STUDIES ON THE CHELATING PROPERTIES OF

THE HYDRAZIDE GROUPING

by

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**NICKEL CHELATES WITH THE LIGANDS FORMED BY THE CONDENSATION OF AROMATIC N-ACYLHYDRAZINES WITH ALDEHYDES OR KETONES**

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STUDIES ON THE CHELATING PROPERTIES OF
THE HYDRAZIDE GROUPING

SUMMARY

The coordinating properties of the N-acylhydrazine grouping,
$\text{RC(O)NHNH}_2$ and the isopropyldiene derivatives thereof,
$\text{RC(O)NHN=C(CH}_3\text{)_2}$ have been extensively investigated in this department and elsewhere. These ligands exhibit keto-enol tautomerism

$\text{RC(O)NHNH}_2 \leftrightarrow \text{RC(OH)=N NH}_2$

Under suitable conditions they may coordinate as bidentates through either the keto form, or by loss of a proton through the enol form.

This thesis presents a study of the variation in coordinating properties brought about by alteration to the structure of the hydrazide grouping.

The complexing power of hydrazides where the $\text{―C=O}$ has been replaced by a $\text{P=O}$ has been examined. Hydrazides such as diphenyl phosphorohydrazidate (i) show practically no complexing power with first row transition metals. Replacement of phenoxy groups with phenyl and oxygen with sulphur in diphenyl phosphonothioic hydrazide (ii) (PSH) causes a notable increase in coordinating power.

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Some complexes with the stoichiometry $M \text{II(PSH)}_4 X_2$, where $M$ is cobalt II or nickel II and $X$ a monovalent anion, have been isolated.

To study the effect on coordinating properties of an oxygen atom linked to the carbonyl group, the phenyl and ethyl esters of carbazic acid and their acetone derivatives have been synthesised. The cobalt II, nickel II and copper II complexes of these four ligands have been identified and their spectral and magnetic properties examined. Not even in the case of the isopropylidene derivatives can any 'enolic' complexes be prepared.

A series of nickel II complexes, the general formula of which is shown in fig. (iii), has been prepared in an effort to correlate the stereochemistry of the complex with the electronic and steric properties of the substituents $X$, $R_1$ and $R_2$.

This series of complexes together with their dipyridinates and dihydrates have been characterised by analysis and their stereochemistry examined by magnetic and visible spectra measurements.
The anhydrous complexes can be divided into two classes. Class A - those which exist as four coordinate square planar complexes, and Class B - complexes which can be isolated in two isomeric forms, a red diamagnetic square planar species and a green paramagnetic species, in which the nickel ion has achieved octahedral coordination via a process of association.

Complexes of class B display equilibria between monomeric and polymeric species in solutions of non-coordinating solvents. These have been studied by means of solution magnetism measurements, spectrophotometric techniques, and molecular weight determinations. The behaviour in solution is consistent with the existence of monomers, dimers and trimers. An attempt has been made to determine the equilibrium constants governing the equilibria.

The ready formation of hydrates in solution by class B compounds is an important consideration in effecting accurate physical measurements. Variation of $R_1$, $R_2$ and $X$ has led to the conclusion that polymerisation is a consequence of the steric and electronic properties of those variables. Apart from the steric effect of substituents, the electronic nature of $R_1$, $R_2$ and $X$, exerts a marked influence on the tendency for association.
To the best of my knowledge this thesis contains no material previously published or written by another person, nor any material previously submitted for a degree or diploma in any University, except where due reference is made in the text.

J.F. ALCOCK
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ERRATUM

Throughout the text KK has been used as the abbreviation for kilokayser instead of kK.
PART A

NICKEL CHELATES WITH THE LIGANDS FORMED

BY THE CONDENSATION OF AROMATIC N-ACYLHYDRAZINES

WITH ALDEHYDES OR KETONES
CHAPTER 1

INTRODUCTION AND REVIEW

1-1 INTRODUCTION

The coordinating properties of the N-acylhydrazine grouping, R\text{C(O)NH-NH}_2, and the isopropylidene derivatives thereof R\text{C(O)NHN} \overset{-}{=}{\text{C(\text{CH}_3)_2}} have been extensively investigated. These ligands exhibit keto-enol tautomerism.

Under suitable conditions they may coordinate as bidentates through either the keto form, or by loss of a proton through the enol form, thus giving rise to cationic or neutral complexes (i) and (ii).

\[
\begin{align*}
\text{(i)} \quad & R-\text{C}-\overset{\text{H}}{\text{N}}-\overset{\text{X}}{\text{NH}_2} \\
\text{(ii)} \quad & R-\text{C}=\overset{\text{I}}{\text{N}}-\overset{\text{M}_2}{\text{NH}}
\end{align*}
\]

Where M is a divalent metal ion and X a monovalent anion.

Some evidence for the keto formulation (i) has resulted from infra-red studies on first row transition metal complexes of N-benzoylhydrazine\textsuperscript{1,2,3} and N-salicoylhydrazine\textsuperscript{3} and their isopropylidene derivatives.\textsuperscript{3,4} The infra-red spectrum of bis(N-isopropylidene-N'-benzoylhydrazino) copper II contains no N-H bond, and verifies that the ligand is coordinated through the enolic form.\textsuperscript{5} A more extensive revue of
the coordinating action of acylhydrazines and related compounds has been presented by Baker.\textsuperscript{5}

A series of nickel II chelates with hydrazones formed by the condensation of aromatic $N$-acylhydrazines with active carbonyl groups has been studied.

\[
\begin{align*}
\text{X} & \quad \text{H} \quad \text{N} \quad \text{NH}_2 \\
\text{O} & \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{O} & \quad \text{O} \quad \text{C} \quad \text{R}_1 \\
\text{R}_2 & \quad \text{C} \quad \text{N} \quad \text{N} \quad \text{C} \quad \text{R}_1 & \quad \text{R}_2
\end{align*}
\]

These ligands form neutral complexes more easily than the parent hydrazines, presumably because the conjugated double bond system stabilises the enolic form. This section is concerned with the nickel complexes with the enolic form of these hydrazones (iii).

\[
\begin{align*}
\text{X} & \quad \text{C} \quad \text{N} \quad \text{N} \quad \text{C} \quad \text{R}_1 \\
\text{O} & \quad \text{N}_2 \\
\text{R}_2
\end{align*}
\]

(iii)

These complexes belong to two types depending on the nature of $X$, $R_1$ and $R_2$.

Class A - Diamagnetic square planar complexes and Class B - complexes which can exist as two distinct isomers, one a red diamagnetic square complex, and the other a green paramagnetic polymeric species. In this section isomerism implies the coexistence of the two spin states of a
metal ion in a metal complex (i.e. for a $d^8$ nickel II system, the existence of a paramagnetic triplet state and a diamagnetic singlet state).

In weakly coordinating solvents there exists an equilibrium between the two isomers, which is dependent on temperature and concentration. It is informative to review the present state of knowledge as regards nickel II complex equilibria. Several series of formally four coordinated nickel II complexes, which in solution exhibit magnetic moments in the range $0 < \mu_{\text{eff}} > 3.3$ B.M. have been reported. Such behaviour can be explained in terms of the equilibrium A and/or B. The nickel ion in both octahedral and tetrahedral environments is spin free and contains two unpaired electrons, whereas in square planar complexes it is spin-paired and diamagnetic.

1-2 A REVIEW OF NICKEL COMPLEXES WHICH EXHIBIT SOLUTION EQUILIBRIA

1-2 (i) Nickel Complexes of Salicylaldimines

Nickel complexes of salicylaldimines which show equilibria in solution are of the structural type (iv).

![Diagram](image)

(iv)

These ligands are the product of the condensation of an o-hydroxybenzaldehyde with a primary amine. The effect of varying R and X in these
ligands on the stereochemical and electronic properties of their complexes has been dramatically illustrated and widely investigated.

1-2 (i) (a) Bis-(N-methylandaldehyde) Nickel II, Ni(Me-sal)₂

An Example of Monomer - Polymer Equilibrium

Interest in salicylaldimine nickel II complexes was aroused by the publication of Wills and Mellor in 1947 in which they reported that bis-(N-methylandaldehyde) nickel II, Ni(Me-sal)₂, and bis-(N-hydroxysalicylaldimine) nickel II, Ni(HO-sal)₂, both diamagnetic in the solid became partially and fully paramagnetic in chloroform and pyridine solutions respectively. Both complexes had magnetic moments of 3.1 B.M. in pyridine, and this was accounted for by the suggestion that the equilibrium

Ni II (R-sal)₂ + 2 Py ⇌ Ni (R-sal)₂ 2 Py

where Py stands for pyridine, lies nearly completely to the right at room temperature. Thus the metal ion is found in an essentially octahedral environment in pyridine solution. Subsequent investigations have showed that these complexes obey the Curie-Weiss law (198 K - 316 K) in pyridine. Additional evidence for the existence and structure of the dipyrindinates, came with their isolation in the solid, and the ready interpretation of their visible spectra in terms of a near octahedral environment.

Initially it was suggested that the weak paramagnetism of Ni(Me-sal)₂ in non-coordinating solvents (e.g. chloroform) was due to an equilibrium between a planar diamagnetic species and a tetrahedral paramagnetic species. However the low dipole moment in benzene precludes the presence of a tetrahedral species.
The magnetic moment of Ni(Me-sal)$_2$ in benzene and chloroform increases with solute concentration, the values at limiting solubility are 1.86 B.M. in chloroform and 2.23 B.M. in benzene. The anomalous paramagnetic behaviour was attributed to an equilibrium between a diamagnetic planar species and an associated species, which must contain one or more paramagnetic nickel ions. A similar situation probably exists for Ni(HO-sal)$_2$ and Ni(H-sal)$_2$, but limited solubility in inert solvents has restricted accurate physical measurements. Neither the extent of association nor the detailed structure of the associated species has been unambiguously assigned in any of the above compounds.

Heat treatment on solid Ni((Me-sal)$_2$ has yielded a number of different forms of the compound. Differences in X-ray powder diffraction patterns, and in solubility has been attributed to the varying degree of polymerisation. The rose coloured form which is insoluble is probably completely polymerised. Evidence for an essentially octahedral environment of the nickel ion is provided by ligand field spectrum.

Other N-alkylsalicylaldimine nickel II complexes behave similarly to Ni(Me-sal)$_2$ and Ni(HO-sal)$_2$. Complexes with R = ethyl, n-propyl, n-butyl, benzyl and allyl have small positive susceptibilities in chloroform and benzene, corresponding to moments of 0.20-1.0 B.M. at room temperature. Magnetic susceptibility has been proved temperature and concentration dependant, and this phenomenon has been ascribed to a monomer-polymer equilibrium. Direct evidence for the existence of a polymer has been provided by molecular weight measurements.
1-2 (i) (b) Bis-(N-sec-alkylsalicylaldimino) Nickel II -

The Existence of Planar — Tetrahedral Equilibria

A further complication in nickel complex equilibria came with the discovery of isomeric tetrahedral species. The salicylaldimine complexes where $R = \text{sec-alkyl}$ are more strongly paramagnetic in solution than their straight chain analogues, however molecular weight measurements in freezing benzene revealed an extent of association which is insufficient to explain the observed paramagnetism. The existence of a second paramagnetic species in solution, viz. tetrahedral was then recognised.\textsuperscript{19,20} Molecular weight measurements showed that at 25°C, association is negligible, and the equilibrium is one between planar and tetrahedral species.\textsuperscript{21,22}

\[
\text{Planar} \quad \xrightarrow{\text{diamagnetic}} \quad \text{Tetrahedral} \quad \xrightarrow{\text{paramagnetic}}
\]

Evidence for the existence of a tetrahedral species in solution may be summarized thus -

1. Despite molecular weight measurements showing the existence of monomers, there still exists appreciable paramagnetism in non-coordinating solvents.
2. Solution magnetic moment increases with increasing temperature whereas polymer formation and hence magnetism would be expected to decrease.
3. Solutions of the complex in benzene show appreciable dipole moments, which is in accord with the presence of a tetrahedral species. The complex with $R = \text{tertiary butyl}$ has a dipole moment of similar magnitude to those of the corresponding cobalt II and zinc II complexes, which have been shown to be tetrahedral.\textsuperscript{21}
4. Visible spectra in solution contain absorption bands characteristic of
both planar and tetrahedral species.\textsuperscript{21,22}

1-2 (i) (c) \textit{Bis-(N-arylsalicyldimino) Nickel II Complexes - Associated – Planar – Tetrahedral Equilibria}

The para and meta substituted phenyl complexes are paramagnetic in solution (range 2.8 to 3.3 B.M.). In solutions of non-coordinating solvents, and below 70°C, only planar and associated species exist,\textsuperscript{23} 1.5 < \bar{n} < 3.0. However measurements up to 200°C have established the existence of tetrahedral species.\textsuperscript{24} Above 70°C the spectral features due to the associated species decrease, and a band at 6.7 K.K., presumably \nu_2 of the tetrahedral form appears. The solution behaviour may be summarised thus -

Increasing Temperature

Associated \rightarrow Planar \rightarrow Tetrahedral

Complexes with an ortho substituted phenyl group e.g. R = o-tolyl and \alpha-naphthyl are monomeric, diamagnetic or weakly paramagnetic, \mu < 1.0 B.M., and show no characteristics of tetrahedral species. Ortho substituents apparently prevent association.\textsuperscript{23,24}

A series of bis-(N-R-salicyldimino) nickel II complexes, where R contains a site capable of coordination [R = CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OCH\textsubscript{3}], has been studied by Holm,\textsuperscript{25} who has concluded that from 40°C to 50°C in chloroform, there exists discreet planar, octahedral and tetrahedral isomers.
Octahedral coordination can be achieved by utilisation of the third coordination site contained on the R group of the ligand.
The Dependence of the Stereochemistry of Bis-(N-R-salicylaldimino) Nickel II Complexes on the Nature of R and X.

Square Planar Versus Tetrahedral

It is primarily steric considerations which determine the stereochemistry. The chemical nature of the substituent X has a real but secondary effect. Steric considerations coupled with X-ray analysis,\textsuperscript{26,27,28} show that the stable planar form of all bis-salicylaldimine complexes is trans. Models indicate that where R contains a branched \textit{a} carbon atom, a trans planar structure involves considerable steric interplay between R and the donor oxygen and \textit{3H} on the opposite half of the molecule (v).

\begin{center}
\includegraphics[width=0.2\textwidth]{image.png}
\end{center}

(v)

Steric interplay is reduced in the tetrahedral species. Thus complexes with R equal to straight chain alkyl do not show the same readiness to form tetrahedral complexes as branched chain alkyl complexes do. As expected, under comparable conditions of temperature and concentration, the proportion of tetrahedral species in the equilibrium mixture has the order, \textit{n}-alkyl < alkyl chain branched at the \textit{\beta} carbon < alkyl chain branched at the \textit{a} carbon atom < a tertiary alkyl group branched at the \textit{a} carbon atom. Likewise increasing the "bulk" of the \textit{3X} substituent causes a marked increase in the tendency to form the tetrahedral isomer in preference to the square complex. The electronic nature and position of the ring
substituent X has a definite but secondary effect on the equilibrium, however in most instances electronic effects are unpredictable.  

1-2 (ii) Nickel "\(\beta\)-keto-amine" Complexes

Similarities between \(\beta\)-keto-amine complexes (vi) and salicylaldimine complexes are to be expected from the common oxygen-nitrogen donor system, and the formation of six-membered chelate rings by both ligands.

![Diagram](image)

(vi)

Nickel complexes with \(R = \text{H, aryl, and alkyl}\) have been prepared.\(^{30,31,32}\)

As with bis-(salicylaldimine) nickel II complexes, the nickel complex stereochemistry is strongly dependant on the nature of \(R\). In the solid all complexes with \(R = \text{H, methyl, \(n\)-alkyl and aryl}\) are diamagnetic and planar, whereas all complexes with \(R = \text{a branched alkyl}\) are paramagnetic and pseudo-tetrahedral. In solutions of non-coordinating solvents, the latter complexes retain full paramagnetism, and thus are wholly tetrahedral. Complexes with \(R = \text{n-alkyl}\) show lower paramagnetism, (μ = 1.4-1.7 B.M.), thereby indicating a substantial proportion of planar species. Complexes with \(R = \text{aryl and methyl}\) are only slightly paramagnetic, with μ < 1.0 B.M. in most cases.

The principal difference in comparison with the salicylaldimines are that for \(R = \text{a branched chain alkyl}\), the tetrahedral configuration is
the most stable, and that for R = aryl, methyl and n-alkyl, molecular
association makes no contribution to the solution composition above -30°C,
(except where R = ortho substituted phenyl).

1-2 (iii) **Nickel Aminotroponeimimates**

The aminotroponeimines act as bidentate ligands, coordinating to
metal ions through two nitrogen atoms, with the formation of a five-membered
chelate ring. The magnetic moments, electronic spectra, and frequencies of
N.N.H. absorption of the bis nickel II chelates of aminotroponeimines, (vii)
depend on the temperature, solvent and ligand structure.\(^{33-36}\)

![Chemical Structure](image)

Complex polymerisation is ruled out by molecular weight measurements, which
correspond to the monomer. The increase in magnetic susceptibility with
temperature is consistent with the production of a tetrahedral species.
The equilibrium behaviour of the complexes is consistent with an equilibrium
of the type,

\[
\text{Tetrahedral} \quad \rightleftharpoons \quad \text{Planar}
\]

\[
\text{paramagnetic} \quad \rightarrow \quad \text{diamagnetic}
\]

Steric difficulties arise when R becomes bulky. The crowding can be
relieved by twisting the molecule so that the nickel atom is approximately
in a tetrahedral configuration.
l-2 (iv) Bis-(β-keto-enolate) Nickel II Complexes

The presence of β-carbonyl groups with at least one hydrogen atom on the carbon atom between allows keto-enol tautomerism to occur.

\[ \text{O} \quad \text{O} \]
\[ \text{R}_1 \quad \text{C} \quad \text{C} \quad \text{R}_2 \]
\[ \text{H} \quad \text{R}_3 \quad \leftrightarrow \]
\[ \text{O} \]
\[ \text{C} \quad \text{C} \quad \text{R}_3 \]
\[ \text{R}_1 \quad \text{R}_2 \]

Under appropriate conditions the enolic proton can be removed. The replacement of this proton by metal ions results in the formation of six-membered chelate systems (viii)

\[ \text{R}_1 \]
\[ \text{R}_3 \quad \text{C} \quad \text{O} \quad \text{M}^n \]
\[ \text{R}_2 \]

(viii)

where M is a metal ion of valence n.

Metal complexes of ligands containing a wide variety of R₁, R₂ and R₃ are known. Accordingly the following abbreviations are used.

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<td>the general β-keto-enolate anion</td>
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</tr>
<tr>
<td>AA</td>
<td>Acetylacetone</td>
<td>(CH₃CO)₂CH₂</td>
</tr>
<tr>
<td>DBM</td>
<td>Dibenzoylmethane</td>
<td>(C₆H₅CO)₂CH₂</td>
</tr>
<tr>
<td>DiBM</td>
<td>Di-isobutylmethane</td>
<td>[(CH₃)₂CHCO]₂CH₂</td>
</tr>
<tr>
<td>DPFM</td>
<td>Di-pivaloylmethane</td>
<td>[(CH₃)₂C₆H₄CO]CH₂</td>
</tr>
<tr>
<td>PAA</td>
<td>3-Phenyl-2,4-pentanedione</td>
<td>(CH₃CO)₂CHC₆H₅</td>
</tr>
</tbody>
</table>
1-2 (iv) (a) **Bis-(Acetylacetonate) Nickel II**

Ni(\(\text{AA}\))\(_2\) is paramagnetic in the solid, \(\mu = 3.27\) B.M. at 27°C.\(^{37}\) In benzene, chloroform and ethanol the moments at 27°C are 3.24, 3.12 and 3.11 B.M. respectively.\(^{38}\) The anhydrous compound readily yields a dihydrate, Ni(\(\text{AA}\))\(_2\) \(\cdot 2\text{H}_2\text{O}\), with a magnetic moment of 3.15 B.M. at 26°C. There is little difference between the spectra of these two compounds.\(^{39}\) A comparison of the spectra of these complexes with the spectra of known tetrahedral nickel complexes, discounts the possibility of Ni(\(\text{AA}\))\(_2\) being a tetrahedral complex.\(^{40}\)

The Ni(\(\text{AA}\))\(_2\) molecule is planar and monomeric in the vapour phase.\(^{41}\) Single X-ray diffraction data on the anhydrous nickel complex collected by Bullen\(^{42}\) revealed that nickel atoms exist in linear chains of three. Mason and Pauling\(^{43}\) were able to deduce the entire structure from Bullen’s\(^{44}\) data. They found that Ni(\(\text{AA}\))\(_2\) was a trimer in the solid state, with the nickel atoms held together in symmetrical chains of three by the acetylacetone oxygen atoms, in such a way that each nickel atom is hexa-coordinate, being surrounded by a distorted octahedron of oxygen atoms, fig. 1-1.\(^{45}\)

\(\text{Ni(\text{AA})}_2\) maintains its trimeric structure when dissolved in solvents of low coordinating power.\(^{46}\) Above 200°C a spectral shift, with the production of a red colour is indicative of some dissociation into monomers. The monomers reassociate on cooling.\(^{45}\)

1-2 (iv) (b) **Nickel Complexes with Substituted Acetylacetones**

**Bis-(2,6-dimethyl-3,5-heptanediono) Nickel II, Ni(DiBM)_2**

\([R_1 = R_2 = \text{CH}(\text{CH}_3)_2, R_3 = \text{H}]\)

Ni(DiBM)_2 is paramagnetic in the solid, but shows a solution spectrum which is both temperature and concentration dependent. The
visible spectrum is roughly a superimposition of the trimeric Ni(II) spectrum and the known monomeric square planar Ni(DPM)$_2$.*

**Bis-(2,2,6,6-tetramethyl-3,5-heptanediono) Nickel II, Ni(DPM)$_2$**

$[R_1 = R_2 = C(CH_3)_3$ and $R_3 = H]$  

Ni(DPM)$_2$ is more sterically hindered than Ni(DiBM)$_2$ and is a red diamagnetic complex, which maintains its planarity in non-coordinating solvents over all ranges of temperature and concentration. A crystal structure study has shown that Ni(DPM)$_2$ is mononuclear and essentially planar.$^{4,5}$

**Bis-(3-phenyl-2,4-pentanediono) Nickel II, Ni(PAA)$_2$ and Bis-(dibenzoyl-methano) Nickel II, Ni(DBM)$_2$**

Both Ni(PAA)$_2$ and Ni(DPM)$_2$ have been isolated in two crystalline forms, a red diamagnetic and a green paramagnetic solid.$^{4,6}$ Further studies on substituted acetylacetones have been carried out by Wolf,$^{4,7}$ who found that whether the Ni(II)$_2$ complex can exist in two isomeric forms or not is a function of the substituents on the chelate ring, which by influencing the chelate ring conformation either favour or hinder the association process.

1-2 (v) Acetylacetonates of Other Divalent First Row Transition Metal Ions

Ni(II) has been shown by X-ray diffraction studies to exist as a trimer in the solid state. X-ray crystal studies on bis-(acetylacetonato) cobalt II, Co(II)$_2$, and bis-(acetylacetonato) zinc II, Zn(II)$_2$, have revealed that these two exist as polymers in the solid state. The structure of no two complexes are the same.$^{4,8}$ As accurate X-ray structure determinations have been completed on this series of complexes, they warrant further consideration.
Bis-(Acetylacetonato) Cobalt II, Co(AA)$_2$

Molecular weight measurements on Co(AA)$_2$ in non-coordinating solvents indicate the presence of monomers, dimers, trimers and tetramers.$^{48}$ The monomeric Co(AA)$_2$ formed at very great dilution has been adjudged after a visible spectrum comparison with Co(DPM)$_2$ to be of tetrahedral symmetry.$^{48}$ Co(DPM)$_2$ and Zn(DPM)$_2$ are isomorphous and tetrahedral.$^{44}$ An X-ray analysis of Co(AA)$_2$ has revealed that the solid is tetrameric$^{50}$ fig. 1-2, with the cobalt ions achieving octahedral coordination by bridging of oxygen atoms.

If a neutral ligand is added to a solution of Co(AA)$_2$ in non-coordinating solvents, complex equilibria are set up, from which the following types of complex can be isolated, [Co(AA)$_2$]L, [Co(AA)$_2$]L$_2$ and [Co(AA)$_2$]$_2$L$_2$, where L is a monodentate ligand. The crystal structure of [Co(AA)$_2$]$_2$ZnH$_2$O has been determined.$^{51}$ The dimer corresponds to the two central cobalt atoms in the tetramer with the bridging positions occupied by :OH$_2$, fig. 1-3.

Bis-(Acetylacetonato) Zinc II, Zn(AA)$_2$

Zn(AA)$_2$ has a trimeric structure in the solid state, in which the two terminal zinc atoms are five coordinated with a slightly distorted trigonal bipyramidal structure, and the central zinc atom is six coordinated. The structure as determined by Cotton$^{52}$ is shown in fig. 1-4. No ligand molecule acts as a bridge through both oxygens. The preference for five coordination is exemplified in the formation of Zn(AA)$_2$L adducts, where L is a monodentate ligand such as pyridine, rather than Zn(AA)$_2$·2L.$^{53-55}$
FIGURE 1-1. The Nickel Acetylacetonate Trimer 43.

FIGURE 1-2. The Cobalt Acetylacetonate Tetramer 50.

FIGURE 1-3. The $[\text{Co(AA)}_2\cdot\text{H}_2\text{O}]_2$ dimer 51.

Portions of the molecules are represented by curved lines.
FIGURE 1-4. The Zinc Acetylacetonate Trimer.

FIGURE 1-5. The Cobalt \( \beta \) keto-phosphonyl Trimer.
Bis-(β-keto-phosphonyl) Cobalt II, Co(PA)$_2$

Co(PA)$_2$ (viii) was first prepared in 1963, and accompanying the preparative details was the observation that the molecular weight in freezing benzene corresponded to a trimer.$^{56}$ As with bis-(β-keto-enolate) nickel II complexes of "intermediate" degree of steric hindrance, there exists a temperature and concentration dependent equilibrium between monomer

![Chemical structure](image)

(viii)

and trimer. The visible spectrum in dilute solution is similar to that of Co II(DPM)$_2$ which has been shown monomeric and tetrahedral.$^{48,57}$ A recent communication reports that the complex is trimeric in the solid state.$^{58}$ Although the structure of Co(PA)$_2$ contains a linear sequence of metal atoms, it differs from Ni(AA)$_2$ in that all six chelate rings are closed about the terminal metal atoms, and none about the central atom, fig. 1-5.
REFERENCES

CHAPTER 2

THE PREPARATION, STEREOCHEMISTRY AND MAGNETISM OF SOME NICKEL COMPLEXES WITH LIGANDS DERIVED FROM THE CONDENSATION OF ACYL HYDRAZINES WITH ALDEHYDES OR KETONES

Substituted benzoylhydrazines readily condense with aldehydes or ketones, to form molecules which act as bidentate ligands.

This work is concerned with the nickel complexes with the enol form of such ligands (i).

2-1 HISTORICAL

The pale blue complex bis-(N-isopropylidenem-N'-benzoylhydrazino) nickel II tetrahydrate was first prepared by Diamantis, who observed that drying in the oven at about 80°C resulted in the production of a chloroform soluble green complex. Recrystallisation of the green compound from chloroform/petroleum spirit mixtures resulted in the production of green and/or red crystals depending on the complex concentration, and solvent
composition.

Analysis revealed that both the red and the green complex were identical in formula, and were in fact bis-(N-isopropylidene-N'-benzoyl-hydrazino) nickel II, Ni(IPBH)_2.

Solid state magnetic moments provided some clue as to the true nature of the complexes, the red complex was found to be diamagnetic, and as such was almost certainly a square planar complex, whilst the green complex was paramagnetic and hence contained high spin nickel. The paramagnetism of the green complex indicated that the complex contained nickel atoms either in a tetrahedral environment or in a quasi-octahedral environment. Coordination number greater than four could only be obtained through a process of association. Absorption spectra in weakly coordinating solvents excluded the presence of tetrahedral species, and thus the two isomers were identified as monomeric square planar, and a high spin polymeric complex.

The behaviour of the complex in weakly coordinating solvents was also characteristic of monomer polymer equilibrium. Dilute solutions displayed the red colour of the monomer, whereas concentrated solutions showed the green colour of the polymeric species. For a given complex concentration, both the red and the green isomer displayed identical spectra in weakly coordinating solvents. In accordance with monomer polymer equilibrium, increasing temperature favours the formation of the monomer, as can be readily observed by the increased intensity of the red colouration, and decreased temperature favours polymer formation.

The influence of donor molecules such as water and ethanol on the solution spectra was observed by Thong. In the presence of these donor
molecules, the nickel atom achieves hexa-coordination by the formation of the bis adducts, at the expense of polymerisation. Although the solid isomers are quite stable in air, solutions in weakly coordinating solvents readily pick up atmospheric moisture. Bis-(N-isopropylidene-N'-benzoyl-hydrazino) nickel II dipyridinate was prepared by Thong,\(^2\) and the magnetic moment and nmr spectrum are characteristic of octahedrally coordinated nickel. The other complex prepared by Thong, bis-(acetaldehyde-N-benzoyl-hydrazone) nickel II, could be isolated only as the square planar complex, and gave no indication of exhibiting association in solution.

2-2 **GENERAL METHODS OF PREPARATION**

The preparations of thirteen new complexes, five which exhibit solution equilibria, two of which are very hygroscopic and cannot be obtained in an analytically pure state, two which can only be obtained as the square planar complex, one which contains another possible coordination site in the ligand molecule and probably exists as an infinite polymer; and five bis pyridine adducts are reported in this work. The individual complexes, magnetic moments, and suggested stereochemistry are given in table 2-2, section 2-4 (iv). Table 2-1 gives a list of ligands and their abbreviations.

2-2 (i) **The Preparation of Hydrazone Complexes**

The preparative method generally employed was that due to Diamantis\(^1\) in the preparation of \(\text{Ni(IPBH)}_2^+\). Ligands were generally prepared "in situ" thus; the dropwise addition of aqueous sodium hydroxide to an acetone-water mixture of nickel chloride and \(N\)-benzoylhydrazine resulted in the separation of \(\text{Ni(IPBH)}_2^+\cdot\text{H}_2\text{O}\). The crude hydrate was then dried, to
give the anhydrous complex, which was recrystallised from a weakly coordinating solvent under moisture free conditions.

A second preparative method developed was to reflux a methanolic solution of nickel acetate and the sodium salt of the hydrazone. The sodium salt of the hydrazone was formed by the addition of an equimolar amount of sodium methoxide in methanol to the hydrazone in methanol. Subsequent removal of the solvent left a mixture of sodium acetate and the complex, from which the complex was removed by extraction into dry petroleum spirit.

Of the complexes which exhibit solution equilibria, the only one which has been isolated in both crystalline forms is Ni(IMPB)_2.\(^1,2\) No deliberate attempt was made to isolate both forms of the new complexes reported in this section. Ni(MKKBH)_2 was isolated in both the green form, and as a mixture of the red and green, Ni(IPP-TH)_2 as red needles, Ni(IPm-TH)_2 and the impure Ni(IPP-CLBH)_2 and Ni(IPo-CLBH)_2 as green polymers.

2-2 (ii) The Preparation of Bis-Pyridine Adducts

Pyridinate readily separate on addition of pyridine to solutions of the complexes in weakly coordinating solvents, but may equally readily be prepared in a pure state by warming the complex or the hydrate in pyridine itself. The latter procedure was generally employed. Solution studies were precluded because of their insolubility.

As can be seen from table 2-2, section 2-4 (iv), the stereochemistry of the nickel complex with a given hydrazone is dependant on the substituents X, R', and R". A possible explanation of stereochemistry in terms of the electronic and steric properties of these variables is presented in Chapter 5. A brief summary of the theoretical interpretation
of the bonding in the two 'competing' structures, the square planar and
the octahedral is given below. Particular attention is devoted to the
bonding in square complexes, in an endeavour to determine the factors
peculiar to metal and ligand which can lead to coordination number four
being the preferred structure.

Table 2-1 - Abbreviations

The Variation of \( X, R_1 \) and \( R_2 \) in the General Ligand

\[
\begin{array}{c}
X \quad R_1 \quad R_2 \\
\hline
H \quad \text{CH}_3 \quad \text{CH}_3 \\
H \quad \text{CH}_3 \quad \text{CH}_2\text{CH}_2 \\
\text{para-CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{meta-CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{para-Cl} \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{ortho-Cl} \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{para-NO}_2 \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{meta-NO}_2 \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{para-OH} \quad \text{CH}_3 \quad \text{H} \\
H \quad \text{CH}_3 \quad \text{H} \\
\end{array}
\]

and the Corresponding Abbreviations are given below:

<table>
<thead>
<tr>
<th>( X )</th>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>IPBH</td>
</tr>
<tr>
<td>H</td>
<td>CH(_3)</td>
<td>CH(_2)CH(_2)</td>
<td>MUXBH</td>
</tr>
<tr>
<td>para-CH(_3)</td>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>Ipp-TH</td>
</tr>
<tr>
<td>meta-CH(_3)</td>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>IPm-TH</td>
</tr>
<tr>
<td>para-Cl</td>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>IPP-ClBH</td>
</tr>
<tr>
<td>ortho-Cl</td>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>IPo-ClBH</td>
</tr>
<tr>
<td>para-NO(_2)</td>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>IPp-NO(_2)BH</td>
</tr>
<tr>
<td>meta-NO(_2)</td>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>IPm-NO(_2)BH</td>
</tr>
<tr>
<td>para-OH</td>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>IPp-OHBH</td>
</tr>
<tr>
<td>H</td>
<td>CH(_3)</td>
<td>H</td>
<td>ABH</td>
</tr>
</tbody>
</table>

\( N\)-Isopropylidene-\( N'\)-isonicotinoylhydrazine is designated IPINH and
Py stands for pyridine.
Crystal field theory is based on a consideration of the electrostatic interaction of the electrons in the donor ligand orbitals, with the five-degenerate d orbitals of the free metal ion, and can be used to give a simple explanation of the bonding and magnetism in nickel complexes.\textsuperscript{3,4} Under the influence of an octahedral field, the five degenerate d orbitals of the free ion are split into two sets, a triply degenerate set, the \( t_{2g} \) orbitals, and a doubly degenerate set of higher energy the \( e_{g} \) orbitals. The energy level scheme, and electron distribution for a \( d^{8} \) ion in an octahedral environment is given in fig. 2-1 (a).

**Figure 2-1 - The Energy Level Scheme for**

(a) Octahedral Coordination (b) Tetrahedral Coordination (c) Tetragonal Distortion (d) Square Planar Coordination
A similar split is observed in the case of tetrahedral coordination, but the $e_g$ level lies lowest in energy, and the separation between the two levels is smaller, fig. 2-1 (b).

The ground state for a $d^8$ square planar structure, contains four orbitals of lower energy, and one of higher energy, the $d_{x^2-y^2}$, with the result that spin-pairing occurs fig. 2-1 (d). Almost invariably square planar nickel complexes are diamagnetic. The energy scheme for the ground state of a high spin complex with weak tetragonal distortion is given in fig. 2-1 (c).

$d^8$ Metal ions, e.g. Ni II, Pd II, Pt II, Au III, Rh I and Ir III provide the bulk of the recognised square planar transition metal complexes reported in the literature. A ligands potentiallity to form square complexes seems dependant on its capacity for double bond formation, and aspect of bonding which is neglected in the simple crystal field model. Double bond formation is a natural extension of the theory of $\sigma$ bonding, as developed in the molecular orbital approach and thus it is not surprising that all attempts to explain the bonding in square planar complexes have been based on molecular orbital calculations.

Fig. 2-2 shows an approximate molecular orbital diagram for a $d^8$ square complex, e.g. PtCl$_4^{2-}$, and the important features may be summarised thus.$^5,6$ The metal orbitals involved in $\sigma$ bonding are the $5d_{z^2}$, $5d_{x^2-y^2}$, $6s$, $6p_x$ and the $6p_y$ orbitals, of which the $5d_{z^2}$ makes only a small contribution. The relative energies of the d orbitals in square planar complexes is not known with certainty, however the dominant feature is that there is one very unstable orbital, the $d_{x^2-y^2}$ and four relatively stable ones. The complex is diamagnetic because the eight metal valence
electrons are paired in the more stable d levels. It is obvious from the energy level diagram, that the best electronic situation for a planar complex will be $d^8$. The most stable levels will be found on the ligand and are expected to be the bonding orbitals with the symmetries of $x^2-y^2$, $s$, $p_x$, and $p_y$. At higher energies are the so-called anti-bonding molecular orbitals derived from the metal d orbitals. Interaction of the $t_{2g}$ orbitals with the electron containing $p$ orbitals of the appropriate symmetry in PtCl$_4^{2-}$ will be an adverse interaction in that it will lead to a destabilisation of the $\pi$ orbitals on the metal.

**Figure 2-2** - A Simplified Molecular Orbital Energy Scheme for a Square Planar Complex such as Pt(CN)$_4^{2-}$, taken from reference 6.
Attempts have been made to interpret the bonding and spectra of the square planar complexes of nickel, platinum and palladium with cyanide.\textsuperscript{6,7,8} This system is more complicated than the \( \text{PtCl}_4^{2-} \) system, because there are two possible types of \( \pi \) bonding with the cyanide ion. Cyanide possesses a filled \( \pi \) bonding orbital which can enter into metal to ligand \( \pi \) bond formation with the \( t_{2g} \) metal orbitals in an analogous bonding process to that described in \( \text{PtCl}_4^{2-} \). However, in addition, cyanide contains an empty \( \pi \) molecular orbital which can enter into metal to ligand back coordination, through interaction with the same metal d orbitals. In this particular case there is a competition between the two possible modes of \( \pi \) bonding, one which is stabilising, and the other destabilising. To predict which will dominate requires a precise knowledge of the actual orbital energies, for cyanide the net effect is to stabilise the complex, i.e. to lower the energy of the \( \pi d \) level.

The ligands discussed in this work contain a delocalised \( \pi \) electron system (ii), as well as p orbitals capable of participating in metal to ligand \( \pi \) bonding. The delocalised \( \pi \) molecular orbital has associated vacant anti-bonding orbitals, which could if they were of sufficiently low energy, participate in metal to ligand back coordination. These ligands may \( \pi \) bond in a similar manner to cyanide, but it is impossible to predict whether back coordination will or will not occur, without a knowledge of
the relative energies of the orbitals.

To decide between the relative energies of the square planar and octahedral structures by a consideration of both \( \pi \) and \( \sigma \) interactions is impossible without a precise knowledge of energy levels. However the following less exact considerations peculiar to the square planar complex are noted.

1. An increased \( \sigma \) bond strength for square complexes.\(^9\) In tetrahedral and square complexes the \( d_{x^2-y^2} \) orbital or more precisely the molecular orbital containing the most \( d_{x^2-y^2} \) character is strongly anti-bonding with respect to the four ligands in the \( xy \) plane. In square complexes this orbital is empty, and thus there is an increased \( \sigma \) bond strength which contributes to the stability of the four coordinate compound. This will be in part compensated for by the energy of pairing in going from a \( (d_{x^2-y^2})^1 (d_z^2) \) to a \( (d_z^2)^2 (d_{x^2-y^2})^0 \) configuration.

   In addition the \( d_z^2 \) orbital which contains two electrons, and is not needed for bonding along the \( z \) axis can be hybridised with the s orbital to provide a greater contribution to the in-plane \( \sigma \) bonding, whilst the pair of non-bonding electrons occupy the hybrid orbital concentrated mainly above and below the molecular plane.

2. Increased \( \pi \) bonding strength. Pauling\(^10\) first invoked the concept of double bond character to explain the strength and shortening of some bonds in metal complexes, and it was suggested that the double bond involved overlap of the \( dx \) electron pairs of the metal with vacant \( p \) or \( d \) orbitals of the donor atom, at right angles to the plane of the complex. It has since been recognised that double bond formation does play an important part in stabilising square nickel complexes.\(^11\)\textsuperscript{-14} \( \pi \) Bonding is even more
pronounced in palladium II and platinum II complexes,\textsuperscript{15,16,17} where the
more extended metal orbitals allow better overlap with ligand π orbitals.

3. A more recent concept to explain the stability of the square complex
is that if the metal \( p_z \) valence orbital is sufficiently involved in a
π orbital net-work, through overlap with a suitable π orbital on the ligands,
the stabilisation through this interaction can lead to it being unavailable
for the formation of \( σ \) bonds with ligands in the axial positions.\textsuperscript{18,19}

2-4. \textbf{MAGNETIC MEASUREMENTS}

Magnetic measurements have been the principal tool untilised in the
recognition and identification of nickel complexes showing solution
equilibration. Accordingly the theoretical interpretation of the magnetism
of nickel complexes, and the susceptibilities encountered in practice are
presented below. The magnetic moments of the complexes prepared in this
work, and their structural implications are then discussed.

Wave mechanics show that for transition metal ions, in their ground
states, the magnetic moment is given by,

\[ \mu_S + L = 4S(S + 1) + (L + 1) \]

where \( S \) is the spin angular momentum quantum number and \( L \) is the orbital
angular momentum quantum number.

For many complexes of the first row transition series, it is
possible to assume that only the spin angular momentum is responsible
for the magnetic dipole - hence

\[ \mu_S = \left[ 4S(S + 1) \right]^{1/2} \text{ B.M.} \]

and \[ \mu = \left[ n(n + 2) \right]^{1/2} \text{ B.M.} \]
where \( n \) is the number of unpaired electrons in the unfilled \( d \) shells

\[
\mu = 2.82 \text{ B.M.}
\]

for either tetrahedral or octahedral nickel.

2-4. (i) Magnetism of Octahedral Nickel Complexes

The free nickel ion exists in a \( 3^3_f \) ground state, and the excited states are \( 3_p, 1_g, 1_d \) and \( 1_s \). The effect of subjecting the \( d^8 \) nickel system to an octahedral field is shown in fig. 2-3. The \( 3_p \) energy term is split into three levels, the low lying \( 3^3_A_{2g} \) triplet, and two higher energy levels, the triply degenerate \( 3^3_T_{2g} \) and \( 3^3_T_{1g} \) levels. Theoretically there should be no contribution to the magnetic moment through orbital angular momentum.

Magnetic moments for octahedral complexes lie mainly in the range 2.9 to 3.4 B.M., and are generally in excess of the spin-only value of 2.82 B.M.\textsuperscript{20}

Few exactly "spin-only" moments are found, even in cases where orbital angular momentum contributions are zero. This is due to spin-orbit coupling, which is a process whereby a ground state which has no orbital angular momentum can mix in with a higher state (of the same \( S \) value), which does contain orbital angular momentum. It is this process which results in octahedral nickel II complexes generally showing a magnetic moment in excess of the "spin-only" value.

2-4. (ii) The Magnetism of Tetrahedral Complexes

The effect of replacing octahedral coordination by tetrahedral is to reverse the order of splitting of the \( d \) levels. The ground state is the triply degenerate \( 3^3_T_{1}(P) \) state fig. 2-5, and hence there should be an appreciable orbital angular momentum contribution to the magnetic moment.

Regular tetrahedral complexes should have moments in the range 3.6 - 4.0 B.M.
In agreement with theory complexes in which ligands are identical, or come close in the spectrochemical series have moments in the range 3.6-4.0 B.M. In complexes containing ligands which are well separated in the spectrochemical series, ground state degeneracy is lost, and only second order contributions are possible. Thus many tetrahedral complexes have magnetic moments in the same range as octahedral ones, and magnetic moments cannot be used to differentiate between tetrahedral and octahedral stereochemistry. Figure 2-6 summarizes the magnetic behaviour of a $d^8$ tetrahedral complex.

2-4 (iii) The Magnetism of Square Complexes

All square planar nickel II complexes are diamagnetic. The nickel ion has a spin singlet ground state, the $^3A_g$. Deviations from strict diamagnetism, or colour changes are usually indicative on one of the series of compounds which exhibit so-called "anomalous behaviour".

2-4 (iv) The Magnetic Moment of Some Nickel Complexes in the Solid State

Magnetic moments on powdered solids were determined by the Gouy method. All measurements were duplicated and the sample tube repacked in each case.
Figure 2-3 - The Energy Level Diagram for a \( ^8 \) Ion in an Octahedral Field, taken from reference 4.

Figure 2-4 - The Perturbations Experienced by the Nickel Ion in an Octahedral Complex, taken from reference 20.
Figure 2-5 - The Energy Level Diagram for a $^8$ Ion in a Tetrahedral Field, taken from reference 4.

Figure 2-6 - The Perturbations Experienced by the Nickel Ion in a Tetrahedral Complex, taken from reference 20.
Table 2-2 - The Magnetic Moments of Some Solid Samples of Nickel Complexes

<table>
<thead>
<tr>
<th>Formula</th>
<th>Colour</th>
<th>Temperature K</th>
<th>Magnetic Moment B.M.</th>
<th>Suggested Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(IPBH)(_2) **</td>
<td>green</td>
<td>297.0</td>
<td>3.36</td>
<td>octahedral</td>
</tr>
<tr>
<td>Ni(IPBH)(_2) **</td>
<td>red</td>
<td>297.0</td>
<td></td>
<td>diamagnetic</td>
</tr>
<tr>
<td>Ni(NH(_2)KBH)(_2) **</td>
<td>green</td>
<td>296.3</td>
<td>3.31</td>
<td>octahedral</td>
</tr>
<tr>
<td>Ni(IPP-TH)(_2) **</td>
<td>red</td>
<td>295.8</td>
<td></td>
<td>diamagnetic</td>
</tr>
<tr>
<td>Ni(IPm-TH)(_2) **</td>
<td>green</td>
<td>297.7</td>
<td>3.27</td>
<td>octahedral</td>
</tr>
<tr>
<td>Ni(IPmNH)(_2)</td>
<td>light green</td>
<td>290.7</td>
<td>3.26</td>
<td>octahedral</td>
</tr>
<tr>
<td>Ni(IPm-NO(_2)BH)(_2)</td>
<td>brown</td>
<td>290.7</td>
<td></td>
<td>diamagnetic</td>
</tr>
<tr>
<td>Ni(IPP-NO(_2)BH)(_2)</td>
<td>brown</td>
<td>290.7</td>
<td></td>
<td>diamagnetic</td>
</tr>
<tr>
<td>Ni(ABH)(_2) +</td>
<td>red</td>
<td>291.6</td>
<td></td>
<td>diamagnetic</td>
</tr>
<tr>
<td>Ni(IPBH)(_2) 2Py</td>
<td>blue grey</td>
<td>290.7</td>
<td>3.32</td>
<td>octahedral</td>
</tr>
<tr>
<td>Ni(IPBH)(_2) 4H(_2)O(^+)</td>
<td>pale blue</td>
<td>290.0</td>
<td>3.21</td>
<td>octahedral</td>
</tr>
<tr>
<td>Ni(IPm-NO(_2)BH)(_2) 2Py</td>
<td>yellow</td>
<td>290.7</td>
<td>3.30</td>
<td>octahedral</td>
</tr>
<tr>
<td>Ni(IPP-NO(_2)BH)(_2) 2Py</td>
<td>yellow</td>
<td>290.7</td>
<td>3.34</td>
<td>octahedral</td>
</tr>
<tr>
<td>Ni(IPP-Cl.BH)(_2) 2Py</td>
<td>pale blue</td>
<td>289.6</td>
<td>3.11</td>
<td>octahedral</td>
</tr>
</tbody>
</table>
** Paramagnetism itself is not sufficient to distinguish between octahedral and tetrahedral nickel. Spectral evidence, Chapter 3, discounts the possibility of tetrahedral stereochemistry.

** Complexes which exhibit solution equilibria. Spectral evidence, Chapter 3, suggests that the complex contains five or six coordinated nickel.

+ Moments taken from the work of Thung.
Magnetic Moments in Solution

A consideration of visible spectra bands, coupled with the initial observation that in the solid state Ni(IPBH)₂ can exist in two distinct isomeric forms, leads to the conclusion that in solutions of Ni(IPBH)₂ in weakly coordinating solvents there exists an equilibrium between a red diamagnetic species and a green paramagnetic species.

Accordingly a series of solution susceptibility measurements were undertaken with the Ni(IPBH)₂ complex in a weakly coordinating solvent with the aim of quantitatively characterising the equilibrium between the two complexes.

Measurements were carried out using a Couy balance, and a stoppered sample tube. Samples were thermostated, and all moments measured at two field strengths. No dependance of susceptibility on field strength was observed.

Accuracy in measurement necessitated the usage of "high" complex concentration. On the score of solubility chloroform was chosen as solvent. Unfortunately at these "high" concentrations, the green complex is the dominant species, and over the concentration range studied only small variations in susceptibility are evident, table 2-3. Solution susceptibility measurements are neither of sufficient accuracy, nor sufficiently extensive to allow an evaluation of association constants, but are consistent with spectral and molecular weight data, and do serve to illustrate the following points.

1. The magnetic susceptibility of Ni(IPBH)₂ in weakly coordinating solvents increases with increasing solute concentration, and decreases with decreasing temperature.
2. Over the concentration range studied \((0.5-4.0) \times 10^{-1}\) molar, association is very nearly complete. This is in accord with subsequent molecular weight measurements. Assuming that a solution in which all the complex is in the associated state would have a magnetic moment equivalent to that of the green solid, 3.36 B.M., a 5.16 \times 10^{-2} M. solution in chloroform contains 96% polymer at 20.6°C.

3. The results are consistent with a red diamagnetic species in solution in equilibrium with a green paramagnetic species, as was expected from the existence of two isomeric forms of the solid.

### Table 2-3 — The Magnetic Moment of Na(IPBH)₂ in Chloroform over a Range of Temperature and Concentration

<table>
<thead>
<tr>
<th>Concentration of Total Monomer in Moles/Litre</th>
<th>(\mu) eff.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20.6°C</td>
</tr>
<tr>
<td>5.16 \times 10^{-2}</td>
<td>3.11</td>
</tr>
<tr>
<td>13.90 \times 10^{-2}</td>
<td>3.12</td>
</tr>
<tr>
<td>27.31 \times 10^{-2}</td>
<td>3.18</td>
</tr>
<tr>
<td>38.05 \times 10^{-2}</td>
<td>3.23</td>
</tr>
</tbody>
</table>

2-4 (vi) **Nuclear Magnetic Resonance Spectra**

The N.M.R. spectra of \(\text{Na(IPBH)}_2\) and \(\text{Zn(IPBH)}_2\) were recorded at a resonance frequency of 60 M.c./sec, using a D.A. 60/I.L. Varian Spectrophotometer, at 29.0°C, with the hope that the spectrum of \(\text{Na(IPBH)}_2\) would be sufficiently well defined to provide a further technique for the quantitative study of the equilibrium, and perhaps provide some information as to the structure of the participating species. Deutero-chloroform was used as solvent, and tetramethyl silane as internal reference.
The limited solubility of the zinc complex reduced the sensitivity of these measurements. The spectrum contained two absorptions, one a multiplet, and the other at higher field a doublet, which as near as could be ascertained were in the ratio 5:6. The spectrum contained two peaks of equal intensity presumably due to the methyl groups. Resonances were centred at $\tau = 8.8$ and 8.95. The lower field absorption was made up of a poorly resolved quartet at $\tau = 5.95$, and a multiple absorption centred at $\tau = 6.6$.

The spectrum of $\text{Ni(IPP)}_2$ showed little evidence of fine structure, and at the concentrations employed c.a. $10^{-1}$ molar was probably due to the paramagnetic polymeric species, which predominates (95%) in solutions of these concentrations.
REFERENCES

18. S.J. Shupack, E. Billig, R.J.H. Clark, R. Williams and H.B. Gray, 

19. E. Billig, R. Williams, I. Bernal, J.H. Waters and H.B. Gray,

20. B.N. Figgis and J. Lewis, "Progress in Inorganic Chemistry",
CHAPTER 3

SPECTRA

3-1 THE SPECTRA OF NICKEL COMPLEXES EXHIBITING SOLUTION EQUILIBRIA

The spectrum of Ni(IPBH)₂ is fairly complex in that there are a large number of bands, table 3-1. The major null spectrum of the red isomer shows a single absorption at 20.0 k.k., which is also present in solution, (εₘ ~ 100), and the proportion of the red species in solution increases with increasing temperature and decreasing concentration. The wavelength of absorption, extinction coefficient, magnetic behaviour and temperature concentration relationship, identify the red isomer as a monomeric square planar complex.¹ The remaining absorptions in solution coincide with the null spectrum of the green complex, and may be interpreted in terms of a nickel atom in a tetragonal or five coordinated environment, see sections 3-4 and 3-5. The absorption band in the region 14.17.0 k.k., although at a wavelength characteristic of tetrahedral nickel, is only weak and contrary to the general behaviour of tetrahedral nickel increases in intensity with decreasing temperature.⁵,⁶,⁷ The increasing proportion of the green species with increasing concentration or decreasing temperature is characteristic of the polymeric species. The close correlation between solid and solution spectra indicate that the structures existing in the solid isomers are preserved in solutions of weakly coordinating solvents. The concentration dependence of the spectrum of Ni(IPBH)₂ in benzene under moisture free conditions is shown in fig. 3-1, and the concentration and temperature dependence of Ni(MMXBH)₂ in chlorobenzene in figs. 3-2 and 3-3 respectively.
A measure of the extinction coefficients for the absorption characteristic of a particular species can be used as an estimate of the relative proportion of that species present in the solution (see Chapter 4).

The similarity between the solution spectra, table 3-1 of Ni(MeKBH)\textsubscript{2}, Ni(IPp-TH)\textsubscript{2} and Ni(IPm-TH)\textsubscript{2}, which are also concentration and temperature dependant, to the spectrum of Ni(IPBH)\textsubscript{2} in benzene suggests strongly that an equilibrium involving the same associative mechanism is operative in all cases.

**Table 3-1 - The Absorption Spectra of Complexes Exhibiting Solution Equilibria. Absorption Maxima are in cm\textsuperscript{-1}.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Transition</th>
<th>ν\textsubscript{2}\textsuperscript{*}</th>
<th>ν\textsubscript{1}\textsuperscript{*}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(IPBH)\textsubscript{2} \textsuperscript{**}</td>
<td>17.0-14.0</td>
<td>12.20</td>
<td>8.75</td>
</tr>
<tr>
<td>mull of red isomer</td>
<td>broad</td>
<td>weak</td>
<td>sh</td>
</tr>
<tr>
<td>Ni(IPBH)\textsubscript{2}</td>
<td>20.4 cm 100</td>
<td>weak</td>
<td>sh</td>
</tr>
<tr>
<td>mull of green isomer</td>
<td>17.0-14.0</td>
<td>12.20</td>
<td>8.75</td>
</tr>
<tr>
<td>Ni(MeKBH)\textsubscript{2}</td>
<td>20.4 cm 100</td>
<td>weak</td>
<td>sh</td>
</tr>
<tr>
<td>benzene</td>
<td>17.0-14.0</td>
<td>12.20</td>
<td>9.00</td>
</tr>
<tr>
<td>Ni(IPp-TH)\textsubscript{2}</td>
<td>20.4 cm 100</td>
<td>weak</td>
<td>sh</td>
</tr>
<tr>
<td>benzene</td>
<td>17.0-13.0</td>
<td>12.30</td>
<td>8.75</td>
</tr>
<tr>
<td>Ni(IPm-TH)\textsubscript{2}</td>
<td>20.4 cm 100</td>
<td>weak</td>
<td>sh</td>
</tr>
<tr>
<td>benzene</td>
<td>16.0-14.5</td>
<td>12.20</td>
<td>9.25</td>
</tr>
</tbody>
</table>

* ν\textsubscript{1} and ν\textsubscript{2} refer to the assignment of the absorption bands of the polymeric species, in terms of a possible tetragonally distorted nickel atom see 3-4 (1).

** This complex was originally prepared by Thong. The complex has been reprepared and its spectra re-examined.

+ The absorption characteristic of the square planar complex.
FIGURE 3-1 THE SPECTRUM OF Ni(IPBH)_2 IN BENZENE AT 25.80°C

\[ \varepsilon_M \]

- \( 2.248 \times 10^{-2} \) Molar
- \( 0.4861 \times 10^{-2} \) Molar

KK
FIGURE 3-2. THE SPECTRUM OF Ni(MEKBH)$_2$ IN CHLOROBENZENE, IN THE REGION OF MONOMER ABSORPTION. T = 25.8°C.

--- 0.02782 Molar
--- 0.0388 Molar
--- 0.007285 Molar
FIGURE 3.3. THE TEMPERATURE DEPENDENCE OF Ni(MEKBH)₂, 2.781 × 10⁻² M, AT THE WAVELENGTH CHARACTERISTIC OF POLYMER ABSORPTION. SOLVENT CHLOROBENZENE.
3-2 THE SPECTRA OF SQUARE PLANAR NICKEL COMPLEXES

A summary of the theory of bonding in square planar complexes has been given in section 2-3. The energy level diagrams for the nickel $d^8$ system in a trans square planar environment are to be found in papers given by Makl$^2,3$ and also by Balhausen$^9$ and Liehr.$^{10}$ All square planar $d^8$ complexes are diamagnetic with a singlet $^1A_{1g}$ ground state. There are three allowed d-d transitions; generally the second and third transitions are not observed because they are obscured by the strong charge transfer bands which are characteristic of square planar complexes. The four coordinate complexes prepared in this section contain nickel atoms surrounded by $2N$ and 20 atoms, which from steric considerations are almost certainly in the trans configuration and their spectra are characterised by an absorption at $\sim 2000$ K.K. Those complexes for which suitable solvents may be found, show extinctions of the order of $10^2$ which are characteristic of square complexes.$^1$ Table 3-2 gives the spectra of the square complexes discussed in this section.
Table 3-2 - The Absorption Spectra of Some Square Complexes. Absorption Maxima are in K.K.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Environment</th>
<th>Absorption Maxima</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(IPBH)₂</td>
<td>red isomer mull</td>
<td>20.0</td>
</tr>
<tr>
<td>Ni(IPBH)₂*</td>
<td>in benzene</td>
<td>20.4 (εm ~ 100)</td>
</tr>
<tr>
<td>Ni(MKKBH)₂</td>
<td>in benzene</td>
<td>20.4 (εm ~ 100)</td>
</tr>
<tr>
<td>Ni(IP-TH)₂*</td>
<td>in benzene</td>
<td>20.45 (εm ~ 100)</td>
</tr>
<tr>
<td>Ni(IPm-TH)₂*</td>
<td>in benzene</td>
<td>20.45 (εm ~ 100)</td>
</tr>
<tr>
<td>Ni(IP-InO₂BH)₂</td>
<td>solid</td>
<td>20.4</td>
</tr>
<tr>
<td>Ni(IPm-InO₂BH)₂</td>
<td>solid</td>
<td>20.3</td>
</tr>
</tbody>
</table>

* These complexes exhibit solution equilibria phenomena, their spectra in benzene show absorptions due to associated species as well as absorptions due to square complexes. For this reason εm values are only approximate.

3-3 The Spectra of Octahedrally Coordinated Nickel Complexes

The tendency of the nickel atom in Na(IPBH)₂, Ni(MKKBH)₂, Ni(IP-TH)₂, and Ni(IPm-TH)₂ to achieve coordination number greater than four, is evident not only through the polymerisation reaction, but also in the readiness with which they form bis adducts with donor molecules. The water sensitivity of solutions of these complexes necessitates the adoption of special techniques to ensure the exclusion of moisture whilst conducting physical measurements.

The absorption bands of the ethanolate, hydrate and pyridinate of Na(IPBH)₂ as well as the pyridinates of three complexes, Ni(IPp-OHBN)₂, Ni(IPp-Cl,BH)₂ and Ni(IP-Cl,BH)₂, which themselves could not be obtained in analytically pure states, are given in table 3-3 and in all
cases the nickel may be considered to be octahedrally coordinated.

The square planar complexes, Ni(IPp-NO₂BH)₂ and Ni(IPo-C₁BH)₂ also yield octahedrally coordinated bis pyridine adducts, but do so less readily than the complexes that exhibit association.

Hexa-coordinated nickel II usually shows three spin allowed absorption bands, in the near infra-red, the visible, and the near ultra-violet positions.¹ Using the d⁸ energy scheme in an octahedral field proposed by Liehr and Balhausen,¹⁰ fig. 3-4, in O₃₃ symmetry these absorptions correspond to transitions from the ground ³A₂g state to the states ³T₂g (F), ³T₁g (P) and ³T₁g (P) in order of increasing energy. Molar absorbances are generally low.

The absorption at lowest energy corresponds to the transition from the ³A₂g ground state to the excited ³T₂g (F) state with ν₁ = 10 D_q, and the complexes reported here generally occur at about 10 kK. In some cases the absorption of second highest energy, from the ³A₂g (F) → ³T₁g (F) state, with ν₂ = 18 D_q, is split into two bands, probably because spin orbit coupling mixes the ³T₁g (F) and the ¹Eg states, which have very similar energies under the influence of weak ligand fields. A similar split is observed in the spectrum of Ni(H₂O)₆.¹¹ No split is observed in the complexes, Ni(IPp-NO₂BH)₂ and Ni(IPp-OH₂BH)₂ because the higher energy component of ν₂ is masked by the strong charge transfer absorptions. In every case the third allowed d-d transition, which occurs in the near ultra-violet is obscured by the charge transfer absorption.

The null spectrum of Ni(IPNH)₂ which is also included in table 3-3, is typical of octahedral nickel and provides strong evidence that hexa-coordination has been achieved through the use of the heterocyclic nitrogen
atom, rather than through the associative process operative in Ni(IPB)₂ and related systems. The stability of the complex is indicated by its inability to form a pyridine adduct.
Table 3-3 - The Absorption Spectra of Some Octahedral Nickel Complexes.

Maxima are given in K.K.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Maxima</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(IPBH)_{2}</td>
<td>benzene/ethanol</td>
<td>15.0</td>
</tr>
<tr>
<td>Ni(IPBH)_{2}</td>
<td>H_{2}O</td>
<td>16.0-13.0 broad and weak</td>
</tr>
<tr>
<td>Ni(IPBH)_{2}</td>
<td>benzene/pyridine</td>
<td>18.2, 16.4</td>
</tr>
<tr>
<td>Ni(IPBH)_{2}</td>
<td>2Py mull</td>
<td>18.0, 16.2 sh</td>
</tr>
<tr>
<td>Ni(IPp-Cl.BH)_{2}</td>
<td>2Py mull</td>
<td>18.5, 16.2 sh</td>
</tr>
<tr>
<td>Ni(IPo-Cl.BH)_{2}</td>
<td>2Py mull</td>
<td>18.2, 16.4 sh</td>
</tr>
<tr>
<td>Ni(IPp-OH.BH)_{2}</td>
<td>2Py mull</td>
<td>16.6</td>
</tr>
<tr>
<td>Ni(IP INH)_{2}</td>
<td>mull</td>
<td>18.7, 16.2 sh</td>
</tr>
<tr>
<td>Ni(IPp-NO_{2}.BH)_{2}</td>
<td>2Py mull</td>
<td>16.5 sh</td>
</tr>
<tr>
<td>Ni(IPm-NO_{2}.BH)_{2}</td>
<td>2Py mull</td>
<td>18.4, 16.6</td>
</tr>
</tbody>
</table>

* Ni(IPBH)_{2} and its aquo and pyridine adduct were first prepared by Thong. They have subsequently been re-prepared and their spectra re-examined.

3-4 THE SPECTRA OF THE POLYMERIC SPECIES

3-4 (1) The Spectrum of Tetragonally Distorted Nickel

The polymeric isomers may conceivably contain nickel atoms in a tetragonal environment and accordingly a summary of the spectral characteristics of octahedral d^8 complexes with D_{4h} symmetry is presented below.

In D_{4h} symmetry, the $^3T_{2g}$ state of Oh symmetry is split into two states, the $^3E$ and also the $^3B_2$, and similarly the $^3T_{1g}$ state is split into the $^3A_2$ and the $^3E$, whilst the ground state transforms into the $^3B_1$ state, fig. 3-5.
The subscript $g$ has been omitted for states in $O_h$ and $D_{4h}$ symmetry for the sake of clarity.

Nelson\textsuperscript{13} has assigned the spectra of a series of $\text{NiL}_4X_2$ complexes, where $L$ is an amine and $X$ a halogen, in terms of $D_{4h}$ symmetry. A crystal structure determination has established unambiguously that $\text{NiPy}_4\text{Cl}_2$ has a trans tetragonal structure.\textsuperscript{14} The spectra observed for the series of complexes $\text{NiL}_4X_2$ may be taken as typical tetragonally distorted nickel and are characterised by the following absorptions:

a sharp band, $\nu_3$, (15-20) at 25.0 K.K.

a broad and unsymmetrical band, $\nu_2$, (6-12) at 15.0-16.0 K.K.
a weak absorption at 11.0 K.K. and a broad band, \( \Psi_1 \) in the near infra-red. Jorgensen\textsuperscript{15} has assigned the bands at 10.90 K.K. and 8.50 K.K. in NiPy\(_4\)Cl\(_2\) as the components of the transition \( ^3A_{2g} \rightarrow ^3T_{2g} (\Psi) \) in octahedral symmetry, i.e. from the \( ^3A_{2g} \rightarrow ^3B_{2g} \) and \( ^3E \) in \( D_{4h} \) symmetry. The extent of the splitting depends on the degree of tetragonality. The split of \( \Psi_2 \) is more difficult to see, but a weak shoulder exists at 14.0 K.K. No split of \( \Psi_3 \) is observed. The weak absorption at 12.6 K.K. is a spin forbidden transition. The detailed absorptions of several complexes of this series are given in table 3-4.

The complex Ni[Hi-SA Len N(CH\(_3\))\(_2\)]\(_2\), where Hi-SA Len N(CH\(_3\))\(_2\) is C\(_6\)H\(_5\)(OH).CH=NN(CH\(_2\))\(_2\)N(CH\(_3\))\(_2\), has been shown by X-ray analysis to contain a nickel atom surrounded by 4N and 20 atoms in a distorted trans octahedral arrangement, with nitrogen atoms in the axial positions. The detailed spectrum is reported in table 3-4, and is analogous to the other spectra reported by Nelson.

The spectra of the polymeric forms of the complexes exhibiting solution equilibria may be interpreted in terms of \( D_{4h} \) symmetry. The bands at 7.5 K.K. and 8.75 K.K. in Ni(IPBH)\(_2\) can be assigned to the split components of \( \Psi_1 \); the band at 12.20 is very weak and probably spin forbidden. The broad absorption from 14.00 to 17.00 K.K. is probably \( \Psi_2 \), and \( \Psi_3 \) would be obscured by the strong charge transfer band. No split of \( \Psi_2 \) is observable in either solid or solution, however the weak absorption \( \Psi_2 \) is found at the tail of the relatively strong monomer absorption which makes resolution in solution difficult (c.f. table 3-1 and fig. 3-1).
Table 3-4. The Spectra of Some Known Tetragonally Distorted Nickel Complexes. Maxima are in K.K.

Data from references 13 and 16.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solid Chloroform</th>
<th>Chloroform</th>
<th>Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiPy(_4)Cl(_2)</td>
<td>25.6</td>
<td>15.8</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>25.5 (12.5), 15.82 (5.5) - 14.0 sh, 12.6 w, 10.9, 8.5 (5.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(β-picoline)(_4)Cl(_2) solid</td>
<td>25.30</td>
<td>15.75</td>
<td>14.30 sh</td>
</tr>
<tr>
<td></td>
<td>25.90 (12.5), 15.70 (5.0) - 14.0 sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.60 w, 11.6 - 10.5, 8.4 (5.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni[3-A-Len N(CH(_3)](_2)] solid</td>
<td>17.40 sh, 13.30, 11.90, 9.10, 7.50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3-4 (ii) High Spin Five Coordinated Nickel Complexes

If association occurs through a sharing of oxygen atoms, then five coordinated nickel atoms are a possibility in the polymer structure. The spectra of some five coordinated nickel complexes are presented in table 3-5. The first such complex Ni(5-Cl-SA Len NEt\(_2\))\(_2\) formed from the Schiff base 5-Cl-C\(_6\)H\(_3\)(OH).CH=N(CH\(_2\)]\(_2\) N(C\(_2\)H\(_5\)] was described by Sassone,\(^{17,18}\) and the diffuse reflectance spectrum showed bands at c.a. 7.70 m, 9.50 w, 12.70 sh and 16.50 K.K., which were assigned to the transitions from the \(^3\)B\(_1\) ground state to the excited states, \(^3\)E, \(^3\)A\(_2\), \(^3\)B\(_2\) and \(^3\)E respectively, derived from the \(^3\)F state of the free ion. The energy states of the five coordinated nickel atom have been discussed by Ciampolini\(^{19}\) in terms of possible square pyramidal or trigonal bipyramidal stereochemistry.

Ni(5-Cl-SA Len NEt\(_2\))\(_2\) has been recognised through X-ray analysis studies to be five coordinate in which the nickel atom is surrounded by five atoms, 3N and 2O, in a distorted square pyramidal arrangement.\(^{17,18}\)
Physical measurements indicate that \( \text{Ni(Tren.Me.Cl)} \text{Cl} \), where Tren.Me is \( N[\text{CH}_2\text{CH}_2\text{N}({\text{CH}_3})_2]_3 \), is a five coordinate complex in which the stereochemical requirements of the ligand suggest trigonal bipyramidal stereochemistry.\(^{20}\) \( \text{Ni(H-SA Len NBT}_2\) (catec)\), where one salicylaldimine molecule has been replaced by a molecule of catechol, exists as a dimer, with each nickel surrounded by a distorted trigonal bipyramidal array of 30 and 2N atoms.\(^{21}\) Included in the table is the spectrum of \( \text{Ni(Me-sal)}_2 \) which has a trigonal bipyramidal configuration.\(^{22}\) when it is the guest in the lattice of the zinc analogue whose structure has been determined by X-ray analysis.\(^{23}\)

**Table 3-5 - The Spectra of Some Five Coordinated Nickel Complexes.**

Maxima are in K.K.

Data from references 17, 18, 20, 21 and 22.

\[
\begin{align*}
(5-\text{Cl-SA Len NBT}_2\) \text{Ni}^{\infty} & \text{ reflectance spectrum,} \quad 16.50, \quad 12.70 \text{ w}, \quad 9.50 \text{ w}, \\
& \text{ 7.70 m}
\end{align*}
\]

\[
\begin{align*}
(X-\text{SA Len NBT}_2\) \text{ (catec)Ni}^{**} & \text{ reflectance spectrum,} \quad \lambda_4.0, \quad 11.30 \text{ sh}, \\
& \text{ 9.70 w}, \quad 6.70 m
\end{align*}
\]

\[
\text{Ni(Tren.Me.Cl)}^{+} \text{ reflectance spectrum,} \quad 23.3, \quad 20.0 \text{ sh}, \quad \lambda_4.6, \\
& \text{ 11.5 sh - 10.7, 7.1}
\]

\[
\begin{align*}
\text{chloroform,} \quad 23.5 \text{ (17.2)}, \quad 20.6 \text{ sh}, \quad \lambda_4.9 \text{ (30),} \\
& 11.6 \text{ (19.0) - 10.9 (22.0), 7.1 (26)}
\end{align*}
\]

\[
\begin{align*}
\text{Ni(Me-sal)}_2 \text{ reflectance spectrum,} \quad 20.4 \text{ sh}, \quad \lambda_4.4, \quad 11.8 \text{ sh}, \\
& \text{ 9.1, 7.3}
\end{align*}
\]

* This spectrum may be taken as typical of the 3-CH\(_3\), 5-CH\(_3\), 5-ethyl and 5-NO\(_2\) complexes which are all five coordinated.

** The absorptions quoted are typical for \( \mathbf{X} = \mathbf{H, 5-Cl, 5-Br or 3,4-benzo.} \)

+ A typical spectrum chosen from a series of such complexes reported in reference 20.
The spectra of the five coordinated complexes cited above are similar to the spectra of the polymers discussed in this section (c.f. table 3-1). Polymerisation via an oxygen sharing process, see Chapter 5, would result in the five coordinated nickel atoms having three oxygen and two nitrogen atoms in their inner coordination sphere and a resultant crystal field and spectrum similar to that of Ni(H-SA Len NeEt₂)₂(catse).

In concluding, the overall spectrum (30-5 K.K.) is compatible with nickel in a tetragonal or penta-coordinate environment and may well be ascribed to a superimposition of the two.

3-5 THE APPARENT LIGAND FIELD STRENGTH OF N-ISOPROPYIDENE-N'-BENZOYL-HYDRAZINE IN [Ni(IPBH)₂]

The break-down of the polymeric unit in the presence of donor molecules (e.g. water, ethanol and pyridine) has been demonstrated by Thong. ³ The spectra of the solvated complexes are typical of octahedral complexes and have been discussed previously. Changes in ligand field are observed on solvation and an examination of ν₁, table 3-6, reveals that the average ligand field strengths lie in the order,

Ni(IPBH)₂₂Py > Ni(IPBH)₂₂H₂O > Ni(IPBH)₂₂EtOH > [Ni(IPBH)₂]n > Ni(H₂O)₆²⁺

Spectral observations on the complex Cu(IPBH)₂(ClO₄)₂ suggest that IPBH lies between water and ammonia in the spectrochemical series ²¹ and hence the observation that the average ligand field strength of the ethanolate and hydrate are greater than IPBH in [Ni(IPBH)₂]n does at first seem surprising. However, an analogous system has been reported in the literature. Bis(acetylacetonato) nickel II is known to exist as trimer in both the solid state and in solution. ²⁰,²⁵ Some selected spectral data
for \([\text{Ni(AA)}_2]_3\) and its addducts are reported in table 3-6 whence it is evident that the average ligand field strength observed here is, 
\[\text{Ni(AA)}_2 2\text{Py} > \text{Ni(AA)}_2 2\text{H}_2\text{O} > [\text{Ni(AA)}_2]_3 > \text{Ni(H}_2\text{O)}_6^{2+}.\] The ligand field exerted by acetylacetone in \([\text{Ni(AA)}_2]_3\) is similar to that of water.

A Gaussian analysis on the monomeric bis-(acetylacetonato) copper II complex in 1-pentanol,\(^{27}\) and on \(\text{CuSO}_4\cdot\text{5H}_2\text{O}\)\(^{28}\) has proved that acetylacetone does in fact exert a stronger ligand field than water. The apparent decrease in ligand field strength in the case of \([\text{Ni(AA)}_2]_3\) has been attributed to the specific configuration of the nickel complex.\(^{29}\) The small nickel-nickel distance in the trimer implies some degree of nickel-nickel interaction. Interaction of filled \(t_{2g}\) orbitals of the nickel atoms should lead to a decreased stability of the \(t_{2g}\) orbital and an increased stability of the \(e_g\) orbital, thus producing a smaller ligand field split. Consequently break-down of the polymer structure through coordination with solvent molecules should lead to an increased splitting of the \(e_g\) and \(t_{2g}\) levels and an increase in the average ligand field. The anomalous ligand field strength of IPBH in its nickel complex is probably analogous to the \([\text{Ni(AA)}_2]_3\) situation and a direct consequence of the structure of the polymer.

<table>
<thead>
<tr>
<th>Table 3-6</th>
<th>Selected Absorption Bands in K·K.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ni(IPBH)}_2) in benzene</td>
<td>(7.4)</td>
</tr>
<tr>
<td>(\text{Ni(IPBH)}_2) benzene-ethanol</td>
<td>(9.10)</td>
</tr>
<tr>
<td>(\text{Ni(IPBH)}_2) in H(_2)O</td>
<td>(10.0)</td>
</tr>
<tr>
<td>(\text{Ni(IPBH)}_2) 2Py</td>
<td>(10.55)</td>
</tr>
<tr>
<td>(\text{Ni(H}_2\text{O)}_6)</td>
<td></td>
</tr>
</tbody>
</table>
REFERENCES

    Acta Crys., 10, 784 (1957).
CHAPTER 4

THE EVALUATION OF EQUILIBRIUM CONSTANTS FOR THE
ASSOCIATION OF BIS-[N-ISOPROPYLDENE-N'-BENZOYLHYDRAZINO]
NICKEL II IN BENZENE

4.1 INTRODUCTION

Solutions of the complex in weakly coordinating solvents may be
-described by the equilibria

\[ A_1 \xrightarrow{k_1} \frac{1}{2} A_2 \xrightarrow{k_2} \frac{1}{3} A_3 \xrightarrow{k_3} \frac{1}{4} A_4 \quad \ldots \ldots \text{etc.} \]

where \( A_1 \) is the monomeric unit \( \text{Ni(IPBH)}_2 \),
\( A_2 \) is the dimer \( [\text{Ni(IPBH)}_2]_2 \) and so on,
and \( k_1, k_2, k_3 \) etc. are the equilibrium constants for the successive
association steps. Let \( A_T \) be the total concentration of monomer units,
such that,

\[ A_T = A_1 + 2A_2 + 3A_3 + \quad \ldots \ldots \text{etc.} \]

where \( A_1, A_2, A_3 \) etc. are the molar concentrations of monomer, dimer and
trimer respectively and let \( \epsilon_1, \epsilon_2, \epsilon_3, \) etc. be the molar extinction
coefficients of the species \( A_1, A_2 \) and \( A_3 \) etc. at a given wavelength.

Now, \( D = \epsilon_1 A_1 + \epsilon_2 A_2 + \epsilon_3 A_3 + \ldots \ldots \text{etc.} \)

where \( D \) is the measured optical density at the given wavelength and

\( \epsilon m A_T = \epsilon_1 A_1 + \epsilon_2 A_2 + \epsilon_3 A_3 + \ldots \ldots \text{etc.} \)

where \( \epsilon m \) is the extinction coefficient per mole of total monomer, \( A_T \).

Hence-forth the quantities defined above, such as \( \epsilon m \) and \( A_T \) will
be used without any further explanation.
4-2 The Dependence of the Average Molecular Weight and the Spectrum of the Associating System on Concentration - An Estimate of \( k_1 \) and \( k_2 \) in Benzene

4-2 (i) Data

Table 4-1 shows \( \epsilon_m \) and \( \Lambda_T \) values at 7,46 K.K. for \( \Lambda_T \) values ranging from 0.500 to 6.75 \( \times \) \( 10^{-2} \) M. Solutions of the complex Ni(II)OH in dry A.R. benzene, were prepared and handled under moisture free conditions, see 6-3 (ii) (a), and optical density measurements performed with a Shimadzu spectrophotometer, type Q.R. 50, using matched stoppered silica cells. Isosbestic molecular weight determinations, performed with the rigorous exclusion of moisture at 25.0°C, see 6-3 (iii), are shown in table 4-2 for \( \Lambda_T \) concentrations ranging from 0.800 to 11.0 \( \times \) \( 10^{-2} \) M. Molecular weights and the corresponding \( \Lambda_T \) values are tabulated in table 4-2. Thus the degree of association lies between 1.5 and 2.5. The concentration range over which the spectrum was studied was not extended to cover the range of molecular weight measurements, owing to the difficulty in effecting dissolution of these quantities of complex, with the preparative technique used to exclude moisture from these solutions, and to the increase of the optical density beyond the accurate range of the instrument.

4-2 (ii) Analysis of Data

4-2 (ii) (a) Preliminary Observations

1. It was assumed that only monomer, dimer and trimer co-exist over the range of spectral measurements, viz. 0.5 \( \times \) \( 10^{-2} \) \( < \) \( \Lambda_T < 6.75 \) \( \times \) \( 10^{-2} \) M. This assumption has a two-fold basis, firstly a mixture of these species can explain the molecular weights and secondly, a study of the spectrum dependance on concentration, fig. 4-1, using the S.P. 700 recording
spectrophotometer reveals an isosbestic point at 15.75 K.K. and an approximate isosbestic in the region 21.3-21.7 K.K. This suggests the presence of more than two species, two of which may have nearly equal extinctions per unit at the former wavelength but different extinctions at the latter. This would be consistent with the \( \alpha_2 \) and \( \alpha_3 \) species having the same absorptions on the d-d region of the spectrum but different from each other and from the monomer in the charge transfer region.

Hence

\[
\alpha_T = \alpha_1 + 2\alpha_2 + 3\alpha_3 \quad \cdots \quad (1)
\]

and

\[
\epsilon_m\alpha_T = \epsilon_1\alpha_1 + \epsilon_2\alpha_2 + \epsilon_3\alpha_3 \quad \cdots \quad (2)
\]

2. Optical density measurements on solutions which might reasonably be expected to contain pure monomer, at concentrations less than \( 10^{-3} \) M, using 5 cm cells, showed that the monomer does not absorb at 7.46 K.K.

i.e.

\[
\epsilon_1 = 0
\]

substituting in (2) gives,

\[
\epsilon_m\alpha_T = \epsilon_2\alpha_2 + \epsilon_3\alpha_3 \quad \cdots \quad (3)
\]

3. The \( \alpha_T \) versus \( \epsilon_m \) curve, fig. 4-2, approaches a limiting value of \( \epsilon_m \) for \( \alpha_T \) 5.0 \( \times \) \( 10^{-2} \) M, over which concentration range the molecular weight curve, fig. 4-3, is still rising steadily. These observations can be explained by the assumption that,

\[
\frac{\epsilon_2}{\epsilon_3} = \frac{2}{3}
\]

or if \( \epsilon' \) is defined as the extinction coefficient per monomer unit,

\[
\epsilon_2 = 2\epsilon',
\]

\[
\epsilon_3 = 3\epsilon'
\]

and (3) gives

\[
\epsilon_m\alpha_T = 2\alpha_2\epsilon' + 3\alpha_3\epsilon' \quad \cdots \quad (4)
\]
Table A-1 - The Dependence of $\epsilon_m$ at 7.6 K.K. on $A_T$ for Ni(IPBH)$_2$ in Benzene. Temperature 25.0°C

<table>
<thead>
<tr>
<th>$A_T \times 10^{-2}$ M</th>
<th>$\epsilon_m$ (7.6 K.K.)</th>
<th>$A_T \times 10^{-2}$ M</th>
<th>$\epsilon_m$ (7.6 K.K.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3725</td>
<td>8.6</td>
<td>2.142</td>
<td>16.91</td>
</tr>
<tr>
<td>0.4861</td>
<td>9.67</td>
<td>3.351</td>
<td>17.70</td>
</tr>
<tr>
<td>0.7207</td>
<td>11.58</td>
<td>3.967</td>
<td>18.15</td>
</tr>
<tr>
<td>0.9795</td>
<td>12.86</td>
<td>5.166</td>
<td>18.55</td>
</tr>
<tr>
<td>1.324</td>
<td>14.69</td>
<td>6.753</td>
<td>18.66</td>
</tr>
<tr>
<td>1.628</td>
<td>15.24</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A-2 - The Apparent Molecular Weight of Ni(IPBH)$_2$ in Benzene at 25.0°C as a Function of Concentration

<table>
<thead>
<tr>
<th>$A_T \times 10^{-2}$ M</th>
<th>Molecular Weight</th>
<th>$A_T \times 10^{-2}$ M</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>635</td>
<td>5.58</td>
<td>932</td>
</tr>
<tr>
<td>1.025</td>
<td>735</td>
<td>7.54</td>
<td>990</td>
</tr>
<tr>
<td>1.376</td>
<td>743</td>
<td>8.95</td>
<td>1002</td>
</tr>
<tr>
<td>1.80</td>
<td>750</td>
<td>11.05</td>
<td>1031</td>
</tr>
<tr>
<td>4.1</td>
<td>885</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 4-1. THE SPECTRUM OF Ni(IPBH)₂ IN BENZENE AT DIFFERENT CONCENTRATIONS (A₀).

- 0.1665 × 10⁻² M
- 0.4861 × 10⁻² M
- 1.3420 × 10⁻² M
- 2.2480 × 10⁻² M

εₘ

23 22 21 20 19 18 17 16 15
cm⁻¹ × 10⁻³
FIGURE 4-2. THE DEPENDENCE OF $\varepsilon_M$ ON $A_T$, AT 7.46 KK.
Figure 4-3. The average molecular weight of Ni(IPBH)$_2$ in benzene at 25.0°C as a function of $A_T$. 

![Graph showing the average molecular weight as a function of $A_T$]
FIGURE 4-4. $\epsilon_M$ VERSUS THE RECIPROCAL OF $A_T$. 

$\epsilon_M$ 

$10^2$ 

$A_T$
4-2 (ii) (b) The Evaluation of $\varepsilon'$

1. The dependance of $\varepsilon_m$ on $A_T$.

A plot of $\varepsilon_m$ versus $1/A_T$ is shown in fig. 4-4. The two points of highest concentration, provide a break in the smooth curve; possible explanations for this will be mentioned later. No estimate of $\varepsilon'$ can be obtained from the plot of $\varepsilon_m$ against $A_T$, or its reciprocal other than $\varepsilon' > 18.75$.

2. The Relationship between $A_1$ and $A_T$.

The equilibrium relationships

$$k_1 [A_1]^2 = [A_2]$$
$$k_2 [A_1] [A_2] = [A_3]$$

and $A_T = A_1 + 2A_2 + 3A_3$

gives $A_T = A_1 + 2k_1A_1^2 + 3k_2k_3A_1^3$ .....(5)

3. The Relationship between $A_1$, $A_T$ and $\varepsilon'$

Combining (4) and (1) gives,

$$\varepsilon_m A_T = \varepsilon' (A_T - A_1)$$

Thus

$$A_1 = A_T \frac{\varepsilon' - \varepsilon_m}{\varepsilon'}$$ .....(6)

$A_1$ values calculated from the formula,

$$A_1 = \frac{\varepsilon' - \varepsilon_m}{\varepsilon'} \cdot A_T$$

Using the experimental quantities $A_T$ and $m$ and assuming $\varepsilon'$ values of 18.70, 20.0, 21.0, 22.0, 23.0 and 24.0, are shown in table 4-3. Plots of $A_1$ versus $A_T$, fig. 4-5, show that the minimum temporary value of $\varepsilon'$ which results in the $A_1$ versus $A_T$ plot having a positive slope at all values of $A_T$ as required by equation (5) above is $\varepsilon' = 21.0$.

i.e. $\varepsilon' > 21.0$
Table 4.3 - The Calculated Free Monomer Concentrations $A_1$ Corresponding to the Experimentally Determined Total Monomer Concentration $A_T$ for a Range of $\epsilon'$ Values

<table>
<thead>
<tr>
<th>$\epsilon'$</th>
<th>18.70</th>
<th>20.0</th>
<th>21.0</th>
<th>22.0</th>
<th>23.0</th>
<th>24.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_T \times 10^{-2}$ M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.725</td>
<td>0.201</td>
<td>0.212</td>
<td>0.220</td>
<td>0.227</td>
<td>0.233</td>
<td>0.239</td>
</tr>
<tr>
<td>4.861</td>
<td>0.234</td>
<td>0.251</td>
<td>0.262</td>
<td>0.273</td>
<td>0.282</td>
<td>0.290</td>
</tr>
<tr>
<td>7.207</td>
<td>0.282</td>
<td>0.311</td>
<td>0.330</td>
<td>0.343</td>
<td>0.364</td>
<td>0.379</td>
</tr>
<tr>
<td>9.795</td>
<td>0.306</td>
<td>0.350</td>
<td>0.379</td>
<td>0.407</td>
<td>0.432</td>
<td>0.455</td>
</tr>
<tr>
<td>13.42</td>
<td>0.287</td>
<td>0.356</td>
<td>0.403</td>
<td>0.446</td>
<td>0.485</td>
<td>0.521</td>
</tr>
<tr>
<td>24.12</td>
<td>0.231</td>
<td>0.373</td>
<td>0.469</td>
<td>0.558</td>
<td>0.638</td>
<td>0.713</td>
</tr>
<tr>
<td>33.51</td>
<td>0.179</td>
<td>0.385</td>
<td>0.526</td>
<td>0.655</td>
<td>0.772</td>
<td>0.879</td>
</tr>
<tr>
<td>39.67</td>
<td>0.117</td>
<td>0.367</td>
<td>0.538</td>
<td>0.694</td>
<td>0.837</td>
<td>0.967</td>
</tr>
<tr>
<td>51.66</td>
<td>0.155</td>
<td>0.375</td>
<td>0.603</td>
<td>0.810</td>
<td>0.999</td>
<td>1.173</td>
</tr>
<tr>
<td>67.53</td>
<td>0.270</td>
<td>0.453</td>
<td>0.752</td>
<td>1.025</td>
<td>1.275</td>
<td>1.503</td>
</tr>
</tbody>
</table>

4. A Second Criterion for $\epsilon'$

Equation (5) reduces to,

$$\frac{A_T - A_1}{A_1^2} = 2k_1 + 3k_1k_2A_1$$

.....(7)

and hence a plot of $A_1$ versus $\frac{A_T - A_1}{A_1^2}$ should result in a straight line, provided the preceding assumptions, viz.

(1) that there are only three species, $A_1$, $A_2$ and $A_3$ present

(2) that $\epsilon' = 0$ and $\epsilon_2 / \epsilon_3 = 2/3$ and
(3) the correct value of \( \epsilon' \) is used to calculate \( \lambda_1 \). Table 4-4 shows \( \lambda_1 \) and \( \lambda_T - \lambda_1 \) values calculated from the experimental quantities \( \lambda_T \) and \( \epsilon_m \) for assumed \( \epsilon' \) values of 21.0, 22.0, 23.0 and 24.0. \( \epsilon' = 22.0 \) and \( \epsilon' = 23.0 \) provide \( \lambda_1 \) versus \( \lambda_T - \lambda_1 \) plots, Fig. 4-6 which more closely resemble a straight line than the \( \epsilon' = 21.0 \) plot, whilst \( \epsilon' = 24.0 \) gives a line with a negative slope at high \( \lambda_T \) values. Hence \( 22.0 \leq \epsilon' < 23.0 \).

In an endeavour to determine \( \epsilon' \) more accurately \( \lambda_1 \) and \( \lambda_T - \lambda_1 \) values were calculated for \( \epsilon' \) values of 22.4, 22.6 and 22.8. Plots of \( \lambda_1 \) versus \( \lambda_T - \lambda_1 \) lend themselves to the following observations.

1. The last point corresponding to \( \lambda_T = 6.753 \times 10^{-2} \) appears to be in error. The most likely source of error lies in the measurement of the high optical density value at this concentration.

2. It is difficult to decide which value of \( \epsilon' \) gives the best straight line. An \( \epsilon' \) value of 22.4 was chosen and a least squares analysis on eight points, neglecting the two points with the highest and the one with the lowest value of \( \lambda_T \), gave a best fit straight line with intercept \( 2k_1 = 53.0 \) l.mole\(^{-1}\) and slope \( 3k_1k_2 = 7.14 \times 10^4 \) l.mole\(^{-2}\). The resulting values of \( \lambda_1 \) and \( \lambda_T - \lambda_1 \) and the graph thereof are shown in Table 4-4 and Fig. 4-7 respectively. The values \( k_1 = 26.5 \) l.mole\(^{-1}\), \( k_2 = 898.2 \) l.mole\(^{-1}\) and \( \epsilon' = 22.4 \) provide a satisfactory reproduction of the experimental \( \lambda_T \) versus \( \epsilon_m \) curve, Fig. 4-3, up to concentrations of about \( 5.0 \times 10^{-2} \) M.
FIGURE 4-5. THE DEPENDENCE OF $A_1$ ON $A_T$ FOR VARIOUS $\epsilon'$ VALUES.
Table 4-14 - $A_1$ and $A_T - A_1$ Values Calculated from $A_T$ and $C_m$ for a Range of $C'$

<table>
<thead>
<tr>
<th>$C'$</th>
<th>21.0</th>
<th>22.0</th>
<th>23.0</th>
<th>24.0</th>
<th>21.0</th>
<th>22.0</th>
<th>23.0</th>
<th>24.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_T \times 10^{-2}$ M</td>
<td>$A_1 \times 10^{-2}$ M</td>
<td>$A_T - A_1 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>0.3725</td>
<td>0.220</td>
<td>0.227</td>
<td>0.229</td>
<td>0.237</td>
<td>0.239</td>
<td>3.151</td>
<td>2.820</td>
<td>2.716</td>
</tr>
<tr>
<td>0.4361</td>
<td>0.262</td>
<td>0.273</td>
<td>0.276</td>
<td>0.282</td>
<td>0.290</td>
<td>3.253</td>
<td>2.877</td>
<td>2.748</td>
</tr>
<tr>
<td>0.7207</td>
<td>0.330</td>
<td>0.348</td>
<td>0.354</td>
<td>0.364</td>
<td>0.379</td>
<td>3.583</td>
<td>3.082</td>
<td>2.913</td>
</tr>
<tr>
<td>0.9795</td>
<td>0.379</td>
<td>0.407</td>
<td>0.417</td>
<td>0.432</td>
<td>0.455</td>
<td>4.163</td>
<td>3.459</td>
<td>3.230</td>
</tr>
<tr>
<td>1.32</td>
<td>0.403</td>
<td>0.416</td>
<td>0.462</td>
<td>0.485</td>
<td>0.521</td>
<td>5.778</td>
<td>4.508</td>
<td>4.127</td>
</tr>
<tr>
<td>1.628</td>
<td>0.447</td>
<td>0.500</td>
<td>0.521</td>
<td>0.549</td>
<td>0.594</td>
<td>5.924</td>
<td>4.512</td>
<td>4.090</td>
</tr>
<tr>
<td>2.41</td>
<td>0.469</td>
<td>0.555</td>
<td>0.591</td>
<td>0.639</td>
<td>0.713</td>
<td>8.801</td>
<td>5.952</td>
<td>5.210</td>
</tr>
<tr>
<td>3.351</td>
<td>0.526</td>
<td>0.655</td>
<td>0.703</td>
<td>0.772</td>
<td>0.879</td>
<td>10.193</td>
<td>6.286</td>
<td>5.358</td>
</tr>
<tr>
<td>3.967</td>
<td>0.538</td>
<td>0.694</td>
<td>0.753</td>
<td>0.837</td>
<td>0.967</td>
<td>11.835</td>
<td>6.767</td>
<td>5.676</td>
</tr>
<tr>
<td>5.166</td>
<td>0.603</td>
<td>0.810</td>
<td>0.888</td>
<td>0.999</td>
<td>1.173</td>
<td>12.552</td>
<td>6.639</td>
<td>5.126</td>
</tr>
<tr>
<td>6.753</td>
<td>0.752</td>
<td>1.025</td>
<td>1.127</td>
<td>1.275</td>
<td>1.503</td>
<td>10.695</td>
<td>5.455</td>
<td>4.317</td>
</tr>
</tbody>
</table>
FIGURE 4-6. THE DEPENDENCE OF $\frac{A_T - A_1}{A_1^2}$ ON $A_1$ FOR VARIOUS $t'$ VALUES.
FIGURE 4-7 THE DEPENDENCE OF $\frac{A_{T}-A_{1}}{A_{1}^{2}}$ ON $A_{1}$ FOR $\epsilon' = 22.4$. 
The constants \( k_1 \) and \( k_2 \) calculated from the spectral data, can be used to construct a molecular weight versus \( A_T \) curve for the system \( M(\text{IPBH})_2 \) in benzene at 25.0°C, fig. 4-9. Comparison with the experimental values shows agreement within the accuracy of the molecular weight determinations (5%) over the entire range of \( A_T \) (0.3 to 0.6 \( \times 10^{-2} \)). Table 4-5 shows the \( A_T \), \( \epsilon_m \) and molecular weight values expected for given \( A_1 \) values.

Additional support for the validity of the foregoing polymer peak analysis, is afforded by an examination of the absorption at 20.4 K.K. which is characteristic of the monomeric species.

4-3 \( \epsilon_m \) AS A FUNCTION OF \( A_T \) AT THE WAVELENGTH CHARACTERISTIC OF MONOMER ABSORPTION

Fig. 4-10 shows the dependence of \( \epsilon_m \) on \( A_T \) at 20.4 K.K. over the concentration range 0.1 \( \times 10^{-2} \) \(< A_T < 5.5 \times 10^{-2} \). Experimental \( \epsilon_m \) and \( A_T \) values are given in table 4-6.

If we assume that the relationship between \( \epsilon_2 \) and \( \epsilon_3 \) assumed in the treatment of the polymer analysis, holds at 20.4 K.K.
then
\[
\epsilon_2 = 2 \epsilon'
\]
\[
\epsilon_3 = 3 \epsilon'
\]
where \( \epsilon' = \epsilon_m \) at high \( A_T \)
and \( \epsilon_1 = \epsilon_m \) at low \( A_T \)
then equation (6) gives us,
\[
( \epsilon_m - \epsilon') A_T = (\epsilon_1 - \epsilon') A_T
\]
or
\[
\frac{A_1}{A_T} = \frac{\epsilon_m}{\epsilon_1 - \epsilon'} - \frac{\epsilon'}{\epsilon_1 - \epsilon'}
\]
Table A-5: $A_n$, $\bar{\epsilon}m$ and Average Molecular Weight for $\text{Ni(IPBH)}_2$ in Benzene calculated for a given value $A_n$ using the Constants $k_1$ and $k_2$ determined in the Polymer Peak Analysis.

<table>
<thead>
<tr>
<th>$A_n \times 10^{-2} M$</th>
<th>$A_T \times 10^{-2} M$</th>
<th>Average Molecular Weight</th>
<th>$\bar{\epsilon}m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.10</td>
<td>.1124</td>
<td>4.37</td>
<td>2.46</td>
</tr>
<tr>
<td>.14</td>
<td>.1700</td>
<td>4.58</td>
<td></td>
</tr>
<tr>
<td>.18</td>
<td>.2388</td>
<td>4.82</td>
<td></td>
</tr>
<tr>
<td>.20</td>
<td>.2783</td>
<td>4.96</td>
<td>6.28</td>
</tr>
<tr>
<td>.24</td>
<td>.3692</td>
<td>5.24</td>
<td></td>
</tr>
<tr>
<td>.28</td>
<td>.4783</td>
<td>5.54</td>
<td></td>
</tr>
<tr>
<td>.30</td>
<td>.5405</td>
<td>5.69</td>
<td>9.93</td>
</tr>
<tr>
<td>.32</td>
<td>.6082</td>
<td>5.85</td>
<td></td>
</tr>
<tr>
<td>.36</td>
<td>.7618</td>
<td>6.16</td>
<td></td>
</tr>
<tr>
<td>.40</td>
<td>.9118</td>
<td>6.48</td>
<td>12.86</td>
</tr>
<tr>
<td>.45</td>
<td>1.208</td>
<td>6.86</td>
<td></td>
</tr>
<tr>
<td>.50</td>
<td>1.525</td>
<td>7.22</td>
<td>15.02</td>
</tr>
<tr>
<td>.55</td>
<td>1.898</td>
<td>7.56</td>
<td></td>
</tr>
<tr>
<td>.60</td>
<td>2.333</td>
<td>7.89</td>
<td>16.6</td>
</tr>
<tr>
<td>.65</td>
<td>2.835</td>
<td>8.19</td>
<td></td>
</tr>
<tr>
<td>.70</td>
<td>3.409</td>
<td>8.47</td>
<td>17.80</td>
</tr>
<tr>
<td>.75</td>
<td>4.060</td>
<td>8.72</td>
<td></td>
</tr>
<tr>
<td>.80</td>
<td>4.779</td>
<td>8.90</td>
<td>18.65</td>
</tr>
<tr>
<td>.85</td>
<td>5.560</td>
<td>9.19</td>
<td></td>
</tr>
<tr>
<td>.90</td>
<td>6.491</td>
<td>9.39</td>
<td>19.30</td>
</tr>
<tr>
<td>.95</td>
<td>7.577</td>
<td>9.56</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>8.670</td>
<td>9.75</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 4-8. THE CALCULATED $\epsilon_M$ AT CURVE FOR Ni(IPBH)$_2$ IN BENZENE. THE CIRCLED PLOTS ARE THE EXPERIMENTAL VALUES.
FIGURE 4-9 THE THEORETICAL $A_T$ VERSUS MOLECULAR WEIGHT PLOT.

Experimental values are circled.
Table 4-6 - $A_T$ and $\epsilon_m$ values for Ni(II)BF$_4$ at 204 K K.

<table>
<thead>
<tr>
<th>$A_T \times 10^{-2}$ M</th>
<th>$\epsilon_m$</th>
<th>$A_T \times 10^{-2}$ M</th>
<th>$\epsilon_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.134</td>
<td>99.20</td>
<td>0.9738</td>
<td>56.48</td>
</tr>
<tr>
<td>0.1572</td>
<td>97.32</td>
<td>1.506</td>
<td>47.79</td>
</tr>
<tr>
<td>0.1665</td>
<td>94.91</td>
<td>2.073</td>
<td>42.73</td>
</tr>
<tr>
<td>0.3724</td>
<td>80.30</td>
<td>2.695</td>
<td>37.84</td>
</tr>
<tr>
<td>0.4224</td>
<td>77.39</td>
<td>5.408</td>
<td>13.07</td>
</tr>
<tr>
<td>0.4460</td>
<td>74.66</td>
<td>5.496</td>
<td>12.47</td>
</tr>
</tbody>
</table>

Provided the correct values of $A_1$ are used the plot of $A_1/A_T$ versus $\epsilon_m$, should result in a straight line. The required $A_1$ values were obtained by a graphical solution of equation (5), using the values for $k_1$ and $k_2$ determined in 4-2 (ii). The plot of $A_1/A_T$ versus $\epsilon_m$ is shown in fig. 4-11 and the corresponding data in table 4-7, as can be seen, the plot is linear, from which by extrapolation,

$$\epsilon_m = 113.0$$

$$\epsilon' = 16.0$$
FIGURE 4-10  THE DEPENDENCE OF $\varepsilon_M$ ON $A_T$, AT 20.4 KK

$\varepsilon_M$ vs. $A_T \times 10^{-2}$ Molar
FIGURE 4-11. $\frac{A_1}{A_T}$ AGAINST $\varepsilon_M$ AT 20.4 KK

$A_1$ values were calculated from $k_1$ and $k_2$ determined in the polymer peak analysis.
Table 4-7 - $A_T$, $A_1$ and $A_1/A_T$ values for the Monomer Peak Analysis.

$A_1$ values were calculated from $k_1$ and $k_2$ determined from the Polymer Peak Analysis.

<table>
<thead>
<tr>
<th>$A_T \times 10^{-2} M$</th>
<th>$A_1 \times 10^{-2} M$</th>
<th>$A_1/A_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.134</td>
<td>0.118</td>
<td>0.877</td>
</tr>
<tr>
<td>0.1572</td>
<td>0.134</td>
<td>0.851</td>
</tr>
<tr>
<td>0.1665</td>
<td>0.114</td>
<td>0.844</td>
</tr>
<tr>
<td>0.3724</td>
<td>0.238</td>
<td>0.638</td>
</tr>
<tr>
<td>0.4224</td>
<td>0.255</td>
<td>0.604</td>
</tr>
<tr>
<td>0.4460</td>
<td>0.263</td>
<td>0.588</td>
</tr>
<tr>
<td>0.9738</td>
<td>0.415</td>
<td>0.426</td>
</tr>
<tr>
<td>1.506</td>
<td>0.495</td>
<td>0.329</td>
</tr>
<tr>
<td>2.073</td>
<td>0.556</td>
<td>0.268</td>
</tr>
<tr>
<td>2.695</td>
<td>0.620</td>
<td>0.230</td>
</tr>
<tr>
<td>5.408</td>
<td>0.906</td>
<td>0.168</td>
</tr>
<tr>
<td>5.96</td>
<td>0.915</td>
<td>0.167</td>
</tr>
</tbody>
</table>

4-4. EVALUATION OF $\Delta G^0$ AT 25.0°C FOR THE REACTION $3 \text{Na(IPBH)}_2 \rightarrow [\text{Na(IPBH)}_2]_3$

IN BENZENE

The free energy change for a chemical reaction is given by,

$$\Delta G^0 = -RT \ln K$$

where

- $R$ is the gas constant
- $T$ is the absolute temperature

and

- $K$ is the equilibrium constant.

At 25.0°C for the reaction

$$2 \text{Monomer} \rightleftharpoons \text{Dimer}$$
where \[ k_1 = 26.5 \text{ l.mole}^{-1} \]
\[ \Delta G^0 = -1.94 \text{ K.Cal.mole}^{-1}. \]

At 25.0°C for the reaction

\[ \text{Monomer} + \text{Dimer} \xrightarrow{k_2} \text{Trimer} \]

where \[ k_2 = 898.0 \text{ l.mole}^{-1} \]
\[ \Delta G^0 = -4.03 \text{ K.Cal.mole}^{-1}. \]

At 25.0°C for the overall reaction

\[ 3 \text{ Monomer} \xrightarrow{K} \text{Trimer} \]

where \[ K = k_1k_2 \]
\[ = 2.38 \times 10^4 \text{ l.mole}^{-2} \]
\[ \Delta G^0 = -5.97 \text{ K.Cal.mole}^{-1}. \]

Cotton and Fackler have reported \[ \Delta F = -5.7 \text{ K.Cal.mole}^{-1} \] at 25.0°C for the reaction

\[ 3 \text{ Ni(DIBM)}_2 = [\text{Ni(DIBM)}_2]_3 \]

where \( \text{Ni(DIBM)}_2 \) is bis-(2,6-dimethyl3,5-heptanediono) nickel II.

4.5 MISCELLANEOUS MEASUREMENTS

4.5 (1) The Effect of Temperature on Association

A series of spectra of \( \text{Ni(IPBH)}_2 \) in chlorobenzene were determined over the range 28.0 to 64.0 K.K. at temperatures of 25.80°C, 29.60°C, 37.55°C and 45.90°C. Between four and six solutions of different concentration were examined at each temperature. The \( \epsilon_m \) (20.4 K.K.) versus \( A_T \) plots at these four temperatures are shown in fig. 4-12, the experimental \( \epsilon_m \) and \( A_T \) data is given in table 4-8. However it was not possible to evaluate \( k_1 \) and \( k_2 \) at different temperatures using the procedure successfully employed with solutions of the complex in benzene.
The measurements illustrate qualitatively that the higher the temperature, the lower the association which is in accord with increasing temperature favouring dissociation because of a favourable entropy change, i.e. ΔS° is positive for the reaction

\[ \text{[Ni(IPBH)_2]}_n \rightleftharpoons n \text{Ni(IPBH)_2} \]

4-5 (ii) The Effect of Solvent on Association

Comparison of figs. 4-9, which shows \( C_m (20.6 \text{ K.K.}) \) versus \( A_T \) for Ni(IPBH)_2 at 25.0°C in benzene, with fig. 4-12, the \( C_m (20.4 \text{ K.K.}) \) versus \( A_T \) plot in chlorobenzene at 25.8°C, shows that if the monomeric species has the same limiting extinction coefficient in both solvents, then chlorobenzene favours the formation of the monomer relative to benzene. Similarly an estimate of the monomer concentration at 25.80°C in chlorobenzene, based on experimental \( C_m (7.45 \text{ K.K.}) \), \( A_T \) values, and an assumed \( C' = 22.4 \) gives values which although not in agreement with the corresponding monomer analysis, are also higher than the percentage of monomer in a benzene solution of the same concentration.

Thong has examined the spectrum of Ni(IPBH)_2 in chloroform at 25.0°C for a range of \( A_T \). Comparison with the spectral data obtained in benzene leads to the same conclusion reached above, viz. that the \( C' \) values for the individual species are different from those in benzene, or that formation of the monomer is favoured in chloroform relative to benzene. Thus it appears that the nature of the solvent affects the overall composition of the equilibrium mixture. Further discussion as to the effect of solvent on the equilibrium is presented in section 5-3.
4-5 (iii) Apparent Molecular Weights in the Ni(MEKBH)$_2$ Benzene System

Molecular weight determinations at 25.0°C using the isopiestic method for the complex Ni(MEKBH)$_2$ in benzene, indicate that the increase in association with increasing concentration follows a very similar pattern to Ni(IP$_2$BH)$_2$ and the equilibria in solution are probably very similar.

Table 4-9 gives the experimentally determined values of molecular weight for Ni(MEKBH)$_2$ in benzene, and fig. 4-13, the average molecular weight versus $A_T$ plot. Probably the apparent molecular weight at a given $A_T$ is slightly higher for Ni(MEKBH)$_2$ than Ni(IP$_2$BH)$_2$.

Table 4-8 - $C_m$ and $A_T$ values for Ni(IP$_2$BH)$_2$ in Chlorobenzene over a range of temperatures. Wavelength = 20.4 K.K.

<table>
<thead>
<tr>
<th>$A_T \times 10^{-2} M$</th>
<th>25.30°C</th>
<th>29.60°C</th>
<th>37.55°C</th>
<th>45.90°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.885</td>
<td>45.75</td>
<td>49.21</td>
<td>57.40</td>
<td>67.48</td>
</tr>
<tr>
<td>2.670</td>
<td>46.44</td>
<td>49.82</td>
<td>58.51</td>
<td>68.17</td>
</tr>
<tr>
<td>2.022</td>
<td>50.44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.738</td>
<td>52.37</td>
<td>56.39</td>
<td>65.09</td>
<td>73.41</td>
</tr>
<tr>
<td>0.9219</td>
<td>67.25</td>
<td>71.48</td>
<td>78.34</td>
<td>84.72</td>
</tr>
<tr>
<td>0.3228</td>
<td>80.54</td>
<td>83.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4-9 - The Average Molecular Weight of Ni(MEKBH)$_2$ in Benzene at 25.0°C as determined by the Isopiestic Method

<table>
<thead>
<tr>
<th>$A_T \times 10^{-2} M$</th>
<th>Average Molecular Wt.</th>
<th>$A_T \times 10^{-2} M$</th>
<th>Average Molecular Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.03</td>
<td>64.7</td>
<td>7.17</td>
<td>960</td>
</tr>
<tr>
<td>4.58</td>
<td>865</td>
<td>7.54</td>
<td>1020</td>
</tr>
<tr>
<td>6.91</td>
<td>987</td>
<td>8.57</td>
<td>1030</td>
</tr>
</tbody>
</table>
FIGURE 4-12. THE DEPENDENCE OF $\varepsilon_M$ ON $A_T$ FOR THE COMPLEX Ni(IPBH)$_2$ IN CHLOROBENZENE. WAVELENGTH 20.4 KK.

$T = 45.90^\circ C$
$T = 37.55^\circ C$
$T = 29.60^\circ C$
$T = 25.80^\circ C$
FIGURE 4-13. THE DEPENDENCE OF THE AVERAGE MOLECULAR WEIGHT OF Ni(MEKBH)$_2$ IN BENZENE ON $A_T$.

Temperature 25.0°C

Average Molecular Weight

$A_T \times 10^{-2}$ Molar
Mathematical analysis of the absorption band at 7.46 K.K. spectral data was possible because of the coincidence that $\epsilon_2 : \epsilon_3 = 2 : 3$. Proof that this analysis is correct, is provided by the fact that the constants $k_1$ and $k_2$ so determined, can explain both the experimental molecular weight curve and the spectral data from the band at 20.4 K.K. The assumption that $\epsilon_2 : \epsilon_3 = 2 : 3$ is not as important in the "latter" analysis because in this case $\epsilon_1 > \epsilon_2$ or $\epsilon_3$.

The fact that the $\epsilon m$ versus $A_T$ curve at 7.46 K.K. comes to a limit a little before the theoretical curve, i.e. the $\epsilon m$ versus $A_T$ curve constructed from the constants $k_1$ and $k_2$, may mean that the assumption that $\epsilon_2 : \epsilon_3 = 2 : 3$ is not entirely correct and that $\epsilon_2 / \epsilon_3$ is slightly greater than $\epsilon_2 / \epsilon_3$. If this is the case then $[A_3]$ would have been underestimated in the calculated curve.

An underestimation of $[A_3]$ might also be the explanation for the calculated molecular weight versus $A_T$ curve, lying below the experimental molecular weights, at high $A_T$. 
REFERENCES


CHAPTER 5

CONCLUSIONS

5-1 GENERAL REMARKS

A series of nickel complexes with the ligands resulting from the condensation of benzoylhydrazine or substituted benzoylhydrazines with aldehydes and ketones has been examined, the members of which can be divided into two classes.

A those which exist as four coordinate square complexes and were identified through spectral and magnetic measurements

B complexes which can be isolated in two isomeric forms, a red diamagnetic square planar species and a green paramagnetic species, in which the nickel ion has achieved quasi-octahedral coordination via a process of association.

Complexes of class B display equilibria between monomeric and associated species in solutions of non-coordinating solvents. An analysis of the behaviour of Ni(IPBH)₂ in benzene, as exemplified in spectral and molecular weight measurements, over the concentration range 10⁻² to 10⁻¹ molar, is consistent with the existence of monomers, dimers and trimers and the equilibrium constants for the two associative steps have been evaluated. Molecular weights of Ni(IPBH)₂ and Ni(MKKBH)₂ in benzene at 25.0°C show no sign of approaching a limiting value; at limiting solubility (ca. 12 x 10⁻² molar) the average molecular weight corresponds to about 2½ monomer units and there is no reason to suppose that higher oligomers may not exist in more concentrated solutions in other solvents (e.g. chloroform).

Association arises from the tendency of the nickel atom to have
coordination number greater than four and presumably arises from a sharing of oxygen atoms. The tendency for hexa-coordination is also evident in the ready formation of dipyridinates and dihydrates. Spectral and magnetic data are consistent with the nickel atom in Ni(IPINH)$_2$ having six donor atoms in the inner coordination sphere; in addition Ni(IPINH)$_2$ does not form a pyridinate, even on boiling with pyridine. Presumably the heterocyclic nitrogen coordinates to the nickel atom of an adjacent molecule, as simple considerations of molecular structure preclude the function of IPINH as a tridentate.

5-2 THE EFFECT OF $R_1$, $R_2$ AND $X$ ON STEREOCHEMISTRY

Variation of $R_1$, $R_2$ and $X$, (i) has led to the conclusion that polymerisation is a consequence of the steric and electronic properties of these variables.

(i)

Apart from the steric effect of substituents, the electronic nature of $R_1$, $R_2$ and $X$, exerts a marked effect on the tendency for association. Table 5-1, which summarizes the variation of $X$, $R_1$ and $R_2$ studied in this section, and also some work of Ohta's, lends itself to the following observations.

All ligands prepared by condensing benzoylhydrazine with aldehydes
give rise to square planar complexes. Thong\textsuperscript{2} has prepared the complex (N-acetaldehyde-N\textsuperscript{1}-benzoylhydrazino) nickel II and has concluded that the complex is square planar and maintains its planarity in solutions of non-coordinating solvents. A molecular weight determination at 25.0°C, in benzene, performed by the present author, has revealed that the complex still exists as the monomer at a concentration of 8.0 x 10\textsuperscript{-2} moles/litre.

Ligands formed by the condensation of benzoylhydrazine and a ketone, i.e. $X = H$ and $R_1$ and $R_2$ are straight chain alkyl groups, give nickel complexes which exhibit solution equilibria phenomena.

Likewise, the isopropylidene derivatives of substituted benzoylhydrazines, where $X$ is an electron releasing group, such as methyl, give nickel complexes which exhibit solution equilibria, whereas a strongly electron withdrawing $X$ group, such as NO\textsubscript{2} gives rise to square planar nickel complexes. $\text{Mn}(\text{IPm-NO}_2\text{BH})_2$ and $\text{Mn}(\text{IPp-NO}_2\text{BH})_2$ have only been prepared as brown diamagnetic solids, but their insolubility in non-coordinating solvents makes it impossible to say with absolute certainty that they cannot polymerise.

In general it appears that when $R = H$, or $X$ an electron withdrawing group such as $-\text{NO}_2$, only square planar complexes are formed, whilst if both $R_1$ and $R_2$ are alkyl groups or $X$ an electron donor such as methyl, the complex will polymerise and an equilibrium between monomeric and associated species exists in non-coordinating solvents.

Electron withdrawing $X$ (e.g. NO\textsubscript{2}) and $R$, (e.g. H as compared to alkyl groups), cause stabilisation of the four coordinate structure, possibly by facilitating back coordination from metal to ligand. Double bond formation is an important mechanism in stabilising square planar
complexes and enables the nickel atom to decrease some of the negative charge which would result from the formation of coordinate σ bonds by use of the 3 d electron pairs of the nickel atom and a vacant p orbital of the ligand. All attempted preparations of \( \text{Ni(IPp-ClBH)}_2 \) and \( \text{Ni(IPm-ClBH)}_2 \) resulted in products which did not analyse satisfactorily and which were deliquescent. These products readily yielded the pure dipyridinates and were also observed to change colour from green to red on heating under vacuum, the colour change being reversed on cooling. The change of colour which was also observed in benzene solution suggests that the pure complexes can polymerise and exhibit monomer-polymer equilibrium in solution. The \( X \) group, \( \text{Cl} \), is mildly electron withdrawing, whilst \( R_1 = R_2 = \text{methyl} \) are electron donating groups, hence the electron density at the donor \( N \) and \( O \) atoms has not been reduced sufficiently to favour exclusively the formation of a square planar complex.

The electronic effect of the heterocyclic nitrogen atom in \( \text{(IPNH)}_2\text{Ni} \) would be expected to favour the monomer formation. \( \text{(IPNH)}_2\text{Ni} \) is paramagnetic (\( \mu = 3.26 \text{ B.M.} \)) and the nul spectrum has a marked likeness to that of \( \text{Ni(IPBH)}_2 \text{ZPy} \). In this case hexa-coordination most probably occurs through utilisation of the heterocyclic nitrogen atom.

Similarly on electronic grounds \( \text{Ni(MEKBH)}_2 \) should have a higher percentage of monomer, for a solution of given concentration, than would \( \text{Ni(IPBH)}_2 \). Molecular weight measurements (Chapter 4) show that there is little difference in association between the two, but at higher concentrations, contrary to expectations, \( \text{Ni(MEKBH)}_2 \) has a slightly higher molecular weight.

Intuitively steric factors would be expected to be of primary importance in determining stereochemistry. By consideration of molecular
structure and because of the steric interaction between R groups of the
two ligands in a cis planar complex, almost certainly the four coordinate
complexes have a trans planar structure (i). In a trans planar structure
steric interactions are to be expected between the R groups on one ligand,
and the substituents in the 2 and 3 positions on the aromatic nucleus of
the other.

Steric interplay in the square complex would be at a minimum when
R = H, and this fits with the observation that all ligands made from
aldehydes give exclusively square complexes. Increased bulkiness of the
group R (as in replacing the H atom by an alkyl group), would cause a
decrease in the stability of the square complex. Presumably, increased
bulkiness of R would also cause increased interactions within the polymeric
species, but lack of precise structural information precludes a more
detailed discussion of this likelihood. More detailed discussions on the
dependance of the nickel complex stereochemistry on the steric and electronic
properties of X and R, must await a more extensive variation of ligand type
and detailed structural analyses.
Table 5-1 - The Dependence of the Stereochemistry of the Complex on X, R₁ and R₂

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>X</th>
<th>R₁</th>
<th>R₂</th>
<th>Stereochemistry of the Nickel Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPBH</td>
<td>H</td>
<td>CH₃</td>
<td>CH₃</td>
<td>square planar and polymeric</td>
</tr>
<tr>
<td>MKBH</td>
<td>H</td>
<td>CH₃</td>
<td>CH₂CH₃</td>
<td>square planar and polymeric</td>
</tr>
<tr>
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</table>
IPo-ClBH

ortho-Cl \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{square planar and polymeric}

IP’p-ClBH

para-Cl \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{square planar and polymeric}

* A complex not reported in this thesis, but preliminary observations indicate that a monomer polymer equilibrium exists in solution.

** This complex has not been obtained in a pure state and is hygroscopic, but red-green colour changes are observed on heating.

† Those complexes with ligands formed from the condensation of aliphatic aldehydes with N-benzoylhydrazine have been examined by Ohta. No abbreviations are given.
5-3 The Nature of the Associated Species

Any discussion as to the exact nature of the polymeric species is merely conjectural, however, the following comments may be made.

1. An analysis of the behaviour of Ni(IPSH)₂ in benzene solution can be explained by the coexistence of monomers, dimers and trimers, possibly under suitable conditions of solvent and concentration higher oligomers may exist.

2. The ligands coordinate through nitrogen and oxygen atoms with the formation of five membered chelate rings. Polymerisation is probably effected by a sharing of the donor oxygen atoms of the ligand, as for example, in the acetylacebonates.⁶ The coordinated nitrogen atom has no spare pair of electrons and cannot act as a bridging group; the uncoordinated nitrogen atom does have a spare pair of electrons and is the only other possible bridging site. Use of this atom in a bridging process does seem unlikely.

3. To stabilise a triplet ground state it is necessary to invoke a structure in which nickel II is at least five coordinate. The visible spectrum of the associated species is similar to the spectrum of the nickel atom in a tetragonal environment but can also be reconciled with penta-coordinated nickel.

A similar situation exists in the case of bis-(N-R-salicylaldimine) nickel complexes which associate in both the solid state and in solution. The mode of association shown diagrammatically in fig. 5-1 has been proposed for the "γ" (associated) form of bis-(N-methyl-salicylaldimino) nickel and related complexes,⁷ ⁸ ⁹ but an X-ray determination has been impossible because single crystals cannot be isolated. The diamagnetic isomer has
been shown to be square planar in structure.\textsuperscript{10} A similar dimeric structure has been shown to exist in \(\text{[Fe(salen)Cl]}\text{Cl}_2\).\textsuperscript{11}

\(\text{Ni(Me-sal)}\text{\textsubscript{2}}\) is associated to a higher degree in solution than the \(n\)-alkyl complexes, which is consistent with the proposed structure in which the lateral interaction of monomers will be influenced by the steric properties of \(\text{Me}\). Molecular weight studies show that bis-(\(N\)-aryl-salicylaldimino) nickel II complexes are associated in solution.\textsuperscript{12,13} It is difficult to envisage polymers of the type depicted in fig. 5-1 because the steric properties of the aryl groups would cause a considerable departure from planarity. \(\text{Zn(Me-sal)}\text{\textsubscript{2}}\) has been shown to be a pentacoordinate dimer,\textsuperscript{14} fig. 5-2, as are the cobalt and manganese analogue.\textsuperscript{14} The \(\alpha\) and \(\beta\) forms of \(\text{Ni(Me-sal)}\text{\textsubscript{2}}\) although planar give binary solid solutions with \(\text{Zn(Me-sal)}\text{\textsubscript{2}}\). In solutions rich with \(\text{Zn(Me-sal)}\text{\textsubscript{2}}\), the planar nickel complex assumes the crystalline structure of the zinc complex and is crystalline and paramagnetic,\textsuperscript{15} however the visible spectrum is different to that of the paramagnetic \(\gamma\) form.

Structure determinations have established that some related copper complexes do associate in a similar manner to that proposed for \(\text{Ni(Me-sal)}\text{\textsubscript{2}}\), \(e.g.\) bis-(salicylaldehyde-ethylenediamine) copper is a dimer,\textsuperscript{16} and bis-(dimethylglyoxime) copper\textsuperscript{17} dimerises by a similar sharing of oxygen atoms, fig. 5-3.

In the light of X-ray determination on similar complexes, the proposed mode of association of \(\text{Ni(Me-sal)}\text{\textsubscript{2}}\) is feasible. The polymers discussed in this thesis could well associate by a similar mechanism.
FIGURE 5-1. The basic structural unit of the associated form of bis (N-methylsalicylaldimino) nickel(II).
FIGURE 5-3. Dimeric bis (Dimethylglyoxime) copper (II), reference 17

FIGURE 5-2. The bis (N-methylsalicylaldimino) zinc (II) dimer 14.

Portions of the molecule are represented by curved lines.
5-4. EQUILIBRIA IN SOLUTION

The dependance of the equilibrium position on solvent has been mentioned in Chapter 3. Chloroform and chlorobenzene appear to favour the formation of low molecular weight species relative to benzene. The solid polymer may be envisaged as either of finite length, say a trimer, or being the product of an infinite associative process. Entropy and enthalpy changes being favourable, dissolution in weakly coordinating solvents results in a break-down of the polymer structure to give species which are associated to a lesser degree, with the weakly coordinating solvent molecules occupying terminal positions. A pictorial representation of the break-down of such a hypothetical polymer structure on dissolution in a weakly coordinating solvent is given in fig. 5-4.

![Diagram of polymer structure dissolution](image)

The longer the polymer length, the greater are the number of nickel atoms achieving six coordination via bridging ligand atoms and the smaller the number of solvent molecules occupying coordination sites. The presence of a solvent, such as ethanol, capable of exerting a ligand field comparable with the average field experienced by a nickel atom in the polymer structure, leads to the exclusive formation of the paramagnetic monomeric species.
REFERENCES

CHAPTER 6

EXPERIMENTAL

6-1 PREPARATION OF LIGANDS

N-acylhydrazines were prepared by refluxing the methyl or ethyl esters of the corresponding acids with hydrazine hydrate. Methyl esters not in stock were prepared by refluxing the free acid with at least a five fold excess of methanol and a few ml. of sulphuric acid. The compounds were identified by melting or boiling point determinations. The following methyl esters were prepared:

- methyl o-chlorobenzoate, b.p. 148°C at 14 mm, pressure, literature
- methyl p-chlorobenzoic acid, m.p. 44°C from methanol, literature
- methyl o-nitrobenzoic acid, b.p. 174°C at 31 mm, literature
- methyl p-nitrobenzoic acid, m.p. 95°C from methanol, literature
- methyl m-nitrobenzoic acid, m.p. 47°C from methanol, literature

Hydrazides used in this section were,

- N-benzoylhydrazine, m.p. 113°C from ethanol-water, literature
- p-chlorobenzoylhydrazine, m.p. 163-165°C from ethanol-water, literature
o-chlorobenzoylhydrazine, m.p. 117.5°C from ether,
literature m.p. 117-118°C
p-nitrobenzoylhydrazine, m.p. 210°C from methanol-water,
literature m.p. 214°C
o-nitrobenzoylhydrazine, m.p. 121°C from water
literature m.p. 123°C
m-nitrobenzoylhydrazine, m.p. 152°C from methanol-water,
literature m.p. 152°C
m-toluic acid hydrazide, m.p. 97°C from water-methanol,
literature m.p. 97°C
p-toluic acid hydrazide, m.p. 115°C from aqueous-ethanol,
literature m.p. 117°C

The isonicotinic acid hydrazide used was manufactured by Hamilton Laboratories Pty. Ltd., Adelaide.

The N-isopropylidene-N'-acylhydrazines were generally prepared in situ.

6-2 PURIFICATION OF SOLVENTS

(i) Benzene

Thiophene was removed from the A.R. grade solvent by repeated extraction with sulphuric acid. After preliminary drying with calcium chloride and then sodium, the benzene was distilled (boiling point 80-81°C) and stored under nitrogen over fresh sodium wire.

(ii) Chlorobenzene

A similar purification process was used for both benzene and chlorobenzene, except that calcium hydride was employed as the final drying agent. The pure solvent boiled at 131.5°C.
(iii) Methyl Alcohol

Methanol was purified by fractionation through an efficient fractionating column.8

(iv) Petroleum Spirit

The petroleum spirit commonly used in recrystallisation was of the boiling range 40-60°C. The A.R. solvent was dried first over anhydrous calcium chloride and finally over sodium wire.8

(v) Chloroform

A.R. chloroform was shaken about five times with water, dried for twenty-four hours over calcium chloride and then distilled (b.p. 61°C).8 The pure solvent was stored under nitrogen in a dark bottle to prevent photo-chemical decomposition.

6-3 PHYSICAL MEASUREMENTS

6-3 (i) (a) The Magnetic Moments of Solids

Magnetic measurements on solid samples were determined at room temperature by the Gouy method using a water cooled Newport 4.25 electromagnet type A fitted with a voltage stabiliser and a manual current control.

A Mettler H 16 balance weighing to .01 mg. was used to detect weight changes. All measurements were performed in duplicate at two different field strengths using currents of 5.0 and 8.0 amps. In all cases duplicate determinations involved a repacking of the tube. A current of 8.0 amps produced a weight change of 25.16 mg. on 0.36807 g. of calibrant mercury tetrathiocyanato-cobaltate II.9 β values were reproducible to better than 0.5% and agreement to within 1% was obtained for duplicate determinations of sample susceptibilities.
Solution of Magnetic Susceptibilities

Solution susceptibilities were determined using a stoppered tube carrying 8.751 ml. of sample. Calibrants employed were nickel chloride solution and pure water. The susceptibility of nickel chloride solution was taken as,

$$10^6 \chi = \frac{10030}{T} \frac{y}{100} - 0.72 \left(1 - \frac{y}{100}\right)$$

where \( T \) is the absolute temperature

and \( y \) is the percentage nickel in the solution.

Nickel content was determined by standard assay as the dimethylglyoxime complex. The susceptibility of water was taken as,

$$\chi_{20^\circ C} = -0.72 \times 10^{-6}$$

and

$$\frac{d\chi}{dT} = 0.12 \text{ per cent per degree at } 20^\circ C.$$  

Suitable thermostatting was achieved by surrounding the Gouy tube with a large jacket, through which thermostatted water was passed. The bath temperature was less than 0.1\% different from that of the return liquid. Solutions were allowed ample time to equilibrate before measurements were attempted.

All measurements were performed in duplicate using two different field strengths. No dependance on field strength was observed. A typical set of constants were at 8 amps \( a = 0.254 \), and \( \beta = 0.420 \) and at 13 amps \( \beta = 0.299 \).

Corrections for the diamagnetism of the ligand were made using Pascal's constants as given in Selwood's "Magnetoochemistry". Solvent susceptibility corrections were calculated from the measured susceptibility of chloroform, \( -\chi \times 10^6 = 0.5100 \).
6-3 (ii) (a) Solution Spectra

Solutions of some of the complexes mentioned in this section readily pick up water to form hydrates. Thus all accurate optical density measurements on these compounds, e.g. the optical densities of Ni(IPBH)$_2$ in benzene used to evaluate the constants $k_1$ and $k_2$, were performed in anhydrous conditions with the acid of "Schlenk Technique", and the apparatus shown in fig. (i). The stepwise procedure was as follows:

1. The complex was weighed into a volumetric flask, usually 5 ml. in size, which was fitted with a standard ground glass neck and stopper.

2. The volumetric flask was then filled with dry nitrogen fig. 6-1. A T-piece which was joined to the flask by means of a quick fit joint, was connected at one arm via a liquid air trap to the pump and at the other arm to a dry nitrogen supply. Partial evacuation was followed by admission of nitrogen. This process was repeated several times and finally the lead to the pump disconnected and a steady flow of nitrogen maintained over the flask.

3. A pipette and a Griffin three-valve pipette filler, for syringing solvent were filled with nitrogen.

4. Dry solvent was drawn into the pipette, whilst a steady flow of nitrogen was maintained over the solvent store. Benzene was stored in a stoppered flask over sodium wire under a positive nitrogen pressure, fig. 6-2.

5. The solvent was run into the volumetric flask fig. 6-3, whilst maintaining the steady nitrogen flow over the flask. Dissolution was effected by gentle agitation and the solvent made up to the mark.

6. The spectrophotometric cell, with a standard ground glass mouth was filled with nitrogen in an analogous manner to the filling of the
volumetric flask in step 2.

7. Using a nitrogen flushed pipette and the apparatus shown in fig. 6-3, solution was drawn into the pipette.

8. A steady flow of nitrogen was maintained over the cell mouth whilst the solution was added from the pipette. The pipette was withdrawn and the top of the T-piece stoppered. In the presence of a slight positive nitrogen pressure, the T-piece was withdrawn and quickly replaced by a ground glass stopper. The spectrum was then recorded. Matched silica cells were used for all spectral measurements. Owing to the temperature dependance of the spectrum of Ni(IPBH)₂, and related compounds, strict temperature control was exercised. Individual recordings of optical density were made with a Shimadzu Spectrophotometer type Q.R. 50. The cell compartment was maintained at constant temperature by circulation of water from a thermostatted tank. Spectra runs over the range 30,000 cm⁻¹ to 5,000 cm⁻¹ were made using an S.P. 700 recording spectrophotometer, wherein temperature was monitored by determining the resistance of a calibrated thermistor placed in the optical cell.

6-3 (ii) (b) **Solid Spectra**

Solid absorption spectra were taken in mull mills. A mull between the finely powdered solid and mull was placed on a filter paper and pressed between glass discs. An identical system, with the filter paper wet with mull served as a blank. All mull spectra were recorded with the S.P. 700 spectrophotometer. Resolution using the mull technique was found to be the equal of reflectance spectra.
6-3 (iii) Molecular Weight Determinations

Molecular weights of Ni(IPBH)₂, Ni(MXKBH)₂ and Ni(ABH)₂ were determined at 25.0°C in benzene by the isopiestic method. Solvent and temperature were chosen with the aim of correlating molecular weight and spectral data. Conditions essential for accuracy are precise thermostatting and the vigorous exclusion of moisture from the system. The method used was essentially that due to Signer, but with the inclusion of a solvent reservoir to hasten the process of distillation, and the introduction of a more efficient technique to ensure the complete absence of moisture.

The apparatus used is shown in fig. 6-4) and the stepwise procedure was as follows:

1. About 5-10 mg. of the standard A.R. benzoic acid was weighed by difference into the bulb A, and between 2-5 times as much complex weighed into the bulb B, the side-arm of which was filled with a B 14 socket. A T-piece was fitted to the apparatus through the quick-fit joint, one arm of which was connected via a vacuum tap to the dry nitrogen supply and the other to a vacuum pump.

2. After first passing nitrogen through the system, the side-arm A was sealed off.

3. The apparatus was then filled completely with dry nitrogen by repeated evacuation and admission of nitrogen.

4. The lead to the pump was then removed and whilst maintaining a steady flow of nitrogen over the open end B, the required volume of solvent was run into bulb B, using an identical pipetting technique to that described in the section dealing with the preparation of solutions.
5. The benzene was frozen and then the nitrogen flow halted, (tap C), at the same instant as the system was re-evacuated. The arm B was then sealed off.

6. The solvent was redistilled, leaving some in each arm, and the rest in the reservoir and the apparatus placed in a tank thermostatted at 25.0°C.

7. Readings were commenced after all the solvent had distilled from the reservoir. A drainage time of about ten minutes was allowed for the solutions to drain from the bulbs to the pipettes. Equilibrium was attained after four to fourteen days, the more concentrated solutions coming to equilibrium fastest.

In the test runs the molecular weight of azobenzene was determined to within 5% using benzoic acid as standard. Molecular weights were calculated from the formula,

\[ M_1 = \frac{W_1 M V}{\bar{W} V_1} \]

where \( M_1 \) is the molecular weight of the unknown,
\( W_1 \) is the weight of unknown,
\( V_1 \) is the volume of the unknown,
and \( M, \bar{W} \) and \( V \) are the corresponding values of the reference.

6-4. ANALYTICAL PROCEDURES

(i) Nickel

Nickel was determined gravimetrically as the dimethylglyoximate following the oxidation of organic material with fuming sulphuric and nitric acids.
(ii) **Hydrazine**

Hydrazine was determined by titration with standard potassium bromate in hydrochloric acid. Acetone was observed to cause a fading of the end point, and consequently was removed by gentle boiling with hydrochloric acid. The end point was marked by the presence of free bromine and was readily detected by extraction into chloroform.

(iii) **Carbon, Hydrogen and Nitrogen**

Carbon, hydrogen and nitrogen analyses were determined by the Australian Micro-Analytical Service, Melbourne.

(iv) **Water**

Hydrated complexes were dried to constant weight in a vacuum pistol at 70°C over P₂O₅ unless otherwise stated.

6-5 **PREPARATION OF COMPLEXES**

**Bis-(N-isopropylidine-N'-benzoylhydrazine) Nickel II**

The complex was isolated in two isomeric forms according to the method of Thong.¹⁷

**Ni(IPBH)₂**

Benzhydrazide 3.0 g. (0.022 mole) in 25 ml. of water and an excess of acetone (20 ml.) was added to a solution of 2.4 g. (0.01 mole) of nickel chloride hexahydrate in about 20 ml. of water. The blue colour of the Ni₄(IPBH)₂Cl₂ complex was immediately evident. Aqueous sodium hydroxide (ca. 0.9 g. in 20 ml. of water) was added dropwise with constant stirring, until the pH of the solution was about 8.5, whence a light blue precipitate of Ni₂(IPBH)₂H₂O was formed. After standing for several hours, the compound was filtered at the pump and washed with water, until the washings were
chloride free. The hydrate was converted to the anhydrous green complex by
drying in the vacuum pistol.

**Green** [Ni(IPBH)$_2$]$_n$

The crude Ni(IPBH)$_2$ was recrystallised from a hot chloroform-
petroleum spirit mixture, with the exclusion of moisture. The green crystals
were collected under nitrogen and dried.

**Analysis:** Found - C, 58.80%; H, 5.39%; N$_2$H$_4$, 15.61%; Ni, 14.30. Calculated
for NiC$_{20}$H$_{22}$N$_4$O$_2$: C, 58.73%; H, 5.42%; N$_2$H$_4$, 15.67%; Ni, 14.35%.

**Red** Ni(IPBH)$_2$

Recrystallisation of the crude green complex from a solvent mixture
of 1 volume of chloroform to 16 of petroleum spirit yields red crystals.
About 15 gm. of complex were dissolved in 80 ml. of solvent. Mixed solvents
containing a lesser proportion of petroleum spirit, result in mixtures of
red and green crystals.

**Analysis:** Found - C, 58.63%; H, 5.41%; N$_2$H$_4$, 15.63%; Ni, 14.30%. Calculated
for NiC$_{20}$H$_{22}$N$_4$O$_2$: C, 58.73%; H, 5.42%; N$_2$H$_4$, 15.67%; Ni, 14.35%.

**Bis-(N-isopropylidene-$$N'$$-benzoylhydrazino) Nickel II Dipyridinate**

This complex was prepared by the method of Thong, or otherwise
by warming Ni(IPBH)$_2$ in pyridine. The blue pyridinate which formed was
collected, washed with petroleum spirit, and dried over sodium hydroxide.

**Analysis:** Found - C, 62.90%; H, 5.91%; N, 14.50%; Ni, 12.46%. Calculated
for C$_{30}$H$_{34}$N$_6$O$_2$Ni: C, 62.26%; H, 6.02%; N, 14.77%; Ni, 12.51%.

**Bis-(N-methyl-ethyl ketone-$$N'$$-benzoylhydrazino) Nickel II**

A mixture of N-methyl-ethyl ketone-$$N'$$-benzoylhydrazones, 11.4 g.
(26 mole) nickel acetate tetrahydrate, 7.4 g. (0.03 mole), and fresh sodium
methoxide 1.1 g. in 400 ml. of methanol was refluxed for about ten minutes.
A clear dark green solution resulted. The solvent was removed under vacuum and the resulting solid mixture thoroughly dried before being placed in a soxhlet thimble and extracted with dry petroleum spirit. The petroleum spirit was removed under vacuum and the green solid which remained purified by re-extracting with dry ether. The solution in petroleum spirit was kept in a stoppered flask under positive nitrogen pressure until the appearance of green crystals, which were collected under nitrogen and dried.

Analysis: Found - C, 60.68%; H, 5.99%; N, 12.81%; Ni, 13.40%. Calculated for NiC_{22}H_{26}N_{4}O_{2}: C, 60.42%; H, 5.97%; N, 12.96%; Ni, 13.33%.

**Bis-(N-isopropylidene-N'-meta-tolucylhydrazino) Nickel II**

Meta-toluic acid hydrazide 3.0 g. (2 x 10^{-2} mole) in 20 ml. of acetone and 15 ml. of water was added to 2.4 g. of (10^{-2} mole) of nickel chloride hexahydrate in 20 ml. of water. The dropwise addition of sodium hydroxide (ca. 0.8 g. in 20 ml. of water) resulted in the gradual formation of a green oil which was transformed into a green solid by the addition of more acetone. The green complex was filtered at the pump, washed with acetone and after drying in the vacuum pistol, recrystallised from benzene-petroleum spirit whence it was recovered as a green solid.

Analysis: Found - C, 60.63%; H, 6.11%; N, 12.40%; N_{2}H_{4}, 14.70%; Ni, 13.38%. Calculated for NiC_{22}H_{26}N_{4}O_{2}: C, 60.45%; H, 5.99%; N, 12.82%; N_{2}H_{4}, 14.61%; Ni, 13.33%.

**Bis-(N-isopropylidene-N'-para-toluocylhydrazino) Nickel II**

Para-toluic acid hydrazide 3.0 g. (2 x 10^{-2} mole) in 20 ml. of acetone and 15 ml. of water was added to 2.4 g. (10^{-2} mole) of nickel chloride hexahydrate in 20 ml. of water. Sodium hydroxide (ca. 0.8 g. in 20 ml. of water) was added dropwise with stirring until the pH rose to about
8.5. The addition of sodium hydroxide was accompanied by the gradual formation of a green oil which changed into a green solid on the addition of more acetone. After filtering, the complex was dried in the vacuum pistol and changed in colour from green to red. The red solid was recrystallised from benzene under nitrogen free conditions and recovered as red needles.

Analysis: Found - C, 59.66%; H, 5.92%; N, 12.82%; N₂H₄, 14.70%; Ni, 13.40%.

Calculated for C₂₂H₂₆N₂O₂Ni: C, 60.45%; H, 5.99%; N, 12.82%; N₂H₄, 14.61%; Ni, 13.33%.

Bis-\(N\)-isopropylidene-\(N\)′-isonicotinoylhydrazino) Nickel II

Isonicotinoylhydrazino 2.75 g. \((2 \times 10^{-2}\) mole) and nickel chloride hexa-aquo 2.37 g. \((10^{-2}\) mole) were dissolved in acetone/water and sodium hydroxide (ca. 0.8 g. in 20 ml. of water) added dropwise with stirring until the pH reached about 8.5. The pale slurry which formed was separated from the solution by centrifugation, washed with ethanol and acetone and dried.

Analysis: Found - C, 51.17%; H, 4.81%; N, 20.15%; Ni, 14.16%. Calculated for C₁₅H₁₀N₂O₂Ni: C, 52.60%; H, 4.91%; N, 20.45%; Ni, 14.28%.

Attempted preparation of Bis-\(N\)-isopropylidene-\(N\)′-para-hydroxybenzoylhydrazino) Nickel II

The addition of aqueous sodium hydroxide to acetone/water solutions of nickel chloride and para-hydroxybenzoylhydrazine gave a blue-green precipitate which was collected, washed with water, ethanol and acetone. After drying in the vacuum pistol, a dark green-brown material was obtained but analyses were not in agreement with those expected for the bis complex.
Bis-(N-isopropylidene-N'-para-hydroxybenzoylhydrazino) Nickel II

Dipyridinate

About 1.0 g. of the impure product obtained in the above preparation was dissolved in boiling pyridine. On standing, green crystals separated which were collected, washed with petroleum spirit and dried over sodium hydroxide pellets.

Analysis: Found - C, 60.07%; H, 5.56%; N, 13.86%; Ni, 9.86%. Calculated for $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_2\text{Ni}$: C, 60.15%; H, 5.39%; N, 14.03%; Ni, 9.80%.

Attempted preparation of Bis-(N-isopropylidene-N'-ortho-chlorobenzoylhydrazino) Nickel II

Ortho-chlorobenzoylhydrazine 3.5 g. ($2.1 \times 10^{-2}$ mole) in 30 ml. of water and 25 ml. of acetone was added to nickel chloride hexahydrate 2.4 g. ($10^{-2}$ mole) in 25 ml. of water and sodium hydroxide (ca. 0.8 g. in 20 ml.) added dropwise with stirring until a pH of 8.5 was obtained. The sea-green precipitate which resulted was collected, washed several times with water and dried in the vacuum pistol at 70°C over $\text{P}_2\text{O}_5$. The green compound so obtained absorbed water from the atmosphere so rapidly their further studies were not attempted.

Bis(N-isopropylidene-N'-ortho-chlorobenzoylhydrazino) Nickel II Dipyridinate

The crude hydrated complex prepared above was dissolved in pyridine to give a blue solution. The blue complex which separated on cooling was collected, washed with petroleum spirit and dried over sodium hydroxide.

Analysis: Found - C, 56.38%; H, 4.86%; N, 13.35%; Ni, 9.03%. Calculated for $\text{C}_{32}\text{H}_{30}\text{N}_2\text{O}_2\text{Cl}_2\text{Ni}$: C, 56.63%; H, 4.75%; N, 13.21%; Ni, 8.95%.
Attempted preparation of Bis-(N-isopropylidene-N'-para-chlorobenzoylhydrazino) Nickel II

Para-chlorobenzoylhydrazine 3.5 g. (2.1 x 10^{-2} mole) in 40 ml. of water and 35 ml. of acetone was added to nickel chloride hexa-hydrate 2.4 g. (10^{-2} mole) in 25 ml. of water and sodium hydroxide (ca. 0.8 g. in 20 ml. of water) added dropwise with stirring until a pH of about 8.5 was obtained. A grass-green precipitate separated in good yield and after collecting and washing with water, was dried in the vacuum pistol. As with the case of the ortho-chloro derivative, the dry complex was so hygroscopic that no further measurements were attempted.

Bis-(N-isopropylidene-N'-para-chlorobenzoylhydrazino) Nickel II Dipyridinate

The crude hydrated complex obtained in the preparation above was dissolved in boiling pyridine to give a blue solution. The blue complex which separated on cooling was collected, washed with petroleum spirit and dried over sodium hydroxide.

Analysis: Found - C, 57.08%; H, 4.69%; N, 13.15%; Ni, 8.99%. Calculated for C_{32}H_{30}N_{6}O_{2}Cl_{2}Ni: C, 8.95%; H, 4.75%; N, 13.21%; Ni, 8.95%.

Bis-(N-isopropylidene-N'-para-nitrobenzoylhydrazino) Nickel II

3.62 g. (2 x 10^{-2} mole) of para-nitrobenzoylhydrazine in 4.5 ml. of water and 40 ml. of acetone were added to 2.4 g. (10^{-2} mole) of nickel chloride hexa-aquo in 25 ml. of water and sodium hydroxide (ca. 0.8 g. in 20 ml. of water) was added dropwise with stirring. The red-brown precipitate which separated, was collected, washed with acetone/water and dried in the vacuum pistol.

Analysis: Found - C, 48.14%; H, 4.25%; N, 17.00%; Ni, 11.75%. Calculated for C_{20}H_{20}N_{6}O_{6}Ni: C, 48.12%; H, 4.45%; N, 16.85%; Ni, 11.76%.
Bis-(N-isopropylidene-\(N'\)-para-nitrobenzoylhydrazino) Nickel II Dipyrindinate

1.0 g. of Ni II(1Pp-N\(_2\)BH\(_2\)\(_2\)) was dissolved in hot pyridine to give a red solution. The yellow crystalline product which separated on standing was collected, washed with petroleum spirit and dried over sodium hydroxide.

Analysis: Found - C, 54.99%; H, 5.03%; N, 17.10%; Ni, 9.09%. Calculated for C\(_{32}\)H\(_{20}\)N\(_8\)O\(_6\)Ni: C, 54.61%; H, 4.60%; N, 17.04%; Ni, 8.95%.

Bis-(N-isopropylidene-\(N'\)-meta-nitrobenzoylhydrazino) Nickel II Dipyrindinate

0.7 g. (0.04 x 10\(^{-2}\) mole) of meta-nitrobenzoylhydrazine in 10 ml. of water and 10 ml. of acetone was added to 0.47 g. (0.2 x 10\(^{-2}\) mole) of nickel chloride hexa-hydrate in 10 ml. of water and aqueous sodium hydroxide added slowly with stirring until a pH of about 8.5 was reached. The brown precipitate which separated on standing was collected, washed with acetone/water and dried in a vacuum pistol.

Analysis: Found - C, 58.38%; H, 4.32%; N, 17.10%; Ni, 11.74%. Calculated for C\(_{20}\)H\(_{20}\)N\(_8\)O\(_6\)Ni: C, 58.12%; H, 4.45%; N, 16.85%; Ni, 11.76%.

Bis-(N-isopropylidene-\(N'\)-meta-nitrobenzoylhydrazino) Nickel II Dipyrindinate

1.0 g. of Ni II(1Pm-N\(_2\)BH\(_2\)\(_2\)) was dissolved in hot pyridine and the solution set aside to stand. The mustard coloured precipitate was collected, washed with petroleum spirit and finally dried over sodium hydroxide.

Analysis: Found - C, 55.20%; H, 4.65%; N, 17.31%; Ni, 8.73%. Calculated for C\(_{32}\)H\(_{30}\)N\(_8\)O\(_6\)Ni: C, 54.81%; H, 4.60%; N, 17.04%; Ni, 8.95%.

Bis-(N-isopropylidene-\(N'\)-benzoylhydrazino) Zinc II

Aqueous sodium bicarbonate was added dropwise with stirring to 2.18 g. (10\(^{-2}\) mole) of zinc acetate dihydrate and 2.72 g. (2 x 10\(^{-2}\) mole) of benzoylhydrazine in acetone/water until the evolution of carbon dioxide ceased. The white precipitate was washed with water, then acetone and
dried at 50-60°C for twelve hours in the drying pistol. The dried product was recrystallised from chloro-benzene and redried to constant weight.

Analysis: Found - N₂H₄, 15.50%; Zn, 15.65%. Calculated for C₂₀,H₂₂,N₄,O₂,Zn:
N₂H₄, 15.42%; Zn, 15.72%.
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PART B

COMPLEXES OF ETHYL CARBAZATE,

PHENYL CARBAZATE AND THEIR ISOPROPYLIDENE DERIVATIVES

WITH FIRST ROW TRANSITION METALS
SUMMARY

This section is concerned with the preparation of metal complexes of ethylocarbazate, ESC, phenylcarbazate, PC and of their isopropylidene derivatives IPSC and IPPC respectively. The investigation was undertaken in an endeavour to determine the effect of an OR group, where R is phenyl or ethyl on the chelating properties of the hydrazide group. The properties of the complexes examined were their solid state absorption spectra and magnetic moments.

The ligands were prepared by using the general method of preparation for carbasates, viz. reaction of a suitable ester of carbonic acid with hydrazine hydrate.¹

\[ R\text{C=O} + \text{NH}_2\text{NH}_2 \rightarrow R\text{O}\text{C=O} + \text{NH}_2\text{NH} \]

Ethylocarbazate was readily formed from the reaction of equimolar quantities of diethyl carbonate and hydrazine hydrate.² Purification was effected by vacuum distillation. Phenylcarbazate was prepared from diphenyl carbonate and hydrazine hydrate. The following method of purification was devised: phenylcarbazate was separated from unreacted diphenyl carbonate by virtue of the latter's insolubility in chloroform and from the by-product phenol as the amine hydrochloride formed by bubbling dry hydrogen chloride through the dry chloroform solution. Phenylcarbazate decomposes above 80°C thus,¹

\[ 2\text{NH}_2\text{NH C(O)C}_6\text{H}_5 \rightarrow 2\text{C}_6\text{H}_5\text{OH} + \text{C}_2\text{H}_4\text{H}_4\text{N}_2 \]
The acetone adducts were prepared for the first time by dissolution
of the carbazate in a minimum volume of hot acetone.

Eleven new complexes of PC, IPFC, BC and IPSC and 3 of BH and IPBH
are reported in this work. The complexes are all ionic with the cobalt II
or nickel II nitrate. These ligands readily reduce copper II and only one
cupric complex has been prepared.

The addition of sodium bicarbonate to solutions of metal complexes
of the keto form of IPBH, results in the production of the internal complex.
However this procedure appears to be unsuccessful with IPPC and IPSC. This
may be the result of the additional resonance stabilisation afforded by the
conjugated benzene ring in IPBH, but seems surprising in view of the fact
that N-isopropylidene-N' -propionylhydrazine,3 the analogous acetylhydrazine
derivative,3 and semi-carbazide,4 \( \text{NH}_2\text{CONNH}_2 \) have been observed to
coordinate in the enol form. A literature survey yields the following
information which serves as a basis for discussing the chelating action
of carbazates.
1-1 HISTORICAL

The first reported synthesis of a complex of an acylhydrazone came in 1929, with the synthesis of bis-(N-benzoylhydrazone) copper II sulphate dihydrate, Cu(BH)$_2$SO$_4$·2H$_2$O. Later in 1936, in two separate publications, Jensen reported the preparation of the anhydrous complex Cu(BH)$_2$SO$_4$, the corresponding N-acetylhydrazone complex, Cu(AH)$_2$SO$_4$, and Ni(AH)$_3$SO$_4$. Since then, there has been little published concerning the complexes of simple acylhyrazines, however two fields involving hydrazine containing ligands have been thoroughly explored. Firstly, Sacconi has investigated the nickel complexes of N-acylhyrazines condensed with a variety of aldehydes and ketones and secondly, an examination of the copper complexes of N-isonicotinoylhydrazone has resulted from the observation that copper II increases the in vitro tuberculostatic activity of this compound by ten fold. The cobalt II, nickel II and copper II complexes of N-acylhyrazines and their isopropylidene derivatives, in particular N-benzoylhydrazone and N-isopropylidene-N'-benzoylhydrazone, have been extensively studied in this department.*

1-2 THE CHELATING ACTION OF ACYLHYDRAZINES

These ligands show keto-enol tautomerism

$$\text{RC(O)NHNH}_2 \leftrightarrow \text{RC(OH) = NH}_2.$$ 

Under suitable conditions these ligands may coordinate through the keto (i), or by loss of a proton through the enol form (ii), forming five membered chelate rings, by coordination through the 0 atom and the
terminal N atom,

\[ R - C = O \xrightarrow{M/2} X \]
\[ R - C - O \xrightarrow{M/2} X \]

(i)  (ii)

where \( M \) is a divalent metal ion and \( X \) a monovalent anion.

Evidence that these are the two atoms involved in coordination is provided by the infra-red studies of Nagano et al.\(^{12}\)

Acylhydrazines readily condense with organic molecules containing an active carbonyl group. The coordinating properties of the isopropylidene derivatives of \( N \)-acylhydrazine, in particular \( N \)-isopropylidene-\( N' \)-benzoylhydrazine have been extensively investigated in this department.\(^*\)

\[ R - C - N H N H_2 \xrightarrow{O=C} \xrightarrow{CH_3} R - C - H \xrightarrow{N=N} \xrightarrow{CH_3} \]

These ligands coordinate in a similar manner to the parent hydrazide, with the exception that inner complexes form more readily.

The stability of the inner complexes of these ligands can be attributed to the effect of conjugated.

\[ R - C = N - N = C \xrightarrow{CH_3} \xrightarrow{CH_3} \]

\( * \) Department of Physical and Inorganic Chemistry, University of Adelaide.
The complexing action of N-benzoxyldrazine, BH, N-acetyldrazine, 
\(\text{AN}\) and N-propionylhydrazine, PH, and their isopropylidene derivatives 
with cobalt II, nickel II and copper II is summarised below.

1-2 (i) Complexes of Enol-N-Acylhydrazines

Co III(BH)\(_3\)\(^{13}\) and Cu II(BH)\(_2\)\(^{14}\) have been synthesised in this 
department, but only in an impure state. The imperfect analyses of these 
complexes is probably due to the presence of reduced species formed 
because of the reducing action of the ligand. No suitable solvent can 
be found for their recrystallisation.

1-2 (ii) Complexes of Keto-N-Acylhydrazines

The tris-benzoxyldrazine complexes of cobalt II and nickel II 
have been synthesised using a variety of anions and their magnetism and 
spectra are consistent with six coordinated metal complexes. The complexes 
crystallise with from one to three water molecules, the number of which 
varies with the anion, indicating that they are waters of crystallisation 
and are not coordinated. Recently a series of complexes with general 
formulae \(M(BH)\(_2\)X\(_2\)\) and \(M(SH)\(_2\)X\(_2\)\), where \(M\) is Co II, Ni II, Cu, II or Zn II, 
BH is benzoyldrazine and SH salicyldrazine and X sulphate or acetate, 
has been reported.\(^{15}\)

Baker has thoroughly investigated the N-benzoxyldrazine copper 
system. A series of copper II complexes with the formula Cu(BH)\(_2\)Cl\(_2\) 
where \(n = 1, 2, 3\) or 4 has been prepared by varying the BH:Cu preparative 
ratio. The copper complexes with acetyldrazine \((\text{AH})\(_2\)\)CuSO\(_4\) and 
propionylhydrazine \((\text{PH})\(_2\)\)CuSO\(_4\) \(\frac{1}{2}\)H\(_2\)O have also been prepared.
1-2 (iii) **Mixed Copper II-Copper I Complexes - The Reducing Action of N-Acylhydrazines**

Hydrazine itself has wide application as a reducing agent, depending on the conditions cupric can be reduced to cuprous or the metal. Although the keto complex \((BH)_2Cu\ \text{II}\ Cl_2\) can be isolated from cold aqueous solutions of benzoylhydrazine and copper II chloride in hot solutions, there is an evolution of nitrogen, and a complex analysing for \((BH)_2CuCl_3\) can be isolated. In addition \(N-N'\)-dibenzyolhydrazine can be isolated from the reaction mixture. Magnetic measurements and work since performed by Baker indicate that the complex should be formulated as \(Cu\ \text{II}(BH)_2\ Cl_2\ CuCl\). The analogous acetylhydrazine complex \((AH)_2CuCl_2\) has also been prepared. Reduction is catalysed by alkaline conditions. Variation of the preparative conditions has also led to the isolation of \((BH)_2CuCl_2\ \text{3CuCl}\). The production of dibenzyolhydrazine has led to investigations into the benzoylating properties of benzoylhydrazine. Oxidation by persulphate is catalysed by trace amounts of cupric ion and when carried out in the presence of amines, e.g. \(p\)-toluidine gives good yields of the benzoyl derivative.\(^{17}\)

1-2 (iv) **Complexes of Enol-\(\text{H}\)-Isopropylidene-\(N'\)-Acylhydrazines**

The four coordinate copper complex \(Cu(\text{IPBH})_2\) and some adducts with weak bases, wherein copper is both five coordinate as in \(Cu(\text{IPBH})_2\ \text{H}_2\text{O}\), \(Cu(\text{PAH})_2\ \text{H}_2\text{O}\) and \(Cu(\text{IPBH})_2\ 2\text{Me Py}\) and hexa-coordinate as in \(Cu(\text{IPBH})_2\ 2\text{Py}\) have been described by Baker.\(^{16}\)

The nickel complex \(Ni(\text{IPBH})_2\) is of considerable interest because it can be isolated in two isomeric forms, a red planar form and a green
green polymeric species. The studies of its solution behaviour provides a considerable proportion of the material presented in section A of this thesis. The bis-(N-isopropylidene-N'-benzoylhydrazine) complex of cobalt II has been obtained as an insoluble mono or dihydrate. No suitable solvent can be found for the recrystallisation of the complex which does not give consistent analysis from preparation to preparation. The crude compound does however, dissolve in pyridine to give Co(IPBH)₂₂Py which from spectral and magnetic measurements contains cobalt in an octahedral environment.

1-2 (v) Complexes of Keto-N-Isopropylidene-N'-Aerylhydrazines

The following copper complexes have been prepared by Baker,¹⁴

Cu(IPBH)₂(ClO₄)₂ in which copper is four coordinated, a complex which analyses for Cu(IPBH)₂ ¹/₂H₂OCl₂; Cu(IPBH)₂H₂OCl₂ which probably contains a coordinated water molecule making the copper atom five coordinated and Cu(IPBH)₂ ₂H₂OCl₂ which is also suspected of being a five coordinate complex. The insoluble cobalt complex Co(IPBH)₂Cl₂ separates from acetone mixtures of cobalt chloride and benzoylhydrazine.¹¹ The mull spectra show bands which are characteristic of both tetrahedral and octahedral species, the relative intensities of which vary from preparation to preparation. Complexes with the general formula M II(IPBH)₂Cl₂ and M II(IPSH)₂Cl₂, M is Mn, Co, Ni, Cu, Zn or Cd and IPBH and IPSH, the isopropylidene derivatives of benzoylhydrazine and salicylhydrazine have been reported recently by Issa.¹⁸
COMPLEXES WITH HYDRAZINE CARBOXYLIC ACID

No complexes of the esters of carbazic acid have been reported, however, complexes of hydrazine carboxylic acid, \( \text{NH}_2\text{NHCOC}_2\text{H}_4 \) are known, and the various types may be summarized thus,

(a) \( \text{M II(N}_2\text{H}_4)_2 \text{ hyc}_2 \)

where \( \text{M} \) is Mn, Co, Ni or Zn

and \( \text{hy c} \) is \( \text{NH}_2\text{NHCOC}^- \).

(b) \( \text{N}_2\text{H}_6 \text{ M II hyc}_3 \text{ H}_2\text{O} \)

where \( \text{M} \) is Fe, Co, Ni or Zn.

(c) \( \text{K (M II hyc}_3 \) \)

where \( \text{M} \) is Fe, Co, Ni or Zn.

The crystals of each set are isostructural, and crystal structure determinations have led to the conclusion that the complexes are chelates of hydrazine carboxylic acid.\(^{19}\) The structures of \( \text{Zn II(N}_2\text{H}_4)_2 \text{ hyc}_2 \), representative of class A compounds, has been determined and found to contain octahedrally coordinated zinc, with the hyc molecules acting as bidentates and the trans hydrazine molecules as monodentates.

Compounds of class (b) contain metal ions surrounded by three bidentate hyc molecules and hydrazinium cations. Prior to a structural determination, these were incorrectly formulated as \( \text{M II hyc}_2 \text{ (N}_2\text{H}_2)_2\text{CO}_3 \).\(^{20,21}\) Type (c) complexes also contain \( \text{M II hyc}_3 \) octahedra.

A complex with the formula \( \text{Co(hyc)}_2\text{N}_2\text{H}_4 \) has been reported by Russian workers and they suggest that cobalt is six coordinated, the hyc molecules acting as bidentates, with the formation of five membered rings, and the other two positions being taken by the hydrazine molecule, with the formation of a three membered ring. Treatment with hydrochloric acid gives
either \((\text{hye})_2 \text{Co} \cdot 2\text{H}_2\text{O}\) or \(\text{Co(hey)}_2\).

RESULTS AND DISCUSSION

2-1 NICKEL COMPLEXES OF BENZOYLHYDRAZINE, ETHYLCARBAZATE AND
PHENYLCARBAZATE

Issa\(^{15}\) has reported the preparation of bis-(benzoylhydrazino)nickel complexes with sulphate and acetate as anions. The complexes were prepared by mixing ethanolic solutions of the ligand and metal in the ratio 2:1. The tris complexes \(\text{M}(\text{BH})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}\) and \(\text{M}(\text{BH})_3(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}\) are reported in this section, and were prepared by mixing ligand and metal in aqueous solution, in a molar ratio of 3:1. The insoluble tris complex separated from aqueous solution even when the ligand to metal ratio was 2:1.

Prior to this work there has been no reported study of the complexing properties of ethyl or phenylcarbazate. The tris complexes, \(\text{M}(\text{EC})_3(\text{NO}_3)_2\) and \(\text{M}(\text{PC})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}\) have been prepared from aqueous and ethanolic solutions respectively, using ligand to metal ratios of 3:1. It seems possible that by varying ligand to metal ratio and using suitable solvents complexes with new stoichiometry may be isolated. This has been done by Baker\(^{16}\) in the preparation of copper-benzoylhydrazine complexes.

The tris (benzoylhydrazino) cobalt complexes have been isolated with sulphate, chloride and nitrate as anion.\(^{13}\) These complexes contain water molecules, the number of which depends on the anion, and so are presumably water of crystallisation. Vigorous drying gives rise to the anhydrous complexes. Drying the nickel phenylcarbazate complex over
phosphorus pentoxide gave the anhydrous complex.

The magnetic moments of the tris complexes of all three ligands are typical of octahedral nickel, table 2-1, as are the mull spectra. The mull spectra of Ni(BH)\(_2\)Cl\(_2\) \(\cdot\) 2H\(_2\)O and Ni(BH)\(_3\)(NO\(_2\))\(_2\) \(\cdot\) 2H\(_2\)O are independent of anion, and assuming that the water molecules are waters of crystallisation, the benzoylhydrazine molecules act as bidentate ligands. Stoichiometry, visible spectrum and magnetic moment indicate that EC acts as a bidentate in Ni(EC)\(_3\)(NO\(_2\))\(_2\). There is no reason to suppose that the coordinating action of PC is any different from that of EC or BH.

The visible spectra contain three bands at approximately 10.4 K.K., 16.7 K.K. and 28.6 K.K. which are typical of octahedrally coordinate nickel and correspond to transitions from the \(^3\Delta_{2g}\) ground state to the \(^3\Pi_{1g}\), \(^3\Pi_{1g}\) (F) and \(^3\Pi_{1g}\) (P) states respectively.\(^{22}\) This means that the ligands exert a ligand field which is slightly less in strength than that of ammonia. The hydrazides themselves exert ligand fields which have the order BH > EC > PC, table 2-2. This can be accounted for by the strongly electronegative oxygen atom diminishing the electron donating power of the hydrazide grouping in EC and PC more so than the phenyl group of BH. The phenol grouping is more electronegative than the ethoxy group and hence EC is a stronger ligand than PC. Spectral data collected by Baker\(^{16}\) for (BH)\(_2\)CuSO\(_4\) and (AH)\(_2\)CuSO\(_4\) indicate that acetylhydrazine is a slightly stronger ligand than benzoylhydrazine, which is in accord with the alkyl group being a stronger electron donor than the phenyl.
Ni(IPBH)₂Cl₂ has been prepared by Issa.¹⁸ The analogous complex with nickel nitrate, Ni(IPBH)₂(NO₃)₂ and its dihydrate Ni(IPBH)₂(NO₃)₂·2H₂O are reported here. Both the solid state spectra and the paramagnetism 3.2 < µ < 3.6 B.M. table 2-1 are indicative of octahedrally coordinated nickel. Octahedral coordination is most probably achieved by utilisation of the anion in the fifth and sixth position, or by a bridging process. There is no difference in the solid state spectra of Ni(IPBH)₂(NO₃)₂ and Ni(IPBH)₂(NO₃)₂·2H₂O.

The average ligand field strength of the isopropylidene complexes is weaker than the parent ligands. The ³T₁g (F) and ¹Eₕ states are apparently sufficiently close in energy to permit mixing and the middle band is split into two components in these four complexes. The addition of sodium bicarbonate to solutions of the ionic isopropylidene complexes does not result in the formation of the inner IP₃C and IPPC complexes, whereas with IPBH the internal complexes are formed. The stability of complexes with the enolic forms of IPBH may be due to the more extensive conjugated double bond system.
Table 2-1 - The Magnetic Moments of Some Nickel Complexes in the Solid State

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temperature °K</th>
<th>μ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(BH)$_3$Cl$_2$ 2H$_2$O</td>
<td>306.0</td>
<td>3.21</td>
</tr>
<tr>
<td>Ni(BH)$_3$(NO$_3$)$_2$ 2H$_2$O</td>
<td>306.0</td>
<td>3.28</td>
</tr>
<tr>
<td>Ni(PC)$_3$(NO$_3$)$_2$ H$_2$O</td>
<td>299.0</td>
<td>3.31</td>
</tr>
<tr>
<td>Ni(SC)$_3$(NO$_3$)$_2$</td>
<td>303.0</td>
<td>3.18</td>
</tr>
<tr>
<td>Ni(IPBH)$_2$(NO$_3$)$_2$</td>
<td>299.0</td>
<td>3.35</td>
</tr>
<tr>
<td>Ni(IPBH)$_2$(NO$_3$)$_2$ 2H$_2$O</td>
<td>299.0</td>
<td>3.37</td>
</tr>
<tr>
<td>Ni(IPPC)$_2$(NO$_3$)$_2$</td>
<td>300.0</td>
<td>3.31</td>
</tr>
</tbody>
</table>

Table 2-2 - The Absorption Spectra of Some Nickel Complexes

Maxima are in K.K.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Energy</th>
<th>Absorption</th>
<th>μ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(BH)$_3$Cl$_2$ 2H$_2$O</td>
<td>28.6</td>
<td>16.7</td>
<td>10.5</td>
</tr>
<tr>
<td>Ni(BH)$_3$(NO$_3$)$_2$ 2H$_2$O</td>
<td>28.5</td>
<td>16.7</td>
<td>10.4</td>
</tr>
<tr>
<td>Ni(SC)$_3$(NO$_3$)$_2$</td>
<td>28.0</td>
<td>16.5</td>
<td>10.4</td>
</tr>
<tr>
<td>Ni(PC)$_3$(NO$_3$)$_2$ H$_2$O</td>
<td>27.7</td>
<td>16.5</td>
<td>10.3</td>
</tr>
<tr>
<td>Ni(IPBH)$_2$(NO$_3$)$_2$</td>
<td>26.0 sh.</td>
<td>16.5 sh.</td>
<td>14.3, 9.8</td>
</tr>
<tr>
<td>Ni(IPBH)$_2$(NO$_3$)$_2$ 2H$_2$O</td>
<td>26.0 sh.</td>
<td>16.5 sh.</td>
<td>14.5, 9.9</td>
</tr>
<tr>
<td>Ni(IPPC)$_2$(NO$_3$)$_2$</td>
<td>27.0</td>
<td>16.1</td>
<td>14.5, 9.3</td>
</tr>
<tr>
<td>Ni(IPPC)$_2$(NO$_3$)$_2$</td>
<td>27.0</td>
<td>16.1</td>
<td>14.3, 9.3</td>
</tr>
</tbody>
</table>
2-3 COBALT II COMPLEXES WITH N-BENZOYLHYDRAZINE, ETHYL CARBAZATE
AND PHENYL CARBAZATE

The tris complexes of benzoylhydrazine and cobalt II have been reported previously and their magnetism and spectra are typical of octahedral cobalt II.¹³

The solid absorption spectra, table 2-3, and magnetic moments, table 2-4, of Co(PC)₃(NO₃)₂ and Co(EC)₃(NO₃)₂ are also indicative of octahedrally coordinated cobalt. As was observed with the analogous nickel complexes, ligand field strength has the order, BH > EC > PC. The d-d band responsible for the red colour of the complexes, at approximately 20 K.K., is the ℏ₉₄₄ (F) to ℏ₃₅₄₄ (P) transition.²³ The shoulder evident in the spectra of Co(EC)₃(NO₃)₂ and Co(PC)₃(NO₃)₂ is a consequence of spin-orbit coupling in the ℏ₉₄₄₄ (P) state. The lower energy band is the ℏ₉₄₄₄ (F) to ℏ₃₂₄₄ transition.²³ Magnetic moments of approximately 5.0 B.M. are typical of octahedrally coordinated cobalt.²₄

2-4 COBALT COMPLEXES OF N-ISOPROPYLIDENE-N'-BENZOYLHYDRAZINE, ISOPROPYLIDENE-ETHYL CARBAZATE AND ISOPROPYLIDENE-PHENYL CARBAZATE

Co(IPB)₂Cl₂ has been previously prepared by the present author,¹³ and has since been reported by Issa.¹⁸ The complex has since been repreared several times and its mull spectrum and magnetic moment re-examined. Magnetic moments, table 2-4, generally lie in the narrow range 4.65 to 4.70 B.M. This is the range common for tetrahedrally coordinated cobalt.²₄ The colour of the various preparation as seen by the naked eye vary from pale pink to light blue. The spectra show a large number of absorptions, table 2-3, which may be summarized thus,
a band at 20.9 K.K. with shoulders at 19.9 and 18.3
a band at 15.7 K.K. with shoulder at 14.9
a broad absorption at 7.5 K.K.

The absorption at ca. 20.0 K.K. may be due to octahedral cobalt and the
band at 14.9 K.K. is indicative of tetrahedrally coordinated cobalt. The
absorption at 7.5 K.K. may be the \( h_{1g} \) (F) to \( h_{2g} \) in an octahedral complex,
and/or the \( h_{A_2} \) to \( h_{T_1} \) (F) transition in a tetrahedral complex.\(^{25}\)

In any case, the ratio of the two high energy absorptions varies
from preparation to preparation. The preparative factors which govern these
variations are obscure. The ratio of tetrahedral to octahedral has not
exceeded 1:1 which means that the tetrahedral species probably constitutes
less than 10% of the mixture. Whether the 10% is present as an impurity
which cannot be detected by analysis, or is the result of the complexes
ability to exist in more than one isomeric form is difficult to say, but
all due precautions were taken to ensure that the complex was not
contaminated with cobalt chloride. Solution studies are precluded because
no suitable solvent can be found. \( \text{Co(IPBH)}_2 \text{Cl}_2 \) is soluble in pyridine and
the bis pyridinate \( \text{Co(IPBH)}_2 \text{2PyCl}_2 \) has been isolated. Solution spectra
and magnetic moment indicate that the pyridinate is octahedral.\(^{13}\)

\( \text{Co(IPPC)}_2 \text{Cl}_2 \text{2H}_2\text{O} \) has a magnetic moment typical of tetrahedral cobalt and
an absorption spectrum similar to that of \( \text{Co(IPBH)}_2 \text{Cl}_2 \) and is probably
a mixture of tetrahedral and octahedral species.

The remaining isopropylidene complexes, \( \text{Co(IPEC)}_2(\text{NO}_3)_2 \),
\( \text{Co(IPEC)}_2(\text{NO}_3)_2 \text{2H}_2\text{O} \), and \( \text{Co(IPPC)}_2(\text{NO}_3)_2 \text{2H}_2\text{O} \) all show spectra which are
indicative of octahedral cobalt. The magnetic moments of these complexes
are all lower than generally observed for octahedral complexes, possibly
they are not magnetically dilute. The average ligand field strength in these isopropylidene complexes is greater than the average field exerted by the parent ligands, in Co(BH)$_3$(NO$_3$)$_2$, which is surprising if the former set of complexes involves coordinate nitrate.

2-5 COPPER COMPLEXES

Ethyl and phenylcarbazate readily reduce copper II and only one copper II complex has been isolated, Cu(IPPC)$_2$Cl$_2$.

Table 2-3 - The Absorption Spectra of Some Cobalt Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelengths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(BH)$_3$SO$_4$ZH$_2$Cl</td>
<td>20.3, 8.8</td>
</tr>
<tr>
<td>Co(PC)$_3$(NO$_3$)$_2$</td>
<td>20.2, 19.0 sh., 8.7</td>
</tr>
<tr>
<td>Co(PC)$_3$(NO$_3$)$_2$</td>
<td>20.1, 18.9, 8.5</td>
</tr>
<tr>
<td>Co(IPPH)$_2$Cl$_2$</td>
<td>20.9, 20.0 sh., 18.2 sh., 15.8 sh., 14.9, 7.0 broad</td>
</tr>
<tr>
<td>Co(IPPC)$_2$Cl$_2$ZH$_2$O</td>
<td>22.8, 21.6 sh., 20.7 sh., 15.9 sh., 15.0, 14.5 sh., 9.3</td>
</tr>
<tr>
<td>Co(IPPC)$_2$(NO$_3$)$_2$ZH$_2$O</td>
<td>22.0, 20.0, 9.5</td>
</tr>
<tr>
<td>Co(IPPC)$_2$(NO$_3$)$_2$</td>
<td>22.0, 20.0, 9.5</td>
</tr>
<tr>
<td>Co(IPPC)$_2$(NO$_3$)$_2$</td>
<td>21.6, 20.7, 8.5</td>
</tr>
</tbody>
</table>

Table 2-4 - The Magnetic Moments of Some Cobalt Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature $\Theta_K$</th>
<th>$\mu$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(PC)$_3$(NO$_3$)$_2$</td>
<td>301.0</td>
<td>5.01</td>
</tr>
<tr>
<td>Co(PD)$_3$(NO$_3$)$_2$</td>
<td>301.0</td>
<td>4.95</td>
</tr>
<tr>
<td>Co(IPPH)$_2$Cl$_2$</td>
<td>298.0</td>
<td>4.65 - 4.69</td>
</tr>
<tr>
<td>Co(IPPC)$_2$Cl$_2$ZH$_2$O</td>
<td>298.0</td>
<td>4.67</td>
</tr>
<tr>
<td>Co(IPSC)$_2$(NO$_3$)$_2$ZH$_2$O</td>
<td>299.0</td>
<td>4.63</td>
</tr>
<tr>
<td>Co(IPSC)$_2$(NO$_3$)$_2$</td>
<td>300.0</td>
<td>4.61</td>
</tr>
<tr>
<td>Co(IPPC)$_2$(NO$_3$)$_2$</td>
<td>297.0</td>
<td>4.67</td>
</tr>
</tbody>
</table>
EXPERIMENTAL

3-1 THE VISIBLE SPECTRA AND MAGNETISM OF SOLID SAMPLES

Visible spectra and magnetic moment measurements on solid samples were performed in the manner reported in part A of this thesis.

3-2 ANALYTICAL TECHNIQUES

The analytical techniques used to determine, nickel, chlorine, hydrazine, carbon, hydrogen and nitrogen, are reported in part A of this thesis.

Cobalt

Cobalt was determined gravimetrically as the pyridine thiocyanate. 26

3-3 PREPARATION OF LIGANDS

Phenylcarbazate

Hydrazine hydrate 12.61 g. (.25 mole) was added slowly to diphenyl carbonate 45 g. (.21 mole). During the addition, the temperature was about 65°C and was maintained at that for a further five minutes. The solution was placed in a vacuum desiccator over phosphorus pentoxide. After the solution had been thoroughly dried, the colourless solution was dissolved in chloroform, filtered, and dry hydrogen chloride bubbled through until no further precipitate was formed. The colourless hydrochloride of phenylcarbazate was filtered at the pump, washed well with chloroform and dried under vacuum over phosphorus pentoxide.

About 95% of the theoretical quantity of 2N sodium hydroxide was added to a stirred solution of the hydrochloride in water (130 ml.).
The solution was cooled and the colourless crystals collected and dried over phosphorus pentoxide, m.p. 103.5°C, literature m.p. 105°C.

Analysis: Found - C, 55.22%; H, 18.15%; N, 5.46%. Calculated for C7H8N2O2: C, 55.29%; H, 18.43%; N, 5.27%.

**Ethylcarbazate**

100 g. (0.85 mole) of ethyl carbonate were shaken for 25 minutes with 44 g. (0.88 mole) of hydrazine hydrate, until the solution became homogeneous. The mixture was allowed to stand for half a day prior to vacuum distillation. Pure ethylcarbazate boiled at 86°C at 8\(\frac{1}{2}\) mm. pressure, m.p. 44°C.

Analysis: Found - C, 34.35%; H, 7.65%; N, 26.90%. Calculated for C7H8N2O2: C, 34.61%; H, 7.69%; N, 26.93%.

**Isopropylidene Phenylcarbazate**

The acetone adduct of phenylcarbazate was prepared by dissolving the hydrazine in a minimum volume of A.R. acetone. Cooling the solution induced precipitation, and the colourless compound so obtained was collected at the pump and dried under vacuum, m.p. 97.5°C.


**Isopropylidene Ethylcarbazate**

Ethylcarbazate was dissolved in about its own weight of boiling acetone. On cooling a poorly crystalline precipitate was obtained, which was collected, dried and then recrystallised from acetone, m.p. 72°C.

Analysis: Found - C, 50.01%; H, 8.43%; N, 19.76%. Calculated for C6H12N2O2: C, 49.97%; H, 8.38%; N, 19.43%. 
3-4. PREPARATION OF COMPLEXES

**Tris (N-benzoylhydrazino) Nickel II Dichloride Dihydrate**

Nickel chloride hexahydrate 1.19 g. in 10 ml. of water was added to 2.05 g. N-benzoylhydrazine in 20 ml. of water. An instant blue colouration resulted and blue crystals separated. The crystals were collected, washed several times with water and dried to constant weight over silica gel.

Analysis: Found - C, 43.57%; H, 5.15%; N, 14.58%; Ni, 10.18%.

Calculated for \( \text{C}_{21}\text{H}_{28}\text{N}_{6}\text{O}_5\text{Ni} \): C, 43.92%; H, 4.93%; N, 14.61%; Ni, 10.22%.

**Tris (N-benzoylhydrazino) Nickel II Dinitrate Dihydrate**

Nickel nitrate hexahydrate 1.9 g. in water was added to N-benzoylhydrazine 2.72 g. in water. A blue precipitate was formed immediately and after collecting was washed well with water and air dried.

Analysis: Found - C, 42.83%; H, 4.99%; N, 14.72%; Ni, 10.40%.

Calculated for \( \text{C}_{21}\text{H}_{28}\text{N}_{6}\text{O}_{11}\text{Ni} \): C, 40.20%; H, 4.50%; N, 17.87%; Ni, 10.28%.

**Tris (ethylcarbazate) Nickel II Dinitrate**

Nickel nitrate hexahydrate 1.93 g. in warm water, was added to 2.0 g. of ethylcarbazate in water. After allowing the solution to stand for a short time, the blue precipitate which had formed was collected, washed with cold water, and dried under vacuum over phosphorus pentoxide.

Analysis: Found - C, 22.06%; H, 5.15%; N, 22.30%; Ni, 11.90%.

Calculated for \( \text{C}_{24}\text{H}_{24}\text{N}_{8}\text{O}_{12}\text{Ni} \): C, 21.84%; H, 4.36%; N, 22.65%; Ni, 11.86%.

**Tris (phenylcarbazate) Nickel II Dinitrate Monohydrate**

Nickel nitrate hexahydrate .58 g. in ethanol was added to phenylcarbazate .90 g. in ethanol. The light blue solution was allowed to stand for twenty four hours, whilst a pale blue precipitate separated. The
precipitate was collected, washed with ethanol and dried to constant weight under vacuum over silica gel.

Analysis: Found - C, 37.84%; H, 4.05%; N, 17.04%; Ni, 8.85%.

Calculated for C_{21}H_{26}N_{2}O_{7}Ni: C, 38.37%; H, 3.99%; N, 17.06%; Ni, 8.93%.

**Bis-(N-isopropylidene-N'-benzoylhydrazino) Nickel II Dinitrate**

1.9 g. of nickel nitrate hexahydrate in acetone was added to N-benzoylhydrazine 2.72 g. The blue precipitate separated which was collected, washed with acetone and dried to constant weight under vacuum over P_{2}O_{5}.

Analysis: Found - C, 44.83%; H, 4.68%; N, 16.17%; Ni, 10.60%.

Calculated for C_{20}H_{24}N_{2}O_{6}Ni: C, 44.90%; H, 4.52%; N, 15.72%; Ni, 10.62%.

**Bis-(N-isopropylidene-N'-benzoylhydrazino) Nickel II Dinitrate Dihydrate**

Nickel nitrate hexahydrate 1.9 g. in acetone was added to N-benzoylhydrazine 2.72 g. in acetone (total volume 45 ml.). The blue precipitate which separated was collected, washed with acetone, and air dried.

Analysis: Found - C, 42.83%; H, 4.99%; N, 14.72%; Ni, 10.40%.

Calculated for C_{20}H_{26}N_{2}O_{10}Ni: C, 42.07%; H, 4.92%; N, 14.72%; Ni, 10.28%.

**Bis-(isopropylidene ethylocarbazate) Nickel II Dinitrate**

An acetone solution of 1.9 g. of nickel nitrate hexahydrate was added to 2.08 g. of ethylocarbazate in acetone (total volume 20 ml.). The blue-green precipitate which separated, was collected, washed with acetone and dried under vacuum over phosphorus pentoxide.

Analysis: Found - C, 30.6%; H, 5.25%; N, 17.58%; Ni, 12.46%.

Calculated for C_{12}H_{21}N_{3}O_{10}Ni: C, 30.58%; H, 5.13%; N, 17.85%; Ni, 12.46%.
Bis-(isopropylidene phenylcarbazate) Nickel II Dinitrate

An acetone solution of nickel nitrate hexahydrate, 0.86 g. was added to 0.9 g. of ethyl carbazate in acetone. A pale blue crystalline product separated, which was filtered, washed with acetone and dried under vacuum over phosphorus pentoxide.

Analysis: Found - C, 42.61%; H, 4.66%; N, 15.21%; Ni, 10.24%.
Calculated for $\text{C}_{20}\text{H}_{24}\text{N}_{6}\text{O}_{10}\text{Ni}$: C, 42.36%; H, 4.26%; N, 14.83%; Ni, 10.36%.

Tris-(phenylcarbazate) Cobalt II Dinitrate

Cobalt nitrate hexahydrate, 0.5 g. in ethanol was added to phenylcarbazate, 0.9 g. in ethanol. The pink crystals which separated on standing were collected, washed with ethanol and dried to constant weight under vacuum over phosphorus pentoxide.

Analysis: Found - C, 39.64%; H, 3.80%; N, 17.37%; Co, 11.40%
Calculated for $\text{C}_{21}\text{H}_{24}\text{N}_{6}\text{O}_{12}\text{Co}$: C, 39.47%; H, 3.79%; N, 17.53%; Co, 11.40%

Tris-(ethylcarbazate) Cobalt II Dinitrate

Cobalt nitrate hexahydrate, 1.94 g. and ethylcarbazate, 2.08 g. was dissolved in a minimum volume of water and allowed to stand at room temperature. The red crystals which separated were washed with water and dried under vacuum over silica gel.

Analysis: Found - C, 22.27%; H, 5.05%; N, 22.82%; Co, 11.80%
Calculated for $\text{C}_{9}\text{H}_{24}\text{N}_{6}\text{O}_{12}\text{Co}$: C, 21.83%; H, 4.86%; N, 22.64%; Co, 11.91%

Bis-(N-isopropylidene-N'-benzoylhydrazino) Cobalt II Dichloride

The preparative method was that previously employed. Cobalt chloride hexahydrate, 0.65 g. in A.R. acetone was added to N-benzoylhydrazine, 1.36 g. in A.R. acetone. The pale blue precipitate which separated was collected and washed with acetone.
Analysis: Found - Cl, 14.68%; N₂H₄, 13.27%; Co, 12.17%. Calculated for C₂₇H₂₄N₄Cl₂Co: Cl, 14.7%; N₂H₄, 13.20%; Co, 12.2%.  

**Bis-(isopropylidene phenylcarbazate) Cobalt II Dinitrate Dihydrate**

Cobalt nitrate hexahydrate 0.85 g. in A.R. acetone was added to phenylcarbazate 0.9 g. in A.R. acetone. The pink precipitate which separated was collected, washed well with acetone and air dried.

Analysis: Found - C, 41.92%; H, 4.59%; N, 14.65%; Co, 10.2%. Calculated for C₂₀H₂₄N₂O₁₀Co: C, 42.5%; H, 4.27%; N, 14.5%; Co, 10.39%.

**Bis-(isopropylidene phenylcarbazate) Cobalt II Dichloride Dihydrate**

Cobalt chloride hexahydrate 0.47 g. in acetone was added to 0.9 g. of phenylcarbazate in acetone. On standing a pale green solid separated from the blue solution. The green compound was collected washed well with acetone and air dried.

Analysis: Found - C, 13.12%; H, 5.07%; N, 10.2%; Cl, 13.3%; Co, 10.62%. Calculated for C₂₀H₂₄N₂O₁₀Cl₂Co: C, 43.69%; H, 5.12%; N, 10.10%; Cl, 12.89%; Co, 10.71%.

**Bis-(N-isopropylidene ethylcarbazate) Cobalt II Dinitrate**

Cobalt nitrate hexahydrate 0.97 g. and ethylcarbazate 1.0 g. were separately dissolved in warm acetone and then mixed. A pink-brown precipitate was formed immediately on mixing. After collecting and washing with acetone, the complex was dried to constant weight under vacuum over phosphorus pentoxide.

Analysis: Found - C, 30.68%; H, 5.38%; N, 17.60%; Co, 12.41%. Calculated for C₁₂H₂₄N₂O₁₀Co: C, 30.58%; H, 5.1%; N, 17.8%; Co, 12.50%.
Bis-\(\text{N-isopropylidene ethylcarbazate}\) Cobalt II Dinitrate Dihydrate

Air drying the complex prepared above gave the dihydrate.

Analysis: Found - C, 28.31%; H, 5.30%; N, 16.89%; Co, 11.57%.

Calculated for \(\text{C}_{20}\text{H}_{28}\text{N}_{6}\text{O}_{6}\text{Co}\): C, 28.40%; H, 5.56%; N, 16.58%; Co, 11.62%.

Bis-\(\text{N-isopropylidene phenylcarbazate}\) Copper II Dichloride

A solution of copper chloride dihydrate 0.51 g. in acetone, at approximately 0°C, was added dropwise to phenylcarbazate 0.9 g. in acetone, at the same temperature. There was little evidence of reduction and the solution was set aside to stand for several days. A light green product was obtained, which was filtered, washed with acetone, and dried to constant weight under vacuum over phosphorus pentoxide.

Analysis: Found - C, 45.97%; H, 4.59%; N, 10.41%.

Calculated for \(\text{C}_{20}\text{H}_{24}\text{N}_{6}\text{O}_{6}\text{Cu}\): C, 46.30%; H, 4.66%; N, 10.80%.
REFERENCES

17. A.A. Diamantis, unpublished work.
21. P.V. Gogorishi, L.D. Tsitsishirili and M.L. Karkarashvili,
PART C

THE COMPLEXING ACTION OF DIPHENYL PHOSPHOROHYDRAZIDATE,

SODIUM PHENYL PHOSPHOROHYDRAZIDATE AND DIPHENYL THIOPHOSPHONYL HYDRAZIDE WITH FIRST ROW TRANSITION METALS
SUMMARY

The chelating action of the hydrazide group has been previously examined for acylhydrazines, semi-carbazones and phenyl and ethyl-carbazate. A further variation of this ligand type has been examined in this section, firstly by changing the $\text{C} = \text{O}$ grouping to a $\text{P} = \text{O}$ group in diphenyl phosphoroxydrazide DPH (i) and sodium phenyl phosphoroxydrazide SPH (ii).

There have been no reported studies of the complexing action of these or any other hydrazidophosphoric acids.

DPH was synthesised by the method of Audrieth, and gave no evidence of complexing with Co II, Ni II, Zn II, Co II or Fe II in alcoholic solution. Spectral studies in ethanol dimethylformamide mixtures gave no indication of any interaction between DPH and these metals; DPH readily reduced Cu II and Fe III. By analogy to the benzylation action of $N$-benzoylhydrazine, DPH was considered to be a potential phosphorylating agent, however the intended investigation

* Reviewed in Part B of this thesis.
into its phosphorylating action was curtailed by the publication of Hamer et al., who reported that when phenyl or benzyl phosphorohydrazidate is oxidised by iodine or N-bromosuccinimide it gives an intermediate which phosphorylates alcohols and phosphate anions.

The complexing action of the water soluble SPH, which was difficult to prepare was examined with a variety of metals. A blue complex Cu(SP)₂Zn₂O separated from aqueous solutions of Cu II and SPH, but with Fe II, Co II, Ni II and Cd II precipitates were formed which had a low content in hydrazine.

In the presence of the latter metals, SPH appears to decompose with the loss of hydrazine.

The lack of, or very weak complexing action of DPH is difficult to explain. The proximity of the two electronegative oxygen atoms may reduce the electron donating power of the hydrazide group, however this explanation seems inadequate in view of the close similarity in ligand field strength between acylhydrazines and the corresponding carbazates. This consideration prompted the synthesis of a third ligand, diphenylthiophosphonyl hydrazide (PSH), (iii), in which the two C₆H₅ groups of DPH have been replaced by phenyl groups, and as an additional variation the P=O group by P=S.

Ethanolic solutions of PSH and CoCl₂, CoBr₂ or NiCl₂ give crystalline complexes analyzing for M₂(PSH)ₓX₂, where M is the divalent metal and X the monovalent anion. These complexes are obviously associated and visible spectra indicate that the metal ion is probably in an octahedral environment.
(iii)
RESULTS AND DISCUSSION

1-1 DIPHENYL PHOSPHORHYDRAZIDATE

DPH was prepared from the mono-chloro ester and hydrazine hydrate.\(^1\) The chloro ester \((\text{C}_6\text{H}_5\text{O})_2\text{P(0)Cl}\) was prepared by method of Rapp,\(^3\) viz. by refluxing for eleven hours, two moles of phenol with one of phosphorus oxychloride. This method was found to be equally as satisfactory as the method of Muller,\(^4\) who recommended strict temperature control and the use of \(1\frac{1}{2}\) moles of phenol to 1.0 of phosphorus oxychloride. The products of the reaction, \((\text{C}_6\text{H}_5\text{O})_2\text{P(0)Cl}, (\text{C}_6\text{H}_5\text{O})_2\text{P(0)Cl}_2\) and \((\text{C}_6\text{H}_5\text{O})_3\text{P(0)}\) were separated by vacuum distillation. After several redistillations the required ester was obtained in about 35% yield.

Initial investigations into the complexing properties of DPH were performed in the manner which was successful in the case of carboxylic acid hydrazides, however, methanolic solutions of the ligand with Zn, Co, Ni and Cd gave no indication of complex formation. DPH readily reduced Cu II and Fe III.

The isopropylidene derivative was prepared and it too showed no visible sign of complexing. In an attempt to determine whether or not there was an interaction between the hydrazide and its isopropylidene derivative, and either cobalt or nickel, visible spectra with either the metal nitrate or halide and excess ligand were run in 30% N-N'-dimethylformamide-, 70% methanol. The spectra were no different either in absorption maxima or extinction coefficient to those of the metal salt under the same conditions of solvent and concentration. Thus it appears
that the ligand exerts little or no coordinating action in this solvent system, i.e. it is not a stronger ligand than the solvent. It does appear now that a better approach to the complexing action of this hydrazide could have been made through the utilisation of non-aqueous systems with a weakly coordinating solvent such as tetrahydrofuran.

1-2 SODIUM PHENYL PHOSPHOROHYDRAZIDATE (SPH)

This compound was synthesised as it was considered that it may act as a uncharged bidentate ligand. The first attempt at synthesis was based on the method of Klemment, i.e. by warming diphenyl phosphorohydrazone with strong alkali until the first vigorous reaction ceased, then cooling and precipitating with ethanol. The method was unsuccessful, C, H, N, P and N₂H₄ analyses were variable and far from the required values. The main difficulty seemed to be in determining when the hydrolysis had proceeded to the desired degree, generally analytical and chromatographic evidence suggested that the disodium salt and inorganic phosphate were present as impurities.

The problem of synthesis was solved by the publication of Hamer et al who developed a second and improved method of controlled hydrolysis. This process consisted of heating a propanol-water solution of sodium hydroxide and diphenyl phosphorohydrazone at 100°C in a sealed tube for 15 minutes. Generally this method gave a satisfactory product, as judged from analytical data, but occasional difficulty in reproducing results was experienced even though freshly prepared samples of diphenyl phosphorohydrazone were used.

The mono-sodium salt, usually prepared as a hemi-hydrate, was
water soluble, and accordingly its complexing action was investigated by mixing aqueous solutions of the metal salt and ligand. Precipitates were formed with Co II, Ni II, Cu II, Fe II and Cd II. Mixing aqueous solutions of SPH and copper sulphate resulted in the immediate formation of a blue precipitate which was insoluble in all solvents except pyridine, wherein reduction and decomposition occurred. Analysis revealed that the compound was Cu (SPH)$_2$ H$_2$O and the visible spectrum showed an absorption maximum at 16.3 K K. with a shoulder at lower energy. This indicates that the copper atom is under the influence of a ligand field which is slightly stronger than that experienced in the ionic copper benzoyl-hydrazine complexes, which suggests that the nitrogen atoms are probably involved in the inner coordination sphere of the copper ion. The complex has a magnetic moment of 1.9 B.M. which is in the range generally observed for Cu II complexes. The copper complex decomposes over a period of time.

Aqueous solutions of SPH and Co II, Ni II, Cd II or Fe II give a precipitate which begins to form soon after mixing and continues over a period of hours or days. Metal and hydrazine analyses on these precipitates indicate that the ligand has decomposed with the loss of hydrazine, because hydrazine figures are low for a complex M (SPH)$_2$ where M is Co, Ni, Cd or Fe and metal analyses are too high for a complex with this formulation. These observations are in agreement with those of Klemment who reported that SPH slowly forms precipitates with lead and uranyl which contain practically no hydrazine.
DIPHENYLTIOPHOSPHONYL HYDRAZIDE (PSH)

PSH was prepared for the first time using a similar method to that employed for the preparation of diphenyl phosphorohydrazide, viz. by the reaction of two moles of hydrazine hydrate with one of diphenyl-thiophosphonyl chloride in ethanol. The starting material \((C_6H_5)_2P(S)Cl\) was prepared as a yellow liquid by refluxing diphenylchlorophosphine and powdered sulphur in benzene.\(^7\)

PSH prepared by this method and recrystallised several times from ethanol gave only imperfect C, H, N and S analyses. The analytical figures obtained for the sample used in the preparation of complexes were:

- Found: C, 56.88%; H, 5.49%; N, 10.40%; S, 12.91%.
- Calculated for \(C_{12}H_{13}N_2PS\): C, 58.03%; H, 5.28%; N, 11.28%; S, 12.91%.

When warm ethanolic solutions of PSH and CoCl\(_2\), CoBr\(_2\) or NiCl\(_2\) were mixed, crystalline products separated which analysed for \(M(PSH)_{4n}X\)\(_2\), where \(M\) is Co or Ni and \(X\) Cl or Br. The analytical figures for these three complexes are given in table 1-1. The pale blue nickel complex has an absorption spectrum which is characteristic of octahedrally coordinated nickel, with absorption maxima of 11.0 K.K., 16.4 K.K. and 26.8 K.K. The formula may be written \([Ni_2(PSH)_{9n}Cl_{4n}]\) where \(n\) is unknown. For the nickel atoms to achieve octahedral coordination, some of the PSH molecules must act as bidentates and others as monodentates. Bridging between nickel atoms may be established by the sharing of a sulphur atom, or by one of the donor atoms of the bridging PSH molecule being coordinated to one nickel atom and the other donor atom being coordinated to the neighbouring nickel.
Table 1-1 - Analyses of Metal Complexes with \((\text{C}_6\text{H}_5)_2\text{P}(\text{S})\text{NH}_2\) (PSh)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Anion</th>
<th>Found %</th>
<th>Calculated for (\text{M}_2(\text{PSh})_9\text{X}_2) %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Metal C</td>
<td>H</td>
</tr>
<tr>
<td>Co</td>
<td>Cl</td>
<td>4.80</td>
<td>52.44</td>
</tr>
<tr>
<td>Ni</td>
<td>Cl</td>
<td>4.85</td>
<td>51.88</td>
</tr>
</tbody>
</table>
The solid state absorption spectra of the pale blue complexes \( \text{Co}_2(\text{PSH})_9 \text{Cl}_2 \) and \( \text{Co}_2(\text{PSH})_9 \text{Br}_2 \) are characterised by an absorption from 8.5 - 9.2 K.K. and another at 19.1 K.K. with shoulders at 17.1 K.K. and 21.1 K.K. The positions of the maxima are indicative of octahedrally coordinated cobalt. The presence of more bands than are generally observed may be due to the fact that all the cobalt atoms in the polymer are not in identical ligand fields. Magnetic moments of about 4.70 B.M. are low for octahedral complexes and may be indicative of metal metal interaction.
**EXPERIMENTAL**

**Monochlorodiphenylphosphate**

\((\text{C}_6\text{H}_5\text{O})_2\text{POCl}\) was prepared by both the method of Muller and by that due to Rapp, the latter was generally employed. A mixture of two mole of phenol and one of phosphorus oxychloride was warmed to reflux during 11 hours. Fractionation separated the products \((\text{C}_6\text{H}_5\text{O})_2\text{POCl}\), \((\text{C}_6\text{H}_5\text{O})\text{POCl}_2\) and \((\text{C}_6\text{H}_5\text{O})_3\text{PO}\). The required ester was identified by chloride analysis.

**Found:** Cl = 13.1%. Calculated for \(\text{C}_{12}\text{H}_{10}\text{ClP}O_3\): Cl = 13.2%.

**Diphenyl Phosphorylhydrazide**

The hydrazide was prepared by the method of Audrieth.\(^1\) 26.0 g. (.103 mole) of \((\text{C}_6\text{H}_5\text{O})_2\text{POCl}\) was added dropwise to 10.1 ml. (.203 mole) of hydrazine hydrate in 8 ml. of 95% ethanol. The solution was stirred throughout, and a heavy clear oil, hydrazine hydrochloride, settled out.

The hydrochloride was brought back into solution by the addition of water and diphenyl phosphorylhydrazide recovered by cooling the solution. The crude product was recrystallised from methanol water, m.p. 116°C, literature = 116°C.

**Analysis:** Found - \(\text{N}_{2}\text{H}_4\), 12.08%. Calculated for \(\text{C}_{12}\text{H}_{13}\text{N}_{2}\text{O}_3\text{P}: \text{N}_{2}\text{H}_4\), 12.12%.

**Diphenyl \(N^2\)-isopropylidene Phosphorylhydrazide**

The acetone derivative of diphenyl phosphorylhydrazide was prepared by dissolving the hydrazide in boiling acetone and allowing to crystallise. The compound was recrystallised from methanol, m.p. 142°C, literature 142°C.
Analysis: Found - C, 59.0%; H, 5.68%; N, 9.17%. Calculated for
C₁₅H₁₇N₂O₂P: C, 59.2%; H, 5.63%; N, 9.21%.

Sodium Phenyl Phosphorohydrazide

(NaO)(C₆H₅O) P(O) NH NH₂ was prepared by two methods of those
due to Klement and to Brown. The method of Klement was unsatisfactory
in that analyses were variable and at no time agreed with the figures
expected for the sodium salt, whilst the second method was much more
successful and generally resulted in the preparation of an analytically
pure sample. The procedure employed was as follows:
(5.4 g.) of (C₆H₅O)₂ P(O)NH₂ dissolved in 10 ml. of propan-2-ol was
added to a hot solution of sodium hydroxide (1.6 g. in 10 ml. of water).
The mixture was maintained at 100°C for 15 minutes in a sealed tube, and
then a further 80 ml. of propanol were added. The sodium salt crystallised
on cooling as the semi-hydrate and was recrystallised from water-propan-
2-ol. Drying at room temperature over P₂O₅ gave the semi-hydrate, drying
under the same conditions, but at 95°C gave the anhydrous complex.
Analysis: Found - C, 32.51%; H, 4.07%; N₂H₄, 14.58%. Calculated for
C₆H₈N₂NaO₂P O.5H₂O: C, 32.30%; H, 4.10%; N₂H₄, 14.63%.

Bis-(phenyl phosphorohydrazide) Copper II Dihydrate

1.05 g. (0.005 mole) of (NaO)(C₆H₅O) P(O)NH₂ in water was added
to 0.25 g. (0.0025 mole) of copper sulphate in water. The blue precipitate
which formed immediately on mixing was centrifuged, washed with water
and dried over silica gel.
Analysis: Found - C, 30.13%; H, 4.46%; N, 11.87%; Cu, 13.3%. Calculated
for C₁₂H₂₀N₀₄P₂Cu: C, 30.42%; H, 4.25%; N, 11.82%; Cu, 13.41%. 
Diphenylthiophosphonyl chloride

Diphenylthiophosphonyl chloride was prepared by slowly adding powdered sulphur (1.5 mole) to diphenylchlorophosphine. Diphenylchlorophosphine was obtained from the Aldrich Chemical Company and was redistilled before use. During the addition of the sulphur, which was performed under nitrogen, the temperature rose to 110°C. The solution was maintained at this temperature for one hour, excess sulphur was removed by filtration and the required \((\text{C}_6\text{H}_5)_2\text{P(S)Cl}\) recovered and purified by vacuum distillation. Sulphur deposits indicated that distillation did in fact cause some decomposition. Diphenylthiophosphonyl chloride was recovered as a yellow liquid and was identified by chloride analysis.

Found: Cl, 14.35%. Calculated for \(\text{C}_{10}\text{H}_{10}\text{Cl}\) PS: Cl, 14.0%.

Diphenylphosphonothioic Hydrazide

12.6 g. \((5 \times 10^{-2} \text{ mole})\) of \((\text{C}_6\text{H}_5)_2\text{P(S)Cl}\) was added dropwise with stirring to 5 g. \((10^{-1} \text{ mole})\) of hydrazine hydrate in 12 ml. of ethanol. At first the solution assumed a red colour but this diminished as the reaction proceeded and a white precipitate formed. Sufficient water was added to dissolve the hydrazine hydrochloride and the mixture cooled and the product collected. The crude diphenylphosphonothioic hydrazide was recrystallised from either benzene or ethanol, m.p. 87°C.

Analysis: Found – C, 58.88%; H, 5.48%; N, 10.40%; S, 12.91%.

Calculated for \(\text{C}_{12}\text{H}_{13}\text{N}_2\text{PS}\): C, 58.03; H, 5.29%; N, 11.29%; S, 12.91%.
Complexes of nickel chloride, cobalt chloride and cobalt bromide with diphenylphosphonothioic hydrazide were prepared by the following general method.

A warm solution of the metal salt in ethanol was added to a warm solution of the ligand in the same solvent, a molar ratio of 5 moles of ligand to one of metal was used. A crystalline precipitate separated immediately and this was collected, washed with ethanol and dried under vacuum. Analytical figures for these complexes have been presented in table 1-1.
REFERENCES

3. M. Rapp, Ann., 224, 156 (1884).
4. P. Brigl and H. Muller, B., 72, 2173 (1938).