Characterization of New Metal Complexes of Schiff Bases and Macrocyclic Ligands and Some Mononitrosyl Derivatives

A Thesis Submitted to the University of Surrey in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Science

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Abstract

Work on iron mononitrosyl complexes of bidentate Schiff base anions derived from salicylaldehyde is described. The complex bis(N-benzylsalicylideneiminato)nitrosyliron and its 4-methyl and 4-methoxy derivatives are the first examples of such compounds to be synthesised. The magnetic properties over the temperature range 293 to 87 K show that they are high spin \{FeNO\}7 with slightly temperature dependent effective magnetic moments. Infrared investigations suggest that the Fe-N-O groups are linear.

Attempts to prepare an iron mononitrosyl with Schiff base derived from 2-hydroxyacetophenone and ethylenediamine resulted in the formation of a binuclear iron(III) oxo-bridged complex \( \mu \)-oxo-bis[N,N'-bis(2-hydroxyacetophenone)ethylenediiminato]iron(III)], which, when investigated by X-ray crystallography, is shown to contain a bent bridging group with a Fe-O-Fe bond angle of 156.7°. This is the first example of a \( \mu \)-oxo iron(III) complex with a 2-hydroxyacetophenone-derived Schiff base.

A series of cobalt mononitrosyls, mainly with bidentate Schiff base co-ligands derived from salicylaldehyde has been prepared and characterized by infrared, \(^1\)H, \(^{15}\)N and \(^{59}\)Co NMR spectroscopies as well as magnetic measurements. The infrared and \(^{15}\)N NMR indicate that the Co-N-O groups in these complexes are bent. Cobalt(II) complexes of the macrocycle 6,13-diphenyl-1,8-dihydro-2,3:9,10-dibenzo-1,4,8,11-tetraaza-cyclotetradecane-4,6,11,13-tetraene (dptaaH₂) and its methyl, methoxy, bromo and nitro derivatives have been prepared. On reaction with nitric oxide, they form mononitrosyls. Similar investigations show that the Co-N-O groups are bent and this has been confirmed by an X-ray
investigation carried out on Co(dptaa)NO from which the Co-N-O bond angle is 122.6°. All the mononitrosyls show temperature independent paramagnetism with fractional magnetic moments at room temperature in the range 0.59-1.31 B.M.

X-ray investigations carried out on two cobalt(II) Schiff base complexes, bis(N-n-butylsalicylideneiminato)cobalt(II) and bis(N-t-butylsalicylideneiminato)cobalt(II), suggest that the unreactivity of the t-butyl derivative to nitric oxide and dioxygen in contrast to the n-butyl derivative is due to steric hindrance of the t-butyl group.

The reactivity of Co(dptaa) towards chloroform, Br₂ and I₂ was investigated in attempts to prepare complexes of the type Co(dptaa)X where X = Cl, Br and I. Although reasonable microanalyses were obtained, the magnetic moments of the chloride and bromide were higher than expected for cobalt(III) complexes. Unfortunately, they could not be recrystallised to remove possible paramagnetic impurities.

Several chromium(II) complexes of Schiff bases derived from 2-hydroxyacetophenone have been prepared via the sodium and lithium salts of the bases. The instability of the complexes has however, prevented complete characterization.

Some miscellaneous investigations, mainly of chromium(II) complexes are also reported.
To my husband
and our coming baby, for Him.
Acknowledgements

I am greatly indebted to my supervisor, Prof. L.F. Larkworthy who has guided and helped me enormously academically and otherwise during the course of my studies. Without him, I could never have been able to reach the present state of my degree. His understanding and support during difficult times are very much appreciated.

Thanks are also due to Dr. D.C. Povey in his capacity as supporting supervisor, and Mr. G.W. Smith who has provided the much needed help in solving the crystal structures presented in this work.

Heartfelt thanks to Ms. N.J. Walker for her friendship and invaluable microanalysis service, Mr. J. Bloxsidge for his help in obtaining the NMR spectra, Mrs. R. Archer and Mr. A.P. Hill for their constant helpfulness and friendship in the lab and the forever cheerful and efficient Departmental secretaries, Pat, Kathy and Caron. Not forgetting the final year project students Miss J. Lowe and Miss C. Souris who have worked together with me in some nitrosyl complexes.

To my dearest husband, Azmi, it is difficult to find appropriate words to thank him for being what he is to me. He has been a constant source of strength, a friend, a company, and everything else, sticking with me through thick and thin, for better for worse. His faith and belief in me have kept me going all this while and forever.

To my special friend Dr. C. McGarry, words of gratitude are not enough for her unfailing support and understanding, through good and bad times, making this period of four years bearable and even enjoyable. Also Kak Ina, my very accommodating and kind friend; Jamila, Naila and so many other wonderful friends whom I cannot possibly list out in this limited page.

To my parents, all my sisters and brother and their families, you have all been inspirational. Thank you for your prayers for me.

Thank you to the Government of Malaysia and the MARA Institute of Technology for the financial support during the course of my study.
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\([\text{Mn(hap-1,3-pn)}]\)

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\([\text{Mn(happram)}_2]\)

References

Publication
## Abbreviations

### Ligands

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<th>Description</th>
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<td>SalenH₂</td>
<td><em>N</em>,<em>N</em>-Ethylenebis(salicylideneimine)</td>
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<tr>
<td>NEt₂SalenH₂</td>
<td><em>N</em>,<em>N</em>-Ethylenebis(4-diethylaminosalicylideneimine)</td>
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<td>SalbamH</td>
<td><em>N</em>-Benzylsalicylideneimine</td>
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<tr>
<td>SalMebamH</td>
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<tr>
<td>SalMeObamH</td>
<td><em>N</em>-4-Methoxybenzylsalicylideneimine</td>
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<td>SalFbamH</td>
<td><em>N</em>-4-Fluorobenzylsalicylideneimine</td>
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<td>fsa₂enH₂</td>
<td><em>N</em>,<em>N</em>-Ethylenebis(3-carboxysalicylaldimine)</td>
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<td>Bis(2-hydroxyacetophenone)ethylendiamine</td>
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<td>HapbamH</td>
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<tr>
<td>nbsal</td>
<td><em>N</em>-n-butylsalicylideneimine</td>
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<td>tbsal</td>
<td><em>N</em>-t-butylsalicylideneimine</td>
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<tr>
<td>dptaaH₂</td>
<td>6,13-Diphenyl-1,8-dihydro-2,3:9,10-dibenzo-1,4,8,11-tetraazacyclotetradecane-4,6,11,13-tetraene</td>
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<td>BrdptaaH₂</td>
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\[
\begin{align*}
\text{NO}_2\text{dptaH}_2 & \quad 6,13-\text{Di}(4\text{-nitrophenyl})-1,8\text{-dihydro}-2,3:9,10\text{-dibenzo}-1,4,8,11\text{-tetraazacyclotetradecane-}4,6,11,13\text{-tetraene} \\
[H_4]\text{HapenH}_2 & \quad \text{Bis}(2\text{-hydroxyacetophenone})\text{ethylenediamine} \\
[H_4]\text{Hap1,3-pnH}_2 & \quad \text{Bis}(2\text{-hydroxyacetophenone})-1,3\text{-propanediamine} \\
\text{DAN} & \quad 1,8\text{-Diaminonaphthalene} \\
\text{depe} & \quad 1,2\text{-Bis(diethylphosphino)ethane} \\
\text{dmpe} & \quad 1,2\text{-Bis(dimethylphosphino)ethane} \\
\text{TMEDA} & \quad N,N,N',N'\text{-Tetramethylethylenediamine} \\
\end{align*}
\]

**Solvents**

<table>
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<th>Solvent</th>
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<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulphoxide</td>
</tr>
</tbody>
</table>

**Apparatus Diagrams**

In the apparatus diagrams, a tap with a greased key is represented as in (a) whereas one with a greaseless key is presented as in (b).
CHAPTER

ONE

INTRODUCTION
1. Introduction

The work covered in the thesis is on the synthesis and characterization of:

(a) new metal complexes of Schiff bases and a macrocyclic compound 6,13-diphenyl-1,8-dihydro-2,3:9:10-dibenzo-1,4,8,11-tetraazacyclotetradecane-4,6,11,13-tetraene (dptaaH₂) and its various substituted derivatives and

(b) nitrosyl compounds formed by reaction of these metal complexes with nitric oxide.

In this Chapter, some background is given to the physical techniques used to study the complexes and the general chemistry of the nitrosyl ligand. Since most of the complexes and the metal salts used as starting materials are air sensitive, the general experimental techniques and the preparations of starting materials are described in Chapter Two. The work covered in Chapter Three is on some iron and cobalt Schiff base mononitrosyl complexes, some Schiff bases being tetradeutate and others bidentate. In Chapter Four, preparations of some cobalt(II) complexes of the macrocycle 6,13-diphenyl-1,8-dihydro-2,3:9,10-dibenzo-1,4,8,11-tetraaza-cyclotetradecane-4,6,11,13-tetraene (dptaaH₂) and its various substituted derivatives are presented as well as investigations of their mononitrosyls. Attempts to prepare dptaa complexes of other metals i.e. iron(II), chromium(II) and manganese(II) are also included. Chapter Five covers work that has been done on complexes of chromium(II) with Schiff base anions and Chapter Six is a compilation of several miscellaneous topics which have been investigated.

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1.1. Theory of Magnetism

Only a brief account of magnetism is given here. Further details are given by Earnshaw.¹

\( \chi_g, \) the gram susceptibility, is given by:

\[
\chi_g = \frac{\kappa}{d}
\]

where \( \kappa = \) volume susceptibility

\( d = \) density

\( \chi_M, \) the molar susceptibility, is defined as:

\[
\chi_M = RMM \chi_g
\]

where \( RMM = \) relative molecular mass of the material

The atomic susceptibility \( \chi_A \) of any material is the resultant of two terms:

\[
\chi_A = \chi_M + \chi_L
\]

where \( \chi_L = \) diamagnetic correction for ligands

The diamagnetic correction for ligands is usually made using Pascal's constants¹ which give each atom a fixed diamagnetism \( \chi_i \).

Therefore \( \chi_L = \sum_{n} \chi_i \)
For any paramagnetic compound, the molecular magnets resulting from the presence of unpaired electrons tend to align themselves with an applied magnetic field, whilst the thermal energy (kT) opposes this alignment. As the temperature decreases, the thermal energy decreases and susceptibility increases. It can be deduced that if the molecular magnets behave independently of each other, i.e. the substance is magnetically dilute, the expression $\chi_A = \frac{N^2 \mu^2}{3RT}$ should be obeyed when $\mu$, the magnetic moment, is independent of temperature. This corresponds to the Curie law $\chi_A = \frac{C}{T}$.

However, few paramagnetic substances obey the Curie law exactly because $\mu$ often varies with temperature, then a more general equation, the Curie-Weiss law $\chi_A = \frac{C}{T+\theta}$ is obeyed, where $\theta$ is a measure of the departure from ideal behaviour. The magnetic moment, however, is usually calculated from $\chi_A = \frac{N^2 \mu^2}{3RT}$. It is then termed the 'effective magnetic moment', $\mu_{\text{eff}}$, the unit of which is the Bohr Magneton (B.M.). Substituting values for the constants $N$ and $R$ leads to the equation:

$$\mu_{\text{eff}} = 2.828 \sqrt[3]{\chi_A T} \text{ B.M.}$$

Elements of the first transition series are expected to have magnetic moments obeying the expression:

$$\mu = \sqrt{4S(S+1)+L(L+1)} \text{ B.M.}$$

where $S$ and $L$ are the spin and orbital moments respectively in units of $\frac{\hbar}{2\pi}$. 

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However, the orbital angular momentum is often quenched since the electrostatic fields of the ligands remove the degeneracy of the 3d orbitals. Then the above formula reduces to the 'spin-only' formula $\mu_{so}$:

$$\mu_{so} = \sqrt{4S(S+1)} \text{ B.M.}$$

If $n$ is the number of unpaired electrons, then $S = \frac{n}{2}$.

Therefore

$$\mu_{so} = \sqrt{n(n+2)} \text{ B.M.}$$

The spin only magnetic moment values for various numbers of unpaired electrons are listed in Table 1.1.

Table 1.1. Values of the spin only magnetic moment $\mu_{so}$ for various numbers of unpaired electrons.

<table>
<thead>
<tr>
<th>No. of unpaired electrons</th>
<th>$\mu_{so}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.73</td>
</tr>
<tr>
<td>2</td>
<td>2.83</td>
</tr>
<tr>
<td>3</td>
<td>3.88</td>
</tr>
<tr>
<td>4</td>
<td>4.90</td>
</tr>
<tr>
<td>5</td>
<td>5.92</td>
</tr>
</tbody>
</table>

When the orbital angular momentum is incompletely quenched, moments in excess of the above values are obtained and are said to include an 'orbital contribution'.
1.2. Temperature Independent Paramagnetism

The atomic susceptibility, $\chi_A$, may contain a small temperature independent paramagnetism contribution. A magnetic field can be considered to distort the electron distribution of an ion on which it acts such that the description of the ground state is changed to a very small extent.

This new description is achieved by 'mixing in' a small amount of some higher state into the ground state. The level which is 'mixed in' usually lies much more than $kT$ above the ground level so that thermal population cannot occur and the contribution made to the susceptibility is independent of temperature, hence the term temperature independent paramagnetism (T.I.P.).

For T.I.P. the expression

$$\mu_{\text{eff}} = 2.828 \sqrt{\chi_A T}$$

reduces to

$$\mu_{\text{eff}} \propto (T)^{1/2}$$

since $\chi_A$ is a constant.

The above formula only applies in the absence of normal paramagnetism, since the effect of unpaired electrons will swamp the temperature independent contribution. This phenomenon is also called 'Van Vleck Paramagnetism'.
1.3. Compounds Containing the Nitrosyl Ligand

The nitrosyl ligand is found in many transition metal complexes and can be considered derived from nitric oxide.

1.3.1. Nitric oxide

Nitric oxide is the simplest thermally stable odd-electron molecule known, and consequently, its electronic structure and reaction chemistry have been extensively studied. It is a colourless, monomeric and paramagnetic gas ($\chi_M = 1.46 \times 10^{-3}$ c.g.s. at 20°C; temperature dependent $\mu_{\text{eff}}$) with a melting point of -163.6°C and boiling point of -151.8°C. Upon heating at elevated temperature (1100-1200°C), it decomposes to oxygen and nitrogen and at high pressure and moderate temperature (about 50°C) it rapidly disproportionates:

$$3\text{NO} \rightarrow \text{N}_2\text{O} + \text{N}_2\text{O}_3 \quad \Delta H = 155.3 \text{ kJ/mol}$$
$$\Delta G = 92.1 \text{ kJ/mol}$$

Little dimerization occurs at room temperature:

$$2\text{NO} \rightarrow \text{N}_2\text{O}_2 \quad \Delta H = 10.5 \text{ kJ/mol}$$

However, this dimerization is predominant in the liquid and even more in the solid phase; in both phases the molecule is colourless and exists in planar cis- and trans- forms, the latter being the more stable:
The NO molecule has an electron configuration of \((\sigma_1)^2 \ (\sigma_1^*)^2 \ (\sigma_2)^2 \ (\sigma_2^*)^2 \ (\pi_1)^4 \ (\sigma_3)^2 \ (\pi_1^*)^1\) and the bonding is best understood by MO theory as illustrated in Figure 1.1.

![Qualitative molecular orbital scheme of nitric oxide](image)

Figure 1.1. Qualitative molecular orbital scheme of nitric oxide.
The scheme is similar to those of CO and N₂, but NO has an extra electron in the \( \pi^* \) antibonding orbital. This unpaired electron renders the molecule paramagnetic and partly cancels the effect of the \( \pi \) bonding electrons. Thus the bond order is 2.5 (as opposed to 3.0 in CO and N₂), consistent with an interatomic distance of 1.15 Å, which is intermediate between the triple-bond distance in NO⁺ of 1.06 Å and representative double bond distances of about 1.20 Å.

1.3.2. Modes of Bonding of NO

Many studies have been carried out to understand the modes of bonding of this molecule which exhibits greater coordination versatility compared with that of many other simple molecules, including carbon monoxide and dinitrogen.

Because of the lability of coordinated NO in redox processes and its versatility as a ligand, upon complexation with transition metal centres, various modes of bonding are found in nitrosyl compounds. In many cases, the MNO bond angle is linear (close to 180°), but in other cases, the ligand is strongly bent (MNO angle of 120°-130°). However, in between the two extreme cases, compounds with partially bent MNO groups have been reported. Complexes containing single-³, double- and triple-bridging nitrosyls are also known. The geometry of the MNO group can also be fluxional in solution. It is difficult, however, to predict beforehand the preferred geometry for the whole range of complexes.

As early as 1934, it was recognised that nitric oxide could lose or gain one electron in its bonding interaction with a transition metal to give complexes.
of NO$^+$ and NO$^-$ i.e. complexes in which NO serves as a three-electron donor or a one electron donor respectively.

1.3.2.1. Linear Nitrosyl Coordination

Linear nitrosyl coordination is a much more common occurrence than bent nitrosyl coordination. Even though the term used here is 'linear', the designation does not disallow a small amount of bending in cases where the group is not in an axially symmetric environment. Thus, MNO angles of 161° to 175° may be found in 'linear' MNO groups. In this case, the coordination can be imagined as transfer of the antibonding electron ($\pi^*$)$^1$ to an empty orbital of the metal, followed by formal coordination as NO$^+$ (bond order 3), with donation of the ($\sigma_3$)$^2$ sp-hybridised lone pair electron into empty metal orbitals, giving effectively three electron donation. This can be described by Figure 1.2.

Figure 1.2. Schematic diagram of linear nitrosyl coordination.
The loss of the unpaired electron from the $\pi^*$ orbital of the nitric oxide molecule to the metal can be quite facile if the metal centre has an empty low energy $d$-orbital, which effectively encourages the transfer to take place. This loss of an electron from the NO reinforces the N-O bond so that the resultant NO$^+$ species has a shorter bond length (by 0.09 Å), a greater dissociation energy (251 kcal/mol) and a higher $v_{\text{NO}}$ (between 2250-2300 cm$^{-1}$ in most nitrosonium compounds) than the neutral NO which exhibits a vibrational frequency at 1888 cm$^{-1}$.\(^\text{10}\)

In linear metal nitrosyls, back-bonding into the $\pi^*$ orbital occurs and this is indicated by the short M-N bond distances. This is especially true for complexes of metal atoms with relatively high electron density. However, this process does not remove electrons from the formal valence shell of the metal. The $\pi^*$ orbitals are predominantly nitrogen in character and the nitrogen preferentially donates its electron pair to the metal to avoid a positive charge on the more electronegative oxygen atom\(^\text{11}\), therefore maximising $d_{\pi^-p_{\pi}}$ backbonding. As well as the short M-N bond characteristics of good $\pi$-backbonding, the N-O bond is also short; but it is nominally a triple bond weakened and lengthened by the extensive metal-to-nitrogen back-bonding.

### 1.3.2.2. Bent Nitrosyl Coordination

Truly bent MNO groups have angles between 120° - 140° and this mode of bonding is rarer than the linear coordination. In such systems, neutral NO can be thought of as a one electron donor, as in the analogous (bent) nitrosyl halides XNO or organic nitroso compounds, RNO with a single $\sigma$ bond between the nitrogen atom and the substituent and a lone pair on the nitrogen.
Using the similar description to the linear nitrosyl above, coordination in this mode is imagined as transfer of an electron of opposite spin from the metal to the nitric oxide to give NO$^-$ (bond order 2). Donation of the two electrons $(\sigma_3)^2$ from NO$^-$ to a metal orbital gives the bent nitrosyl group. This process can be illustrated schematically in Figure 1.3.

The nitrogen which is formally sp$^2$ hybridised causes the strongly bent MNO angle. Unlike linear complexes, it is said that no $\pi$-backbonding occurs in bent complexes$^9$, however Figure 1.3 above shows that backbonding is feasible.
1.3.2.3. Molecular Orbital Studies

Since the early 1960's scientists have put a great deal of effort into determining the factors that influence the geometry of coordination of diatomic and related polyatomic molecules to transition metal centres. The first MO scheme to account for the electronic spectra of linear nitrosyl and carbonyl compounds such as Fe(S₂CNMe₂)₂NO and Mn(CO)₅X (X = NO₃⁻, Br⁻, Cl⁻, I⁻) was presented by Gray et. al\(^1\). Subsequently, this scheme has been improved upon by several workers\(^1\), using molecular orbital techniques. A detailed account of the development of these studies has been outlined by Thompson\(^1\).

It has been pointed out\(^2\) that the mode of coordination of the metal nitrosyl group in a complex is dependent on the relative energies of the π\(^*\) orbital of the NO and the d orbital of the metal. If there exists an empty low energy d orbital on the metal, the pair of electrons forming the coordinate bond will be localized on the metal and the ligand may be described as NO\(^+\), i.e. a linear MNO angle, if not, the electrons will fill the π\(^*\) orbital of the nitrosyl and the species may be written as NO\(^-\), i.e. a bent MNO angle.

However, since the π\(^*\) orbital is similar in energy to the metal d orbitals, and since their mutual overlap is sizeable, any assignment of electrons in the complex to one fragment or the other is arbitrary, a situation that is especially acute for the nitrosyl ligand. For example, the complex [Rh(NO)(PPh₃)₃] can be considered formally as Rh(-1) and NO\(^+\) or Rh(+1) and NO\(^-\), but the extensive delocalization between the metal and nitrosyl group means that the actual electron distribution diverges significantly from both of these extreme descriptions. This dichotomy has been partially overcome by using the \{MNO\}\(^n\) notation, introduced by Feltham and Enemark\(^2\), in which \(n\) is the...
number of $d$-type electrons on the metal when the nitrosyl is formally considered to be NO$^+$. This system avoids any partition of the electrons to one fragment or another. Thus the preceding rhodium example$^{21}$ is described as \{RhNO\}$^{10}$.

There are three general factors which influence the linearity or otherwise of the MNO angle in nitrosyl complexes:$^9$

1. The coordination geometry and number,
2. The value of $n$,
3. The nature of the one-electron molecular orbitals.

Table 1.2 summarises the effect of 1 and 2 on the angle of the MNO group.

Table 1.2. The dependence of M-N-O angles of nitrosyl complexes on coordination number and geometry and the value of $n$.

<table>
<thead>
<tr>
<th>Coordination no.</th>
<th>Coordination geometry</th>
<th>$n$</th>
<th>M-N-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>octahedral</td>
<td>≤6</td>
<td>linear</td>
</tr>
<tr>
<td>6</td>
<td>octahedral</td>
<td>≥7</td>
<td>bent</td>
</tr>
<tr>
<td>5</td>
<td>square pyramidal and</td>
<td>≤6</td>
<td>linear</td>
</tr>
<tr>
<td></td>
<td>trigonal bipyramidal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>square pyramidal</td>
<td>8</td>
<td>bent</td>
</tr>
<tr>
<td>5</td>
<td>trigonal bipyramidal</td>
<td>8</td>
<td>linear</td>
</tr>
<tr>
<td>4</td>
<td>tetrahedral</td>
<td>10</td>
<td>linear</td>
</tr>
<tr>
<td>4</td>
<td>planar</td>
<td>10</td>
<td>bent</td>
</tr>
</tbody>
</table>
The ability of the NO ligand to bend, in contrast to related ligands such as CO or N$_2$ is explained in terms of the similarity of the energies of the HOMO and LUMO at nitrogen, the n(N) and (π*NO) orbitals to those of the ligand field orbitals.$^{22,23}$

An excellent review on the transition metal nitrosyl complexes by Mingos and Sherman$^5$ discusses some molecular orbital calculations for five and six coordinate complexes. Modifications of the MNO angle can be carried out by either:

(a) changing the energy of the π$_1^*$ orbitals or
(b) changing the energy of the metal d$_{z^2}$ and d$_{xz}$ orbitals.

As the nitrosyl bends, the d$_{z^2}$ orbital interacts favourably with π$_1^*$ and decreases its antibonding interaction with the nitrogen lone pair. At the same time, the metal d$_{xz}$ orbital decreases its bonding interaction with π$_1^*$. Therefore, to enhance the driving force to bend in these complexes, increasing the stabilizing interaction of the d$_{z^2}$ orbital and decreasing the stabilizing interaction of the d$_{xz}$ orbital in the metal are important, therefore, strong π-donor ligands are required. However, the relationship between the position of the central atom in the periodic table and the nitrosyl geometry is much harder to evaluate.

Since the present work is mainly concerned with pentacoordinate cobalt mononitrosyls {MNO}$^8$ and iron mononitrosyls {MNO}$^7$, these two systems will be discussed briefly here.
1.3.2.3.1. Pentacordinate Cobalt Mononitrosyls \(\{\text{MNO}\}^8\)

The principal geometries of five coordinate \(\{\text{MNO}\}^8\) are square pyramidal (SP) with bent apical nitrosoyl (NO\(^-\)) and trigonal bipyramidal (TBP) with linear MNO group (NO\(^+\)). In a study carried out by Hoffmann et al.,\(^2\) a molecular orbital model of pentacordinate nitrosyls was constructed based on the MNO bonding scheme derived from the interaction of an ML\(_4\) fragment of varying geometry with an NO group. For \(\{\text{MNO}\}^8\) species, the model leads to the following conclusions:

1. The better the \(\sigma\)- or \(\pi\)-donating capability of the basal ligands in a square pyramid, the more likely is the nitrosyl to bend. In compounds of the type ML\(_2\)L\(_2\')(NO), L trans to L', the nitrosyl group should bend in the plane containing the poorer donors. In a compound of the type ML\(_2\)DA(NO) where D = \(\pi\) donor trans to A = \(\pi\) acceptor, if the NO group bends in the DMA plane, then it should bend toward the acceptor.

2. A nitrosyl ligand is less likely to bend in the equatorial position of a trigonal bipyramid than in the apical site of a square pyramid. If a nitrosyl in a trigonal bipyramid bends, then it would prefer to do so in the axial plane rather than the equatorial one. Nitrosyl groups in equatorial positions in a trigonal bipyramid and basal sites in a square pyramid should be linearly coordinated.

3. In ML\(_4\)(NO) species, if L are strong \(\pi\)-acceptor substituents, a trigonal bipyramid with an equatorial nitrosyl will be preferred. If the ligands are strong \(\pi\)-donors, a range of geometries is possible, from a strongly bent square pyramid to a less bent trigonal bipyramid. A bent nitrosyl will move its nitrogen off the coordination axis in the direction of \(\pi\) coordination.
Enemark and Feltham\textsuperscript{25} in a review on metal nitrosyl complexes suggested the molecular orbital correlation diagram for \{MNO\}\textsuperscript{8} systems in Figure 1.4.

![Correlation Diagram](image)

Figure 1.4. A correlation diagram relating the molecular orbitals of five-coordinate \{MNO\}\textsuperscript{8} complexes in fields of $C_2$, $C_{4v}$, $C_s$ symmetry.

Figures 1.4(b) and 1.4(c) show two possible orbital schemes for a pentacoordinate complex having $C_{4v}$ symmetry and show the correlation diagrams relating these two schemes to each other. The 3e orbitals are antibonding, and from the analysis of triatomic MNO, placing electrons in an antibonding orbital results in the distortion of the MNO group. In Figure 1.4(b), all the eight electrons are placed in bonding and non-bonding orbitals which
results in linear coordination of NO to the metal centre. However, when the 3e orbitals are lower in energy than the $4a_1$ (Figure 1.4(c)) then there will be two electrons in the 3e anti-bonding orbitals which would lead to bending of the MNO group. Figure 1.4(d) shows the resultant ordering of the orbital in a TP complex with a strongly bent MNO group.

1.3.2.3.2. Pentacoordinate Iron Mononitrosyls {MNO}$^7$

Most known pentacoordinate iron mononitrosyls have linear MNO groups and the molecular orbital diagram suggested for the tetragonal pyramidal complexes with linear MNO group is illustrated in Figure 1.5. Depending on the relative positions of the antibonding orbitals $3b_1$ and $3b_2$ with the non-bonding $5a_1$, {FeNO}$^7$ complexes can have only a single electron in either of the three orbitals. A complex with a bent MNO species will have a molecular orbital correlation diagram with the $3b_1$ and $3b_2$ orbitals at a lower position than the $5a_1$, thus having the seventh electron in either one of the two former orbitals.
Figure 1.5. The molecular orbital diagram for a tetragonal pyramidal (TP) pentacoordinate iron mononitrosyl.
1.3.2.4. Synthesis of Nitrosyl Complexes

Many methods are used for the synthesis of nitrosyl complexes and some examples of the most widely used routes are listed here.

a) Addition reaction

Passing gaseous nitric oxide through a solution of a coordinatively unsaturated transition metal complex may result in a simple addition. As nitric oxide contains an unpaired electron, this method is most commonly applied to paramagnetic starting materials. An example is shown below:

Apart from using NO gas as in the case above, nitrosonium salts (usually of tetrafluoroborate or hexafluorophosphate) also provide an easy synthetic route to nitrosyl complexes.

b) Substitution of other ligands

Nitric oxide can replace ligands such as CO, tertiary phosphines and alkenes. An example of a CO substitution is:
c) Reductive nitrosylation

Reacting nitric oxide with high oxidation state metal halides can lead to reduction to low-valent nitrosyl compounds with elimination of nitrosyl halides\textsuperscript{28}.

\[
\text{NO, MeCN} \quad [\text{MoCl}_5] \quad \rightarrow \quad [\text{MoCl}_3(\text{NO})(\text{MeCN})_2]
\]

Reductive nitrosylation also occurs on reaction of hydroxylamine with transition metal oxo-compounds\textsuperscript{29}:

\[
\text{NH}_2\text{OH, MeOH} \quad (n\text{-Bu}_4\text{N})_4[\alpha\text{-Mo}_8\text{O}_{26}] \quad \rightarrow \quad (n\text{-Bu}_4\text{N})_2[\text{Mo}_5\text{O}_{13}(\text{OCH}_3)_4(\text{NO})]-\{\text{Na(MeOH)}\}.3\text{MeOH}
\]

\textbf{d) Use of organonitrosyl reagents}

A versatile reagent Diazald (\textit{N}-methyl-\textit{N}-nitroso-\textit{p}-toluenesulfonamide), which is also known as MNTS, is used extensively in the preparation of many nitrosyl complexes. An example of such reactions is given below\textsuperscript{30}:

\[
\text{Diazald} \quad \text{Mo(CO)}_6 + \text{Cp}^\Phi\text{Li} \quad \rightarrow \quad \text{Cp}^\Phi\text{Mo(NO)(CO)}_2
\]

\[\text{(Cp}^\Phi = \text{tetraphenylcyclopentadienide)}\]
Other nitroso derivatives like Me(N(NO)CONH₂), Cl₃CNO, Et₂NNO, and Me₂NNO³¹ have also been used:

\[
\begin{align*}
\text{Fe}_2(\text{CO})_9 & \quad \text{Me}_2\text{NNO} \\
\text{Fe} & \quad \text{Fe}(\text{CO})_2\text{NO}
\end{align*}
\]

**e) Reduction of coordinated nitrite or nitrate ligands**

These synthetic methods are based on oxygen transfer reactions which are an important general feature of transition metal nitrosyl chemistry. The following examples³²,³³ are illustrations of such reactions:

\[
\begin{align*}
\text{HCIO}_4 & \quad [\text{Ru}(\text{bpp})(\text{NO}_2)(\text{PMe}_3)_2]\text{ClO}_4 \quad \text{[Ru}(\text{bpp})(\text{NO})(\text{PMe}_3)_2]\text{[ClO}_4]\text{]}_3 \\
& \quad (\text{bpp} = 2,6\text{-bis(pyrazol-1-yl)pyridine})
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{COOH} & \quad \text{W}(\text{CO})_6 + \text{NaNO}_3 \quad \text{HW}_2(\text{CO})_6(\text{NO})
\end{align*}
\]

**f) Reaction with nitrosyl halides**

As opposed to reductive nitrosylations which eliminate nitrosyl halides, this type of reaction uses nitrosyl halides to cause oxidative nitrosylations³⁴:

\[
\begin{align*}
\text{NOCl} & \quad [\text{V}(\eta-\text{C}_5\text{H}_5)_2] \quad [\text{V}(\eta-\text{C}_5\text{H}_5)_2\text{Cl(NO)}]
\end{align*}
\]
g) Nitrosyl transfer reaction

A number of transition metal nitrosyl complexes are capable of transferring a nitrosyl group to another metal centre. An example of such transfer is:

\[
\text{[CoCl(NO)₂]₂} \rightarrow \text{[VH(CO)₃(NO)(dppe)]}
\]

(dppe = 1,2-bis(diphenylphosphino)ethene)
1.3.2.5. Characterization of Metal Nitrosyl Complexes

There are many techniques which are used in the characterization of metal nitrosyl complexes. The most commonly employed techniques are outlined below.

1.3.2.5.1. Vibrational Spectroscopy

In the past, much effort has been made to determine the relationship between the geometry of coordination of nitrosyl complexes and the stretching frequency values of the NO group ($v_{NO}$). Indeed, from as early as 1958, infrared spectroscopy has been the accepted method for characterising metal nitrosyl complexes. After comprehensive investigations of the infrared spectra of metal nitrosyls, it was concluded that coordinated NO groups absorb in the range of 1045 to 1940 cm$^{-1}$, the majority being in the range of 1626 to 1938 cm$^{-1}$. It was suggested that these nitrosyls contained NO$^+$ ions. The complexes which exhibit $v_{NO}$ values in the range of 1000 to 1200 cm$^{-1}$ were then considered to contain NO$^-$. Symons et al. further suggested that NO$^-$ ion would show an absorption band around 1900 cm$^{-1}$ and NO$^+$ at around 1650 cm$^{-1}$.

In 1965, Gans re-classified these ranges by suggesting that, since ionic NO$^+$ is isoelectronic with dinitrogen ($N_2$), $v_{NN}$ being 2331 cm$^{-1}$, nitrosyls showing $v_{NO}$ in the range of 1900 to 1700 cm$^{-1}$ can be considered to contain NO$^+$ species; and since NO$^-$ ion is isoelectronic with dioxygen ($O_2$), $v_{OO}$ being 1555 cm$^{-1}$ (Raman active band), nitrosyls with $v_{NO}$ between 1700 and 1500 cm$^{-1}$ were regarded to contain NO$^-$. In 1968, the ability of NO to coordinate to transition metals in linear and bent fashions was first established unambiguously as a result of X-ray crystallographic studies,
particularly by Ibers and co-workers\textsuperscript{39}, in which the first accurately documented example of a distinctly bent M-N-O linkage was presented. In 1971, Mingos and Ibers\textsuperscript{40} suggested that the NO\textsuperscript{-} ligand coordinates through an sp\textsuperscript{2} hybrid orbital and gives an M-N-O bond angle of approximately 120° i.e. bent coordination, whereas the NO\textsuperscript{+} ligand coordinates to a metal linearly, with an M-N-O bond angle of approximately 180°. Following this work, it was pointed out that the ν\textsubscript{NO} values alone were inadequate to diagnose the mode of coordination of the nitrosyl ligand.\textsuperscript{41} The ranges of 2000 - 1600 cm\textsuperscript{-1} and 1720 - 1525 cm\textsuperscript{-1} have been quoted for linear and bent MNO respectively. The overlap of the ranges has therefore rendered the infrared correlation alone insufficient for characterisation of these two modes of coordination of certain nitrosyl complexes. The gap can now be filled by \textsuperscript{15}N NMR spectroscopy for diamagnetic metal nitrosyls.\textsuperscript{42}
1.3.2.5.2. Nitrogen Nuclear Magnetic Resonance Spectroscopy

Work on nitrogen NMR has been extensively reviewed\textsuperscript{43}. Table 1.3 below presents the properties of a few NMR active isotopes.

Table 1.3. Properties of some NMR active isotopes.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Nuclear Spin</th>
<th>Natural Abundance N (%)</th>
<th>Receptivity Relative to Proton</th>
<th>Magnetogyric Ratio ν</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{1}\text{H})</td>
<td>1/2</td>
<td>99.99</td>
<td>1.0000</td>
<td>26.75</td>
</tr>
<tr>
<td>(^{14}\text{N})</td>
<td>1</td>
<td>99.63</td>
<td>1 x 10(^{-3})</td>
<td>1.933</td>
</tr>
<tr>
<td>(^{15}\text{N})</td>
<td>1/2</td>
<td>0.370</td>
<td>3.85 x 10(^{-6})</td>
<td>-2.712</td>
</tr>
<tr>
<td>(^{59}\text{Co})</td>
<td>3/2</td>
<td>100.0</td>
<td>0.2770</td>
<td>6.317</td>
</tr>
</tbody>
</table>

From the following relationship:

\[
\text{Receptivity} = N \cdot ν^3 \cdot I(I+1) \cdot B_0^2
\]

since \(^{14}\text{N}\) and \(^{15}\text{N}\) have low magnetogyric ratios (ν), their NMR sensitivities are low compared to that of \(^{1}\text{H}\).

Nitrogen-14 has spin \(I = 1\) and it is the major isotope of nitrogen at 99.63\% natural abundance. At times, its presence has to be taken into account in interpreting an NMR spectrum because of the effect of its quadrupole moment. Because of its rapid relaxation time, the signals tend to be broad
and it is often difficult to identify the signal above the baseline except in simple cases.

On the other hand, $^{15}$N has spin $I = \frac{1}{2}$ which gives an intrinsic advantage of high resolution over $^{14}$N, but because of its low natural abundance of 0.37%, its NMR sensitivity is very much lower than that of $^{14}$N. However, the problem of low natural abundance can be overcome by using relatively inexpensive isotopically enriched starting materials. Nitrogen-15 also suffers from a long relaxation time (170 seconds), which necessitates long accumulation times; therefore relaxation agents e.g. Cr(acac)$_3$ are often used for reasonable acquisition times. The availability of wide-bore high-field FT NMR spectrometers developed by Roberts et al.$^{44}$ makes these measurements more practicable. The increase in accessibility of $^{15}$N NMR spectroscopy has led to a marked decline in $^{14}$N NMR.

Nitrogen-14 and Nitrogen-15 chemical shifts (Figure 1.6) are interchangeable because primary isotope effects are very small and of the order of the experimental uncertainties.$^{45}$ The electron shielding mechanism is also the same for all nitrogen nuclei in the same environment. The range of the chemical shift is wide (more than 1000 ppm) with the shifts within each functional type commonly limited to less than 100 ppm. Nitrogen NMR spectroscopy is particularly suitable for distinguishing between bent and linear MNO conformations because of the large downfield shift (by hundreds of ppm) that is expected for the bent as compared to the linear nitrosyl ligand.
Figure 1.6. Range of nitrogen chemical shifts (ppm) observed for nitrosyl complexes and related compounds.
Chemical shifts in nitrogen NMR spectroscopy are dominated by the paramagnetic term which arises from the mixing of excited states with ground states under the perturbing influence of a magnetic field. These second order effects are mediated by the magnetic dipole operator and involve changes in the orbital angular momentum associated with the rotation of electronic charge around the nucleus. Such electron density currents interact with the magnetic dipole of the nucleus, giving rise to changes in the effective field experienced by that nucleus, which are measured as changes in the shielding.

Linear nitrosyls show chemical shifts in the range of -100 to 100 ppm (MeNO₂ as reference) which means that the nitrogen is highly shielded in this coordination geometry. As the MNO angle becomes smaller, the chemical shift moves further downfield and compounds which have truly bent MNO species show chemical shifts as high as 850 ppm. This shift to the lower field can be explained by the presence of the lone pair of electrons on the nitrogen which is being deshielded by low-energy \( n_N \rightarrow \pi^*_{NO} \) paramagnetic circulations in the magnetic field.⁴⁶

1.3.2.5.3. X-Ray Crystallography

The most reliable method for the assignment of the coordination mode of nitric oxide in transition metal complexes in the solid state is single crystal X-ray crystallography. Crystallographic disorder can lead to characterisation problems for bent nitrosyl groups. Both two-fold (Figure 1.7(a)) and four-fold (Figure 1.7(b)) crystallographic disorder have been observed and have led to some confusion and ambiguity about the identity of the ligands. The various positions for the oxygen atoms of the disordered ligands can usually be resolved, but the nitrogen atom position can also be disordered (Figure
1.7(c)), giving anomalously high mean-square vibrational amplitudes for these atoms if the disorder remains unresolved. This makes it impossible to define the nitrogen positions uniquely and leads to inaccurate bond lengths and angles for the coordinated nitrosyl ligand.

Figure 1.7. Crystallographic disorder of metal nitrosyl complexes.

Feltham and Enemark\textsuperscript{47} have given an excellent summary of the results of X-ray crystallographic structural determinations on metal nitrosyl complexes. The following conclusions are particularly noteworthy:

1. The M-N distances are rather short, indicating substantial multiple bond character between the nitrosyl and the metal. The average value for the N-O distance in a wide range of complexes is 1.15 Å. The M-N-O bond angles range from 180° to 109° with clustering near 180° and 120°.
2. The most common coordination number for mononitrosyl complexes is 6 and \( \{\text{MNO}\}^n \) complexes with \( n = 4, 5, 6, 7, \) and 8 are known. The M-N-O bond angle is linear (± 10°) provided that \( n < 6 \). The range of bond angles for \( \{\text{MNO}\}^7 \) and \( \{\text{MNO}\}^8 \) is larger, but the average bond angles of 146(11)° and 126(9)°, respectively, show clearly the way in which \( n \) influences the M-N-O bond angle.

3. Comparisons of the differences in bond lengths for the cis- and trans-ligands in octahedral complexes with linear M-N-O groups with \( \nu_{\text{NO}} > 1800 \text{ cm}^{-1} \) have trans-M-L bonds slightly shorter (0.013 - 0.075 Å) than those of the cis-ligands.

4. The structures of mononitrosyl square pyramidal complexes follow the same basic pattern as that established for octahedral complexes, with \( n < 6 \), having essentially linear geometries. For \( n = 7 \), the M-N-O bond angles vary from 127(6)° to 178(1)°. When \( n = 8 \), the mononitrosyls have a strongly bent M-N-O group with the bond angles ranging from 141° to 109°.

5. \( \{\text{MNO}\}^8 \) trigonal bipyramidal complexes have bond angles much closer to linearity and lie in the range 159° - 180°. When no steric constraints are imposed, the NO group prefers the equatorial site of the TBP; however, with bulky ligands, it is frequently observed in the axial site.

6. Four coordinate \( \{\text{MNO}\}^{10} \) complexes with three equivalent ligands have pseudo-tetrahedral coordination geometries and linear M-N-O groups (bond angles between 174° - 180°). In complexes for which the symmetry deviates significantly from \( C_{4v} \), the M-N-O bond angle may vary substantially form 180°.
CHAPTER TWO

EXPERIMENTAL METHODS
2. Experimental Methods

This Chapter describes the general techniques and apparatus used in handling air sensitive compounds. The preparations of air sensitive starting materials are also outlined.

2.1. Air Sensitive Compounds

All chromium(II), manganese(II) and many iron(II) and cobalt(II) compounds are highly susceptible to aerial oxidation, therefore, precautions have to be taken to exclude traces of air during the preparation and storage of these compounds. For these purposes, a highly efficient all-glass nitrogen line with specially designed glassware for various experimental manipulations, first described by Larkworthy\textsuperscript{48} and recently, modified\textsuperscript{49} (Figure 2.1), as well as a neoprene nitrogen (Figure 2.2) line were used in conjunction with an inert-atmosphere box (Figures 2.3 and 2.4) as well as Schlenk and syringe techniques.\textsuperscript{50}

2.1.1. Nitrogen Lines

The all-glass nitrogen line (Figure 2.1) is an essential piece of apparatus for air sensitive work. It is evacuated with an oil pump protected by a trap immersed in liquid nitrogen at A. Reaction vessels were usually attached by a flexible rubber tubing to B and C, whereas D was used if the use of rubber tubing was to be avoided. Deoxygenation of a small amount of solvent can be carried out by bubbling nitrogen through it in vessel H and then transferring it by suction to a vessel attached at D. The vessels J and K act as gas reservoirs as well as being used as traps when drying compounds on D. The key F controls the nitrogen input into the line and
any excess gas can be bubbled out through keys L and M and a set of liquid paraffin traps N.

Figure 2.1. The all-glass nitrogen line.
Another type of nitrogen line illustrated in Figure 2.2, which is less rigid than the all-glass nitrogen line previously mentioned, was also used during the course of this work. Y glass junctions were connected using pieces of neoprene tubing to make up the main network of the line which was connected to a vacuum pump, protected by a set of traps immersed in liquid nitrogen, and a nitrogen supply from the bench via a three way tap F. This line was also fitted with a pressure gauge E and a mercury manometer M which had a sulphur trap G attached at the gas outlet to remove mercury vapour when nitrogen was being bubbled through the mercury into the atmosphere. Reaction flasks and other apparatus were attached to A, B, C and/or D which had to be blocked with short pieces of blunted fire-polished glass rod if not in use to prevent air from entering the system. The neoprene tubing was tightly wired on with copper wire at the connections to the glass tubing.
Figure 2.2. The neoprene nitrogen line.
2.1.2. Inert Atmosphere Box

An inert atmosphere box is very useful in air sensitive chemistry. After a complex has been synthesised, most manipulations such as transferring solids into storage tubes, the preparation of nujol mulls and KBr discs for infrared spectra, filling and packing magnetic susceptibility tubes, and the weighing out of samples for microanalyses can be carried out in the box. It can also be used for storing and weighing out air sensitive reagents for an experiment.

The inert atmosphere box used during the course of this work was a Faircrest Engineering Mark 4A model illustrated in Figure 2.3. The gas recirculation and purification (Figure 2.4) system allows the atmosphere in the box to be constantly recycled and repurified. This enables the box to be used for several hours continuously without the level of oxygen rising above 5 ppm, although a level of about 1 ppm is more desirable. The purification train consists of a heated BTS catalyst column, C, a water-cooled heat exchanger, H and a column of Linde 4A molecular sieves M. The taps are arranged so that each section can be individually sealed off without disturbing the gas flow.

Purified nitrogen from the recirculation and purification system enters the box (Figure 2.3) at A and leaves at A'. If pressure rises above the hydrostatic pressure of the liquid paraffin in the outlet bubbler, gas bubbles out through the bubbler. If the pressure falls below a value set on the valve B, B admits nitrogen automatically from the supply. If a more rapid nitrogen flow is required, there is an auxiliary nitrogen inlet valve on the purification system which is operated by a foot switch. The inlet ports P and P' are purged with nitrogen before use, the smaller port requiring
only about 15 minutes sweeping as opposed to 30 minutes for the larger port.

Since the gloves are made of rubber, there is the possibility of oxygen and moisture permeating through them. Two gas-tight removable internal covers seal the gloves from the box when it is not in use, and allow the gloves to be evacuated and filled with nitrogen before use. Disposable surgical gloves are worn to reduce permeation of moisture from the hands into the box.

The level of oxygen within the inert atmosphere box was monitored using a Model EC90 oxygen meter supplied by Systech Instruments Ltd.
Figure 2.3. Top view of the inert atmosphere box.

Figure 2.4. Gas recirculation and purification system.
2.1.3. Purification and Deoxygenation of Solvents and Reagents

It was necessary to remove dissolved oxygen (deoxygenate), and, in certain cases, further purify reagents and solvents used during the preparations.

The deoxygenation of solvents was carried out either by distillation under nitrogen or, if only small quantities of solvents and reagents were needed, the freeze-pump-thaw method described by Shriver was used. The liquid was cooled under continuous pumping until it was completely frozen. The flask was then refilled with nitrogen and evacuated a few times and while still under vacuum, the liquid was allowed to warm up and thaw. It was assumed that repeating the procedure three times was sufficient to remove completely all gases dissolved in the liquid (when bubbles no longer appeared at the cooling and thawing stage).

All the solvents used in non-aqueous chelation procedures which involved the use of highly moisture sensitive reagents such as sodium hydride or lithium alkyls (tetrahydrofuran, toluene and diethyl ether) required rigorous drying and purification before use as described below.

2.1.3.1. Tetrahydrofuran

Potassium hydroxide pellets (50.00 g) were added to a winchester of Analar tetrahydrofuran and left to stand for a day. The solvent was then passed through a column of activated alumina into a two litre Schlenk flask under vacuum before adding a die (approximately 5 g) of potassium metal. The flask was then attached to a specially designed still-head (Figure 2.5.) connected to a Schlenk line in a fume cupboard under
nitrogen for heating under reflux for one hour and then the solvent was cooled slightly prior to the addition of benzophenone (5 g). Heating under reflux was then carried out for another four hours before the solvent was ready to be distilled off for use as needed. The solvent in the flask turned to a deep blue-purple colour upon the addition of the benzophenone and remained that colour as long as the system was kept under nitrogen. Contamination by air or moisture can easily be detected by the change of colour through green to dirty brown.

2.1.3.2. Diethyl Ether

To a Winchester of Analar diethyl ether, hydrated iron(II) sulphate (50 g) was added and left to stand for a day to destroy the peroxide. The solvent was then decanted off into an empty winchester, and potassium hydroxide pellets (100 g) were added to dry the solvent. This was left standing for two days before three dies of sodium wire (approximately 15 g) were pressed into the winchester for further drying. After being left for three days, the solvent was decanted into a one litre Schlenk flask and lithium aluminium hydride (20 g) added. The ether was heated to boiling point under nitrogen with a condenser attached to a Schlenk line until after cooling no effervescence was observed. This indicated that the solvent was dry enough to be distilled off as needed.
2.1.3.3. Toluene

Three dies of sodium wire (approximately 15.00 g) were added to a winchester of Analar toluene which was allowed to stand for at least one day before the solvent was decanted into a two litre Schlenk flask. This was then attached to a still head connected to a Schlenk line in a fume cupboard under nitrogen. About 5 g of sodium chunks were added and the solvent was heated under reflux for 5 hours before it was ready to be used.
Figure 2.5. Solvent still.
2.1.4. Generation of $^{14}$NO

The nitric oxide was generated by Blanchard's method in an NO line (Figure 2.7). Equal volumes of aqueous iron(II) sulphate heptahydrate (1 M solution, acidified with 55 cm$^3$ of 36 M sulphuric acid per litre of acidified solution) from funnel A and aqueous sodium nitrite (1 M solution) from funnel B were allowed to mix in reaction vessel C (previously evacuated with screwclip SC closed, to remove any traces of NO$_2$ or H$_2$O present). This produces a large 'brown-ring' reaction, and thermal decomposition of the brown-ring complex ($[\text{FeNO(H}_2\text{O)}]^{2+}$) gives nitric oxide as represented in the overall equation below:

$$2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4$$

$$+ 2\text{H}_2\text{O} + 2\text{NO}$$

Previous IR analysis of the reaction gases showed that nitric oxide generated from the decomposition of the brown ring complex contained very little impurities, mainly unreactive N$_2$O and NO$_2$, although no quantitative estimates were made.

The nitric oxide generated was allowed to fill vessel C and the excess of gas was stored in vessel D over aqueous NaOH (12 M solution). The pressure of nitric oxide in flasks C and D could be varied by moving reservoir D' vertically up and down with screwclips SC open. The gas was purified by passage through column F containing KOH pellets and column G containing 4A type molecular sieves to remove NO$_2$ or moisture present. The pressure of nitric oxide in the apparatus was adjusted to atmospheric with the mercury manometer M. The gas was then stored and measured for each nitrosylation reaction in the gas burette J. More
nitric oxide could be generated as required by draining off the spent reaction mixture through tap T in the bottom of flask C and then allowing more reactants to mix in C.

The glassware assembly used for a typical nitrosylation reaction is illustrated in Figure 2.6. The reactants (either solid or dissolved in appropriate solvent) were placed in flask L and side-arm N and the system was evacuated. Nitric oxide was admitted from the NO line by opening taps X, Z and R until the pressure was equalised to atmospheric. Tap X was closed and Y opened to allow the NO in the gas burette J to be taken up by the reaction mixture. The mercury in the arms of the gas burette was levelled and the magnetic stirrer S was started. Stirring was continued until the NO uptake was complete. The nitric oxide uptake was measured by the difference in the mercury levels in burette J before and after the reaction.
Figure 2.6. Apparatus for nitrosylation reaction.
Figure 2.7. The nitric oxide (NO) line.
2.1.5. Generation of $^{15}$NO

The Brauer method, modified for small quantities, was used to generate the labelled nitric oxide. The apparatus, illustrated in Figure 2.8, consists of a bulb E and three taps A, B and C with capillary tubing to lessen dead-space, connected via a right-angled bend to a two-necked 100 cm$^3$ pear-shaped flask F, equipped with a tap D on the side arm and a subaseal wired on.

In a typical experiment, Analar iron(II) sulphate heptahydrate (0.638 g, 2.265 mmol), anhydrous sodium bromide (0.638 g, 6.201 mmol) and $^{15}$N-labelled sodium nitrite (0.300 g, 4.348 mmol) were layered alternately in the flask F, and a small stirring bar was placed carefully on top of the undisturbed reaction mixture. Air was pumped from the system, which was then filled with nitrogen and placed in a Dewar of liquid nitrogen to just above the level of the solids. Deoxygenated water (0.5 cm$^3$) was injected via the subaseal through the side-arm tap D onto the reaction mixture and tap D was closed. The reaction flask F with the frozen contents was then evacuated and tap B closed. The Dewar was removed from flask F, the contents of which were allowed to warm to room temperature with stirring to initiate the production of $^{15}$NO. The colour changed to brown, with vigorous effervescence of nitric oxide. After the reaction was complete, (about 30 minutes with warming), some of the $^{15}$NO was transferred to the burette J, which had been filled with mercury to tap Y. To transfer the remaining $^{15}$NO to the burette, taps Y and A were closed and the Dewar was placed under bulb E to condense the nitric oxide in E (the level of the liquid nitrogen was not too high to avoid condensation of $^{15}$NO within the capillary tube).
As the Dewar was removed from bulb E, tap A and tap Y on the burette were quickly opened to allow the rapidly evaporating $^{15}$NO into the burette. This preparation could generate about 90 - 95 cm$^3$ of $^{15}$NO at atmospheric pressure.

Figure 2.8. Apparatus for generation of $^{15}$NO.
2.1.6. Preparation of Starting Materials

2.1.6.1. Chromium(II) Chloride Tetrahydrate

Chromium metal (10.00 g, 192.3 mmol) was added to a mixture of concentrated Analar hydrochloric acid (16 cm³, 1.18 g cm⁻³, 517.8 mmol) and distilled water (36 cm³) which had been deoxygenated by the freeze-pump-thaw method. The system was evacuated and refilled with nitrogen three times to remove any trace of air. Hydrogen was slowly evolved and the colour of the solution turned sky blue.

The reaction was stirred in a warm water bath (75°C) until the effervescence stopped (about 6 hours). After cooling to room temperature, the excess of metal was removed by filtration, and the filtrate was concentrated under vacuum aided by a water bath (60°C) to the point of crystallisation. Deoxygenated acetone (100 cm³) was then added to precipitate the product. Any oxidised compound (green) dissolved in the acetone while most of the chromium(II) salt was insoluble in the solvent. The blue solid was filtered off, washed with ice-cold deoxygenated acetone to remove any remaining chromium(III) impurity and the product was dried under vacuum. Yield, 20.52 g (40%).

2.1.6.2. Chromium(II) Bromide Hexahydrate

The bromide was prepared in a similar manner to the chloride from the equivalent amount of Analar hydrobromic acid. The bromide was a deeper blue than the chloride. Yield, 22.30 g (27%).
2.1.6.3. Chromium(II) Iodide Hexahydrate

Approximately 7 g of chromium chunks were heated in a deoxygenated mixture of Analar hydriodic acid (17 cm$^3$) and distilled water (20 cm$^3$). The reaction was much slower than those of the hydrochloric and hydrobromic acids described above. After heating for about one hour, the brown colour of the hydriodic acid slowly disappeared and the solution turned blue. The heating was continued for 10 hours before the unreacted metal was removed by filtration. The filtrate was concentrated to dryness and blue crystals formed in the flask. Further heating and pumping resulted in a change of colour to green, however, upon rehydration, the blue compound was obtained. It was not possible to wash the product with acetone as chromium(II) iodide is very soluble in it. Therefore, the salt was scraped from the flask in the inert atmosphere box for storage. Yield, 18.66 g (66%).

The unwashed salt turned green within three weeks on storage so washing it with different solvents was tried. Diethyl ether was the most suitable solvent for this purpose and was used in later preparations.

2.1.6.4. Chromium(II) Tetrafluoroborate Hexahydrate

An excess of chromium chunks (2.560 g) was added to deoxygenated tetrafluoroboric acid (3.9 cm$^3$, 1.31 gcm$^{-3}$, 58.18 mmol) and water (15 cm$^3$) and the reaction mixture was heated to 80°C for 4 hours until the reaction ceased. After cooling to room temperature, the excess of metal was removed by filtration and the blue filtrate taken to dryness, yielding a sky blue product. Yield, 1.69 g (26%).
2.1.6.5. Chromium(II) Triflate Tetrahydrate

Chromium chunks (12.00 g) were added to trifluoromethanesulphonic (triflic) acid (30 cm$^3$) in water (50 cm$^3$) which had been deoxyygenated, and placed in a warm water bath (65°C) for 5 hours until evolution of hydrogen ceased. The unreacted metal was filtered off and the filtrate taken almost to dryness when the blue solid which first appeared turned whitish. When purified diethyl ether (30 cm$^3$) was added to the mixture, the whitish product became blue again. It was filtered off and dried under vacuum.

2.1.6.6. Anhydrous Chromium(II) Halides

The hydrated chromium(II) halide was placed in a small round-bottomed Schlenk flask, put under continuous vacuum and placed in an oil bath. The temperature was raised from 80°C to 140°C by 20°C every 2 hours. Heating was continued at 140°C for another two hours until the colour of the product turned from sky blue through green to almost grey. The salt was magnetically stirred occasionally to give a more uniformly dehydrated product.

2.1.6.7. Anhydrous Chromium(II) Acetate

Chromium(II) acetate was prepared by the method of Ocone and Block$^{55}$, adapted for use on the nitrogen line.

Aqueous chromium(II) halide was added to a three-fold molar excess of sodium acetate dissolved in deoxygenated distilled water. A deep pink product formed immediately and the mixture was allowed to stir for 15
minutes. The product was filtered off in a dehydrating sinter (Figure 2.9.) and washed three times with degassed distilled water. After vacuum pumping for about 30 minutes, the apparatus was immersed in a hot oil bath, raising the temperature very slowly to 140°C as described in the section above. The pink colour changed to brown-orange upon dehydration. This method generally gave yields of more than 90%.

Figure 2.9. Sinter for dehydrating compounds in an oil bath.
2.1.6.8. Anhydrous Iron(II) Acetate

A suspension of iron powder (20.00 g, 60 mesh) in Analar acetic acid (200 cm³) and water (20 cm³) was deoxygenated and heated under reflux for seven hours under nitrogen. The resultant solution was very light green in colour. The unreacted iron powder was removed while the mixture was still hot by filtration through pre-purged celite on a sintered disc, and acetic anhydride (300 cm³) was added to the filtrate. The solution turned red and some white precipitate appeared. The mixture was refluxed for 1 hour and after cooling to room temperature, the white solid was filtered off, washed with freshly distilled diethyl ether and dried on the pump.

Analysis for FeC₄H₆O₄  
Calculated: C, 27.62; H, 3.48; N, 0.00 %  
Found: C, 28.44; H, 3.96; N, 0.00 %
2.1.7. Methods of Characterization and Analyses

2.1.7.1. Magnetic Susceptibility Measurements

Temperature variable magnetic susceptibility measurements were carried out using a Gouy Balance supplied by Newport Instruments Ltd., the temperature ranging from room temperature to liquid nitrogen temperature. Field strength, H, was controlled by varying the current supply to the electromagnet using a highly accurate ammeter, which also made precise reproduction of a particular field possible.

Samples were prepared by packing the solid tightly into a flat-based Pyrex glass tube of uniform bore which had been calibrated for its diamagnetism at various field strengths throughout the range of temperatures. The weight, m, of the compound was determined using the difference in weight of the empty and filled tube, taken on a four-decimal-place balance. After tapping the tube on a wooden surface to ensure uniform packing, the length l, of the sample was measured. The tube was then suspended from a chain by cotton to a pre-determined length so that the bottom of the sample was in the region of maximum magnetic field.

To remove errors due to the paramagnetism of the oxygen in air, the chamber containing the specimen was evacuated and flushed with nitrogen. The very low susceptibility of nitrogen (\(-0.0004 \times 10^{-6}\) c.g.s. units) could be neglected in calculations. A further advantage of the nitrogen surroundings was that at very low temperatures (90 K), there was no atmospheric oxygen to condense on the specimen. The sample was suspended from the arm of the balance carefully into the cryostat between the poles of a magnet. With the help of the moveable platform, the
sample could be moved to the centre of the chamber so that it did not touch the walls at any time during measurements, which would introduce errors in the reading. The change in weight, $w$, of the sample, corrected for the diamagnetism of the tube, was determined at various field strengths at room temperature, and then at different temperatures down to liquid nitrogen temperature.

The molar susceptibility, $\chi_M$, is obtained from the equation:

$$\chi_M = \frac{2gMlw}{mH^2}$$

where $g = \text{acceleration due to gravity}$

$I = \text{length of sample}$

$M = \text{relative molecular mass of sample}$

$w = \text{pull on sample due to field } H$

$m = \text{mass of sample}$

$H = \text{applied field (from calibration curves)}$

The atomic susceptibility, $\chi_A$, of the metal was obtained by correcting $\chi_M$ for the diamagnetism of the ligands and groups present using Pascal's constants.

The effective magnetic moment, $\mu_{\text{eff}}$, was calculated from the equation:

$$\mu_{\text{eff}} = 2.828 \sqrt{\chi_A T} \quad \text{where } T = \text{temperature in Kelvin.}$$
2.1.7.2. Infrared Spectra

The infrared spectra were recorded on a Perkin Elmer System 2000 Fourier Transform Infrared (FTIR) from the range 4000 - 400 cm⁻¹. Samples for infrared spectra were made up in KBr disks. Spectroscopic grade potassium bromide purchased from Sigma was pre-dried in a 400°C oven overnight and allowed to cool in a desiccator before use. The KBr disks for air sensitive compounds were prepared in the inert atmosphere box.

2.1.7.3. X-ray Crystal Structure Determinations

Crystallographic data were collected on the Enraf-Nonius CAD4 X-ray diffractometer and the structures solved by Mr. G.W. Smith.

2.1.7.4. Microanalyses

Analyses for carbon, hydrogen and nitrogen were carried out by Ms. N. Walker of the University of Surrey Microanalysis Service. Air sensitive samples were weighed out and sealed by crimping in the inert atmosphere box.
2.1.7.5. Nuclear Magnetic Resonance Spectra

Proton NMR spectra were recorded by Mr. J. Bloxsidge of the Chemistry Department on a Bruker AC-300E Pulse Fourier Transform NMR Spectrometer, operating at 300 MHz. Solution nitrogen-15 and cobalt-59 NMR spectra were recorded by Mr. G. Thompson on the high field (400 MHz) NMR facility at Warwick University. Solid state $^{15}$N NMR spectra were recorded with the use of cross polarisation and magic angle spinning on a Bruker MSL-300 spectrometer at University College London by Dr. P. Barrie.
CHAPTER THREE

IRON AND COBALT MONONITROSYLS WITH SCHIFF BASE CO-LIGANDS
3. Reactions of Iron(II) and Cobalt(II) Schiff Base Complexes with Nitric Oxide

3.1. Introduction

3.1.1. Historical background

Prior to the 1960's, very little work had been done on iron(II) chelates of Schiff bases mainly because of their susceptibility to aerial oxidation. However, with the development of techniques of handling air-sensitive compounds, work of this nature has been made possible and many new compounds have been isolated and their properties investigated. A brief discussion of Schiff bases generally is given at the beginning of Chapter Five.

In 1964, Hewlett\textsuperscript{57} found that $N,N'$-ethylenbis(salicylideneiminato)iron(II) [Fe(salen)] reacted with nitric oxide in 1:1 ratio to give a mononitrosyl which exhibited a $\nu_{NO}$ of 1712 cm$^{-1}$. The preparation was repeated and a magnetic investigation\textsuperscript{58} was carried out on the compound which revealed that it underwent a spin crossover at around 180 K when the spin state abruptly changed from high spin (three unpaired electrons, $S = 3/2$) to low spin (one unpaired electron, $S = 1/2$) with the lowering of the temperature. This corresponded to the weakening of the peak at 1712 cm$^{-1}$ and the appearance of a new peak at around 1630 cm$^{-1}$ in the infrared spectrum. This was the first example of an iron mononitrosyl to exhibit such a phenomenon. The X-ray crystal structure\textsuperscript{59} of this complex was determined at 98 K and 296 K showing that the M-N-O angle was bent at both temperatures, i.e 127° and 147° respectively, but more so at the lower temperature. Marginally significant structural changes above and below the transition temperature
were observed. Mossbauer effect measurements carried out on the complex clearly reflected the $S = 3/2 \leftrightarrow S = 1/2$ isomerism.

The second iron mononitrosyl to show a similar spin-state transition between $S = 3/2$ and $S = 1/2$ was $N,N'$-o-phenylenebis(salicylideneaminato)nitrosyliron [Fe(salphen)NO]$^{61}$. Magnetic susceptibility measurements show a transition temperature of around 180 K. The NO stretching frequency at room temperature which occurred at 1724 cm$^{-1}$ disappeared upon cooling, and a new peak appeared at 1643 cm$^{-1}$ (83 K). There was originally a shoulder at around 1663 cm$^{-1}$ in the room temperature spectrum. A Mossbauer study performed at 300 K and 77 K showed similar results to the salen complex.$^{62}$

Other less dramatic examples$^{63}$ of such behaviour were shown by the 5-NO$_2$, 4-Cl, 5-Cl and 3-NO$_2$ derivatives of Fe(salen)NO. Each exhibited some minor decrease in the values of the effective magnetic moment with lowering of temperature in the order given, though no spin crossover was observed in the temperature range investigated (300 K to 90 K). Apart from the 5-NO$_2$ derivative, which showed an additional peak at 1715 cm$^{-1}$ at liquid nitrogen temperature, none of the other derivatives mentioned showed any major changes in the infrared spectra taken over the temperature range apart from the sharpening of the $\nu_{\text{NO}}$ peak. The additional peak was presumed to be that of the NO stretching frequency of the low-spin isomer of the Fe(5-NO$_2$salen)NO present in small quantity. The $S = 3/2$ and $S = 1/2$ isomer proportions change much more slowly in this case than in the unsubstituted salen and salphen analogues. The 5-Me derivative of Fe(salen)NO obeyed the Curie law and had an effective magnetic moment which was temperature independent, unlike other complexes given above.
The known iron mononitrosyls which show spin crossover behaviour have quadridentate Schiff base co-ligands. These complexes are restricted to square pyramidal configurations by the nature of the co-ligand. This Chapter describes the preparation of some iron mononitrosyls with bidentate Schiff bases which do not impose this restriction so that the complexes may be square pyramidal or trigonal bipyramidal. Some attempts have also been made to prepare iron mononitrosyls with quadridentate Schiff bases not previously investigated.

A number of cobalt mononitrosyls similar in structure to Fe(salen)NO are known, i.e. Co(salen)NO and various derivatives. Since these have the \{CoNO\} \textsuperscript{8} configuration, they are essentially diamagnetic. However, this means that they can be investigated by NMR spectroscopy. From X-ray crystallographic investigations, it has been shown that the CoNO groups are bent, with Co-N-O angle approximately 125°, and this has been confirmed for these complexes in solution by \textsuperscript{15}N NMR spectroscopy (see also Chapter 4). Some new complexes of the Co(salen)NO type have been prepared, and also related compounds containing bidentate Schiff bases.

Unless the correct experimental conditions are chosen, dinuclear \(\mu\)-oxo iron(II) complexes can be formed in the reaction of nitric oxide with Fe(salen) etc. and sometimes, during the preparation of other iron(III) complexes, small amounts of the oxo-bridged iron(III) species are formed. An example of this is [Fe\textsubscript{III}(salen)]\textsubscript{2}O which was obtained while recrystallizing Fe(salen)acetate. One \(\mu\)-oxo derivative, [Fe(hapen)]\textsubscript{2}O, was isolated during the present work.
3.1.2. Spin Crossover

A spin-state crossover phenomenon can be observed if the the energies of high spin and low spin states differ by only about the thermal energy prevailing at or below room temperature. The magnetic properties of the complex therefore change anomalously as a function of temperature. A high spin mononitrosyl with the configuration \( \{ \text{Fe(NO)} \}^7 \) has three unpaired electrons (\( \mu_{\text{s0}} = 3.87 \) B.M.) and a low spin one has one unpaired electron (\( \mu_{\text{s0}} = 1.73 \) B.M.). Figure 3.1 shows illustrations of the crystal field splittings energy of the \( d \) orbitals of a metal in different fields:

![Diagram of crystal field splittings](image)

Figure 3.1. Qualitative crystal field splitting diagrams of the \( d \) orbitals of a metal in different fields and in a mononitrosyl Schiff base complex.
3.2. Experimental

3.2.1. Ligands

3.2.1.1. $N,N'$-Ethylenebis(salicylideneimine) [SalenH$_2$]

On the addition of ethylenediamine (4.922 g, 81.89 mmol) to salicylaldehyde (20.00 g, 163.8 mmol) dissolved in absolute ethanol (70 cm$^3$), the solution turned bright yellow. The mixture was refluxed for one hour and left to cool slowly to room temperature. The yellow needles obtained were filtered off, washed with cold ethanol and dried in air. Yield, 19.97 g (91%).

Analysis for C$_{16}$H$_{16}$N$_2$O$_2$  
Calculated: C, 79.17; H, 5.62; N, 7.10 %  
Found: C, 79.04; H, 5.51; N, 7.06 %

3.2.1.2. $N$-Benzylsalicylideneimine [SalbamH]

To salicylaldehyde (11.40 g, 93.31 mmol) dissolved in diethyl ether (40 cm$^3$), benzylamine (10.00 g, 93.31 mmol) was added. The resultant yellow solution was stirred for two hours and then cooled in liquid nitrogen. A solid separated at a very low temperature but during filtration and drying, some of it became liquid. Yield, 7.939 g (40 %).

Analysis for C$_{14}$H$_{13}$NO  
Calculated: C, 78.36; H, 6.58; N, 7.03 %  
Found: C, 78.30; H, 6.14; N, 6.63 %
3.2.1.3. *N*-4-Methylbenzylsalicylideneimine [SalMebamH]

In absolute ethanol (30 cm³), salicylaldehyde (1.877 g, 15.37 mmol) and 4-methylbenzylamine (1.863 g, 15.37 mmol) were mixed. A yellow solution formed immediately. The reaction mixture was refluxed for 30 minutes and then allowed to cool to room temperature. No solid was obtained by cooling in an ice bath, so the ethanol was taken off using a rotary evaporator and the yellow oil which remained was redissolved in diethyl ether (40 cm³). The solution was then cooled rapidly in liquid nitrogen and the pale yellow solid which appeared was quickly filtered off and dried in air. Yield, 2.501 g (72%).

Analysis for C₁₅H₁₅NO

Calculated: C, 79.97; H, 6.71; N, 6.22 %
Found: C, 80.05; H, 6.70; N, 6.35 %

3.2.1.4. *N*-4-Methoxybenzylsalicylideneimine [SalMeObamH]

Equimolar ethanolic solutions (20 cm³) of salicylaldehyde (5.000 g, 40.94 mmol) and 4-methoxybenzylamine (6.271 g, 40.94 mmol) were mixed and heated under reflux for one hour. The bright yellow crystals obtained on cooling were filtered off, washed with cold ethanol and dried. Yield, 7.914 g (80%)

Analysis for C₁₅H₁₅NO₂

Calculated: C, 74.67; H, 6.27; N, 5.81 %
Found: C, 74.66; H, 6.25; N, 5.76 %
3.2.1.5. **N-4-Fluorobenzylsalicylideneimine [SalFbamH]**

To salicylaldehyde (5.379 g, 44.05 mmol) dissolved in ethanol (20 cm$^3$), an ethanolic solution of 4-fluorobenzylamine (5.512 g, 44.05 mmol) was added and the mixture heated under reflux for one hour. When no solid was obtained on cooling, the ethanol was taken off using a rotary evaporator and a yellow oil was obtained which solidified after being left in the refrigerator. Yield, 6.115 g (61%).

Analysis for $C_{14}H_{12}NOF$

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, 73.35; H, 5.28; N, 6.10 %</td>
<td>C, 73.22; H, 5.06; N, 5.83 %</td>
</tr>
</tbody>
</table>

3.2.1.6. **N-Phenylsalicylideneimine [Sal-N-phenH]**

Equimolar ethanolic solutions (20 cm$^3$) of salicylaldehyde (5.000 g, 40.94 mmol) and aniline (3.813 g, 40.94 mmol) were mixed and heated under reflux for one hour. The bright yellow crystals obtained on cooling were filtered off, washed with cold ethanol and dried. Yield, 7.124 g (88%).

Analysis for $C_{15}H_{15}NO_2$

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, 74.67; H, 6.27; N, 5.81 %</td>
<td>C, 74.66; H, 6.25; N, 5.76 %</td>
</tr>
</tbody>
</table>

3.2.1.7. **N,N'-Ethylenebis(4-diethylaminosalicylideneimine) [NEt$_2$salenH$_2$]**

A solution of 4-diethylaminosalicylaldehyde (5.000 g, 25.87 mmol) in absolute ethanol (40 cm$^3$) was added to ethanolic ethylenediamine (0.777 g, 12.94 mmol). The colour changed from light brown to yellow-brown. The mixture was heated and stirred for half an hour and allowed to cool slowly to room temperature. Microcrystalline plates found after the solution had been
left overnight were filtered off, washed with ice-cold absolute ethanol and air
dried. Yield, 4.573 g (86 %).

Analysis for C$_{24}$H$_{34}$N$_{2}$O$_{2}$

Calculated: C, 70.21; H, 8.35; N, 13.65 %

Found: C, 70.08; H, 8.48; N, 13.59 %

3.2.1.8. N,N'-Ethylenebis(3-carboxysalicylaldimine) [f$_{sa}$$_{2}$enH$_{2}$]

The 3-aldehydosalicylic acid required to prepare this ligand was synthesised
by the Duff and Bills$^{66}$ method outlined below.

To salicylic acid (40.00 g, 289.6 mmol) in water (300 cm$^3$),
hexamethylenetetramine (27.00 g, 184.6 mmol) was added and the mixture
was boiled under reflux for 16 hours. After being allowed to cool to room
temperature, acidification was carried out using hydrochloric acid (4 M, 300
cm$^3$) and the yellow precipitate obtained was filtered off and air dried. The
solid was then extracted with 4 portions of toluene at 70$^\circ$C and the insoluble
portion of the solid was discarded (5-aldehydosalicylic acid). The toluene
from the combined extract was removed by rotary evaporator and the residue
was dissolved in ammonia (3 M, 200 cm$^3$) before adding barium chloride
solution (10 %, 100 cm$^3$) and sodium hydroxide solution (2 M, 200 cm$^3$) at
50$^\circ$C. After 2 hours, the precipitate of barium 3-aldehydosalicylate was
collected, decomposed with dilute hydrochloric acid and the brownish product
was filtered off. Recrystallisation from water yielded light brown crystals
which had a melting point of 173-175$^\circ$C (lit. 178-180$^\circ$C).

Analysis for C$_{8}$H$_{6}$O$_{4}$

Calculated: C, 57.84; H, 3.64; N, 0.00 %

Found: C, 57.06; H, 3.50; N, 0.00 %
The Schiff base was obtained by reacting ethylenediamine (0.270 g, 4.500 mmol) with the 3-aldehydosalicylic acid (1.495 g, 9.000 mmol) obtained above in absolute ethanol (30 cm³) under reflux for 2 hours. The bright yellow precipitate obtained upon cooling to room temperature was filtered off and washed with absolute ethanol. Yield, 0.890 g (56%).

Analysis for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_6$

Calculated: C, 60.67; H, 4.52; N, 7.86 %

Found: C, 60.04; H, 4.51; N, 7.85 %
3.2.2. Mononitrosyl Iron-Schiff Base Complexes

The syntheses of the iron nitrosyl complexes were carried out by the reported method.\textsuperscript{67}

3.2.2.1. Bis(\textit{N}-benzylsalicylideneiminato)nitrosyliron \([\text{Fe(salbam)}_2\text{NO}]\)

The ligand salbam\(\text{H} \) (1.500 g, 7.100 mmol) and anhydrous sodium acetate (0.582 g, 7.100 mmol) were added to methanol (20 cm\(^3\)) and the solution was deoxygenated before iron(II) perchlorate hexahydrate (1.288 g, 3.550 mmol) was added against a stream of nitrogen. The yellow colour of the solution immediately turned bright red and some solid was slowly formed. The reaction was stirred for 5 hours before NO gas was admitted and gas uptake started after stirring for about 1 minute. The colour darkened and the nitrosyl product seemed to be more soluble than the iron(II) complex. When the reaction was complete (80.5 cm\(^3\), 758 mmHg, 22\(^\circ\)C, 4.073 mmol), the NO was replaced by nitrogen. The molar ratio of iron to NO was approximately 1:1. The flask was left overnight in the freezer to obtain more solid. The dark red product was filtered off, washed with cold methanol and dried under vacuum. It was air stable. Yield, 1.45 g (81\%). The infrared spectrum contained a band at 1774 cm\(^{-1}\) assignable to the NO stretching vibration.

Analysis for \(\text{FeC}_{28}\text{H}_{24}\text{N}_{3}\text{O}_3\) 
Calculated: C, 66.42; H, 4.78; N, 8.30 %
Found: C, 65.40; H, 4.59; N, 7.99 %
3.2.2.2. Bis(N-4-methylbenzylsalicylideneiminato)nitrosyliron

\[ \text{[Fe(salMebam)\textsubscript{2}NO]} \]

Iron(II) perchlorate hexahydrate (0.568 g, 1.565 mmol) was added to a deoxygenated methanolic solution (20 cm\textsuperscript{3}) of salMebamH (0.705 g, 3.131 mmol) and anhydrous sodium acetate (0.257 g, 3.131 mmol). The yellow colour changed to bright red and the reaction was stirred for 7 hours before nitrosylation was carried out in the usual manner. As the NO gas was taken up (37 cm\textsuperscript{3}, 758 mmHg, 24\textdegree C, 1.72 mmol), the colour of the solution turned a darker red and some dark red solid appeared. Approximately 1 mole of NO was taken up by 1 mole of iron. The solid was filtered off, washed with ice-cold methanol and dried on the pump. Yield, 0.71 g (85%). The infrared spectrum showed \( \nu_{\text{NO}} \) at 1777 cm\textsuperscript{-1}.

Analysis for FeC\textsubscript{30}H\textsubscript{28}N\textsubscript{3}O\textsubscript{3}

Calculated: C, 67.68; H, 4.92; N, 7.89 %

Found: C, 67.26; H, 5.26; N, 7.75 %

3.2.2.3. Bis(N-4-methoxybenzylsalicylideneiminato)nitrosyliron

\[ \text{[Fe(salMeObam)\textsubscript{2}NO]} \]

The ligand salMeObamH (1.330 g, 5.512 mmol) and anhydrous sodium acetate (0.452 g, 5.512 mmol) were added to methanol (20 cm\textsuperscript{3}) and the solution was deoxygenated before iron(II) perchlorate hexahydrate (1.000 g, 2.756 mmol) was added against a stream of nitrogen. The yellow colour of the solution immediately turned bright red but solid was formed. The reaction mixture was stirred for 5 hours before NO gas was admitted and gas uptake started after stirring for about 1 minute. The colour darkened and some red solid appeared. When the reaction was complete (56 cm\textsuperscript{3}, 762.5 mmHg, 25\textdegree C, 2.508 mmol), the NO was replaced by nitrogen. The molar ratio of iron
to NO was approximately 1:1. The flask was left overnight in the freezer to obtain more solid. The dark red product was filtered off, washed with cold methanol and dried under vacuum. It was air stable. Yield, 1.231 g (82%). The infrared spectrum contained a band at 1777 cm\(^{-1}\) assignable to the NO stretching vibration.

Analysis for FeC\(_{28}\)H\(_{24}\)N\(_{3}\)O\(_{3}\)  
Calculated: C, 63.62; H, 4.98; N, 7.41 %  
Found: C, 65.82; H, 5.26; N, 7.57 %

3.2.2.4. Attempts to Prepare Other Iron Mononitrosyl Complexes of Salicylaldehyde-derived Schiff Bases

The preparations of Fe(salFbam)\(_{2}\)NO, Fe(sal-N-phen)\(_{2}\)NO, Fe(sal-1,3-pn)NO and Fe(NEt\(_{2}\)salen)NO were attempted a few times unsuccessfully. An outline of the experimental conditions and the microanalysis results is given in Table 3.1 and Table 3.2 respectively.

Table 3.1. Experimental conditions.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Iron(II) perchlorate hexahydrate (mmol)</th>
<th>Nitric oxide uptake (mmol)</th>
<th>Molar ratio Fe:NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(salFbam)(_{2})NO</td>
<td>Methanol</td>
<td>2.153</td>
<td>1.885</td>
<td>1:0.88</td>
</tr>
<tr>
<td>Fe(sal-N-phen)(_{2})NO(^a)</td>
<td>Methanol</td>
<td>1.521</td>
<td>1.375</td>
<td>1:0.90</td>
</tr>
<tr>
<td>Fe(sal-N-phen)(_{2})NO(^b)</td>
<td>Methanol  /hexane</td>
<td>2.756</td>
<td>2.396</td>
<td>1:0.87</td>
</tr>
<tr>
<td>Fe(sal-N-phen)(_{2})NO(^c)</td>
<td>Ethanol</td>
<td>2.756</td>
<td>2.374</td>
<td>1:0.86</td>
</tr>
<tr>
<td>Fe(sal-1,3-pn)NO</td>
<td>Methanol</td>
<td>1.565</td>
<td>1.615</td>
<td>1:1.03</td>
</tr>
<tr>
<td>Fe(NEt(_{2})salen)NO</td>
<td>Methanol</td>
<td>1.521</td>
<td>5.361</td>
<td>1:0.35</td>
</tr>
</tbody>
</table>

\(^a\) = first attempt;  \(^b\) = second attempt;  \(^c\) = third attempt.
Table 3.2. Microanalysis results.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Results</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(salFbam)(2)NO</td>
<td>Theoretical</td>
<td>62.01</td>
<td>4.09</td>
<td>7.75</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>46.21</td>
<td>3.24</td>
<td>1.49</td>
</tr>
<tr>
<td>Fe(sal-N-phen)(2)NO(^a)</td>
<td>Theoretical</td>
<td>65.29</td>
<td>4.21</td>
<td>8.79</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>58.86</td>
<td>3.86</td>
<td>8.44</td>
</tr>
<tr>
<td>Fe(sal-N-phen)(2)NO(^b)</td>
<td>Experimental</td>
<td>42.22</td>
<td>3.47</td>
<td>3.23</td>
</tr>
<tr>
<td>Fe(sal-N-phen)(2)NO(^b)</td>
<td>Experimental</td>
<td>64.27</td>
<td>4.47</td>
<td>5.60</td>
</tr>
<tr>
<td>Fe(sal-1,3-pn)NO</td>
<td>Theoretical</td>
<td>55.76</td>
<td>4.40</td>
<td>11.48</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>45.81</td>
<td>4.23</td>
<td>5.48</td>
</tr>
<tr>
<td>Fe(NE(_2)salen)NO</td>
<td>Theoretical</td>
<td>57.42</td>
<td>7.71</td>
<td>10.04</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>54.58</td>
<td>6.45</td>
<td>10.30</td>
</tr>
</tbody>
</table>

\(^a\) = first attempt; \(^b\) = second attempt; \(^c\) = third attempt.

From the results of the microanalyses in Table 3.2, it is clear that the preparations were unsuccessful. No peaks assignable to the stretching frequency of NO were found in the infrared spectra of the products.
3.2.3. Mononitrosyl Cobalt-Schiff Base Complexes

The syntheses of the cobalt nitrosyl complexes were carried out by the reported method.\textsuperscript{58}

3.2.3.1. \textit{N,N’-Ethylenebis(4-diethylaminosalicylideneiminato)nitrosylcobalt} [Co(NEt\textsubscript{2}salen)NO]

A deoxygenated solution of 4-NEt\textsubscript{2}salenH\textsubscript{2} (1.700 g, 4.141 mmol) in methanol (20 cm\textsuperscript{3}) was stirred with a solution of cobalt(II) acetate tetrahydrate (1.030 g, 4.141 mmol), also in methanol (10 cm\textsuperscript{3}) in an atmosphere of nitric oxide. A very rapid uptake of NO was observed (99 cm\textsuperscript{3}, 20°C, 752 mmHg, 5.466 mmol) which was completed in 1 hour. Approximately 1.3 moles of NO were taken up per mole of cobalt(II). The purple microcrystalline solid which appeared was filtered off and washed with cold methanol. Yield, 1.470 g (71%). The NO stretching frequency was not easily assignable as it overlapped with a C=N stretch in the region of 1594 cm\textsuperscript{-1}.

Analysis for CoC\textsubscript{24}H\textsubscript{32}N\textsubscript{5}O\textsubscript{3}

\begin{align*}
\text{Calculated: C,} &\quad 57.94; \text{H,} &\quad 6.48; \text{N,} &\quad 14.08 \% \\
\text{Found: C,} &\quad 57.85; \text{H,} &\quad 6.51; \text{N,} &\quad 13.81 \%
\end{align*}

3.2.3.2. \textit{N,N’-Ethylenebis(salicylideneiminato)nitrosylcobalt} [Co(salen)NO]

A solution of salenH\textsubscript{2} (1.120 g, 4.174 mmol) in methanol (20 cm\textsuperscript{3}) was added to a methanolic solution (10 cm\textsuperscript{3}) of cobalt(II) acetate tetrahydrate (1.040 g, 4.174 mmol) under NO with stirring. An approximately 1:1 molar ratio of nitric oxide to cobalt(II) was taken up in 30 minutes (71 cm\textsuperscript{3}, 21°C, 759 mmHg, 3.778 mmol) after which reaction ceased. The black crystalline product was
filtered off rapidly in air and washed with methanol. Yield, 0.430 g (41%). The infrared spectrum showed a peak at 1622 cm\(^{-1}\) assignable to the NO stretching frequency.

3.2.3.3. \(N,N'\)-Ethylenebis(3-carboxysalicylideneimino)nitrosylcobalt
[Co(fsa\(_2\)en)NO]

The Schiff base fsa\(_2\)enH\(_2\) (0.250 g, 0.722 mmol) and the cobalt(II) acetate tetrahydrate (0.180 g, 0.722 mmol) were each dissolved in dimethylformamide (15 cm\(^3\)). The two solutions were mixed under an atmosphere of nitric oxide, with an immediate uptake of NO (18.5 cm\(^3\), 24°C, 748 mmHg, 0.847 mmol) being observed. After 30 minutes, the reaction was complete and the NO uptake corresponded approximately to 1 NO per 1 Co. Since no solid appeared, the solution was concentrated by pumping. On addition of water, a brown microcrystalline solid was formed which was filtered off, washed with cold methanol and dried in air. Yield, 0.240 g (77%). The NO stretching frequency was obscured by the peaks of the ligand and it was estimated to be at approximately 1595 cm\(^{-1}\).

Analysis for CoC\(_{18}\)H\(_{14}\)N\(_3\)O\(_7\) Calculated: C, 48.78; H, 3.18; N, 9.48 %  
Analysis for Co(fsa\(_2\)en)NO.H\(_2\)O Calculated: C, 46.87; H, 3.50; N, 9.11 %  
Found: C, 46.42; H, 3.10; N, 8.61 %

Another preparation using a mixture of ethanol and water as solvent gave a dark microcrystalline solid which analysed as below:

Found: C, 47.02; H, 3.14; N, 8.84 %

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3.2.3.4. Bis(N-4-methylbenzylsalicylideneiminato)nitrosylcobalt

[Co(salMebam)$_2$NO]

A pink solution of cobalt(II) acetate tetrahydrate (0.515 g, 2.068 mmol) in methanol (10 cm$^3$) was added to a methanolic solution of the ligand SalMebamH (0.932 g, 4.135 mmol) in an atmosphere of nitric oxide. The solution immediately became dark red and was stirred for one hour. When the reaction ceased, approximately a 1:1 molar ratio of nitric oxide to cobalt(II) had been taken up (46 cm$^3$, 18.5°C, 762 mmHg, 1.902 mmol). A peak at 1612 cm$^{-1}$ in the infrared spectrum was assigned to the NO stretching frequency.

Analysis for CoC$_{30}$H$_{26}$N$_3$O$_3$

Calculated: C, 66.78; H, 5.60; N, 7.78 %

Found: C, 66.82; H, 5.18; N, 7.73 %

3.2.3.5. Bis(N-4-methoxybenzylsalicylideneiminato)nitrosylcobalt

[Co(salMeObam)$_2$NO]

A solution of SalMeObamH (0.998 g, 3.879 mmol) in methanol (20 cm$^3$) was allowed to react with cobalt(II) acetate tetrahydrate (0.483 g, 1.939 mmol) in a nitric oxide atmosphere. When the reaction was complete, 1.06 moles of nitric oxide had been taken up per mole of cobalt(II) (50 cm$^3$, 20°C, 762 mmHg, 2.061 mmol). The black solid formed was filtered off, washed with methanol and dried in air. Yield, 0.956 g (80 %). The infrared spectrum showed a peak at 1640 cm$^{-1}$ which was assigned to the NO stretching frequency.
Analysis for CoC_{30}H_{28}N_{3}O_{5}  
Calculated: C, 63.27; H, 4.96; N, 7.27 %  
Found: C, 63.25; H, 4.86; N, 7.27 %

3.2.3.6. Bis(N-4-fluorobenzylsalicylideneiminato)nitrosylcobalt  
[Co(salFbam)_{2}NO]

The solutions of salFbamH (0.947 g, 4.076 mmol) and cobalt(II) acetate tetrahydrate (0.508 g, 2.038 mmol) in methanol (20 cm^{3}) were mixed and stirred in an atmosphere of nitric oxide for one hour until the NO uptake ceased. Approximately 1 molar equivalent of NO (35 cm^{3}, 21^\circ C, 758 mmHg, 1.855 mmol) was taken up per mole of cobalt(II). Yield, 0.819 g (73 %). The peak at 1659 cm\(^{-1}\) in the infrared spectrum was assigned to the NO stretching frequency.

Analysis for CoC_{29}H_{9}N_{3}O_{3}F  
Calculated: C, 61.65; H, 4.06; N, 7.70 %  
Found: C, 61.39; H, 3.86; N, 7.50 %

3.2.4. Attempted Preparations of Iron Mononitrosyl Complexes of Schiff Bases Derived From 2-Hydroxyacetophenone

3.2.4.1. Attempt to prepare Fe(hapen)NO

The ligand hapenH_{2} (2.000 g, 6.748 mmol) was dissolved in deoxygenated methanol (40 cm^{3}) and iron(II) perchlorate hexahydrate (2.449 g, 6.748 mmol) and anhydrous sodium acetate (1.107 g, 13.50 mmol) were added to the solution. The colour of the solution changed from bright yellow to dark red. The mixture was stirred for five hours and then NO gas was admitted into the reaction flask. When the NO uptake had stopped (66 cm^{3}, 755 mmHg, 21^\circ C, 2.967 mmol), the gas was pumped out and replaced with nitrogen. The molar
ratio of iron:NO was 1:0.4. Much less NO was taken up than expected. The dark solid which precipitated was filtered off and dried at the pump. Its infrared spectrum did not contain a band assignable to NO. This and the analytical data indicate that the expected nitrosyl had not been formed.

Dark solid:
Analysis for FeC_{18}H_{16}N_{3}O_{3}  
Calculated: C, 56.86; H, 4.77; N, 11.05 %  
Found: C, 49.07; H, 5.16; N, 5.63 %

The filtrate was left standing in air for 2 days and the dark red crystals which appeared were filtered off and air dried. The crystals were found to be suitable for X-ray crystallography (Section 3.3.5.1.) which showed that a μ-oxo bridged compound [Fe(hapen)]$_2$O had been formed. The analytical data agreed with this formula.

Crystals:
Analysis for (FeHapen)$_2$O  
Calculated: C, 60.36; H, 5.07; N, 7.82 %  
Found: C, 60.02; H, 4.95; N, 7.66 %

3.2.4.2. Attempt to prepare Fe(hap-1,3-pn)NO

The ligand hap-1,3-pnH$_2$ (1.007 g, 3.244 mmol) and anhydrous sodium acetate (0.532 g, 6.488 mmol) were dissolved in methanol (30 cm$^3$) and the solution was deoxygenated. Iron(II) perchlorate hexahydrate (1.177 g, 3.244 mmol) was added whereupon the yellow solution turned bright red, but no solid was observed. After stirring for 4 hours, NO gas was admitted and was taken up almost immediately. The NO uptake stopped after about 20 minutes (70 cm$^3$, 765 mmHg, 25°C, 3.145 mmol) and the system was again put under
nitrogen. Some solid was found after nitrosylation which was filtered off, washed with ice-cold deoxygenated methanol and dried under vacuum. The dry solid was pale, almost rusty brown in colour and there was no NO peak in its infrared spectrum in spite of the uptake of 1 mole of NO per mole of iron(II).

Similar attempts to synthesise Fe(hapbam)$_2$NO and Fe(happram)$_2$NO were also unsuccessful. The results of the microanalyses were in poor agreement with the theoretical ones and there were no obvious peaks due to NO in the infrared spectra; therefore detailed accounts of the preparations are not given.

3.2.5. Preparation of $^{15}$NO-labelled Cobalt Complexes

3.2.5.1. Co(salen)$^{15}$NO

The $^{15}$NO (23 cm$^3$, 21°C, 758 mmHg, 1.219 mmol) was condensed into a reaction flask containing a deoxygenated solution of salenH$_2$ (0.330 g, 1.204 mmol) in methanol (20 cm$^3$) by freezing the salenH$_2$ solution with liquid nitrogen. Cobalt(II) acetate tetrahydrate (0.300 g, 1.204 mmol) was added from the sidearm while the solution was thawing. Upon stirring, the mixture turned dark brown and a dark solid was formed. After 1 hour, any $^{15}$NO remaining in the tubing to the flask was swept into it by allowing nitrogen into the apparatus. After stirring for another hour, the black crystalline solid formed was filtered off and washed with cold methanol. Yield, 0.280 g (66%). The $^{15}$NO stretching frequency appeared at 1593 cm$^{-1}$.
3.2.5.2. Co(NEt₂salen)¹⁵NO

A solution of NEt₂salenH₂ (0.180 g, 0.438 mmol) in methanol (20 cm³) was deoxygenated and ¹⁵NO (8 cm³, 20°C, 757 mmHg, 0.445 mmol) was condensed into the flask by freezing the solution. Cobalt(II) acetate tetrahydrate (0.109 g, 0.438 mmol) was added from the sidearm and the thawed solution was stirred. The black crystals which formed were filtered off, washed with methanol and dried in air. Yield, 0.170 g (77%). The NO band could not be easily assigned due to the overlapping peaks which were due to the ligand. However, it was estimated to be around 1589 cm⁻¹.

3.2.5.3. Co(fsa₂en)¹⁵NO

Labelled nitric oxide (9 cm³, 22°C, 762 mmHg, 0.458 mmol) was condensed on to a frozen solution of fsa₂enH₂ (0.160 g, 0.437 mmol) in methanol (20 cm³) in a flask which was then mixed with cobalt(II) acetate tetrahydrate (0.106 g, 0.437 mmol) by tipping the latter from the sidearm. When thawed, the solution was stirred and the colour of the reaction mixture turned dark brown. The solid was filtered off, washed with methanol and dried in air. There was some yellow solid among the red-brown product which suggested that it was contaminated with some unreacted ligand. The v_NO was obscured by peaks due to the ligand, but it was estimated to be at approximately 1640 cm⁻¹.
3.2.6. Complexes of Cobalt(II) Schiff Bases

The cobalt(II) complex of Co(NEt₂salen) was prepared (Section 3.2.6.1.) to compare its infrared spectrum with that of the Co(NEt₂salen)NO to see if the NO stretching frequency could be more accurately assigned.

Also it had earlier⁶⁸ been found that although bis(N-n-butylsalicylideneiminato)cobalt(II) will react with nitric oxide and oxygen, bis(N-n-butylsalicylideneiminato)cobalt(II) reacts with neither. The preparations of the n-butyl (Section 3.2.6.2) and t-butyl (Section 3.2.6.3) derivatives were repeated and their crystal structures were determined (Sections 3.3.5.2 and 3.3.5.3) to see if this would throw any light on the different reactivities towards nitric oxide and oxygen.

3.2.6.1. N,N'-Ethylenebis(4-diethylaminosalicylideneiminato)cobalt(II) [Co(NEt₂salen)]

Cobalt(II) acetate tetrahydrate (0.607 g, 2.436 mmol) was dissolved in methanol (10 cm³) and the pink solution was deoxygenated. Similarly, the ligand 4-NEt₂SalenH₂ (1.000 g, 2.436 mmol) was dissolved in methanol (20 cm³) and deoxygenated. Both solutions were gently heated in a warm water bath (70°C) and then mixed. The resultant deep blood red solution was stirred for 4 hours and then left in the freezer overnight. Some orange solid was observed which was filtered off and dried on the pump. Yield, 0.973 g (79%)

Analysis for CoC₂₄H₃₂N₄O₂ Calculated: C, 61.66; H, 6.90; N,11.98 %
Analysis for Co(4-NEt₂Salen).2H₂O Calculated: C, 57.25; H, 7.21; N,11.13 %
Found: C, 56.99; H, 6.59;N,11.17 %
3.2.6.2. Bis(N-n-butylnsalicylideneiminato)cobalt(II) [Co(nbsal)$_2$]

An excess of $n$-butylamine (2.500 g, 34.00 mmol) was added under nitrogen to a solution of bis(salicylaldehydato)cobalt(II) dihydrate (3.000 g, 8.900 mmol) in methanol (80 cm$^3$) containing 2 cm$^3$ of 37% aqueous formaldehyde. The solution was stirred at 60°C for 15 minutes, allowed to cool and then placed in a refrigerator overnight. The red needles which separated were quickly filtered off and washed with cold methanol in air and dried in vacuum. The product was stored under nitrogen. Yield, 1.350 g (37%). The crystals were suitable for an X-ray investigation. This compound was prepared by A. Marécaux.

Analysis for CoC$_{22}$H$_{28}$N$_2$O$_2$  
Calculated: C, 64.23; H, 6.86; N, 6.81 %
Found: C, 64.38; H, 7.11; N, 7.00 %

3.2.6.3. Bis(N-t-butylnsalicylideneiminato)cobalt(II) [Co(tbsal)$_2$]

This preparation was carried out in air. To a solution of bis(salicylaldehydato)cobalt(II) dihydrate (3.000 g, 89.00 mmol) in methanol (60 cm$^3$), t-butylnamine (2.500 g, 34.00 mmol) was added and the reaction mixture was heated and stirred at 60°C for 15 minutes and then allowed to cool. The red product was recrystallised from ethanol to give red crystals on which an X-ray crystallographic study was carried out. Yield, 2.600 g (72%).

Analysis for CoC$_{22}$H$_{28}$N$_2$O$_2$  
Calculated: C, 64.23; H, 6.86; N, 6.81 %
Found: C, 63.95; H, 7.01; N, 7.49 %
3.3. Results and Discussion

3.3.1. Magnetic Measurements

Table 3.3. The variation of reciprocal susceptibility and effective magnetic moment of Fe(salbam)_2NO with temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>10^-2\chi_A^-1 (c.g.s.)</th>
<th>\mu_{\text{eff}} (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>1.51</td>
<td>3.94</td>
</tr>
<tr>
<td>261</td>
<td>1.35</td>
<td>3.94</td>
</tr>
<tr>
<td>229</td>
<td>1.19</td>
<td>3.93</td>
</tr>
<tr>
<td>197</td>
<td>1.01</td>
<td>3.93</td>
</tr>
<tr>
<td>165</td>
<td>0.86</td>
<td>3.92</td>
</tr>
<tr>
<td>133</td>
<td>0.69</td>
<td>3.93</td>
</tr>
<tr>
<td>101</td>
<td>0.53</td>
<td>3.89</td>
</tr>
<tr>
<td>87</td>
<td>0.47</td>
<td>3.84</td>
</tr>
<tr>
<td>81</td>
<td>0.44</td>
<td>3.83</td>
</tr>
</tbody>
</table>

Diamagnetic correction = -256.6 \times 10^{-6} c.g.s.

\theta = 10^\circ

Graph 3.3. The plot of the reciprocal susceptibility and effective magnetic moment against temperature.
Table 3.4. The variation of reciprocal susceptibility and effective magnetic moment of Fe(salMebam)$_2$NO with temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^{-2} \chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>1.46</td>
<td>4.00</td>
</tr>
<tr>
<td>261</td>
<td>1.31</td>
<td>3.99</td>
</tr>
<tr>
<td>229</td>
<td>1.14</td>
<td>4.01</td>
</tr>
<tr>
<td>197</td>
<td>1.00</td>
<td>3.97</td>
</tr>
<tr>
<td>165</td>
<td>0.83</td>
<td>3.98</td>
</tr>
<tr>
<td>133</td>
<td>0.67</td>
<td>3.98</td>
</tr>
<tr>
<td>101</td>
<td>0.52</td>
<td>3.95</td>
</tr>
<tr>
<td>85</td>
<td>0.44</td>
<td>3.92</td>
</tr>
</tbody>
</table>

Diamagnetic correction = $-274.5 \times 10^{-6}$ c.g.s.

$\theta = 10$ K

Graph 3.4. The plot of the reciprocal susceptibility and effective magnetic moment against temperature.
Table 3.5. The variation of reciprocal susceptibility and effective magnetic moment of Fe(salMeObam)$_2$NO with temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^{-2} \chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>291</td>
<td>1.47</td>
<td>3.97</td>
</tr>
<tr>
<td>261</td>
<td>1.33</td>
<td>3.96</td>
</tr>
<tr>
<td>229</td>
<td>1.18</td>
<td>3.95</td>
</tr>
<tr>
<td>197</td>
<td>1.01</td>
<td>3.96</td>
</tr>
<tr>
<td>165</td>
<td>0.84</td>
<td>3.96</td>
</tr>
<tr>
<td>133</td>
<td>0.69</td>
<td>3.94</td>
</tr>
<tr>
<td>101</td>
<td>0.53</td>
<td>3.91</td>
</tr>
<tr>
<td>85</td>
<td>0.45</td>
<td>3.90</td>
</tr>
</tbody>
</table>

Diamagnetic correction = $-274.5 \times 10^{-6}$ c.g.s.

$\theta = 10$ K

Graph 3.5. The plot of the reciprocal susceptibility and effective magnetic moment against temperature.
The complexes Fe(salbam)_2NO, Fe(salMebam)_2NO and Fe(SalMeObam)_2NO are the first examples of iron mononitrosyls with bidentate Schiff base co-ligands. All obeyed the Curie-Weiss law with effective magnetic moments of 3.94, 4.00 and 3.97 B.M. at 293 K respectively with small values of the Weiss constant $\theta = 10^\circ$. The $\mu_{\text{eff}}$ values indicate that the complexes contain three unpaired electrons ($\mu_{\text{so}} = 3.87$ B.M.) i.e. high spin $\{\text{Fe(NO)}\}^7$.

It was also noted that lowering the temperature below approximately 100 K resulted in a slight but obvious decrease of the effective magnetic moment probably due to the formation of very small but increasing amounts of low spin complex. This behaviour indicates that spin crossover might occur below liquid nitrogen temperature. In this way, the magnetic behaviour of these complexes resembles that of Fe(5-Clalen)NO$^7$ more than that of Fe(salen)NO$_2$ or Fe(salphen)NO$_5$. The small $\theta$ values could also be due to weak antiferromagnetic interactions. Unfortunately, apparatus to carry out magnetic measurements below liquid nitrogen was not available.
Table 3.6. The variation of reciprocal susceptibility and effective magnetic moment of Co(NEt<sub>2</sub>salen).2H<sub>2</sub>O with temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^{-2}\chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>261</td>
<td>1.36</td>
<td>3.89</td>
</tr>
<tr>
<td>229</td>
<td>1.21</td>
<td>3.89</td>
</tr>
<tr>
<td>197</td>
<td>1.03</td>
<td>3.92</td>
</tr>
<tr>
<td>165</td>
<td>0.86</td>
<td>3.86</td>
</tr>
<tr>
<td>133</td>
<td>0.73</td>
<td>3.82</td>
</tr>
<tr>
<td>101</td>
<td>0.56</td>
<td>3.78</td>
</tr>
<tr>
<td>85</td>
<td>0.51</td>
<td>3.70</td>
</tr>
</tbody>
</table>

Diamagnetic correction = - 316.0 x $10^{-6}$ c.g.s.
$\theta = 25$ K

Graph 3.6. The plot of the reciprocal susceptibility and effective magnetic moment against temperature.
Table 3.7. Room temperature magnetic moments of cobalt mononitrosyl complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(salen)NO</td>
<td>1.01</td>
</tr>
<tr>
<td>Co(fsa$_2$en)NO</td>
<td>1.31</td>
</tr>
<tr>
<td>Co(NEt$_2$salen)NO</td>
<td>0.70</td>
</tr>
<tr>
<td>Co(salMebam)$_2$NO</td>
<td>0.59</td>
</tr>
<tr>
<td>Co(salFbam)$_2$NO</td>
<td>0.88</td>
</tr>
<tr>
<td>Co(salMebam)$_2$NO</td>
<td>0.91</td>
</tr>
<tr>
<td>Co(nbsal)$_2$NO</td>
<td>1.00$^{68}$</td>
</tr>
</tbody>
</table>

Table 3.8. Room temperature magnetic moments of cobalt(II) Schiff base complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(NEt$_2$salen).2H$_2$O</td>
<td>3.92</td>
</tr>
<tr>
<td>Co(nbsal)$_2$</td>
<td>4.19</td>
</tr>
<tr>
<td>Co(tbsal)$_2$</td>
<td>4.23</td>
</tr>
</tbody>
</table>

All the cobalt nitrosyl complexes in Table 3.7 show small effective magnetic moments of 0.70-1.31 B.M. Magnetic moments of this order were previously ascribed$^{58}$ to Van Vleck (temperature independent) paramagnetism which is comparatively large for cobalt(III) compounds. These complexes contain no unpaired electrons ($S = 0$) i.e. the configuration is low spin {Co(NO)}$^8$.

It is interesting to note that the parent cobalt(II) complexes, Co(NEt$_2$Salen).2H$_2$O, Co(nbsal)$_2$ and Co(tbsal)$_2$ (Table 3.8) show effective
magnetic moments of 3.92, 4.19 and 4.23 B.M. respectively, indicative of a high spin cobalt(II) complexes (high spin 3d⁷ configuration). In the case of Co(nbsal)₂ and Co(tbsal)₂, the coordination is tetrahedral, as revealed by X-ray crystallography (Sections 3.3.5.2 and 3.3.5.3). The tetrahedral splitting diagram leads to three unpaired electrons with the 3d⁷ configuration. In the case of Co(NEt₂salen).2H₂O, however, the molecule could be square planar with the two water molecules in the lattice, square pyramidal with one coordinated water molecule or octahedral with both water molecules coordinated. However, planar cobalt(II) complexes are low spin, with magnetic moments in the range 2.1 to 2.9 B.M., and octahedral cobalt(II) complexes are usually high spin, with magnetic moments in the range 4.8 to 5.2 B.M.¹ It is thus thought that this complex is square pyramidal, with one water molecule coordinated and the other in the lattice.

Upon nitrosylation, these complexes were rendered low spin with magnetic moments of 0.70 and 1.00 B.M. respectively. This is in agreement with the fact that NO is situated at the strong-field end of the spectrochemical series causing large splittings in the d orbitals making the low spin arrangement of electrons more favoured energetically.
3.3.2. Infrared Spectroscopy

The infrared spectra of the ligand and nitrosyl complexes were obtained mainly to assign the NO stretching frequencies of these compounds.

Table 3.9. NO and $^{15}$NO stretching frequencies of iron and cobalt nitrosyls.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$v_{\text{NO}}$ (cm$^{-1}$)</th>
<th>$v_{^{15}\text{NO}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(salbam)$_2$NO</td>
<td>1774</td>
<td>-</td>
</tr>
<tr>
<td>Fe(salMebam)$_2$NO</td>
<td>1777</td>
<td>-</td>
</tr>
<tr>
<td>Fe(salMeObam)$_2$NO</td>
<td>1777</td>
<td>-</td>
</tr>
<tr>
<td>Co(NEt$_2$salen)NO</td>
<td>1594</td>
<td>1589</td>
</tr>
<tr>
<td>Co(salen)NO</td>
<td>1622</td>
<td>1593</td>
</tr>
<tr>
<td>Co(fsa$_2$en)NO</td>
<td>1595</td>
<td>1642</td>
</tr>
<tr>
<td>Co(salFbam)$_2$NO</td>
<td>1659</td>
<td>-</td>
</tr>
<tr>
<td>Co(salMebam)$_2$NO</td>
<td>1612</td>
<td>-</td>
</tr>
<tr>
<td>Co(salMeObam)$_2$NO</td>
<td>1640</td>
<td>-</td>
</tr>
</tbody>
</table>

From the values of the $v_{\text{NO}}$ of the complexes in Table 3.9 above, a tentative suggestion can be made that the iron nitrosyl complexes contain approximately linear Fe-N-O groups which might become bent in the low spin isomers if these could be obtained. On the other hand, the cobalt nitrosyl complexes contain bent Co-N-O groups. However, these suggestions need to be substantiated by other methods such as $^{15}$N NMR (cobalt nitrosyls) and if possible, single crystal X-ray diffraction studies.
3.3.3. Proton Nuclear Magnetic Resonance Spectra of the Schiff Bases

![Schiff Base Structures]

Table 3.10. Proton NMR data for SalenH₂ and NEt₂salenH₂.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Residue</th>
<th>No. of H</th>
<th>δ_H (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SalenH₂</td>
<td>Phenyl rings</td>
<td>8</td>
<td>6.80-7.32 (m)</td>
</tr>
<tr>
<td></td>
<td>CH</td>
<td>2</td>
<td>8.45 (s)</td>
</tr>
<tr>
<td></td>
<td>CH₂</td>
<td>4</td>
<td>3.95 (s)</td>
</tr>
<tr>
<td>NEt₂salenH₂</td>
<td>Phenyl rings</td>
<td>6</td>
<td>5.83-6.94 (m)</td>
</tr>
<tr>
<td></td>
<td>CH</td>
<td>2</td>
<td>7.80 (s)</td>
</tr>
<tr>
<td></td>
<td>CH₂ (a)</td>
<td>4</td>
<td>3.71 (s)</td>
</tr>
<tr>
<td></td>
<td>CH₂ (b)</td>
<td>8</td>
<td>3.37 (q)</td>
</tr>
<tr>
<td></td>
<td>CH₃</td>
<td>12</td>
<td>1.15 (t)</td>
</tr>
</tbody>
</table>
Table 3.11. Proton NMR data for SalMebamH and SalMeObamH.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Residue</th>
<th>No. of H</th>
<th>$\delta_H$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SalMebamH</td>
<td>Phenyl rings</td>
<td>8</td>
<td>6.61-7.34 (m)</td>
</tr>
<tr>
<td></td>
<td>CH</td>
<td>1</td>
<td>8.49 (s)</td>
</tr>
<tr>
<td></td>
<td>CH$_2$</td>
<td>2</td>
<td>4.72 (s)</td>
</tr>
<tr>
<td></td>
<td>CH$_3$</td>
<td>3</td>
<td>2.31 (s)</td>
</tr>
<tr>
<td>SalMeObamH</td>
<td>Phenyl rings</td>
<td>8</td>
<td>6.60-7.40 (m)</td>
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<td></td>
<td>CH</td>
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<td>8.46 (s)</td>
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<td></td>
<td>CH$_2$</td>
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<td></td>
<td>CH$_3$</td>
<td>3</td>
<td>3.86 (s)</td>
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Table 3.12. Proton NMR data for SalbamH and SalFbamH.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Residue</th>
<th>No. of H</th>
<th>$\delta_H$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SalbamH</td>
<td>Phenyl rings</td>
<td>9</td>
<td>6.83-7.36 (m)</td>
</tr>
<tr>
<td></td>
<td>CH</td>
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<tr>
<td></td>
<td>CH$_2$</td>
<td>2</td>
<td>4.76 (s)</td>
</tr>
<tr>
<td>SalFbamH</td>
<td>Phenyl rings</td>
<td>8</td>
<td>6.39-7.40 (m)</td>
</tr>
<tr>
<td></td>
<td>CH</td>
<td>1</td>
<td>8.66 (s)</td>
</tr>
<tr>
<td></td>
<td>CH$_2$</td>
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<td>4.60 (s)</td>
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</table>

Note: For Tables 3.10-12, s=singlet; m=multiplet; t=triplet; q=quadruplet.

The OH signals of the Schiff bases were not observed as the solvent used was deuterated methanol, for reasons of solubility limitations. The proton and the deuterium of OH and OD in the ligands and solvent respectively would exchange resulting in the absence of the OH signals, expected in the region of 10.00 to 13.00 ppm for these compounds.$^{100}$
3.3.4. Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy for Cobalt Mononitrosyl Complexes

Table 3.13. Values of $\delta^{15}N$ and $\delta^{59}Co$ of $^{15}NO$ labelled cobalt mononitrosyls.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\delta^{15}N$ (solution) (ppm)</th>
<th>$\delta^{15}N$ (solid) (ppm)</th>
<th>$\delta^{59}Co$ (solution) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(Salen)$_{15}$NO</td>
<td>725 (CD$_2$Cl$_2$) $^{69}$</td>
<td>699</td>
<td>not observed</td>
</tr>
<tr>
<td></td>
<td>737 (CD$_3$)$_2$SO) $^{12}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(NEt$<em>2$Salen)$</em>{15}$NO</td>
<td>757 (DMSO)</td>
<td>739</td>
<td>7954</td>
</tr>
<tr>
<td>Co(fsa$<em>2$en)$</em>{15}$NO</td>
<td>-</td>
<td>806</td>
<td>8414</td>
</tr>
<tr>
<td>Co(nbsal)$<em>2$$</em>{15}$NO</td>
<td>728 (CD$_2$Cl$_2$)</td>
<td>741</td>
<td>9675</td>
</tr>
</tbody>
</table>

The references for $^{15}N$ and $^{59}Co$ were CH$_3^{15}$NO$_2$ and K$_3$Co(CN)$_6$ respectively.

The values of the $^{15}N$ chemical shifts for these complexes fall within the range of 350-850 ppm in support of the suggestion made in the infrared section above that the coordination geometry of the Co-N-O group in these cobalt complexes is indeed bent. An X-ray crystallography investigation carried out on Co(salen)NO$^{70}$ has shown that the Co-N-O group has a mean angle of 127°.
3.3.5. X-Ray Crystallography

The structures of [Fe(hapen)]$_2$O, Co(nbsal)$_2$ and Co(tbsal)$_2$ were solved by Mr. G.W. Smith.

3.3.5.1. X-Ray Crystal Structure of [Fe(hapen)]$_2$O

A single crystal of the $\mu$-oxo bridged compound [Fe(hapen)]$_2$O was investigated by X-ray methods and Tables 3.13 and 3.14 respectively show the bond lengths and bond angles of the chelate rings. Figure 3.3 illustrates the atom numbering scheme for the complex.

Crystal Data

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>(FeC$<em>{18}$H$</em>{18}$N$_2$O$_2$)$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMM</td>
<td>716.40</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
</tr>
<tr>
<td>$a$</td>
<td>11.918(5) Å</td>
</tr>
<tr>
<td>$b$</td>
<td>20.729(12) Å</td>
</tr>
<tr>
<td>$c$</td>
<td>13.709(17) Å</td>
</tr>
<tr>
<td>$\beta$</td>
<td>107.48(7)$^\circ$</td>
</tr>
<tr>
<td>$V_c$</td>
<td>3228.9 Å$^3$</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>$D_x$</td>
<td>1.476 gcm$^{-3}$</td>
</tr>
<tr>
<td>$F$(000)</td>
<td>1488</td>
</tr>
<tr>
<td>$\mu$(Mo K$\alpha$)</td>
<td>9.5 cm$^{-1}$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.71069 Å</td>
</tr>
</tbody>
</table>
A crystal of approximate dimensions 0.28 x 0.15 x 0.18 mm was mounted on a glass fibre and examined on the Enraf-Nonius CAD4 diffractometer, using 25 accurately centred reflections.

Intensity data were collected in the ϑ range 1° to 25° using monochromated MoKα radiation covering the index range 0 ≤ h ≤ 14, 0 ≤ k ≤ 24, -16 ≤ l ≤ 6. Examination of the final data list showed that no reflections were available for the collection of PSI data. After the usual correction for Lorentz and polarisation effects, of the 3087 measured reflections, 1832 had I > 3 σ(I) and 1040 were estimated to be unobserved. The monitored standard reflection showed no significant decay during the data collection period. Examination of the reflection data showed the presence of a c-glide and since the N(z) test yielded a centric distribution, space group C2/c was adopted. The unit cell volume would only allow four molecules in the cell indicating that the bridging O atom was expected to be on the two-fold axis. The alternative position of the O atom at the centre of symmetry would imply the Fe-O-Fe angle to be 180° which was considered unlikely.

Anisotropic refinement was started, initially of iron alone, then all non-hydrogen atoms when R rapidly converged to 0.043, \( R_w = 0.049 \), S = 1.009. The highest peak in the difference map was 0.3 eÅ⁻³.
The molecule of [Fe(hapen)]$_2$O contains two Fe(hapen) moieties linked by a single oxygen atom bridge. The Fe-O-Fe bridge is bent with an angle of 156.7°. Both iron atoms are five coordinate with approximate square pyramidal geometry.
Figure 3.4. ORTEP drawing of $[\text{Fe(hapen)}]_2\text{O}$. 
Table 3.13. Bond lengths of the chelate rings for [Fe(hapen)]$_2$O.

<table>
<thead>
<tr>
<th>Atom1-Atom2</th>
<th>Bond length (Å)</th>
<th>Atom1-Atom2</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-N1</td>
<td>2.154 (4)</td>
<td>Fe-N2</td>
<td>2.092 (4)</td>
</tr>
<tr>
<td>Fe-O1</td>
<td>1.905 (4)</td>
<td>Fe-O2</td>
<td>1.903 (3)</td>
</tr>
<tr>
<td>O1-C1</td>
<td>1.319 (6)</td>
<td>O2-C11</td>
<td>1.307 (5)</td>
</tr>
<tr>
<td>C1-C6</td>
<td>1.398 (8)</td>
<td>C11-C16</td>
<td>1.416 (7)</td>
</tr>
<tr>
<td>C6-C7</td>
<td>1.469 (9)</td>
<td>C16-C17</td>
<td>1.463 (7)</td>
</tr>
<tr>
<td>C7-N1</td>
<td>1.296 (7)</td>
<td>C17-N2</td>
<td>1.280 (6)</td>
</tr>
<tr>
<td>N1-C9</td>
<td>1.461 (8)</td>
<td>N2-C19</td>
<td>1.472 (7)</td>
</tr>
<tr>
<td>C9-C19</td>
<td>1.502 (8)</td>
<td>Fe-O</td>
<td>1.765 (1)</td>
</tr>
</tbody>
</table>

Table 3.14. Bond angles of the chelate rings for [Fe(hapen)]$_2$O.

<table>
<thead>
<tr>
<th>Atom1-Atom2-Atom3</th>
<th>Bond angle (°)</th>
<th>Atom1-Atom2-Atom3</th>
<th>Bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1-C1-C6</td>
<td>123.7 (6)</td>
<td>O2-C11-C16</td>
<td>123.7 (4)</td>
</tr>
<tr>
<td>C1-C6-C7</td>
<td>123.2 (5)</td>
<td>C11-C16-C17</td>
<td>122.9 (4)</td>
</tr>
<tr>
<td>C6-C7-N1</td>
<td>120.3 (5)</td>
<td>C16-C17-N2</td>
<td>120.3 (5)</td>
</tr>
<tr>
<td>N1-C9-C19</td>
<td>109.7 (4)</td>
<td>N2-C19-C9</td>
<td>106.9 (4)</td>
</tr>
<tr>
<td>Fe-N1-C9</td>
<td>111.7 (3)</td>
<td>Fe-N2-C19</td>
<td>104.9 (3)</td>
</tr>
<tr>
<td>O-Fe-O1</td>
<td>112.5 (1)</td>
<td>O-Fe-O2</td>
<td>109.3 (2)</td>
</tr>
<tr>
<td>O1-Fe-N1</td>
<td>84.9 (2)</td>
<td>O2-Fe-N2</td>
<td>85.0 (2)</td>
</tr>
<tr>
<td>N1-Fe-N2</td>
<td>77.6 (2)</td>
<td>Fe-O-Fe</td>
<td>156.7 (3)</td>
</tr>
</tbody>
</table>
The first oxo-bridged iron(III) complex was the Schiff base derivative [Fe(salen)]$_2$O prepared by Pfeiffer and co-workers$^{71}$ who formulated the gross structure correctly without the aid of modern techniques. Since, many other iron(III) oxo-bridged complexes have been isolated and characterised.$^{72}$ These complexes are known with Fe-O-Fe angles in the range 139° - 180° with the majority having angles smaller than 180°. It is difficult to say for certain what controls the Fe-O-Fe angle in a particular complex, since a variety of effects such as ligand repulsions, electronic factors and crystal packing could all play a part.$^{73}$

Tatsumi and Hoffman,$^{74}$ in their study of bridged metalloporphyrin dimers have concluded that the angle found for a given [Fe(L)]$_2$O complex would be decided largely by the extent of intramolecular interaction between the ligands attached to the Fe centres. Thus, in [Fe(PP)]$_2$O$^{75}$ where the bulky, 'flat', inflexible porphyrins will interact quite considerably with each other, the bond approaches linearity at 174°, whereas the quadridentate open-chain ligand salen$^2$ in [Fe(salen)]$_2$O can reduce intramolecular contacts by having the Fe(salen) moieties arranged in a trans fashion about the Fe-O-Fe links allowing the angle to be considerably reduced to 139°. The presence of solvent molecules in the crystal can alter the angle due to packing effects.
Table 3.15 lists the Fe-O-Fe bond angles and Fe-O bond lengths of some oxo-bridged iron(III) Schiff base complexes for comparison with the values for [Fe(hapen)]₂O obtained in the current work.

Table 3.15. Fe-O-Fe geometries of μ-oxo iron(III) Schiff base.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Fe-O-Fe (°)</th>
<th>Fe-0 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(Salen)]₂O</td>
<td>145</td>
<td>1.78</td>
</tr>
<tr>
<td>[Fe(Salen)]₂O.2py⁷⁶</td>
<td>139.1</td>
<td>1.82</td>
</tr>
<tr>
<td>[Fe(Salen)]₂O.CH₂Cl₂⁷⁷</td>
<td>142.4</td>
<td>1.79</td>
</tr>
<tr>
<td>[Fe(N-n-propyl-sal)₂]₂O⁷⁸</td>
<td>164</td>
<td>1.78</td>
</tr>
<tr>
<td>[Fe(N-p-chlorophenyl-sal)₂]₂O⁷⁹</td>
<td>175</td>
<td>1.76</td>
</tr>
<tr>
<td>[Fe(Hapen)]₂O</td>
<td>156.7</td>
<td>1.77</td>
</tr>
</tbody>
</table>

The bridging Fe-O distance is about 1.80 Å in all cases which is shorter than the other iron-ligand Fe-O bond length (ca. 1.92 Å). This bond shortening is generally considered indicative of some degree of π-bonding between the d orbitals of the iron and the p orbitals of the bridging oxygen along the Fe-O-Fe bridge.

The infrared mode commonly used to characterise the oxo bridge in iron(III) and other μ-oxo complexes is the antisymmetric stretch of Fe-O-Fe. This appears as a broad, strong band at around 820-840 cm⁻¹ and in some cases a shoulder is observed at around 860 cm⁻¹. Indeed, the infrared spectrum of [Fe(hapen)]₂O contains a strong band at 843 cm⁻¹, which does not appear in the spectrum of the Schiff base HapenH₂, therefore assignable to the antisymmetric stretch of Fe-O-Fe.
The μ-oxo iron(III) complexes are also characterised by low magnetic moments of around 1.9 B.M. per Fe atom (one unpaired electron). Though these values are reminiscent of those observed in low spin iron(III) complexes, the temperature dependence of the susceptibility shows they cannot belong to this class of compound. The susceptibility drops toward zero as the temperature approaches zero. Lewis and co-workers gave a quantitative analysis of the magnetic behaviour using what they termed the 'dipolar-coupling' approach. The dipoles (spins) become aligned in an antiparallel manner, resulting in antiferromagnetism, and the magnetic moment approaches zero as the temperature is lowered.

The Fe-Fe distances are in the range of 3.4 - 3.6 Å, therefore, the contribution of direct metal-metal orbital overlap to the exchange mechanism is considered to be small with such a big separation. Exchange must occur via overlap of the metal $d$ orbitals with the bridging oxygen $p$ orbital, i.e. a superexchange pathway.
3.3.5.2. X-Ray Crystal Structure of Co(nbsal)$_2$

The molecular structure of the complex Co(nbsal)$_2$ is presented below in Figure 3.5, including the atom numbering scheme.

Figure 3.5. Atom numbering scheme and molecular structure of Co(nbsal)$_2$. 
### Crystal Data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>CoC_{22}H_{28}N_{2}O_{2}</td>
</tr>
<tr>
<td>RMM</td>
<td>411.41</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>P4</td>
</tr>
<tr>
<td>a</td>
<td>14.244(4) Å</td>
</tr>
<tr>
<td>c</td>
<td>5.395(1) Å</td>
</tr>
<tr>
<td>V_c</td>
<td>1094.6 Å^3</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>D_x</td>
<td>1.248 g cm^{-3}</td>
</tr>
<tr>
<td>F(000)</td>
<td>434</td>
</tr>
<tr>
<td>(\mu (\text{Mo K}\alpha))</td>
<td>7.97 cm^{-1}</td>
</tr>
</tbody>
</table>

A needle crystal of approximate dimensions 0.13 x 0.15 x 0.45 mm was mounted on a glass fibre and examined on the Enraf-Nonius CAD4 four-circle diffractometer, using graphite-monochromated MoK\(\alpha\) radiation (\(\lambda = 0.71073\) Å). The unit cell dimensions were obtained by least-squares refinement of a set of 25 reflections in the \(\theta\) range 13\(^o\) to 15\(^o\). Intensity data were collected in a \(\omega-2\theta\) scan mode from one octant of the reciprocal lattice; \(\theta\) range 1\(^o\) to 26\(^o\), 0 \(\leq h \leq 17\), 0 \(\leq k \leq 17\), 0 \(\leq l \leq 6\). After correction for the Lorentz and polarization effects, the data set yielded 1298 independent reflections of which 777 were used (\(l > 3 \sigma (l)\)). The 020 reflection, which was monitored hourly throughout the data collection, showed negligible decay (0.1\%) in spite of the slight sensitivity of the complex to aerial oxidation. Psi-reflections were not available for the application of an empirical absorption correction.

Refinement of the structure with the hydrogen atoms in fixed calculated positions using a C-H distance of 1 Å decreased the value of \(R\) to 0.080.
Application of a pseudo empirical absorption correction by DIFABS\textsuperscript{82} reduced $R$ to 0.075. When an anisotropic refinement was applied to all non-hydrogen atoms, $R$ converged at 0.038, $R_w = 0.045$, $S = 1.073$.

Table 3.16. Bond lengths for Co(nbsal)\textsubscript{2}.

<table>
<thead>
<tr>
<th>Atom1-Atom2</th>
<th>Bond length (Å)</th>
<th>Atom1-Atom2</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-O</td>
<td>1.894(4)</td>
<td>C2-C7</td>
<td>1.422(8)</td>
</tr>
<tr>
<td>Co-N</td>
<td>1.968(4)</td>
<td>C3-C4</td>
<td>1.353(9)</td>
</tr>
<tr>
<td>O-C1</td>
<td>1.311(6)</td>
<td>C4-C5</td>
<td>1.352(9)</td>
</tr>
<tr>
<td>N-C7</td>
<td>1.295(7)</td>
<td>C5-C6</td>
<td>1.352(9)</td>
</tr>
<tr>
<td>N-C8</td>
<td>1.458(8)</td>
<td>C8-C9</td>
<td>1.507(10)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.418(8)</td>
<td>C9-C10</td>
<td>1.488(12)</td>
</tr>
<tr>
<td>C1-C6</td>
<td>1.411(9)</td>
<td>C10-C11</td>
<td>1.426(15)</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.410(7)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3.17. Bond angles for Co(nbsal)$_2$.

<table>
<thead>
<tr>
<th>Atom1-Atom2-Atom3</th>
<th>Bond angle (°)</th>
<th>Atom1-Atom2-Atom3</th>
<th>Bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-Co-O</td>
<td>113.8(2)</td>
<td>C1-C2-C3</td>
<td>118.1(5)</td>
</tr>
<tr>
<td>O-Co-N</td>
<td>96.1(2)</td>
<td>C1-C2-C7</td>
<td>124.9(5)</td>
</tr>
<tr>
<td>O-Co-N</td>
<td>118.3(2)</td>
<td>C3-C2-C7</td>
<td>117.0(5)</td>
</tr>
<tr>
<td>N-Co-N</td>
<td>115.7(2)</td>
<td>C2-C3-C4</td>
<td>121.8(5)</td>
</tr>
<tr>
<td>Co-O-C1</td>
<td>126.8(4)</td>
<td>C3-C4-C5</td>
<td>119.9(5)</td>
</tr>
<tr>
<td>Co-N-C7</td>
<td>121.2(4)</td>
<td>C4-C5-C6</td>
<td>121.1(6)</td>
</tr>
<tr>
<td>Co-N-C8</td>
<td>121.3(3)</td>
<td>C1-C6-C5</td>
<td>121.2(6)</td>
</tr>
<tr>
<td>C7-N-C8</td>
<td>117.5(5)</td>
<td>N-C7-C2</td>
<td>127.8(5)</td>
</tr>
<tr>
<td>O-C1-C2</td>
<td>123.0(5)</td>
<td>N-C8-C9</td>
<td>111.2(6)</td>
</tr>
<tr>
<td>O-C1-C6</td>
<td>119.1(5)</td>
<td>C8-C9-C10</td>
<td>114.9(6)</td>
</tr>
<tr>
<td>C2-C1-C6</td>
<td>117.9(5)</td>
<td>C9-C10-C11</td>
<td>117.4(9)</td>
</tr>
</tbody>
</table>
3.3.5.3. X-Ray Crystal Structure of Co(tbsal)$_2$.

A suitable single crystal was chosen from a sample of Co(tbsal)$_2$ recrystallised from ethanol. The molecular structure and atom numbering scheme are presented in Figure 3.6.

Figure 3.6. Atom numbering and molecular structure of Co(tbsal)$_2$. 
Crystal Data

Molecular formula  CoC_{22}H_{28}N_{2}O_{2}
RMM  411.41
Crystal system  Orthorhombic
Space group  Pbc_{21} (29) [Pca_{21}]

\begin{align*}
a & = 10.977(2) \text{ Å} \\
b & = 20.037(7) \text{ Å} \\
c & = 9.866(3) \text{ Å} \\
V_c & = 2170.0 \text{ Å}^3 \\
Z & = 4 \\
D_x & = 1.259 \text{ gcm}^{-3} \\
F(000) & = 868 \\
\mu(\text{Mo } K\alpha) & = 8.04 \text{ cm}^{-1}
\end{align*}

A crystal of approximate dimensions 0.4 x 0.8 x 0.15 mm was examined as for Co(nbsal)$_2$ above. Intensity data were collected in the $\theta$ range $1^\circ - 24^\circ$, and the index range $0 \leq h \leq 12$, $0 \leq k \leq 23$, $0 \leq l \leq 11$. Of the 2304 reflections measured, 1819 had non-zero intensity and 1458 had $I > 3\sigma(I)$. Correction was made for the Lorentz and polarization effects and analysis of the standard reflection showed negligible decay of intensity throughout the data collection period.

Anisotropic refinement, initially Co alone, then all non-hydrogen atoms, caused $R$ to converge at 0.051, $R_w = 0.073$, $S = 1.179$. Hydrogen atom positions were recalculated during these last refinement cycles. In the final difference Fourier map, the highest peak was 0.48 eÅ$^{-3}$. 

123
Table 3.18. Bond lengths for Co(tbsal)$_2$.

<table>
<thead>
<tr>
<th>Atom1-Atom2</th>
<th>Bond length (Å)</th>
<th>Atom1-Atom2</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-O1</td>
<td>1.899(5)</td>
<td>C13-C14</td>
<td>1.393(15)</td>
</tr>
<tr>
<td>Co-O2</td>
<td>1.901(5)</td>
<td>C14-C15</td>
<td>1.349(15)</td>
</tr>
<tr>
<td>Co-N1</td>
<td>1.998(5)</td>
<td>C15-C16</td>
<td>1.405(12)</td>
</tr>
<tr>
<td>Co-N2</td>
<td>1.999(6)</td>
<td>C17-C18</td>
<td>1.48(2)</td>
</tr>
<tr>
<td>O1-C11</td>
<td>1.296(9)</td>
<td>C17-C19</td>
<td>1.36(2)</td>
</tr>
<tr>
<td>O2-C21</td>
<td>1.296(10)</td>
<td>C17-C20</td>
<td>1.49(2)</td>
</tr>
<tr>
<td>N1-C1</td>
<td>1.276(9)</td>
<td>C21-C22</td>
<td>1.407(11)</td>
</tr>
<tr>
<td>N1-C17</td>
<td>1.497(10)</td>
<td>C21-C26</td>
<td>1.427(11)</td>
</tr>
<tr>
<td>N2-C2</td>
<td>1.283(9)</td>
<td>C22-C23</td>
<td>1.37(2)</td>
</tr>
<tr>
<td>N2-C27</td>
<td>1.499(9)</td>
<td>C23-C24</td>
<td>1.37(2)</td>
</tr>
<tr>
<td>C1-C16</td>
<td>1.37(11)</td>
<td>C24-C25</td>
<td>1.337(12)</td>
</tr>
<tr>
<td>C2-C26</td>
<td>1.464(10)</td>
<td>C25-C26</td>
<td>1.394(12)</td>
</tr>
<tr>
<td>C11-C12</td>
<td>1.414(12)</td>
<td>C27-C28</td>
<td>1.499(12)</td>
</tr>
<tr>
<td>C11-C16</td>
<td>1.425(9)</td>
<td>C27-C29</td>
<td>1.522(13)</td>
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<tr>
<td>C12-C13</td>
<td>1.336(13)</td>
<td>C27-C30</td>
<td>1.491(14)</td>
</tr>
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Table 3.19. Bond angles for Co(tbsal)$_2$.

<table>
<thead>
<tr>
<th>Atom1-Atom2-Atom3</th>
<th>Bond angle ($^\circ$)</th>
<th>Atom1-Atom2-Atom3</th>
<th>Bond angle ($^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1-Co-O2</td>
<td>113.2(2)</td>
<td>N1-C17-C19</td>
<td>114.8(9)</td>
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<tr>
<td>O1-Co-N1</td>
<td>97.5(2)</td>
<td>N1-C17-C20</td>
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<tr>
<td>O1-Co-N2</td>
<td>114.0(2)</td>
<td>C18-C17-C19</td>
<td>110(1)</td>
</tr>
<tr>
<td>O2-Co-N1</td>
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<td>C18-C17-C20</td>
<td>105(1)</td>
</tr>
<tr>
<td>O2-Co-N2</td>
<td>97.4(2)</td>
<td>C19-C17-C20</td>
<td>105(1)</td>
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<tr>
<td>N1-Co-N2</td>
<td>122.4(2)</td>
<td>O2-C21-C22</td>
<td>117.9(8)</td>
</tr>
<tr>
<td>C1-N1-C17</td>
<td>118.8(6)</td>
<td>O2-C21-C26</td>
<td>125.5(7)</td>
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<tr>
<td>C2-N2-C27</td>
<td>116.7(6)</td>
<td>C22-C21-C26</td>
<td>116.6(8)</td>
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<tr>
<td>N1-C1-C16</td>
<td>129.4(6)</td>
<td>C21-C22-C23</td>
<td>121(1)</td>
</tr>
<tr>
<td>N2-C2-C26</td>
<td>128.5(7)</td>
<td>C22-C23-C24</td>
<td>121.0(9)</td>
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<tr>
<td>O1-C11-C12</td>
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<td>C23-C24-C25</td>
<td>119.7(9)</td>
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<tr>
<td>O1-C11-C16</td>
<td>124.1(7)</td>
<td>C24-C25-C26</td>
<td>122(1)</td>
</tr>
<tr>
<td>C12-C11-C16</td>
<td>116.4(7)</td>
<td>C2-C26-C21</td>
<td>122.9(7)</td>
</tr>
<tr>
<td>C11-C12-C13</td>
<td>122.7(9)</td>
<td>C2-C26-C25</td>
<td>117.6(7)</td>
</tr>
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<td>C12-C13-C14</td>
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<td>C14-C15-C16</td>
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<td>N2-C27-C29</td>
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<td>C28-C27-C29</td>
<td>109.2(8)</td>
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<tr>
<td>C11-C16-C15</td>
<td>118.7(7)</td>
<td>C28-C27-C30</td>
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<tr>
<td>N1-C17-C18</td>
<td>109.7(7)</td>
<td>C29-C27-C30</td>
<td>110.1(9)</td>
</tr>
</tbody>
</table>
Both [Co(nbsal)$_2$] and [Co(tbsal)$_2$] have tetrahedral configurations, but the bond angles at the cobalt atoms are unequal and very different from the ideal tetrahedral angle (109.5°), particularly in the tert-butyl substituted compound. This is partly due to the restriction by the chelate rings which form similar angles at cobalt [Co(nbsal)$_2$, 96.1°; Co(tbsal)$_2$, 97.1°]. However, the tert-butyl groups lead to an opening out of the N-Co-N angle from 115.7° to 122.4° and an increase of the Co-N bond distances from 1.968 to 1.998 Å. The Co-O bond distances are the same within experimental error in both compounds. The O-Co-O angles are similar in both compounds (113.8° and 113.2°), although the O-Co-N angle is smaller in [Co(tbsal)$_2$] (114.0° as opposed to 118.3°).

In [Co(nbsal)$_2$], the n-butyl chain lies away from the CoN$_2$ plane leaving regions where NO could attack the cobalt ion to form a mononitrosyl derivative. On the other hand, in [Co(tbsal)$_2$], the Me groups of the tert-butyl substituent block the CoN$_2$ angle as well as lying over the chelate rings and so prevent the attack of NO (and O$_2$). The tert-butyl methyl groups also show considerable disorder which manifests itself in very large thermal ellipsoids and a foreshortening of the bond distances, particularly that for C17-C19. There are no short contacts below the normally expected van der Waals distances in the structure of either cobalt complexes.\textsuperscript{83}
CHAPTER FOUR

MACROCYCLIC COMPLEXES
4. Macrocycles: 6,13-Diphenyl-1,8-dihydro-2,3:9,10-dibenzo-1,4,8,11-tetraazacyclotetradecane-4,6,11,13-tetraene (dptaaH$_2$) and Related Substituted Ligands.

4.1. Introduction

A macrocycle is a cyclic compound with nine or more members, including all hetero atoms, and with three or more donor (ligating) atoms.

4.1.1. Historical Background

The field of macrocycles has been studied since the beginning of the century. However, prior to 1960 very little interest was shown in the coordination chemistry of macrocyclic compounds. It was only in the early 1960's, when several independent groups (Curtis$^8$ in New Zealand, Thompson and Busch$^8$ in the U.S.A and Schrauzer$^{86}$, Umland and Thierig$^{87}$ in Germany) synthesised a variety of new coordination compounds of synthetic macrocyclic ligands, that this field of scientific research started rapid growth.

The chemistry of synthetic macrocyclic ligands can be divided into two broad groups. The first group is the cyclic polyethers of the 'crown' type, and the second is the synthetic ring systems containing donor atoms other than oxygen such as nitrogen, sulphur and/or phosphorus. The current work is concerned with the second type of macrocycle containing nitrogen donor atoms as illustrated in Figure 4.1.
Figure 4.1. The structure of 6,13-diphenyl-1,8-dihydro-2,3:9,10-dibenzo-
1,4,8,11-tetraazacyclotetradecane-4,6,11,13-tetraene (dptaaH$_2$) 
(X = H)

X = H, Me, MeO, Br, NO$_2$.

The structure of the free ligand$^{88}$ (dptaaH$_2$) is slightly saddle-shaped (Figure 4.2.), the X-ray crystal structure determination revealed the deviation of the mean plane through the four nitrogen atoms from planarity was just significant at the 3$\sigma$ level. Nitrogen atoms N(2) and N(4) are at 0.020 Å and 0.019 Å above the plane, whereas N(1) and N(3) sit 0.020 Å and 0.019 Å below the plane (Figure 3). The cavity is 3.826 Å across.

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Figure 4.2. Side view of dptaah$_2$ showing its slight saddle-shape.

Figure 4.3. Molecular structure of dptaah$_2$.  

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The structure of Co(dptaa)\textsuperscript{87} is very similar to that of the free ligand, except that the nitrogen atoms in the complex are exactly planar (Figure 4.4. and 4.5.), the cobalt is at the centre of this plane equidistant from the nitrogens with an average Co-N distance of 1.865 Å.

Figure 4.4. Molecular structure of Co(dptaa).
There has been some work published on these phenyl- and substituted-phenyl-tetraaza[14]annulenes. These publications give an account of the Cr(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) complexes of the diphenyl dibenzotetraaza[14]annulene anion (dptaa) and of the complexes of a few substituted dptaa's with certain of these metals. These publications are mostly concerned with the electrochemical properties of these complexes. However, not much work has been done on the coordination chemistry of these ligands and their metal complexes. This Chapter is mainly concerned with this aspect of the compounds.
4.2. Experimental

4.2.1. Ligand Synthesis

The syntheses of the ligands require the preparation of the appropriate acraldehydes before condensation with o-phenylenediamine. The acraldehydes are obtained by formylating the appropriate phenylacetic acids, and there are numerous methods of formylation. In the current work, the synthesis of α-phenyl-β-dimethylaminoacraldehyde was performed according to the procedure published by Arnold\textsuperscript{93}, with a few modifications in the interest of health and safety as well as ease of synthesis (see Section 4.2.1.1.), even though the yield obtained was marginally lower than that of Arnold.

A mixture of phosphorus oxychloride (functioning as a Lewis acid) and dimethylformamide forms the formylating agent $[\text{CIHCN(CH}_3\text{)}_2]^+$ as illustrated below$^{94}$:
A nucleophilic attack by the double bond of the corresponding diol of the phenylacetic acid or the appropriate *para*-substituted phenylacetic acid on the formylating agent results in an intermediate which in turn attacks a second cation. The resultant intermediate decarboxylates to give a quaternary salt which can be readily hydrolysed under mild conditions to give the desired product as illustrated by the proposed general mechanism which follows:
The acraldehyde is in turn reacted with α-phenylenediamine in 1:1 ratio to obtain the macrocycle:

4.2.1.1. dptaaH₂

Phenylacetic acid (27.22 g, 200.0 mmol) was dissolved in dimethyl formamide (73.16 g, 1000 mmol) in a 1 litre round bottomed flask. Phosphorus oxychloride (92.30 g, 600.0 mmol) was then added dropwise to the solution which became very warm and effervescence occurred after the addition of about 5 cm³ of the phosphorus oxychloride. An ice bath was used to slow down the reaction. The colourless solution slowly turned light
brown. After the addition was complete, a reflux condenser was fitted on the flask and the mixture was stirred in a warm water bath (70°C) for 5.5 hours. The mixture was allowed to cool to room temperature and decomposed slowly using 300 cm³ of crushed ice, until no more fizzing occurred. A large excess of a saturated solution of potassium carbonate (400 cm³) was then used to hydrolyse the intermediate. As this process produced a vigorous effervescence, slow addition was necessary.

Arnold used benzene to extract the acraldehyde, but in the current work toluene was used instead as it is much safer to work with than the allegedly carcinogenic benzene. Toluene (100 cm³) was added to the mixture which was refluxed for fifteen minutes to extract the product. There were three layers in the reaction mixture at this stage, but as the heating continued, the middle layer became thinner. Only the top toluene layer was collected and the two bottom layers were extracted again with smaller portions of toluene (50 cm³) until the middle layer completely disappeared. The combined toluene extract was shaken with anhydrous magnesium sulphate (5.000 g) to remove any water present and the spent magnesium sulphate was filtered off. The filtrate was further dried by stirring overnight with fresh anhydrous magnesium sulphate. The drying agent was filtered off and the toluene was taken off from the filtrate by rotary evaporator.

For ease of synthesis, instead of vacuum distillation of the product at 130-140°C / 0.35 mmHg as used by Arnold, the viscous, honey-coloured residue was redissolved in diethyl ether (300 cm³) and cooled in liquid nitrogen. Two layers formed and the lighter coloured upper layer was decanted from the much smaller dark brown bottom layer which was discarded. The lighter layer was further cooled in liquid nitrogen. An off-white precipitate dropped out on
stirring with a glass rod. This α-phenyl-β-dimethyl aminoacraldehyde was
filtered off and air-dried. Yield, 22.00 g (63%).

Analysis for C₁₁H₁₃N

Calculated: C, 75.20; H, 7.52; N, 7.92%
Found: C, 75.40; H, 7.48; N, 7.99%

The α-phenyl-β-dimethylaminoacraldehyde (20.00 g, 114.1 mmol) was
refluxed for seven hours with o-phenylenediamine (12.34 g, 114.1 mmol) in
dimethylformamide (70 cm³) and the mixture was allowed to cool slowly to
room temperature to obtain dark purple-brown crystals of dptaαH₂ which were
filtered off, washed with methanol and dried in air. Yield, 11.13 g (23%)

Analysis for C₃₀H₂₄N₄

Calculated: C, 81.19; H, 5.49; N, 12.72 %
Found: C, 81.79; H, 5.34; N, 12.73 %

4.2.1.2. MedptaαH₂

Phosphorus oxychloride (46.00 g, 300.0 mmol) was added slowly to
dimethylformamide (36.58 g, 500.0 mmol) with stirring. Some effervescence
occurred and a dark brown coloration appeared as the phosphorus
oxychloride reacted with the dimethylformamide. 4-Tolylacetic acid (15.02 g,
100.0 mmol) was added and the mixture stirred on a water bath at 70°C for
5.5 hours. After being allowed to cool to room temperature, the excess of
phosphorus oxychloride was decomposed with crushed ice (150 cm³) and
hydrolysis was carried out by adding a saturated solution of potassium
carbonate (200 cm³) to the reaction mixture.

Toluene (50 cm³) was used to extract the product by refluxing it for 15
minutes and the dark brown organic layer was collected using a separating
funnel. The aqueous layer was further extracted with two smaller portions (25 cm³) of toluene. The toluene layer was dried with two portions of 3.00 g of anhydrous magnesium sulphate with stirring. The drying agent was then removed by filtration.

The toluene was taken off using a rotary evaporator and a brown solid separated at this stage. The α-4-tolyl-β-dimethylaminoacraldehyde was filtered off, washed with diethyl ether and dried in air. Yield, 11.72 g (62%).

Analysis for C₁₂H₁₅NO
Calculated: C, 76.16; H, 7.99; N, 7.40 
Found: C, 75.90; H, 7.03; N, 7.39 

The acraldehyde (10.00 g, 52.84 mmol) was refluxed for seven hours with o-phenylenediamine (5.71 g, 52.84 mmol) in dimethylformamide (30 cm³). Slow cooling resulted in red-brown crystals of MedptaaH₂. Yield, 4.201 g (17%)

Analysis for C₃₂H₂₆N₄
Calculated: C, 82.02; H, 6.02; N, 11.96 
Found: C, 81.91; H, 5.92; N, 11.92 

4.2.1.3. MeOdpntaaH₂

Phosphorus oxychloride (92.30 g, 600.0 mmol) was added slowly to dimethylformamide (73.16 g, 100.0 mmol). During the addition, fumes and heat were given off and the colourless dimethylformamide turned dark brown. 4-Methoxyphenylacetic acid (33.24 g, 200.0 mmol) was added and when addition was complete, the reaction mixture was stirred on a warm water bath (70°C) for 5.5 hours. After being allowed to cool to room temperature, the excess of phosphorus oxychloride was decomposed using crushed ice (300
cm$^3$) and a saturated solution of potassium carbonate (400 cm$^3$) was added slowly to hydrolyse the intermediate to obtain the product.

Toluene (100 cm$^3$) was added and the mixture was refluxed for 15 minutes to extract the product. Using a separating funnel, the toluene layer was separated from the aqueous layer which was further extracted with two portions of 50 cm$^3$ toluene. The combined extract was then dried with two portions of 3.000 g of anhydrous magnesium sulphate with stirring. After removing the drying agent by filtration, the toluene was then taken off by rotary evaporator, resulting in an oily dark brown layer. Diethyl ether (200 cm$^3$) was added to the oil and shaken. The product separated as a brown-yellow solid. Yield, 17.00 g (41%).

Analysis for $C_{12}H_{15}NO_2$  
Calculated: C, 70.22; H, 7.37; N, 6.82 %  
Found: C, 69.75; H, 7.28; N, 6.56 %

The $\alpha$-methoxyphenyl-$\beta$-dimethylaminoacraldehyde (15.00 g, 73.08 mmol) was refluxed with o-phenylenediamine (7.900 g, 73.08 mmol) in dimethylformamide (70 cm$^3$) for 7 hours and after slow cooling to room temperature, the dark brown-purple crystals appeared which were filtered off and washed with methanol before being air dried. Yield, 5.693 g (16%).

Analysis for $C_{32}H_{28}N_4O_2$  
Calculated: C, 76.78; H, 5.64; N, 11.19 %  
Found: C, 76.33; H, 5.52; N, 11.13 %
4.2.1.4. BrdptaaH$_2$

The acraldehyde needed for the preparation of this macrocyclic ligand was prepared by Mr. D. Tam by the usual method. α-4-Bromophenyl-β-dimethylaminoacraldehyde (2.058 g, 8.100 mmol) was added to dimethylformamide (30 cm$^3$) in a round bottomed flask and o-phenylenediamine (0.876 g, 8.100 mmol) was mixed into the solution. The mixture was refluxed for seven hours and allowed to cool to room temperature resulting in a black-purple microcrystalline solid which was filtered off, washed with methanol and air dried. Yield, 0.882 g (18%).

Analysis for C$_{30}$H$_{22}$N$_4$Br$_2$

Calculated: C, 60.22; H, 3.71; N, 9.36 %

Found: C, 60.39; H, 3.61; N, 9.25 %

4.2.2. Complexes

Essentially, there are two ways of synthesising the metal complexes of these ligands. The first method is by template reaction and the other is by direct insertion. Both methods were used during the course of this work.

4.2.2.1. Co(dptaa)

The ligand dptaaH$_2$ (3.000 g, 6.691 mmol) was added to dimethylformamide which had been deoxygenated (40 cm$^3$) in a 150 cm$^3$ round bottomed flask. Cobalt(II) acetate tetrahydrate (1.670 g, 6.691 mmol) was added. The mixture was refluxed for three hours and then allowed to cool slowly to room temperature to produce some dark purple-brown crystals. The product is stable in air. Yield, 3.112 g (93%)
4.2.2.2. Co(Medptaa)

Dimethylformamide (40 cm³) was deoxygenated using the freeze-pump-thaw method and the ligand MedptaaH₂ (1.612 g, 3.441 mmol) and cobalt(II) acetate tetrahydrate (0.863 g, 3.441 mmol) were added into the reaction flask against a stream of nitrogen. The mixture was then heated under reflux for 3 hours under nitrogen. Slow cooling resulted in formation of deep purple crystals of Co(Medptaa) which were filtered off and washed with methanol before being air dried. The product was not air sensitive. Yield, 1.542 g (85%)

Analysis for CoC₃₀H₂₂N₄ Calculated: C, 72.43; H, 4.46; N, 11.26%  
Found: C, 71.94; H, 4.29; N, 11.11%

4.2.2.3. Co(MeOdptaa)

Dimethylformamide (30 cm³) was deoxygenated by the freeze-pump-thaw method. Cobalt(II) acetate tetrahydrate (0.252 g, 1.000 mmol) and MeOdptaaH₂ (0.501 g, 1.000 mmol) were added to the reaction flask and the flask was evacuated and filled with nitrogen. The mixture was heated under reflux for 3 hours and allowed to cool slowly to room temperature. Some dark purple crystalline solid was obtained which was filtered off, washed with methanol and air dried. The product was air stable. Yield, 0.511 g (91%)

Analysis for CoC₃₂H₂₆N₄O₂ Calculated: C, 68.94; H, 4.70; N, 10.04%  
Found: C, 69.16; H, 4.66; N, 9.87%
4.2.2.4. Co(NO₂dptaa)

Dimethylformamide (30 cm³) was deoxygenated by the freeze-pump-thaw method. NO₂dptaaH₂ (1.683 g, 2.841 mmol) and cobalt(II) acetate tetrahydrate (0.713 g, 2.841 mmol) were added to the flask which was then evacuated and filled with nitrogen before the mixture was heated under reflux for 4 hours. Some reddish-brown solid appeared after cooling. It was filtered off, washed with deoxygenated methanol and dried on the pump. There was no apparent weight change upon long exposure to air suggesting that the dried product is not sensitive to aerial oxidation. Yield, 1.702 g (90 %).

Analysis for CoC₃₀H₂₀N₆O₄

Calculated: C, 61.34; H, 3.43; N, 14.31 %
Found: C, 63.23; H, 3.23; N, 13.95 %

4.2.2.5. Co(Brdptaa)

The ligand BrdptaaH₂ (0.852 g, 1.421 mmol) was dissolved in dimethylformamide (30 cm³) and the mixture was deoxygenated in the usual manner. Cobalt(II) acetate tetrahydrate (0.363 g, 1.421 mmol) was added against a stream of nitrogen and the mixture was then refluxed for 3 hours. Upon slow cooling, some purple-black microcrystalline product formed which was filtered off, washed with methanol and air dried. Yield, 0.822 g (91 %)

Analysis for CoC₃₀H₂₀N₄Br₂

Calculated: C, 54.99; H, 3.08; N, 8.55 %
Found: C, 55.75; H, 3.02; N, 8.52 %
4.2.2.6. Fe(dptaa)

The iron(II) complex of Fe(dptaa) was prepared successfully by direct insertion and by a template synthesis.

(a) Direct Insertion

Triethylamine (5 cm³) and dptaaH₂ (1.000 g, 2.272 mmol) were deoxygenated by the freeze-pump-thaw method and freshly distilled toluene (30 cm³) under nitrogen was added. Anhydrous iron(II) acetate (0.469 g; 2.272 mmol) was added against a flow of nitrogen and the mixture was heated under reflux overnight. Upon cooling, some featherlike crystals were formed. These were filtered off and dried on the pump. The dry product was found to be air stable. Yield, 0.851 g (76%)

Analysis for FeC₃₀H₂₂N₄  Calculated: C, 72.89; H, 4.49; N, 11.33 %
    Found: C, 72.65; H, 4.39; N, 11.23 %

(b) Template Synthesis

Dimethylformamide (20 cm³) was deoxygenated by the freeze-pump-thaw method. Freshly distilled toluene (20 cm³) and o-phenylenediamine (0.800 g, 7.400 mmol) were added and the solution was flushed with nitrogen before the addition of anhydrous iron(II) acetate (0.641 g; 3.700 mmol). The reaction mixture was heated under reflux for 4 hours. No reaction seemed to have taken place as there was a white suspension (anhydrous iron(II) acetate) in a brown solution (o-phenylenediamine). α-Phenyl-β-dimethylaminoacraldehyde (1.291 g, 7.400 mmol) was added when the reaction had cooled to room temperature. The colour immediately changed to blood red and the mixture
was further heated under reflux for 3 hours. The iron(II) acetate slowly dissolved as some purple-brown crystalline product gradually separated from the red-purple solution. The solid was filtered off, washed with toluene and dried on the vacuum pump.

Analysis for FeC₃₀H₂₂N₄

Calculated: C, 72.89; H, 4.49; N, 11.33 %

Found: C, 72.34; H, 4.87; N, 10.77 %

4.2.2.7. Attempts to Prepare Cr(dptaa)

Several attempts have been made to synthesise Cr(dptaa) by the various methods outlined below.

(a) Template Synthesis

Anhydrous chromium(II) chloride (0.284 g, 2.312 mmol) was added against a stream of nitrogen to a deoxygenated dimethylformamide (50 cm³) solution of o-phenylenediamine (0.500 g, 4.623 mmol). The mixture was heated under reflux for 3 hours and then left to cool slowly to room temperature before adding α-phenyl-β-dimethylaminoacraldehyde (0.810 g, 4.623 mmol). The flask was evacuated and refilled with nitrogen and then the solution was heated under reflux for 4 hours. The colour changed to dark purple-brown (almost black) and then to a brighter purple at which point it was thought that the synthesis had failed because of the latter colour change. It was possible that the chromium(II) had been oxidised during the course of the reaction. The reaction was terminated.
(b) Preparation From Na$_2$dptaa

Sodium hydride (0.817 g, 34.04 mmol) was added to a suspension of dptaaH$_2$ (7.700 g, 17.37 mmol) in freshly distilled THF (100 cm$^3$). There was no apparent reaction, but on warming there was a slight evolution of gas (H$_2$). The mixture was then heated under reflux for 7 hours and then for a further 24 hours as a small amount of effervescence was still observed upon cooling. As the reaction proceeded, the colour of the solution changed from dark purple to orange-brown.

The dark crystals obtained were then filtered off through an extractor and the filtrate was removed and left to stand. The dark purple solid on the sintered disc was then extracted with fresh THF (70 cm$^3$). This solution was also allowed to cool to room temperature and left undisturbed to obtain further product. The solid in both flasks was filtered off separately and dried on the pump. Combined yield, 7.172 g (87%).

Analysis for Na$_2$C$_{30}$H$_{22}$N$_4$  
Calculated: C, 74.37; H, 4.58; N, 11.56%

Analysis for Na$_2$dptaa.4THF  
Calculated: C, 71.48; H, 7.04; N, 7.25%

Found: C, 71.20; H, 6.95; N, 7.31%

Anhydrous chromium(II) chloride (0.467 g, 3.801 mmol) was added to Na$_2$dptaa.4THF (2.938 g, 3.801 mmol) in THF (100 cm$^3$). The yellow-brown supernatant immediately became blood red and the reaction was stirred at room temperature overnight. The solution was filtered through an extractor and the purple residue was extracted with purified toluene (100 cm$^3$) for 24 hours. The maroon-purple microcrystalline needle product was filtered off (solid a) and the filtrate was placed in the freezer. After several weeks a crystalline product was isolated from the filtrate (solid b).
Solid a:

Analysis for CrC$_{30}$H$_{22}$N$_{4}$

Calculated: C, 73.46; H, 4.52; N, 11.42 %
Found: C, 64.15; H, 4.15; N, 10.25 %

Solid b:

Analysis for CrC$_{30}$H$_{22}$N$_{4}$

Calculated: C, 73.46; H, 4.52; N, 11.42 %
Found: C, 64.77; H, 4.22; N, 10.32 %

(c) Preparation From Li$_2$dptaa

Freshly distilled toluene (100 cm$^3$) was added to dptaaH$_2$ (0.500 g 1.135 mmol) which had been pumped on for 2 hours. The ligand did not dissolve completely in the solvent. The mixture was cooled to -60°C in an acetone/dry ice mixture and MeLi (1.62 cm$^3$, 2.270 mmol; 1.4 M diethyl ether solution) added, but no colour change to indicate reaction was observed. The cooling bath was removed and the reaction mixture stirred. After five minutes the colour slowly changed to dark red, and the lithiated ligand seemed more soluble in toluene than the starting material. After being left to stir for about 1 hour, the reaction mixture was heated under reflux for 2 hours and then cooled slowly to room temperature. After further cooling to -60°C, anhydrous chromium(II) chloride (0.139 g, 1.135 mmol) was added and the reaction was stirred for 1 hour as it slowly warmed up to room temperature. During the time, the colour of the solution changed from red to almost black and then, after the mixture heated under reflux for 4 hours, it was allowed to cool slowly to room temperature. The dark red-purple solid which appeared was filtered off on an extractor, and extracted with the mother liquor for 7 hours. At first, the extracting solvent was quite heavily coloured (orange-brown) but after about 5 hours, the colour became paler even though some red-purple
solid still remained on the sintered disc. As the extract cooled, some red-purple solid separated. This was filtered off and dried. The solid remaining on the sinter was also vacuum dried.

Solid on sinter:

Analysis for CrC$_{30}$H$_{22}$N$_4$  
Calculated: C, 73.46; H, 4.52; N, 11.42 %  
Found: C, 50.10; H, 3.41; N, 7.63 %

Solid from solution:

Analysis for CrC$_{30}$H$_{22}$N$_4$  
Calculated: C, 73.46; H, 4.52; N, 11.42 %  
Found: C, 71.99; H, 4.91; N, 10.89 %

When the preparation was repeated using THF/Cr$_2$(OAc)$_4$ instead of toluene, the microanalysis results were as follows:

Solid on extractor:

Analysis for CrC$_{30}$H$_{22}$N$_4$  
Calculated: C, 73.46; H, 4.52; N, 11.42 %  
Found: C, 57.24; H, 4.85; N, 5.94 %

Solid from solution:

Analysis for CrC$_{30}$H$_{22}$N$_4$  
Calculated: C, 73.46; H, 4.52; N, 11.42 %  
Found: C, 71.89; H, 4.93; N, 10.76 %

From the results of the microanalyses above, it can be concluded that the products on the extractors were contaminated with the lithium chloride and lithium acetate whereas the solid obtained from the extract contained less lithium salts. However, both the attempts (using toluene/CrCl$_2$ and THF/Cr(OAc)$_2$) did not produce the desired product in reasonable purity.
(d) With Triethylamine as Base

A 20:10:20 mixture of dimethylformamide:triethylamine:toluene was deoxygenated using the freeze-pump-thaw method and dptaaH\(_2\) (1.000 g, 2.270 mmol) was added. The mixture was left stirring overnight to complete deprotonation of the ligand. The triethylamine and toluene were then removed in vacuum, and more deoxygenated dimethylformamide (40 cm\(^3\)) and anhydrous chromium(II) chloride (0.279 g, 2.270 mmol) were added. The reaction mixture was heated under reflux overnight and some crystals appeared which were filtered off, washed twice with deoxygenated methanol and dried on the pump.

Analysis for Cr\(_{30}\)H\(_{22}\)N\(_4\)

Calculated: C, 73.46; H, 4.52; N, 11.42 %

Found: C, 72.93; H, 5.85; N, 10.39 %

Similar synthesis without toluene gave the microanayes results below.

Analysis for Cr\(_{30}\)H\(_{22}\)N\(_4\)

Calculated: C, 73.46; H, 4.52; N, 11.42 %

Found: C, 61.35; H, 6.71; N, 8.55 %

4.2.2.8. Attempt to prepare Mn(dptaa)

Toluene (60 cm\(^3\)) was mixed with triethylamine (0.459 g, 4.540 mmol) and deoxygenated in the usual manner. Anhydrous manganese(II) acetate (0.393 g, 2.270 mmol) and dptaaH\(_2\) (1.000 g, 2.270 mmol) were added and the flask was evacuated and refilled with nitrogen before the mixture was heated under reflux overnight. The white powder of the manganese(II) acetate had disappeared apparently through reaction with the ligand resulting in black-purple microcrystals. These were filtered off after the reaction mixture had
been allowed to cool slowly to room temperature. The solid was washed with deoxygenated methanol and dried under vacuum. Yield, 0.791 g (71%).

Analysis for CrC₃₀H₂₂N₄  
Calculated: C, 73.02; H, 4.49; N, 11.35 %  
Found: C, 77.45; H, 5.58; N, 11.73 %

4.2.3. Reactions with Nitric Oxide

The cobalt(II) complexes were reacted with NO to oxidise the metal centre to cobalt(III) and produce mononitrosyl derivatives.

4.2.3.1. Co(dptaa)NO

Dimethylformamide (15 cm³) was deoxygenated in a two-necked 100 cm³ flask and Co(dptaa) (0.501 g, 1.007 mmol) added to the solvent. It was not very soluble in dimethylformamide. The system was evacuated and filled with nitrogen several times, finally evacuated and then NO gas was admitted, at which point the solution turned darker reddish brown. Stirring was started after noting the mercury level on the gas burette. The level started to rise after about 5 minutes and the NO uptake was complete after 30 minutes (24.00 cm³, 756 mmHg, 24°C, 1.100 mmol). Approximately 1 mole of NO was taken up per mole of cobalt(II). The product was considerably more soluble in dimethylformamide than the starting material, but some microcrystalline product was observed in the mixture. The NO was then pumped out and replaced by nitrogen. The mixture was left overnight in the freezer and methanol (15 cm³) was added quickly to precipitate more product before the solid was filtered off in air, washed with methanol and air dried. Yield, 0.322 g (61%). A peak at 1625 cm⁻¹ was assigned to the stretching frequency of coordinated NO.
Analysis for $\text{CoC}_3\text{H}_2\text{N}_5\text{O}$  
Calculated: C, 61.34; H, 3.43; N, 14.31 %  
Found: C, 63.23; H, 3.23; N, 13.95 %

### 4.2.3.2. Co(Medptaa)NO

Dimethylformamide (15 cm$^3$) was deoxygenated and Co(Medptaa) (0.366 g, 0.696 mmol) was added against a stream of nitrogen. The system was evacuated before NO was admitted. The mixture was stirred and after about 30 minutes, the NO uptake was complete (13.5 cm$^3$, 760 mmHg, 23°C, 0.655 mmol, approximately 1:1 molar ratio of NO to cobalt(II)). The NO gas was pumped out and the system was put under nitrogen. Some dark red-brown microcrystalline product could be seen and the mixture was allowed to stand in a freezer overnight. To obtain more product, methanol (15 cm$^3$) was added before filtration. The product was washed with methanol and air dried. Yield, 0.291 g (75%). The NO stretching frequency was assigned to the peak at 1612 cm$^{-1}$.

Analysis for $\text{CoC}_3\text{H}_2\text{N}_5\text{O}$  
Calculated: C, 69.12; H, 4.32; N, 12.61 %  
Found: C, 68.57; H, 4.77; N, 12.55 %

### 4.2.3.3. Co(MeOdptaa)NO

Dimethylformamide (15 cm$^3$) was deoxygenated and Co(MeOdptaa) (0.416 g, 0.746 mmol) was added to the flask. The nitrogen was removed before NO was admitted. After 5 minutes stirring, the NO gas started to be taken up and the reaction was complete (17.0 cm$^3$, 760 mmHg, 23°C, 0.825 mmol) after about 30 minutes (1:1 molar ratio NO:cobalt(II)). The colour changed from dark purple-brown (solid not very soluble) to dark red-brown (more soluble).
Some microcrystals were found in the reaction mixture and as with the previous two reactions, methanol (15 cm\(^3\)) was added to separate more product before quick filtration and washing with methanol. The product was dried in air. Yield, 0.322 g (73%). The peak at 1624 cm\(^{-1}\) was assigned to the stretching frequency of NO.

Analysis for CoC\(_{32}\)H\(_{26}\)N\(_{5}\)O\(_{3}\).\(\frac{1}{4}\)DMF

Calculated: C, 64.93; H, 4.62; N, 12.14 %

Found: C, 63.35; H, 4.86; N, 12.44 %

4.2.3.4. Co(Brdpta)NO

The complex Co(Brdpta) (0.490 g, 0.748 mmol) was added to deoxygenated dimethylformamide (10 cm\(^3\)) and the flask was evacuated and filled with NO. Stirring was carried out for 1 hour, and after the uptake was complete (8.5 cm\(^3\), 751 mmHg, 19\(^\circ\)C, 0.493 mmol), the NO was pumped out, the flask was filled with nitrogen, and the solid was quickly filtered off in air and washed with methanol before being air dried. The molar ratio of cobalt to nitric oxide was 1:0.66. Despite this low ratio, there was a peak at 1607 cm\(^{-1}\) assignable to the stretching frequency of NO. From the microanalysis results below, it could be concluded that nitrosylation had taken place.

Analysis for CoC\(_{30}\)H\(_{20}\)N\(_{5}\)Br\(_{2}\)O

Calculated: C, 52.58; H, 2.94; N, 10.22 %

Found: C, 54.43; H, 2.99; N, 9.54 %
4.2.3.5. Attempt to prepare Co(NO$_2$dptaa)NO

Dimethylformamide (20 cm$^3$) was deoxygenated by the freeze-pump-thaw method and Co(NO$_2$dptaa) (0.422 g; 0.713 mmol) was added. The system was twice evacuated and refilled with nitrogen, and then NO was allowed in. There was no NO uptake during stirring for 3 hours.

4.2.4. Reactions with $^{15}$NO

The preparations of the nitrosyl complexes above were repeated on a small scale with labelled $^{15}$NO so that $^{15}$N NMR spectroscopy could be applied to determine the geometry of the cobalt-nitrosyl groups in these complexes.

4.2.4.1. Co(dptaa)$^{15}$NO

The cobalt(II) complex, Co(dptaa) (0.921 g, 1.852 mmol) was added to dimethylformamide (10 cm$^3$) in a two-necked 50 ml flask and the mixture was deoxygenated by the freeze-pump-thaw method. Nitrogen-15 oxide was admitted (37.0 cm$^3$, 733 mmHg, 22°C, 1.852 mmol) after evacuating the flask, and the reaction mixture was stirred for one hour to ensure that all the $^{15}$NO had reacted with the cobalt(II) complex. Nitrogen was then admitted into the flask to bring the pressure to atmospheric and the stirring was continued for another two hours to ensure complete nitrosylation. The colour of the complex turned darker as the reaction progressed and the product was slightly more soluble in dimethylformamide than the starting material. The flask was left in a freezer overnight to obtain more solid before filtration; washing with methanol and drying were carried out in air. Yield, 0.891 g (97%). The stretching frequency of coordinated $^{15}$NO appeared at 1607 cm$^{-1}$.
4.2.4.2. Co(Medptaa)\textsuperscript{15}NO

The complex Co(Medptaa) (0.181 g, 0.342 mmol) was added to dimethylformamide (7 cm\textsuperscript{3}) in a two necked 50 ml flask. The mixture was deoxygenated as usual. The system was evacuated before\textsuperscript{15}NO (8.00 cm\textsuperscript{3}, 0.380 mmol, 744 mmHg, 23°C) was admitted into the flask (slightly in molar excess of the cobalt(II) complex). The reaction mixture was stirred vigorously for one hour to ensure that the labelled nitric oxide had reacted with the Co(Medptaa) before the pressure was brought to atmospheric by admitting nitrogen. Upon nitrosylation, the colour of the complex turned redder and it became slightly more soluble in the solvent. The stirring was continued for another two hours and then the flask was placed in a freezer overnight to obtain more solid. The dark purple-black solid was filtered off in air, washed with methanol, and air dried. Yield, 0.171 g (92%). A shoulder at approximately 1578 cm\textsuperscript{-1} was assigned to the stretching frequency of \textsuperscript{15}NO.

4.2.4.3. Co(MeOdptaa)\textsuperscript{15}NO

The complex Co(MeOdptaa) (0.292 g, 0.521 mmol) was added to dimethylformamide (7.0 cm\textsuperscript{3}) and the mixture was de-aerated in the usual manner. After evacuation, \textsuperscript{15}NO was admitted (0.52 mmol, 10.0 cm\textsuperscript{3}, 756 mmHg, 21.5°C) and the reaction mixture was stirred for one hour before admitting nitrogen into the flask. The product was slightly darker in colour than the starting material. Stirring was continued for another two hours before the mixture was place in the freezer to obtain more solid which was then filtered off in air and washed with methanol. Yield, 0.262 g (91%). The \textsuperscript{15}NO stretching frequency appeared at 1606 cm\textsuperscript{-1}. 

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4.2.4.4. Co(Brdptaa)\textsuperscript{15}NO

The cobalt(II) complex, Co(Brdptaa) (0.245 g, 0.374 mmol) was added to dimethylformamide (7 cm\textsuperscript{3}) in a two-necked 50 ml flask and the mixture was deoxygenated by the freeze-pump-thaw method. Nitrogen-15 oxide was admitted (8 cm\textsuperscript{3}, 733 mmHg, 22\textdegree{}C, 0.391 mmol) after evacuating the flask, and the reaction mixture was stirred for one hour to ensure that all the\textsuperscript{15}NO had reacted with the cobalt(II) complex. Nitrogen was then admitted into the flask to bring the pressure to atmospheric and the stirring was continued for another two hours to ensure complete nitrosylation. The colour of the complex turned darker as the reaction progressed and the product was slightly more soluble in dimethylformamide than the starting material. The flask was left in a freezer overnight to obtain more solid before filtration, washing with methanol and drying were carried out in air. Yield, 0.230 g (94%). No \textsuperscript{15}NO peak was observed in the infrared spectrum possibly due to overlap with ligand absorption bands in the expected region of 1580 cm\textsuperscript{-1}.

4.2.5. Halogenation Reactions

In attempts to prepare the cobalt(III) complexes Co(dptaa)\textsubscript{X}, where \textsubscript{X} = Cl, Br and I, the reactions of Co(dptaa) with CH\textsubscript{3}Cl\textsubscript{3}, Br\textsubscript{2} and I\textsubscript{2} were studied as below.

4.2.5.1. Co(dptaa)I

The complex Co(dptaa) (0.500 g, 1.005 mmol) was added to a solution of iodine (0.128 g, 1.005 mmol) in chloroform (20 cm\textsuperscript{3}) and stirred overnight. A dark blue-black, microcrystalline solid was obtained from a dark green
solution. The solid was filtered off and recrystallised from chloroform. Yield, 0.489 g (81%).

Analysis for CoC$_{30}$H$_{22}$IN$_{4}$

Calculated: C, 57.71; H, 3.55; N, 8.97 %
Found: C, 56.27; H, 3.33; N, 8.56 %

4.2.5.2. Co(dptaa)Br

The complex Co(dptaa) (0.546 g, 1.098 mmol) was mixed with hexane (20 cm$^3$) in a stoppered round bottomed flask. Bromine (0.088 g, 0.059 cm$^3$, 1.098 mmol) was injected into the mixture. The bromine dissolved in the hexane to give an orange-brown solution which became paler as the bromine was taken up by the complex upon stirring. The solid was filtered off, washed with hexane and dried in air. Yield, 0.493 g (79%).

Analysis for CoC$_{30}$H$_{22}$N$_{4}$Br

Calculated: C, 54.99; H, 3.08; N, 8.55 %
Found: C, 55.75; H, 3.02; N, 8.52 %

4.2.5.3. Co(dptaa)Cl

The complex Co(dptaa) (0.500 g, 1.005 mmol) was heated under reflux in chloroform (40 cm$^3$) for 48 hours and left to cool slowly. The colour of the solution was dark green and the product obtained was a mixture of dark green needles and microcrystals. However, the crystals were found to be unsuitable for X-ray crystallography. Yield, 0.449 g (72%).

Analysis for CoC$_{30}$H$_{22}$N$_{4}$Cl

Calculated: C, 67.61; H, 4.16; N, 10.51 %
Found: C, 67.72; H, 4.08; N, 10.45 %
4.3. Results and discussion

4.3.1. Infrared spectroscopy

The infrared spectra (KBr discs) of the ligands, cobalt(II) complexes, mononitrosyls and $^{15}$N-labelled mononitrosyls are shown in the tables below.

Table 4.1. Infrared peaks of dptaaH$_2$, Co(dptaa), Co(dptaa)NO and Co(dptaa)$^{15}$NO.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>dptaaH$_2$</th>
<th>Co(dptaa)</th>
<th>Co(dptaa)NO</th>
<th>Co(dptaa)$^{15}$NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-H$_{str}$</td>
<td>3128 w,br</td>
<td>3058 m</td>
<td>3055 m</td>
<td>3055 m</td>
</tr>
<tr>
<td>C-H$_{str}$</td>
<td>3057 m</td>
<td>3030 m</td>
<td>3035 m</td>
<td>3033 m</td>
</tr>
<tr>
<td>C-H$_{str}$</td>
<td>1678 w</td>
<td>1677 w</td>
<td>1673 w</td>
<td></td>
</tr>
<tr>
<td>(arom) C=C$_{str}$</td>
<td>1632 s</td>
<td>1633 s</td>
<td></td>
<td>1632 s</td>
</tr>
<tr>
<td>N-O$_{str}$</td>
<td>1625 s</td>
<td></td>
<td></td>
<td>1607 s,sh</td>
</tr>
<tr>
<td>(arom) C=C$_{str}$</td>
<td>1590 s</td>
<td>1593 s</td>
<td>1596 s</td>
<td>1593 s</td>
</tr>
<tr>
<td>N-H$_{bend}$</td>
<td>1505 s</td>
<td>1552 s</td>
<td>1552 s</td>
<td>1552 s</td>
</tr>
<tr>
<td>(arom) C=C$_{str}$</td>
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<td>1470 s</td>
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<td></td>
<td></td>
<td>1268 m</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>1160 m</td>
<td>1162 w</td>
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<tr>
<td></td>
<td>1115 w</td>
<td>1115 w</td>
<td>1115 w</td>
<td>1115 w</td>
</tr>
<tr>
<td></td>
<td>1104 w</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>C-H$_{def}$ i.p.</td>
<td>1078 w</td>
<td>1078 m</td>
<td>1079 w</td>
<td>1079 w</td>
</tr>
<tr>
<td>substituted</td>
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<tr>
<td>benzene</td>
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<tr>
<td>rings</td>
<td>1023 m</td>
<td>1024 w</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As expected for compounds containing aromatic rings, absorption bands are observed at characteristic regions associated with the aromatic residues. There are two peaks (3057 and 3031 cm\(^{-1}\)) due to the C-H\(_{\text{str}}\) vibrations, four peaks (1632, 1590, 1494 and 1456 cm\(^{-1}\)) in the C=C stretching region, a series of weak bands from 900 to 1160 cm\(^{-1}\) due to C-H\(_{\text{def}}\) in-plane vibrations and two strong C-H\(_{\text{def}}\) out-of-plane peaks at 761 and 699 cm\(^{-1}\) due to the substituted aromatic rings, the former peak being assigned to both the mono- and di-substituted (ortho-) rings, and the latter being the second peak for the monosubstituted rings.
The peaks at 3128 cm\(^{-1}\) and 1505 cm\(^{-1}\) in the ligand spectrum which do not appear in any of the spectra of the metal complexes are assigned to the N-H\(_{\text{str}}\) and N-H\(_{\text{bend}}\) vibrations. C-N\(_{\text{str}}\) vibrations are assigned to bands in the region 1353 to 1336 cm\(^{-1}\). The C-N\(_{\text{str}}\) vibration absorbs at 1353 cm\(^{-1}\) in the ligand, at a lower wavenumber of 1341 cm\(^{-1}\) in Co(dptaa) and lower still at 1334 cm\(^{-1}\) in the \(^{14}\)N mononitrosyl cobalt(III) complexes. This lowering is in accordance with the increased mass of the residues (H < Co < CoNO) attached to the nitrogen atom. The peaks at 1408 - 1372 cm\(^{-1}\) are assigned to the C=N\(_{\text{str}}\) vibration, even though this region is a bit low for such vibrations. There is a lowering of about 40 cm\(^{-1}\) in this band upon complexation with Co, however, it is not significantly affected by the presence of the nitrosyl groups.

The peaks due to Co-N\(_{\text{str}}\) and Co-N\(_{\text{bend}}\) are assigned at 679-681 and 414-416 cm\(^{-1}\) respectively, in agreement with values in the literature\(^{95}\). For the complex Co(dptaa)NO, the N-O\(_{\text{str}}\) absorption band appears at 1625 cm\(^{-1}\), and this peak occurs at a slightly lower wavenumber of 1607 cm\(^{-1}\) in the Co(dptaa)\(^{15}\)NO spectrum. The lower value is due to the higher mass of \(^{15}\)N compared with \(^{14}\)N.
Table 4.2. Infrared peaks for MedptaαH₂, Co(Medptaα), Co(Medptaα)NO and Co(Medptaα)¹⁵NO.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>MedptaαH₂</th>
<th>Co(Medptaα)</th>
<th>Co(Medptaα)NO</th>
<th>Co(Medptaα)¹⁵NO</th>
</tr>
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<tr>
<td>N-H_{str}</td>
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<tr>
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<td>1592 s</td>
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<tr>
<td>C-H_{def i.p.}</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>substituted</td>
<td>1029 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>982 m</td>
<td>984 m</td>
<td>983 m</td>
<td></td>
</tr>
<tr>
<td>ring</td>
<td>958 w</td>
<td>961 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>939 w</td>
<td>935 w</td>
<td>936 w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>915 m</td>
<td>907 m</td>
<td>916 m</td>
<td>915 w</td>
</tr>
<tr>
<td>C-H_{def o.o.p.}</td>
<td>814 s</td>
<td>816 s</td>
<td>812 s</td>
<td>817 s</td>
</tr>
<tr>
<td></td>
<td>781 m</td>
<td>785w</td>
<td>786 w</td>
<td></td>
</tr>
<tr>
<td>C-H_{def o.o.p.}</td>
<td>737 s,sh</td>
<td>736 s</td>
<td>738 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>727 s</td>
<td>729 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-N_{str (lig.)}</td>
<td>662 m</td>
<td>651 m</td>
<td>653 m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>605 w</td>
<td>618 w</td>
<td>619 w</td>
<td>619 w</td>
</tr>
<tr>
<td></td>
<td>578 s</td>
<td>577 s</td>
<td>578 m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>569 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>538 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>518 s</td>
<td>519 m</td>
<td>518 m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>501 m</td>
<td>500 s</td>
<td>495 m</td>
<td>498 m</td>
</tr>
<tr>
<td></td>
<td>483 w</td>
<td>481 w</td>
<td>479 w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>455 w</td>
<td>454 m</td>
<td>451 w</td>
<td>448 w</td>
</tr>
<tr>
<td></td>
<td></td>
<td>439 w</td>
<td>438 w</td>
<td></td>
</tr>
<tr>
<td>Co-N_{bend (lig.)}</td>
<td>416 m</td>
<td>420 w</td>
<td>414 w</td>
<td></td>
</tr>
</tbody>
</table>
For the aromatic residues of the compounds, the peaks at around 3025 cm\(^{-1}\) are the C-H stretching frequencies and there are four absorptions (1632, 1592, 1550 and 1455 cm\(^{-1}\)) due to the in-plane C=C\(_{\text{str}}\) vibrations. A very characteristic band of the para-disubstituted aromatic rings due to the C-H out-of-plane deformation vibrations is shown around 812-817 cm\(^{-1}\) as well as the peak for the ortho-disubstituted rings at 737 cm\(^{-1}\).

There are two peaks (2914 and 2859 cm\(^{-1}\)) at lower wavenumber than the aromatic C-H\(_{\text{str}}\) which indicate the presence of methyl groups. However, the C-H\(_{\text{def}}\) absorption peaks for this methyl residue which should appear around 1460 cm\(^{-1}\) and 1380 cm\(^{-1}\) are being shielded by the strong bands of the aromatic rings which appear around the same region.

The N-H bending vibration at 1504 cm\(^{-1}\) and the N-H stretching frequency at 3468 cm\(^{-1}\) do not occur in the spectra of the cobalt complexes. C-N\(_{\text{str}}\) vibrations, assigned to peaks appearing in the region of 1328-1352 cm\(^{-1}\), show the same trend as found for the dptaa complexes discussed previously. The C=N\(_{\text{str}}\) absorption frequencies are observed around 1407-1371 cm\(^{-1}\) as before.

From comparison of the spectra, the nitrosyl stretching absorption band occurs at 1612 cm\(^{-1}\), but the \(^{15}\)N-O\(_{\text{str}}\) band, which should occur at a slightly lower wavenumber, is not obvious in this case as it appears to be obscured by the C=C\(_{\text{str}}\) bands of the aromatic rings. However, there is a shoulder at approximately 1578 cm\(^{-1}\) which could be due to the stretching vibration of the \(^{15}\)N-O group. The Co-N\(_{\text{str}}\) and the Co-N\(_{\text{bend}}\) (ligand) peaks are assigned to those at 651-663 and 414-416 cm\(^{-1}\) respectively.
Table 4.3. Infrared peaks of MeOdptaaH₂, Co(MeOdptaa)
Co(MeOdptaa)NO and Co(MeOdptaa)₁⁵NO.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>MeOdptaaH₂</th>
<th>Co(MeOdptaa)</th>
<th>Co(MeOdptaa)NO</th>
<th>Co(MeOdptaa)₁⁵NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-Hstr</td>
<td>3479 w</td>
<td>3034 w</td>
<td>3030 w</td>
<td>3033 w</td>
</tr>
<tr>
<td>C-Hstr</td>
<td>3033 w</td>
<td>3059 w</td>
<td>3064 w</td>
<td>3064 w</td>
</tr>
<tr>
<td>(OCH₃) C-Hstr</td>
<td>2830 m</td>
<td>2830 m</td>
<td>2832 m</td>
<td>2831 m</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1677 s</td>
<td>1677 s</td>
</tr>
<tr>
<td>(arom) C=Cstr</td>
<td>1632 s</td>
<td>1633 w</td>
<td>1624s</td>
<td>1606s</td>
</tr>
<tr>
<td>N-Ostr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>¹⁵N-Ostr</td>
<td>1593 s</td>
<td>1592 s</td>
<td>1598 s</td>
<td>1589 s</td>
</tr>
<tr>
<td>(arom) C=Cstr</td>
<td>1510 s</td>
<td>1510 s</td>
<td>1510 s</td>
<td>1510 s</td>
</tr>
<tr>
<td>N-Hbend</td>
<td>1505 s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(arom) C=Cstr</td>
<td>1463 s</td>
<td>1462 s</td>
<td>1451 s</td>
<td>1451 s</td>
</tr>
<tr>
<td></td>
<td>1441 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1426 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=Nstr</td>
<td>1407 s</td>
<td>1369 s</td>
<td>1374 s</td>
<td>1373 s</td>
</tr>
<tr>
<td>C-Nstr</td>
<td>1352 s</td>
<td>1338 s</td>
<td>1328 s</td>
<td>1328 s</td>
</tr>
<tr>
<td></td>
<td>1304 s</td>
<td>1306 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-Ostr</td>
<td>1280 s</td>
<td>1283 s</td>
<td>1281 s</td>
<td>1281 s</td>
</tr>
<tr>
<td></td>
<td>1245 s</td>
<td>1246 s</td>
<td>1245 s</td>
<td>1244 s</td>
</tr>
<tr>
<td></td>
<td>1224 s</td>
<td>1225 s</td>
<td>1225 s</td>
<td></td>
</tr>
<tr>
<td>C-Hdef i.p.</td>
<td>1182 s</td>
<td>1179 s</td>
<td>1180 s</td>
<td>1180 s</td>
</tr>
<tr>
<td>substituted</td>
<td>1159 s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>1113 m</td>
<td>1114 m</td>
<td>1110 w</td>
<td>1110 w</td>
</tr>
<tr>
<td>ring</td>
<td>1104 m</td>
<td>1096 w</td>
<td>1096 w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>983 m</td>
<td>983 m</td>
<td>983 m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>960 m</td>
<td>962 w</td>
<td>964 w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>921 m</td>
<td>918 w</td>
<td>919 w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>908 s</td>
<td>903 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>894 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>832 s</td>
<td>831 s</td>
<td>835 s</td>
<td>836 s</td>
</tr>
<tr>
<td></td>
<td>810 m</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
For the aromatic rings, there are weak peaks at 3033 and 3058 cm\(^{-1}\) due to the C-H\(_{\text{str}}\) vibrations. The C=C\(_{\text{str}}\) in plane absorption frequencies are at 1632, 1593, 1510 and 1463 cm\(^{-1}\). The substituted aromatic rings give rise to the characteristic strong peaks at 832 and 741 cm\(^{-1}\), the former due to the \(\text{para}\)- and the latter to the \(\text{ortho}\)-di-substituted rings.

The presence of the methoxy residue is confirmed by the C-H stretching vibration which occurs at 2830 cm\(^{-1}\), and this group also gives two C-O stretching bands at 1280 and 1245 cm\(^{-1}\) which do not appear in the spectra of the other groups of dptaa complexes under study here.

The N-H\(_{\text{str}}\) and N-H\(_{\text{bend}}\) vibrations give rise to the peaks at 3479 and 1505 cm\(^{-1}\) respectively. The C-N\(_{\text{str}}\) vibrations absorb around 1328-1352 cm\(^{-1}\) whereas the C=N\(_{\text{str}}\) stretching frequencies occur around 1373-1407 cm\(^{-1}\). The patterns of these bands are similar to those for the dptaa and Medptaa
complexes i.e. the vibration absorbs at a lower wavenumber upon complexation with cobalt.

In the spectrum of Co(MeOdpta)NO, there is a peak at 1624 cm$^{-1}$ which does not appear in the spectra of the ligand and cobalt(II) complex and it is assigned to the N-O$_{str}$. This absorption band is lowered by about 20 cm$^{-1}$ in the spectrum of Co(MeOdpta)$_{15}$NO as expected for the heavier$^{15}$N-labelled nitrosyl group. The Co-N$_{str}$ and Co-N$_{bend}$ vibrations are assigned at 660-663 cm$^{-1}$ and 414-415 cm$^{-1}$, similar to those in the groups of dptaa and Medpta compounds.
Table 4.4. Infrared peaks of BrdptaaH$_2$, Co(Brdptaa), Co(Brdptaa)NO and Co(Brdptaa)$^{15}$NO.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>BrdptaaH$_2$</th>
<th>Co(Brdptaa)</th>
<th>Co(Brdptaa)NO</th>
<th>Co(Brdptaa)$^{15}$NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-H$_{str}$</td>
<td>3152 w</td>
<td></td>
<td>3060 w</td>
<td>3059 w</td>
</tr>
<tr>
<td>C-H$_{str}$</td>
<td>3060 w</td>
<td>3060 w</td>
<td>3026 w</td>
<td>3029 w</td>
</tr>
<tr>
<td>C-H$_{str}$</td>
<td>3030 w</td>
<td>3029 w</td>
<td>3059 w</td>
<td>3029 w</td>
</tr>
<tr>
<td>(arom) C=C$_{str}$</td>
<td>1635 s</td>
<td>1633 s</td>
<td>1632 s</td>
<td>1632 s</td>
</tr>
<tr>
<td>N-O$_{str}$</td>
<td>1607 s</td>
<td></td>
<td>1607 s</td>
<td></td>
</tr>
<tr>
<td>(arom) C=C$_{str}$</td>
<td>1593 s</td>
<td>1592 s</td>
<td>1594 s</td>
<td>1594 s</td>
</tr>
<tr>
<td></td>
<td>1585 s</td>
<td>1575 s</td>
<td>1577 s</td>
<td>1573 s</td>
</tr>
<tr>
<td></td>
<td>1554 s</td>
<td>1555 s</td>
<td>1553 s</td>
<td></td>
</tr>
<tr>
<td>N-H$_{bend}$</td>
<td>1507 m</td>
<td></td>
<td>1507 m</td>
<td></td>
</tr>
<tr>
<td>(arom) C=C$_{str}$</td>
<td>1490 s</td>
<td>1473 s</td>
<td>1489 s</td>
<td>1488 s</td>
</tr>
<tr>
<td>(arom) C=C$_{str}$</td>
<td>1457 m</td>
<td>1421 w</td>
<td>1422 m</td>
<td>1446 s</td>
</tr>
<tr>
<td>C=N$_{str}$</td>
<td>1406 s</td>
<td>1406 s</td>
<td>1406 m</td>
<td>1406 m</td>
</tr>
<tr>
<td></td>
<td>1376 s</td>
<td>1372 s</td>
<td>1376 s</td>
<td>1374 s</td>
</tr>
<tr>
<td>C-N$_{str}$</td>
<td>1350 s</td>
<td>1338 s</td>
<td>1335 s</td>
<td>1335 s</td>
</tr>
<tr>
<td></td>
<td>1256 s</td>
<td>1259 s</td>
<td>1258 m</td>
<td>1262 s</td>
</tr>
<tr>
<td></td>
<td>1227 s</td>
<td>1226 s</td>
<td>1226 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1211 s</td>
<td>1211 m</td>
<td>1212 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1195 m</td>
<td>1187 w</td>
<td>1187 w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1158 m</td>
<td>1159 m</td>
<td>1160 w</td>
<td>1159 m</td>
</tr>
<tr>
<td></td>
<td>1103 m</td>
<td>1111 m</td>
<td>1115 m</td>
<td>1111 m</td>
</tr>
<tr>
<td></td>
<td>1073 s</td>
<td>1076 s</td>
<td>1076 s</td>
<td>1075 s</td>
</tr>
<tr>
<td></td>
<td>1054 w</td>
<td>1050 m</td>
<td>1050 m</td>
<td>1050 m</td>
</tr>
<tr>
<td>C-H$_{def}$ i.p.</td>
<td>1027 s</td>
<td>1027 w</td>
<td>1028 w</td>
<td>1027 w</td>
</tr>
<tr>
<td>substituted</td>
<td>1006 s</td>
<td>1007 s</td>
<td>1007 m</td>
<td>1007 s</td>
</tr>
<tr>
<td>benzene</td>
<td>982 s</td>
<td>982 m</td>
<td>982 s</td>
<td></td>
</tr>
<tr>
<td>ring</td>
<td>959 s</td>
<td>959 w</td>
<td>959 w</td>
<td>959 w</td>
</tr>
<tr>
<td></td>
<td>939 w</td>
<td>940 w</td>
<td>939 w</td>
<td>939 w</td>
</tr>
<tr>
<td></td>
<td>923 s</td>
<td>920 m</td>
<td>920 m</td>
<td>920 m</td>
</tr>
<tr>
<td></td>
<td>911 s</td>
<td>902 w</td>
<td>909 w</td>
<td>909 w</td>
</tr>
</tbody>
</table>
Absorption bands are observed at characteristic regions of aromatic residues which are two peaks (3060 and 3030 cm\(^{-1}\)) due to the C-H\(_{str}\) vibrations, four peaks (1633, 1593, 1490 and 1457 cm\(^{-1}\)) in the C=C stretching region and a series of weak bands from 900 to 1160 cm\(^{-1}\) due to C-H\(_{def}\) in-plane vibrations. The para-disubstituted aromatic rings give rise to the strong peaks at 819 cm\(^{-1}\) due to the C-H out-of-plane deformation vibrations and the ortho-substituted rings are characterised by the strong peaks at 734 cm\(^{-1}\).

The peaks at 3152 and 1507 in the ligand spectrum which do not appear in any of the spectra of the metal complexes are assigned to the N-H\(_{str}\) and N-H\(_{bend}\) vibrations respectively. C-N\(_{str}\) vibrations, assigned to peaks appearing in the region of 1350 - 1335 cm\(^{-1}\), show the same trend as other dptaa complexes discussed previously. The C=N\(_{str}\) absorption frequencies are observed around 1406 cm\(^{-1}\) as before.
The nitrosyl stretching frequency occurs at 1607 cm\(^{-1}\), whereas the \(^{15}\text{N-O}_\text{str}\) band could not be assigned in this case as the region where it is expected to appear (1590 - 1580 cm\(^{-1}\)) is heavily obscured by C=C peaks of the ligand. The Co-N\(_\text{str}\) and the Co-N\(_\text{bend}\) (ligand) peaks are assigned to those at 652 - 650 and 418 - 403 cm\(^{-1}\) respectively.

Table 4.5. The \(^{14}\text{NO}\) and \(^{15}\text{NO}\) stretching frequencies of the mononitrosyls.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(v^{(14}\text{NO})) cm(^{-1})</th>
<th>(v^{(15}\text{NO})) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(dptaa)</td>
<td>1625</td>
<td>1607</td>
</tr>
<tr>
<td>Co(Medptaa)</td>
<td>1612</td>
<td>1578 (sh)</td>
</tr>
<tr>
<td>Co(MeOdptaa)</td>
<td>1624</td>
<td>1606</td>
</tr>
<tr>
<td>Co(Brdptaa)</td>
<td>1607</td>
<td>n.o.</td>
</tr>
</tbody>
</table>

n.o. = not observed, sh = shoulder.

The NO stretching frequencies of the mononitrosyls studied here fall in the range 1500-1900 cm\(^{-1}\) earlier assigned\(^{96}\) to coordinated NO groups. This indicates that the complexes contain cobalt(III) and NO\(^-\) species (bent M-N-O), rather than cobalt(I) and NO\(^+\) (linear M-N-O). The latter would be expected to show NO stretching frequencies in the range 1700-1900 cm\(^{-1}\) which is not the case (see also Section 1.3.2.5.1).

However, it has subsequently been shown that there is a sizeable overlap\(^{97}\) between the NO stretching frequencies of nitrosyls considered to contain NO\(^-\)
(bent M-N-O groups) and of nitrosyls containing NO$^+$ (linear M-N-O groups). Therefore, the infrared correlation alone is not an accurate enough diagnostic tool to determine the coordination mode of the nitrosyl group$^{98}$. This is why $^{15}$N NMR spectroscopy has been applied to Co-N-O complexes as the two species would appear in two very distinct regions of chemical shift (see Section 1.3.2.5.2).
4.3.2. Proton Nuclear Magnetic Resonance Spectroscopy

The \(^1\text{H}\) NMR spectra of the ligands and the cobalt mononitrosyls were obtained for characterization purposes.

Table 4.6. Proton NMR peaks and assignments of dptaaH\(_2\), Co(dptaa)NO, MedptaaH\(_2\), Co(Medptaa)NO, MeOdptaaH\(_2\) and Co(MeOdptaa)NO.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>(\delta_H) (ppm)</th>
<th>No. of H</th>
<th>Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>dptaaH(_2)</td>
<td>CDCl(_3)</td>
<td>14.25 (br)</td>
<td>2</td>
<td>NH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.07, 8.05</td>
<td>4</td>
<td>CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.40, 7.39</td>
<td>10</td>
<td>C(_6)H(_5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.16, 6.99</td>
<td>8</td>
<td>C(_6)H(_4)</td>
</tr>
<tr>
<td>Co(dptaa)NO</td>
<td>DMSO</td>
<td>8.13 (br)</td>
<td>4</td>
<td>CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.68, 7.66 (d)</td>
<td>18</td>
<td>C(_6)H(_5) and C(_6)H(_4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.54, 7.52 (d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.40, 7.38, 7.36 (t)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.24, 7.20, 7.19 (t)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MedptaaH(_2)</td>
<td>CDCl(_3)</td>
<td>14.21 (br)</td>
<td>2</td>
<td>NH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.03, 8.01</td>
<td>4</td>
<td>CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.28, 7.26 (d)</td>
<td>4</td>
<td>(p)-subs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.21, 7.17 (d)</td>
<td>4</td>
<td>C(_6)H(_4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.13 (q)</td>
<td>4</td>
<td>(o)-subs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.95 (q)</td>
<td>4</td>
<td>C(_6)H(_4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.38</td>
<td>6</td>
<td>CH(_3)</td>
</tr>
<tr>
<td>Co(Medptaa)NO</td>
<td>CDCl(_3)</td>
<td>8.00</td>
<td>4</td>
<td>CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.62 (d)</td>
<td>4</td>
<td>(\alpha)- and (p)-subs.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.19 (s)</td>
<td>8</td>
<td>C(_6)H(_4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.05 (br)</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.41</td>
<td>6</td>
<td>CH(_3)</td>
</tr>
<tr>
<td>MeOdptaaH(_2)</td>
<td>CDCl(_3)</td>
<td>14.12 (br)</td>
<td>2</td>
<td>NH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.98 (br)</td>
<td>4</td>
<td>CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.25-6.91 (m)</td>
<td>12</td>
<td>C(_6)H(_4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.84</td>
<td>6</td>
<td>OCH(_3)</td>
</tr>
<tr>
<td>Co(MeOdptaa)NO</td>
<td>CDCl(_3)</td>
<td>8.02</td>
<td>4</td>
<td>CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.57 (br)</td>
<td>4</td>
<td>(\alpha)- and (p)-subs.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.48 (br)</td>
<td>12</td>
<td>C(_6)H(_4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.88</td>
<td>6</td>
<td>OCH(_3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.95</td>
<td>3</td>
<td>CH(_3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.68</td>
<td>3</td>
<td>(DMF)</td>
</tr>
</tbody>
</table>
The NMR results in Table 4.6 confirm the indications from the microanalyses and infrared studies that the expected compounds have been synthesised. The presence of the CH\textsubscript{3} group in Medptaah\textsubscript{2} and in its metal and nitrosyl complexes is indicated by the CH absorption band at around 2915 and 2859 \text{cm}^{-1} in the infrared spectra. In confirmation, the NMR spectra of the ligand and the nitrosyl complex show signals at 2.38 and 2.41 ppm respectively which are due to the methyl groups. The same is true for the methoxy-substituted dptaa and its mononitrosyl derivative. The methoxy groups absorb at 2830, 1280 and 1245 \text{cm}^{-1} in the infrared spectra, and in the NMR spectra, these groups give rise to the signals at 3.84 and 3.88 ppm in MeOdptaah\textsubscript{2} and Co(MeOdpta)NO respectively.

The microanalysis of Co(MeOdpta)NO indicated the presence of 0.25 molar equivalents of dimethylformamide which is in agreement with the presence of two peaks at 2.95 and 2.68 ppm in the \textsuperscript{1}H NMR spectrum due to this solvent residue. It is not clear however if the dimethylformamide is incorporated in the lattice or present as impurity. The peaks due to the aromatic rings of the macrocyclic complexes cannot be assigned accurately as they tend to overlap.

In a few of the NMR spectra, there were some additional peaks due to the presence of solvent residues like DMSO and CHCl\textsubscript{3}, as well as some peaks caused by the silicone grease used to seal the joints during the experimental work.
4.3.3. Nitrogen-15 and Cobalt-59 Nuclear Magnetic Resonance Spectroscopy

The $^{15}$N and $^{59}$Co NMR spectra of the $^{15}$NO-labelled complexes of Co(dptaa) and its Me- and MeO-derivatives were obtained. The results are presented in Table 4.7.

Table 4.7. $^{15}$N and $^{59}$Co chemical shifts of Co(dptaa)$_{15}$NO, Co(Medptaa)$_{15}$NO and Co(MeOdptaa)$_{15}$NO.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{15}$N (ppm)</th>
<th>$^{59}$Co (ppm)</th>
<th>Solvent</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(dptaa)$_{15}$NO</td>
<td>756.3</td>
<td>not detected</td>
<td>DMSO</td>
<td>294</td>
</tr>
<tr>
<td></td>
<td>763.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(solid)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(Medptaa)$_{15}$NO</td>
<td>758.2</td>
<td>6060</td>
<td>CDCl$_3$</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td>-2.7 (w,br)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(MeOdptaa)$_{15}$NO</td>
<td>758.7</td>
<td>6060</td>
<td>CDCl$_3$</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td>319.9 (vw)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(Brdptaa)$_{15}$NO</td>
<td>not detected</td>
<td>15679</td>
<td>DMF-$d_7$</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(vbr)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The reference used for the $^{15}$N NMR spectra was CH$_3$NO$_2$, and for the $^{59}$Co NMR spectra the reference was aqueous [Co(CN)$_6$]$^{3-}$.

From the correlation table$^{97}$ (see Section 1.3.2.5.1) the $^{15}$N signals for the compounds Co(dptaa)$_{15}$NO, Co(Medptaa)$_{15}$NO and Co(MeOdptaa)$_{15}$NO in Table 4.7 appear in the region for bent Co-N-O groups. These data confirm the suggestion made from the infrared spectra that the coordination mode of the nitrosyl groups is bent rather than linear. The solid state NMR which was carried out for Co(dptaa)$_{15}$NO also shows a signal in the bent M-N-O region.
which is in agreement with the X-ray crystal structure of Co(dptaa)NO (Section 4.3.5) which shows that the Co-N-O group is indeed bent in the solid state. Even though no crystals of the other nitrosyls suitable for X-ray crystallography were obtained, it is reasonable to conclude from the NMR observations that the nitrosyl groups are in the bent geometry as well. For the complex Co(Brdptaa)\textsuperscript{15}NO, the \textsuperscript{15}N chemical shift was not detected.

The \textsuperscript{59}Co NMR signals appear at 6060 ppm, indicative of oxidation state (III). From the literature, it is found that cobalt(III) compounds exhibit a signal in the region of 3000 to 14000 ppm, and signals typical of lower oxidation state cobalt complexes are found at lower chemical shifts of -4000 to 2000 ppm.

4.3.4. Magnetic Measurements

Room temperature magnetic measurements were carried out on the cobalt(II) complexes and the mononitrosyls. The results are listed in Table 5.8.

Table 4.8. Magnetic measurements for cobalt complexes and corresponding nitrosyls.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$10^{-3} \chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(dptaa)</td>
<td>2.61</td>
<td>2.50</td>
</tr>
<tr>
<td>Co(Medptaa)</td>
<td>1.74</td>
<td>2.03</td>
</tr>
<tr>
<td>Co(MeOdptaa)</td>
<td>2.48</td>
<td>2.27</td>
</tr>
<tr>
<td>Co(dptaa)NO</td>
<td>0.26</td>
<td>0.77</td>
</tr>
<tr>
<td>Co(Medptaa)NO</td>
<td>0.27</td>
<td>0.78</td>
</tr>
<tr>
<td>Co(MeOdptaa)NO</td>
<td>0.17</td>
<td>0.63</td>
</tr>
</tbody>
</table>
Co(dptaa) has an effective magnetic moment of 2.50 B.M. which is higher than the spin-only value for one unpaired electron (1.73 B.M.). This is probably due to incomplete quenching of orbital contributions (Section 1.1). Co(dptaa)NO has a magnetic moment of 0.77 B.M. which is indicative of a Co(III) low spin complex with temperature independent paramagnetism (Section 1.2). It suggests that the nitrosyl here is coordinated as NO⁻, consistent with the conclusion that has been made that the MNO angle is bent.

The cobalt complexes of the dianions Medptaa and MeOdptaa show effective magnetic moments of 2.03 and 2.27 B.M. respectively, and, as the case of Co(dptaa), they are higher than the spin-only value for one unpaired electron. The nitrosyl complexes have effective magnetic moments of 0.78 and 0.63 B.M. (very similar to that of Co(dptaa)NO) which can be considered due to the temperature independent paramagnetism commonly found in cobalt(III) complexes. Weak paramagnetism can arise from the presence of impurities e.g. traces of the cobalt(II) complex, but the good analytical data make this unlikely.

Room temperature magnetic measurements on the products of the halogenation reactions of Co(dptaa) were also carried out.

Table 4.9. Results of room temperature magnetic measurements on Co(dptaa)Cl, Co(dptaa)Br and Co(dptaa)I.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$10^{-3} \chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(dptaa)Cl</td>
<td>1.31</td>
<td>1.77</td>
</tr>
<tr>
<td>Co(dptaa)Br</td>
<td>1.48</td>
<td>1.88</td>
</tr>
<tr>
<td>Co(dptaa)I</td>
<td>2.96</td>
<td>0.84</td>
</tr>
</tbody>
</table>
From Table 4.9, Co(dptaa)Cl and Co(dptaa)Br have effective magnetic moments of 1.77 and 1.88 B.M. respectively, very close to the spin only value of one unpaired electron (1.73 B.M.), indicative of low spin cobalt(II) $d^7$ complexes. These values were not predicted as oxidation to cobalt(III) was expected during reaction. The purity of these complexes is in doubt; attempts at recrystallisation were unsuccessful. It is possible that halogenation of the rings had occurred, but this was not investigated further. In the iodination reaction of Co(dptaa), the expected oxidation seems to have taken place. The complex shows an effective magnetic moment of 0.84 B.M., corresponding to a low spin cobalt(III) $d^6$ complex with the magnetic moment arising from temperature independent paramagnetism.

4.3.5. X-Ray Crystallography

A single crystal of Co(dptaa)NO was investigated using X-ray crystallographic methods. Table 4.10 and 4.11 list the bond lengths and bond angles of the chelate rings respectively. Figure 4.6 shows the atom numbering scheme and molecular structure of Co(dptaa)NO.

The Co-N-O angle of 122.6° obtained from the X-ray study confirms the bent geometry of the Co-N-O group. The cobalt centre is positioned 0.22 Å above the plane of the four nitrogen atoms (Figure 4.7). This is quite different from the Co(dptaa)$^{87}$ complex (Figure 4.5) which has the cobalt atom exactly at the centre of the plane of the nitrogen atoms. A molecule of dimethylformamide is found in the lattice; however, for simplicity, this is not included in the ORTEP drawing of the molecular structure of Co(dptaa)NO (Figure 4.6).
Crystal Data

Molecular formula  \( \text{CoC}_{33}\text{H}_{29}\text{N}_{6}\text{O}_{2} \ [\text{Co(dptaa)}\text{NO}.\text{DMF}] \)

RMM  600.57

Crystal system  Triclinic

Space group  \( \text{P}\bar{1} \)

\( a \)  11.838(11) Å \( \alpha \) 100.64(3)°

\( b \)  13.500(5) Å \( \beta \) 107.11(6)°

\( c \)  9.853(3) Å \( \gamma \) 102.68(5)°

\( V_c \)  1414.9 Å³

\( Z \)  2

\( D_x \)  6.4 gcm⁻³

\( F(000) \)  620

\( \lambda \)  0.71073 Å

A crystal of approximate dimensions 0.4 x 0.4 x 0.4 mm was examined. The triclinic unit cell was measured on a CAD4 diffractometer using 25 accurately centred reflections from the crystal.

Intensity data were collected in the \( \theta \) range 1° - 25° using graphite monochromated Mo-\( K\alpha \) radiation covering the index range \( 0 \leq h \leq 15, -16 \leq k \leq -16, -11 \leq l \leq 11 \). Reflections were not available from the data list for a PSI data collection. After the usual Lorentz and polarisation corrections, from a total of 5226 reflections, 4486 were deemed to have \( I \geq 3\sigma(I) \). Analysis of the standard reflection showed an intensity loss of 23.8% over the data collection period for which a correction was applied. The statistical \( N(z) \) test revealed a centric distribution leading to the assumption of space group \( \bar{P} \) which is consistent with the cell volume containing two molecules.
Anisotropic refinement, initially of Co alone, then all non-hydrogen atoms, except the solvent molecule gave an $R$ value of 0.075. A final refinement with the inclusion of a DMF molecule caused $R$ to converge at 0.048, $R_w = 0.075$, $S = 0.997$. The highest peak in the difference map was 0.5 eÅ$^{-3}$.

Table 4.10. Bond lengths of the chelate rings and the Co-N-O group of Co(dptaa)NO.

<table>
<thead>
<tr>
<th>Atom1-Atom2</th>
<th>Bond length (Å)</th>
<th>Atom1-Atom2</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N</td>
<td>1.812 (3)</td>
<td>N-O</td>
<td>1.183 (4)</td>
</tr>
<tr>
<td>Co-N1</td>
<td>1.888 (3)</td>
<td>Co-N2</td>
<td>1.889 (2)</td>
</tr>
<tr>
<td>Co-N3</td>
<td>1.890 (2)</td>
<td>Co-N4</td>
<td>1.883 (2)</td>
</tr>
<tr>
<td>N1-C1</td>
<td>1.329 (4)</td>
<td>N3-C3</td>
<td>1.325 (4)</td>
</tr>
<tr>
<td>C1-C20</td>
<td>1.398 (4)</td>
<td>C3-C40</td>
<td>1.383 (4)</td>
</tr>
<tr>
<td>C20-C2</td>
<td>1.392 (4)</td>
<td>C40-C4</td>
<td>1.391 (4)</td>
</tr>
<tr>
<td>C2-N2</td>
<td>1.326 (4)</td>
<td>C4-N4</td>
<td>1.328 (4)</td>
</tr>
<tr>
<td>N2-C31</td>
<td>1.403 (3)</td>
<td>N4-C16</td>
<td>1.414 (3)</td>
</tr>
<tr>
<td>C31-C36</td>
<td>1.402 (4)</td>
<td>C16-C11</td>
<td>1.400 (5)</td>
</tr>
<tr>
<td>C36-N3</td>
<td>1.404 (4)</td>
<td>C11-N1</td>
<td>1.411 (3)</td>
</tr>
</tbody>
</table>
Table 4.11. Bond angles of the chelate rings and the Co-N-O group of Co(dptaa)NO.

<table>
<thead>
<tr>
<th>Atom1-Atom2-Atom3</th>
<th>Bond Angle (°)</th>
<th>Atom1-Atom2-Atom3</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-Co-N1</td>
<td>96.1 (1)</td>
<td>N-Co-N3</td>
<td>97.6 (1)</td>
</tr>
<tr>
<td>N-Co-N2</td>
<td>97.3 (1)</td>
<td>N-Co-N4</td>
<td>95.9 (1)</td>
</tr>
<tr>
<td>N1-C1-C20</td>
<td>124.9 (3)</td>
<td>N3-C3-C40</td>
<td>125.5 (2)</td>
</tr>
<tr>
<td>C1-C20-C2</td>
<td>122.8 (3)</td>
<td>C3-C40-C4</td>
<td>122.9 (3)</td>
</tr>
<tr>
<td>C20-C2-N2</td>
<td>125.8 (2)</td>
<td>C40-C4-N4</td>
<td>125.4 (2)</td>
</tr>
<tr>
<td>C2-N2-C31</td>
<td>120.4 (2)</td>
<td>C4-N4-C16</td>
<td>121.4 (2)</td>
</tr>
<tr>
<td>N2-C31-C36</td>
<td>114.0 (2)</td>
<td>N4-C16-C11</td>
<td>114.3 (2)</td>
</tr>
<tr>
<td>C31-C36-N3</td>
<td>113.3 (2)</td>
<td>C16-C11-N1</td>
<td>113.6 (2)</td>
</tr>
<tr>
<td><strong>Co-N-O</strong></td>
<td><strong>122.6 (3)</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.6. Atom numbering scheme of Co(dptaa)NO
Figure 4.7. Side view of Co(dptaa)NO.
The drawing in Figure 4.7 illustrates the side view of the molecule, showing the cobalt atom raised from the 4N plane, the bent Co-N-O group and the 72° rotation of the phenyl rings to each other.

The average Co-N distances are 1.865 Å and 1.888 Å in the cobalt(II) complex and the mononitrosyl respectively. These values are slightly higher than the Co-N (nitrosyl) distance of 1.812 Å. This suggests that a degree of double bonding occurs in the Co-N (nitrosyl), in agreement with the schematic diagram of the bent nitrosyl coordination (Figure 1.3). However, the Co-N (ligand) bond lengths mentioned above are shorter than the available cavity of 3.826 Å for this ligand. Therefore, to accommodate this difference, on coordination, some inherent features must be flexible enough to relieve ligand strain which are:

- A variation in the bond distances of the 14-membered ring.
- A modification of the various interior angles of the 14-membered ring, and
- Torsional distortion about the appropriate bonds to redirect the N₄ lone pairs into the N₄ plane.
4.3.6. Dptaa Complexes of Iron(II), Chromium(II) and Manganese(II)

Magnetic measurements were carried out on Fe(dptaa); however, the samples were not pure enough magnetically to give sensible effective magnetic moment values. The room temperature magnetic moments for the products from the template and insertion methods were 11.7 and 14.5 B.M. respectively. A very small amount of ferromagnetic impurity e.g. in the form of an iron oxide could give a very large effective magnetic moment to an iron(II) complex even though the impurity could not be detected from the microanalysis results. Unfortunately, attempts to recrystallise the Fe(dptaa) were unsuccessful.

The products from the various attempts to synthesise Cr(dptaa) and Mn(dptaa) did not give good microanalysis results, consequently, no further measurements were carried out. Furthermore, the amounts obtained were insufficient to carry out magnetic susceptibility measurements.
CHAPTER FIVE

CHROMIUM(II) SCHIFF BASE COMPLEXES
5. Schiff Bases

5.1. Introduction

A Schiff base is defined as a compound containing one or more azomethine groups (-RC=N-) and it is usually formed by the condensation of a primary amine with an active carbonyl compound. To be able to coordinate to a metal, these bases need to bear another functional group, usually -OH, sufficiently near to the site of condensation that a five- or six-membered chelate ring can be formed with the metal.

The great synthetic flexibility of the bases allows diverse structural types to be formed. The bases may vary in terms of the symmetry of the ligands, the non-symmetrical being the less common. The base can be bidentate or polydentate, whether it is a salicylaldimine or a β-ketoamine. A Schiff base is usually synthesised from the condensation of a substituted primary amine with an α-hydroxy aromatic aldehydes, β-diketones or 1,2-dicarbonyls. The current work is mainly concerned with bidentate (Figure 5.1) and symmetrical quadridentate (Figure 5.2) Schiff bases derived from 2-hydroxyacetophenone.
Bidentate ligand

R = C₃H₇ ; HappramH
R = CH₂C₆H₅ ; HapbamH

(Figure 5.1)

Tetradentate ligand

n = 2 ; HapenH₂
n = 3 ; Hap-1,3-pnH₂

(Figure 5.2)
The Schiff bases (Figure 5.1) could exist as the phenol-imine (Figure 5.3) or the keto-amine (Figure 5.4) tautomers as illustrated above. However, a high resolution proton NMR study on the similar system of salicylaldimines did not show any splitting in the signal due to the methine proton that could be assigned to a long range coupling\(^1\) to an N-H group. Therefore, it was concluded that such a system exists exclusively as the phenol-imine tautomer.

Metal complexes derived from Schiff bases have been known for over one hundred years. However, this field underwent a period of relative inactivity until it attracted a great deal of attention when Pfeiffer\(^1\) carried out his pioneering research in the 1930's. In the period of 1931 - 1942 Pfeiffer and his co-workers produced a prodigious number and variety of complexes derived from Schiff bases of salicylaldehyde and its substitution products. Schiff base complexes have subsequently been found to play an essential role in many biological processes. To date, many Schiff base complexes have been synthesised and characterised especially those derived from salicylaldehyde, however, very little work has been done on those derived from 2-hydroxyacetophenone, especially with chromium(II).
5.2. Experimental

5.2.1. Ligands

The ligands were synthesised from the commercially available 2-hydroxyacetophenone and the appropriate amines using the well established Diehl\textsuperscript{102} method.

5.2.1.1. Bis(2-hydroxyacetophenone)ethylenediimine [HapenH\textsubscript{2}]

An ethanolic (96 %, 40.00 cm\textsuperscript{3}) solution of 2-hydroxyacetophenone (30.00 g, 220.3 mmol) was heated to boiling. Ethylenediamine (6.621 g, 110.2 mmol) was also boiled in ethanol (96%, 40.00 cm\textsuperscript{3}). The two hot solutions were mixed in a round bottomed flask to give a bright yellow solution. Upon further heating, some yellow semicrystalline solid appeared and the mixture was heated under reflux for one hour. More solid appeared when the solution was allowed to cool slowly to room temperature. The solid was filtered off and washed with ice-cold ethanol. Recrystallization from ethanol afforded yellow needles. Yield, 30.00 g (92 %).

Analysis for C\textsubscript{18}H\textsubscript{20}N\textsubscript{2}O\textsubscript{2} Calculated: C,72.92; H,6.80; N,9.45 %

   Found: C,72.99; H,6.91; N,9.51 %
5.2.1.2. Bis(2-hydroxyacetophenone)-1,3-propanediimine [Hap-1,3-pnH₂]

A solution of 2-hydroxyacetophenone (15.00 g, 110.2 mmol) in ethanol (96 %, 20 cm³) was heated and then mixed with a hot solution of 1,3-diaminopropane (4.083 g, 55.09 mmol) in ethanol (96 %, 20 cm³) resulting in a bright yellow solution. The solution was heated under reflux for one hour upon which some yellow semicrystalline solid appeared. After being cooled slowly to room temperature, the solid was filtered off and washed with ice-cold ethanol. Recrystallization from ethanol produced bright yellow needles. Yield, 17.75 g (93%).

Analysis for C₁₉H₂₂N₂O₂

Calculated: C, 73.52; H, 7.14; N, 9.03 %

Found: C, 73.58; H, 7.18; N, 8.99 %

5.2.1.3. 2-Hydroxyacetophenone-n-propylimine [HappramH]

The reagents 2-hydroxyacetophenone (15.00 g, 110.2 mmol) and n-propylamine (6.513 g, 110.2 mmol) were dissolved separately in ethanol (96 %, 20 cm³). On mixing, a yellow solution was produced to which anhydrous sodium sulphate (5.000 g; 35.20 mmol) was added and then the mixture was heated under reflux for one hour. No solid appeared upon cooling, so after filtration to remove sodium sulphate the solvent was taken off using a rotary evaporator. The viscous yellow product was then dissolved in diethyl ether (40 cm³) and the solution cooled very rapidly in liquid nitrogen. The yellow microcrystals which formed were quickly filtered off while the mixture was still very cold and dried in air. Yield, 15.35 g (79 %).
5.2.1.4. 2-Hydroxyacetophenonebenzylimine [HapbamH]

A solution of 2-hydroxyacetophenone (10.00 g, 73.45 mmol) in absolute ethanol (40 cm³) and benzylamine (7.865 g, 73.45 mmol) were mixed in a round bottomed flask. The bright yellow mixture was stirred for two hours at room temperature and the solvent was taken off on a rotary evaporator. The viscous product was dissolved in diethyl ether and then cooled in ice to crystallise the ligand. Yellow needles which formed were filtered off, washed with cold methanol and air dried. Yield, 14.87 g (90%).

Analysis for C_{15}H_{15}NO

Calculated: C, 79.97; H, 6.71; N, 6.22 %

Found: C, 79.97; H, 6.66; N, 6.20 %
5.2.2. Complexes of Chromium(II)

Two general routes were used in attempts to synthesise chromium(II) complexes of the Schiff base anions hapen, hap-1,3-pn and happram. The first route was via the sodium salts prepared from the bases and sodium hydride, and the second was via lithium salts using methyl lithium in diethyl ether.

Before use, all glassware was washed thoroughly in a base bath followed by an acid bath, tap water, distilled water and acetone. The glassware was then left in a 140°C oven for at least one hour to remove all trace of moisture. While the apparatus was still hot, the taps and joints were greased and the glassware was put under continuous vacuum and allowed to cool to room temperature before reagents were added.

5.2.2.1. Preparations via sodium salts

The sodium salts of the ligands were prepared by reacting the ligands with sodium hydride in THF as generally outlined below.

The ligand was pumped on for two hours in a warm water bath (ca. 80°C) to remove any moisture which might be present before it was dissolved in freshly distilled THF. The solution was then cooled in an ice bath and stirred. Sodium hydride (1 molar equivalent for happramH and 2 molar equivalents for hapenH₂ and hap-1,3-pnH₂) which had been weighed into a small Schlenk tube was added very slowly via a bent adapter into the yellow solution of the ligand. This addition resulted in vigorous effervescence as hydrogen was released and the solution turned pale yellow.
After the effervescence had stopped, the solution was filtered slowly through a fine sinter to remove any undissolved impurities (usually a small amount of brown particles). The filtrate was then taken to dryness under vacuum and the pale yellow sodium salt was stored in glass ampoules ready for complexation with anhydrous chromium(II) salts, either chloride or bromide.

5.2.2.1.1. *N,N*-bis(2-hydroxyacetophenone)ethylenediiminatochromium(II) [Cr(hapen)]

The salt Na₂hapen (2.934 g, 8.621 mmol) was dissolved in freshly distilled THF (100 cm³) against a stream of nitrogen and the system was evacuated and refilled with nitrogen. To the pale yellow solution, anhydrous chromium(II) chloride (0.991 g, 8.063 mmol) was added. The colour of the solution immediately changed to blood red and the reaction was left to stir at room temperature overnight. The reaction mixture was filtered through a fine sinter to remove sodium chloride, but some solid product was also found on the sinter, so the mixed solid was not discarded.

The filtrate was concentrated to half volume and placed in a freezer overnight. However, no solid was found, so the THF was taken off on the pump and the mass was redissolved in fresh THF. Some solid which did not redissolve in the solvent was then extracted from the sintered filter together with the product isolated previously. Upon slow cooling, needles were obtained. They were filtered off and dried on the vacuum. However, the crystals rapidly decomposed (turning to a dark green powder) in the apparatus used to mount them for X-ray crystallography. Yield, 0.571 g (20%).
5.2.2.1.2. $N,N'$-bis(2-hydroxyacetophenone)-1,3-propanediiminato-chromium(II) [Cr(hap-1,3-pn)]

The salt Na$_2$hap-1,3-pn (3.118 g, 8.790 mmol) was dissolved in freshly distilled anhydrous THF (100 cm$^3$) and anhydrous chromium(II) chloride (1.080 g, 8.790 mmol) was added to the pale yellow solution resulting in an immediate colour change to deep red. The reaction was left to stir overnight at room temperature. Sodium chloride precipitation was observed.

The mixture was then filtered through a fine sinter to remove the sodium chloride and the filtrate was filtered again as the first filtration did not successfully remove all the salt. The filtrate was then pumped to dryness and the red mass was microanalysed. Yield, 2.582 g (81%)

Analysis for Cr$_{19}$H$_{20}$N$_2$O$_2$ Calculated: C, 63.32; H, 5.59; N, 8.88 %
Analysis for Cr(hap-1,3-pn).THF Calculated: C, 63.88; H, 6.53; N, 6.48 %

Found: C, 61.18; H, 6.40; N, 6.48 %
5.2.2.1.3. Bis(2-hydroxyacetophenone-n-propyliminato)chromium(II)
[Cr(happram)$_2$]

Anhydrous chromium(II) bromide (1.195 g, 5.642 mmol) was added to a slurry of NaHappram (2.430 g, 12.19 mmol) in freshly distilled THF (70 cm$^3$). The mixture immediately became dark red and it was left to stir for three hours at room temperature and then filtered. Much powder came through the sinter, so after standing overnight, the mixture was taken to dryness and freshly distilled toluene (100 cm$^3$) added.

The blood red mixture was filtered and the filtrate placed overnight in a freezer. A small amount of air sensitive orange brown powder was filtered off. The resulting filtrate was concentrated to dryness yielding a red-brown residue which became khaki on exposure to air after several minutes. Yield, 1.273 g (56%).

The filtrate was very sensitive to aerial oxidation, rapidly turning olive green upon exposure to air.

Analysis for CrC$_{22}$H$_{28}$N$_2$O$_2$

| Calculated: C, 65.33; H, 6.98; N, 6.93 % |
| Found: C, 64.86; H, 7.15; N, 5.74 % |
5.2.2.2. Preparations via lithium salts

Magnetic measurements on the chromium(II) Schiff base complexes obtained from the preparations described above were carried out. The results (see Section 5.3.1.) were different from those of Cr(hapram)$_2$ reported by Sandell$^{103}$. Therefore, to investigate the behaviour further, the preparations were repeated using the same method as Sandell.

The lithium salts of the ligands were generated in situ unlike the sodium salts, which were isolated, in the preparations described above.

5.2.2.2.1. $N,N'$-bis(2-hydroxyacetophenone)ethylenediiminatochromium(II) [Cr(hapen)]

The Schiff base hapenH$_2$ (0.840 g, 2.834 mmol) was weighed into the dry glassware and pumped on for one hour to remove any trace of moisture. The ligand was dissolved in freshly distilled THF (80 cm$^3$) giving a bright yellow solution which was then cooled to -60°C in an acetone/dry ice bath. Using a pre-dried needle and syringe, methyl lithium in diethyl ether (4.05 cm$^3$, 5.668 mmol, 1.4 M solution) was injected into the reaction flask through a septum cap. The colour turned to pale yellow upon the addition.

Anhydrous chromium(II) acetate (0.482 g, 2.834 mmol) was added to the mixture against a stream of nitrogen and the flask was evacuated and filled with nitrogen to remove any oxygen that might have entered the system. The mixture was stirred and allowed to warm up to room temperature. The colour of the solution turned dark red-brown with some bright red microcrystals slowly forming.
overnight upon stirring. The solid was then filtered off on a sintered disc and then extracted with fresh THF. On extraction, the solid redissolved in the hot THF quite easily and the residue on the sintered disc was almost white in colour. The solution was dark red and some feathery dark red crystals were formed at the bottom of the flask. They were filtered off and dried under vacuum.

Crystals:
Analysis for CrC\textsubscript{18}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2} Calculated: C, 62.42; H, 5.24; N, 8.09 %
Analysis for Cr(hapen).\textfrac{1}{2}Li(OAc) Calculated: C, 60.16; H, 5.18; N, 7.38 %

Found: C, 59.57; H, 5.06; N, 7.27 %

The filtrate was pumped to dryness and the red solid obtained was washed with freshly distilled dry toluene. Some of the solid redissolved but the bulk was then filtered off and dried under vacuum.

Solid obtained from filtrate:
Analysis for CrC\textsubscript{18}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2} Calculated: C, 62.42; H, 5.24; N, 8.09 %
Analysis for Cr(hapen).Li(OAc) Calculated: C, 58.26; H, 5.13; N, 7.79 %

Found: C, 58.47; H, 5.54; N, 7.82 %

5.2.2.2.2. Bis(2-hydroxyacetophenone-n-propyliminato)chromium(II) [Cr(hapram)\textsubscript{2}]

The Schiff base hapramH (2.000 g, 11.28 mmol) was pumped on for two hours to remove any trace of moisture and dissolved in freshly distilled THF (100 cm\textsuperscript{3}). The solution was cooled in an acetone/dry ice mixture to -60°C before MeLi in
diethyl ether (8.06 cm³, 11.28 mmol, 1.4 M solution) was injected in with a pre-dried syringe and needle. The yellow solution turned to bright red. Anhydrous chromium(II) acetate (0.960 g, 5.642 mmol) was added to the solution against a stream of nitrogen. The mixture was stirred and allowed to warm slowly to room temperature. The colour of the solution started to turn dark red after one hour and when left to stir overnight, some deep red solid was found which was filtered off and dried on the oil pump. Upon drying, some white solid was observed in the product which was thought to be lithium acetate.

The filtrate was pumped to dryness and the red mass was washed with freshly distilled dried toluene. The product was slightly soluble in toluene. The undissolved solid was filtered off and dried under vacuum. Yield, 0.611 g (37%).

Analysis for \( \text{CrC}_{22}\text{H}_{28}\text{N}_{2}\text{O}_{2} \)

- Calculated: C, 65.33; H, 6.98; N, 6.93 %
- Found: C, 64.92; H, 7.22; N, 6.77 %

5.2.2.2.3. \textit{N,N'}-bis(2-hydroxyacetophenone)-1,3-propanediiminato-chromium(II) [Cr(hap-1,3-pn)]

The preparation of this complex was attempted a few times using three different combinations of solvent and chromium(II) salt as detailed below.

(a) \textit{From THF} / Cr\textsubscript{2}(CH\textsubscript{3}COO)\textsubscript{4}

Hap-1,3-pn\textsubscript{2} (0.830 g, 2.674 mmol) was pumped on for two hours to remove any trace of water before being dissolved in freshly distilled THF (100 cm\textsuperscript{3}).
After cooling in an acetone / dry ice mixture to -60°C, methyl lithium in diethyl ether (3.82 cm³, 5.348 mmol, 1.4 M solution) was introduced slowly with a dry syringe and needle through a septum cap. The yellow colour of the solution faded upon the addition. Anhydrous chromium(II) acetate (0.455 g, 2.672 mmol) was added against a stream of nitrogen, but no immediate reaction seemed to have taken place. The mixture was stirred overnight upon which a very slow colour change to deep red occurred. Some jelly-like brown substance found in the solution was filtered off and discarded.

The filtrate was pumped to dryness and the dark red mass was washed with freshly distilled toluene, filtered off and dried on the pump. Yield, 0.372 g.

Analysis for CrC₁₉H₂₀N₂O₂

Calculated: C, 63.33; H, 5.59; N, 7.77 %

Found: C, 47.86; H, 5.25; N, 4.36 %

The method was repeated giving the microanalysis results which follow:

Analysis for CrC₁₉H₂₀N₂O₂

Calculated: C, 63.33; H, 5.59; N, 7.77 %

Found: C, 53.57; H, 6.07; N, 3.87 %

(b) From toluene / Cr₂(CH₃COO)₄

The ligand hap-1,3-pnH₂ (0.865 g, 2.787 mmol) was pumped on to dry it completely before toluene (100 cm³) was added. The ligand was slightly soluble in the solvent. The mixture was cooled in acetone / dry ice to -60°C and methyl lithium in diethyl ether (3.98 cm³, 5.574 mmol, 1.4 M solution) was injected. No
apparent colour change was observed. Anhydrous chromium(II) acetate (0.474 g, 2.787 mmol) was then added against a stream of nitrogen.

The mixture was allowed to warm to room temperature and left to stir overnight but no reaction seemed to have occurred. The chromium(II) salt was insoluble in toluene, therefore THF (30 cm³) was added and the colour of the solution slowly turned red brown. However, no product precipitated. The experiment was terminated at this point as the colour of the solution was slightly tinged with green which was usually an indication that oxidation had taken place in chromium(II)-Schiff base preparations.

(c) From THF / diethyl ether / CrCl₂

From the two attempts above, it was concluded that lithium acetate was soluble in THF and toluene in these preparations. Therefore a third method using anhydrous chromium(II) chloride which would produce lithium chloride was attempted. The lithium chloride had been found from experiments unreported here to be insoluble in diethyl ether. Thus it should be possible to remove the lithium chloride from the reaction mixture by filtration.

The Schiff base hap-1,3-pnH₂ (1.149 g, 3.702 mmol) was pumped on for two hours before diethyl ether / THF (90 : 10) was added. Both solvents had been dried and freshly distilled. The solution was cooled as before to -60°C in acetone / dry ice before MeLi in diethyl ether (5.29 cm³, 7.404 mmol, 1.4 M solution) was injected into the flask through a septum cap. No apparent colour changes were observed. Anhydrous chromium(II) chloride (0.455 g, 3.702 mmol) was added to the mixture and stirred.
The solution turned dark red almost immediately and a fine white precipitate of lithium chloride was formed. The mixture was stirred overnight and then the white precipitate was filtered off. Some of the precipitate passed through the sinter even though the filtration was done very slowly under gravity and the solution had to be filtered three times before no lithium chloride could be seen in the filtrate.

The filtrate was then taken to dryness, washed with toluene and the solid filtered off and dried under vacuum. Yield, 0.541 g (40%).

Analysis for CrC₁₉H₂₀N₂O₂:  
Calculated: C, 63.33; H, 5.59; N, 7.77 %

Analysis for CrC₁₉H₂₀N₂O₂·½LiCl:  
Calculated: C, 61.52; H, 5.28; N, 7.34 %

Found: C, 62.61; H, 7.36; N, 7.01 %

5.2.2.2.4. Bis(2-hydroxyacetophenonebenzyliminato)chromium(II)  
Cr(hapbam)₂

The ligand hapbamH (2.000 g, 8.877 mmol) was pumped on for one hour and dissolved in freshly distilled THF (100 cm³), and the yellow solution was cooled in an acetone/dry ice mixture to -60°C. Methyl lithium in diethyl ether (6.34 cm³, 8.877 mmol, 1.4 M solution) was injected into the reaction flask through a septum cap upon which the colour slowly changed to bright red. The acetone/dry ice bath was removed and stirring was started. After two minutes, anhydrous chromium(II) acetate (0.755 g, 4.439 mmol) was added against a stream of nitrogen. The system was evacuated and refilled with nitrogen to remove any trace of air which could have entered the flask during the addition.
After being stirred for thirty minutes, the colour of the solution changed to dark red and some red solid appeared. After six hours, the solid was isolated and during filtration, some red microcrystals started to appear in the filtrate which was then left for two days to encourage crystal growth. On drying these crystals, much whitish solid (lithium acetate) was seen to contaminate the red solid, so the product was discarded. The second batch of solid which was found in the filtrate was then filtered off and dried under vacuum. Yield, 0.256 g (6 %).

Analysis for CrC$_{30}$H$_{28}$N$_2$O$_2$  
Calculated: C, 71.99; H, 5.64; N, 5.60 %

Analysis for CrC$_{30}$H$_{28}$N$_2$O$_2$·½Li(OAc)  
Calculated: C, 69.78; H, 5.57; N, 5.25 %

Found: C, 70.54; H, 6.35; N, 4.96 %

Subsequent preparations to obtain enough complex for magnetic measurements have given poor microanalyses.
5.3. Results and Discussion

5.3.1. Magnetic Measurements

Table 5.1. Variation of reciprocal susceptibility and effective magnetic moment with temperature of Cr(hapen).THF, prepared from sodium salt.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^{-2} \chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>2.23</td>
<td>3.24</td>
</tr>
<tr>
<td>261</td>
<td>1.97</td>
<td>3.26</td>
</tr>
<tr>
<td>229</td>
<td>1.73</td>
<td>3.25</td>
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<tr>
<td>197</td>
<td>1.48</td>
<td>3.27</td>
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<tr>
<td>165</td>
<td>1.23</td>
<td>3.27</td>
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<tr>
<td>133</td>
<td>1.07</td>
<td>3.14</td>
</tr>
<tr>
<td>101</td>
<td>0.77</td>
<td>3.23</td>
</tr>
<tr>
<td>87</td>
<td>0.67</td>
<td>3.21</td>
</tr>
</tbody>
</table>

Diamagnetic correction = -194.0 x 10^{-6} c.g.s.

$\theta = 10^\circ$

Graph 5.1. Plot of reciprocal susceptibility and effective magnetic moment against temperature.
Table 5.2. Variation of reciprocal susceptibility and effective magnetic moment with temperature of Cr(hap-1,3-pn).THF prepared from sodium salt

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^{-2} \chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>1.93</td>
<td>3.49</td>
</tr>
<tr>
<td>261</td>
<td>1.71</td>
<td>3.49</td>
</tr>
<tr>
<td>229</td>
<td>1.51</td>
<td>3.49</td>
</tr>
<tr>
<td>197</td>
<td>1.30</td>
<td>3.48</td>
</tr>
<tr>
<td>165</td>
<td>1.10</td>
<td>3.46</td>
</tr>
<tr>
<td>133</td>
<td>0.90</td>
<td>3.43</td>
</tr>
<tr>
<td>101</td>
<td>0.70</td>
<td>3.40</td>
</tr>
<tr>
<td>87</td>
<td>0.61</td>
<td>3.37</td>
</tr>
</tbody>
</table>

Diamagnetic correction = -201.3 x 10^{-6} c.g.s.

$\theta = 20^\circ$

Graph 5.2. Plot of reciprocal susceptibility and effective magnetic moment against temperature.
Table 5.3. Variation of reciprocal susceptibility and effective magnetic moment with temperature of Cr(happram)$_2$, prepared from sodium salt.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^{-2} \chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>2.08</td>
<td>3.36</td>
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<tr>
<td>261</td>
<td>1.84</td>
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<td>3.33</td>
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<tr>
<td>165</td>
<td>1.27</td>
<td>3.23</td>
</tr>
<tr>
<td>101</td>
<td>0.80</td>
<td>3.18</td>
</tr>
<tr>
<td>87</td>
<td>0.70</td>
<td>3.15</td>
</tr>
</tbody>
</table>

Diamagnetic correction = $-194.0 \times 10^{-6}$ c.g.s.
$	heta = 50^\circ$

Graph 5.3. Plot of reciprocal susceptibility and effective magnetic moment against temperature.
Table 5.4. Variation of reciprocal susceptibility and effective magnetic moment with temperature of Cr(hapen).Li(OAc), prepared from lithium salt.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^{-2} \chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>261</td>
<td>3.21</td>
<td>2.55</td>
</tr>
<tr>
<td>229</td>
<td>2.91</td>
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<td>197</td>
<td>2.67</td>
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<td>2.13</td>
</tr>
<tr>
<td>87</td>
<td>1.65</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Diamagnetic correction = $-184.2 \times 10^{-6}$ c.g.s.

$\theta = 90^\circ$

Graph 5.4. Plot of reciprocal susceptibility and effective magnetic moment against temperature.
Table 5.5. Variation of reciprocal susceptibility and effective magnetic moment with temperature of Cr(hapram)$_2$, prepared from lithium salt.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^{-2} \chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>1.21</td>
<td>4.40</td>
</tr>
<tr>
<td>261</td>
<td>1.10</td>
<td>4.36</td>
</tr>
<tr>
<td>229</td>
<td>0.99</td>
<td>4.29</td>
</tr>
<tr>
<td>197</td>
<td>0.89</td>
<td>4.22</td>
</tr>
<tr>
<td>165</td>
<td>0.78</td>
<td>4.10</td>
</tr>
<tr>
<td>133</td>
<td>0.69</td>
<td>3.93</td>
</tr>
<tr>
<td>101</td>
<td>0.61</td>
<td>3.65</td>
</tr>
<tr>
<td>87</td>
<td>0.57</td>
<td>3.49</td>
</tr>
</tbody>
</table>

Diamagnetic correction = $-220.9 \times 10^{-6}$ c.g.s.

$\theta = 70^\circ$

Graph 5.5. Plot of reciprocal susceptibility and effective magnetic moment against temperature.
Table 5.6. Summary of magnetic properties of chromium(II) Schiff base complexes prepared from sodium and lithium salts.

<table>
<thead>
<tr>
<th>Method of preparation</th>
<th>Complex</th>
<th>$\mu_{293}$ (B.M.)</th>
<th>$\mu_{87}$ (B.M.)</th>
<th>$\theta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium salt</td>
<td>Cr(Hapen).THF</td>
<td>3.24</td>
<td>3.21</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Cr(Hap-1,3-pn).THF</td>
<td>3.49</td>
<td>3.37</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Cr(Happram)$_2$</td>
<td>3.36</td>
<td>3.15</td>
<td>50</td>
</tr>
<tr>
<td>Lithium salt</td>
<td>Cr(Hapen).Li(OAc)</td>
<td>2.55</td>
<td>2.06</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>Cr(Happram)$_2$</td>
<td>4.40</td>
<td>3.49</td>
<td>70</td>
</tr>
</tbody>
</table>

All the chromium(II) complexes in Table 5.6 above obeyed the Curie-Weiss law. Those prepared from the sodium salts of the ligands have effective magnetic moments in the range of 3.49 - 3.15 B.M., which is in between the spin only values for 2 (2.83 B.M.) and 3 (3.87 B.M.) unpaired electrons. A high spin chromium(II) $d^4$ complex will exhibit a spin only value of 4.90 B.M. whereas a low spin one will have a spin only value of 2.83 B.M., therefore, it could be concluded that the complexes are low spin with some orbital contribution. These complexes show a very small decrease in the effective magnetic moments on lowering the temperature especially Cr(hapen).THF, and the $\theta$ values are quite small. These suggest that the complexes are magnetically dilute, i.e. showing no interaction between the metal centres.

A different magnetic behaviour was observed for the complexes prepared from the lithium salts. Cr(hapen).LiOAc has an effective magnetic moment of 2.55 B.M. at 293 K, and lowering the temperature to 87 K decreased the effective
magnetic moment to 2.06 B.M. These values are lower than the spin only value for two unpaired electrons expected for a low spin chromium(II) complexes. The $\theta$ value for this complex is also quite large (90 K) suggesting an antiferromagnetic interaction between the metal centres. It could be possible that an intermolecular bridging occurs in the complex, similar to that found in the Cu(salen) discussed in Section 6.6, enabling this interaction to take place. Alternatively, the low magnetic moments observed in these complexes are probably due to some degree of oxidation to chromium(III) even though precautions were taken to avoid this from happening during preparations.

However, the sample of Cr(hapram)$_2$ prepared from the lithium salt has effective magnetic moments of 4.40 and 3.49 B.M. at 293 and 87 K respectively. These values are indicative of a high spin chromium(II) undergoing a slow transition to a low spin state with the lowering of temperature. Below 100 K, the reciprocal susceptibility started to increase slowly when the temperature was lowered. When the complex was first prepared by Sandell, the same magnetic behaviour was observed. Taking measurements below the available liquid nitrogen temperature would very likely show the full spin state transition of this complex. Unfortunately, since no crystals were obtained from the preparations, the structure of this complex cannot be characterised by X-ray crystallography.
5.3.2. Proton NMR Spectroscopy of the Ligands

The solvent used for the NMR spectra of these Schiff bases was deuterated methanol for reasons of solubility limitations. However, the use of this solvent enabled an isotopic exchange to occur in the solution between the -OH groups in the bases and the -OD group in the solvent. This caused the virtual disappearance of the -OH signals from these spectra which is expected in the region of 10.00 - 13.00 ppm.\textsuperscript{100}

\[ \text{HapenH}_2 \quad \text{Hap-1,3-pnH}_2 \]

Table 5.7. Proton NMR data of HapenH\textsubscript{2} and Hap-1,3-pnH\textsubscript{2}.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Residue</th>
<th>No. of H</th>
<th>$\delta_H$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HapenH\textsubscript{2}</td>
<td>Phenyl rings</td>
<td>8</td>
<td>6.71-7.64 (m)</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{2}</td>
<td>4</td>
<td>4.05 (s)</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{3}</td>
<td>6</td>
<td>2.48 (s)</td>
</tr>
<tr>
<td>Hap-1,3-pnH\textsubscript{2}</td>
<td>Phenyl rings</td>
<td>8</td>
<td>6.66-7.63 (m)</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{2} (a)</td>
<td>4</td>
<td>3.83 (t)</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{2} (b)</td>
<td>2</td>
<td>2.24 (p)</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{3}</td>
<td>6</td>
<td>2.48 (s)</td>
</tr>
</tbody>
</table>
Table 5.8. Proton NMR data for HapramH and HapbamH.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Residue</th>
<th>No. of H</th>
<th>$\delta_H$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HapramH</td>
<td>Phenyl ring</td>
<td>4</td>
<td>6.58-7.58 (m)</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_3$ (a)</td>
<td>3</td>
<td>2.45 (s)</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2$ (b)</td>
<td>2</td>
<td>3.57 (t)</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2$ (c)</td>
<td>2</td>
<td>1.77 (s)</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_3$ (d)</td>
<td>3</td>
<td>1.08 (t)</td>
</tr>
<tr>
<td>HapbamH</td>
<td>Phenyl rings</td>
<td>9</td>
<td>6.66-7.65 (m)</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_3$</td>
<td>3</td>
<td>2.53 (s)</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2$</td>
<td>2</td>
<td>4.85 (s)</td>
</tr>
</tbody>
</table>

Note: In Tables 5.7 and 5.8, m=multiple; s=singlet; t=triplet; sx=sextuplet; p=pentuplet.
CHAPTER SIX

MISCELLANEOUS WORK
6. Miscellaneous Work

6.1. Cr(DMSO)$_2$Cl$_2$

In 1965, Holah and Fackler$^{104}$ prepared CrCl$_2$.2DMSO, CrBr$_2$.3DMSO and CrI$_2$.4DMSO which, from their visible reflectance spectra, appeared to contain six-coordinate (distorted octahedral) chromium(II). This indicated that in the cases of the chloride and bromide, the complexes did not exist as simple monomers. However, all displayed normal high-spin magnetic moments at room temperature.

In the present work, the preparation of Cr(DMSO)$_2$Cl$_2$ was repeated to carry out a magnetic susceptibility measurement over a temperature range of 295 - 87 K to see if the results would throw some light on the nature of the bonding in the complex. Recrystallisation of the product was attempted several times in the hope that a suitable crystal could be obtained to determine the structure of the complex. It would be interesting to see if the complex was planar, with or without a stacked structure, tetrahedral or even chloride bridged. However, the recrystallization attempts were unsuccessful. The preparation of the complex is outlined below.

Chromium(II) chloride tetrahydrate (2.370 g, 12.15 mmol) was added to de-gassed dimethylsulphoxide (30 cm$^3$) and the initially blue solution turned turquoise when gently heated. It was left to cool slowly to room temperature and then in placed in the freezer overnight. No solid was observed, so the mixture was concentrated to half volume under vacuum when the solution turned a darker green and a light blue precipitate
appeared. The solvent was taken off completely and the blue solid was washed with deoxygenated absolute ethanol, filtered off and dried under vacuum. Yield, 1.102 g (33%)

Analysis for CrC₄H₁₂S₂O₂Cl₂  Calculated: C, 17.21; H, 4.33; N, 0.00 %  
Found: C, 17.95; H, 4.07; N, 0.00 %

The results of the magnetic measurement carried out on the complex are summarised in Table 6.1 below and a plot of the reciprocal susceptibility and effective magnetic moment against temperature is illustrated in Graph 6.1.

The values of the effective magnetic moments are temperature dependent, decreasing at lower temperatures indicating that the complex is not magnetically dilute. The Curie-Weiss law is obeyed with a $\theta$ value of approximately 35°.

Table 6.1. Variation of reciprocal susceptibility and effective magnetic moment with temperature of Cr(DMSO)$_2$Cl$_2$.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^{-2} \chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>1.05</td>
<td>4.75</td>
</tr>
<tr>
<td>261</td>
<td>0.93</td>
<td>4.73</td>
</tr>
<tr>
<td>229</td>
<td>0.82</td>
<td>4.72</td>
</tr>
<tr>
<td>197</td>
<td>0.71</td>
<td>4.70</td>
</tr>
<tr>
<td>165</td>
<td>0.60</td>
<td>4.68</td>
</tr>
<tr>
<td>133</td>
<td>0.50</td>
<td>4.63</td>
</tr>
<tr>
<td>101</td>
<td>0.39</td>
<td>4.55</td>
</tr>
<tr>
<td>87</td>
<td>0.83</td>
<td>4.50</td>
</tr>
</tbody>
</table>

Diamagnetic correction = $-145.1 \times 10^{-6}$ c.g.s.

$\theta = 35^\circ$
Graph 6.1. Plot of reciprocal susceptibility and effective magnetic moment against temperature for Cr(DMSO)$_2$Cl$_2$. 

$10^{-2}\chi_A^{-1}$ (c.g.s.) vs. Temperature (K)

$\mu_{\text{eff}}$ (B.M.)
6.2. 1,8-Diaminonaphthalene (DAN) Complexes

There has been very little work done on the 1,8-diaminonaphthalene (DAN) complexes of chromium(II) except for the preparation and characterisation of Cr(DAN)$_2$Cl$_2$ and Cr(DAN)$_2$(CF$_3$SO$_2$)$_2$. From infrared spectra which showed no bands corresponding to the free DAN, it was concluded that the complexes comprised bidentate diamine. Magnetic measurements over the temperature range 293 - 87 K showed both to contain high-spin chromium(II) with no significant interactions between the metal centres. The diffuse reflectance spectrum of Cr(DAN)$_2$(CF$_3$SO$_2$)$_2$ was as expected for high-spin, distorted six-coordinate chromium(II) complex.

Following this work, the preparations of the iodide and bromide complexes of chromium(II) DAN were carried out to complete the series. In addition, attempts were made to synthesise macrocyclic complexes from Cr(DAN)$_2$Br$_2$ by reacting the complex with acetylacetone or acetone illustrated in Figure 6.1 and Figure 6.2. It was hoped that these reactions would produce the planar macrocyclic complexes which could be related to those prepared in Chapter Four. Curtis obtained a nickel(II) macrocyclic complex by reaction of [Ni(1,2-diaminoethane)$_3$]$^{2+}$ and dry acetone. However, in the present work, both reaction failed probably due to the incompatibility of the sizes of the metal centre and the cavity of the macrocycle. The Cr$^{2+}$ ion is larger than the size of Ni$^{2+}$ ion by about 0.08 Å.
Figure 6.1. Attempted reaction of Cr(DAN)$_2$Br$_2$ with acetylacetone to obtain a planar macrocyclic complex.

Figure 6.2. Attempted reaction of Cr(DAN)$_2$Br$_2$ with acetone to obtain a planar macrocyclic complex.
6.2.1. Cr(DAN)$_2$I$_2$

The ligand 1,8-diaminonaphthalene (2.000 g, 12.66 mmol) was dissolved in absolute ethanol (50 cm$^3$) under nitrogen to give a brown-red solution to which chromium(II) iodide hexahydrate (5.410 g, 13.07 mmol) was slowly added against a stream of nitrogen. A dark green precipitate appeared when the mixture was stirred and heated. After three hours, the suspension was cooled to room temperature and the green solid filtered off, washed with deoxygenated ethanol and dried under vacuum resulting in a green powder which turned brown when exposed to air. Yield, 3.841 g (61%).

Analysis for CrC$_{20}$H$_{20}$N$_4$I$_2$  
Calculated: C, 38.61; H, 3.24; N, 9.00 %  
Found: C, 39.16; H, 3.39; N, 8.66 %

6.2.2. Cr(DAN)$_2$Br$_2$

A blue methanolic (20 cm$^3$) solution of chromium(II) bromide hexahydrate (2.720 g, 8.504 mmol) was slowly added to a red-brown solution of 1,8-diaminonaphthalene (2.000 g, 12.66 mmol) in methanol (50 cm$^3$) with stirring. An apple green precipitate rapidly appeared and the suspension was heated at 90°C for two hours before it was allowed to cool slowly to room temperature. The solid was filtered off, washed with absolute ethanol and dried under vacuum. The dry apple green product immediately turned brown upon exposure to air. Yield, 4.652 g (90%).

Analysis for CrC$_{20}$H$_{20}$N$_4$Br$_2$  
Calculated: C, 45.48; H, 3.82; N, 10.61 %  
Found: C, 44.79; H, 4.06; N, 10.09 %
Table 6.2. Variation of reciprocal susceptibility and effective magnetic moment with temperature of Cr(DAN)$_2$I$_2$.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^{-2} \chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>1.06</td>
<td>4.71</td>
</tr>
<tr>
<td>261</td>
<td>0.94</td>
<td>4.70</td>
</tr>
<tr>
<td>229</td>
<td>0.83</td>
<td>4.71</td>
</tr>
<tr>
<td>197</td>
<td>0.71</td>
<td>4.70</td>
</tr>
<tr>
<td>165</td>
<td>0.60</td>
<td>4.67</td>
</tr>
<tr>
<td>133</td>
<td>0.49</td>
<td>4.65</td>
</tr>
<tr>
<td>101</td>
<td>0.38</td>
<td>4.63</td>
</tr>
<tr>
<td>87</td>
<td>0.33</td>
<td>4.60</td>
</tr>
</tbody>
</table>

Diamagnetic correction = $-306.9 \times 10^{-6}$ c.g.s.

$\theta = 8^\circ$

Graph 6.2. Plot of reciprocal susceptibility and effective magnetic moment against temperature.
Table 6.3. Variation of reciprocal susceptibility and effective magnetic moment with temperature of Cr(DAN)$_2$Br$_2$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^{-2} \chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>1.06</td>
<td>4.71</td>
</tr>
<tr>
<td>261</td>
<td>0.94</td>
<td>4.72</td>
</tr>
<tr>
<td>229</td>
<td>0.81</td>
<td>4.75</td>
</tr>
<tr>
<td>197</td>
<td>0.69</td>
<td>4.77</td>
</tr>
<tr>
<td>165</td>
<td>0.59</td>
<td>4.74</td>
</tr>
<tr>
<td>133</td>
<td>0.47</td>
<td>4.73</td>
</tr>
<tr>
<td>101</td>
<td>0.36</td>
<td>4.71</td>
</tr>
<tr>
<td>87</td>
<td>0.31</td>
<td>4.70</td>
</tr>
</tbody>
</table>

Diamagnetic correction = -236.4 x $10^{-6}$ c.g.s.  
$\theta = -5^\circ$

Graph 6.3. Plot of reciprocal susceptibility and effective magnetic moment against temperature.
The values of $\mu_{\text{eff}}$ of approximately 4.70 B.M. are almost independent of temperature and the $\theta$ values are small. These results indicate that the complexes contain high spin chromium(II) and are monomeric entities which show very weak interaction between the metal centres.
6.3. $N,N,N',N'$-Tetramethylethlenediame (TMEDA) Complexes

It has been reported that the vanadium(II) complex of $N,N,N',N'$-tetramethylethlenediamine $V$(TMEDA)$_2$Cl$_2$ is a good starting material for the preparation of vanadium(II) complexes generally.\textsuperscript{108} It was hoped that Cr(TMEDA)$_2$Cl$_2$ would be similarly useful, but unfortunately, neither it nor the bromo-derivative could be isolated. The attempts are outlined below.

6.3.1. Attempt to prepare Cr(TMEDA)$_2$Cl$_2$

Chromium(II) chloride tetrahydrate (2.610 g; 12.56 mmol) was added to a mixture of methanol (20 cm$^3$) and 2,2-dimethoxypropane (20 cm$^3$). A light blue solution was obtained which turned greenish blue with heating and stirring. The solution was taken to dryness under vacuum which afforded a white solid.

Tetramethylethlenediamine (4.24 cm$^3$, 28.13 mmol, 2:1 + 5% excess) was dissolved in methanol (20 cm$^3$) and deoxygenated before being added to the white solid to give a dark blue solution. After heating and stirring for 30 minutes and cooling to room temperature, the solvent was taken off under vacuum. This yielded a sky blue solid which was washed with freshly distilled diethyl ether, filtered off and vacuum dried. Upon exposure to air, the blue colour changed to grey.

Analysis for Cr(TMEDA)$_2$Cl$_2$  Calculated: C, 40.56; H, 9.08; N, 15.77 %
Analysis for Cr(TMEDA)Cl$_2$  Calculated: C, 30.14; H, 6.74; N, 11.72 %

          Found: C, 31.40; H, 8.65; N, 11.09 %
6.3.2. Attempt to prepare Cr(TMEDA)$_2$Br$_2$

Chromium(II) bromide hexahydrate (1.926 g, 6.022 mmol) was dissolved in a mixture of 2,2-dimethoxypropane (20 cm$^3$) and methanol (20 cm$^3$), and the blue solution was stirred and heated for 30 minutes before it was taken to dryness under vacuum giving a white solid. Tetramethylethylenediamine (1.90 cm$^3$, 12.60 mmol, 2:1 + 5% excess) was dissolved in methanol (20 cm$^3$) and added to the white solid. The deep blue solution which formed was heated to boiling and then cooled to room temperature. A dark green solid separated which was filtered off and dried; the filtrate was taken to dryness yielding a purplish blue solid which was washed with freshly distilled diethyl ether, filtered off and dried under vacuum.

Dark green solid:
Analysis for CrC$_{12}$H$_{32}$N$_4$Br$_2$  
Calculated: C, 32.45; H, 7.26; N, 12.61 %  
Found: C, 21.93; H, 6.41; N, 4.22 %

Purplish blue solid:
Analysis for CrC$_{12}$H$_{32}$N$_4$Br$_2$  
Calculated: C, 32.45; H, 7.26; N, 12.61 %
Analysis for Cr(TMEDA)$_{1.5}$Br$_2$.H$_2$O  
Calculated: C, 26.75; H, 6.48; N,10.40 %
Found: C, 25.58; H, 6.72; N, 9.85 %
6.4. Complexes of Reduced Schiff Bases

Many attempts to synthesise planar chromium(II) Schiff base complexes have been carried out during the course of this work and for a long while, no progress was made. Parallel work on vanadium(II) was also being carried out\textsuperscript{109} and some crystals of what was thought to be V(happram)\textsubscript{2}.n(Toluene) were isolated. However, an X-ray crystallographic investigation revealed that it was a vanadium(III) complex, V(happram)\textsubscript{3}, which indicated that oxidation had taken place during the reaction. It was then thought that a reduced Schiff base would be a better ligand to work with as the possibility of the reduction of the C=N groups by the chromium(II) would be removed. The Schiff bases were reduced by reaction with sodium borohydride (Figure 6.3) in methanol as described by Hoss and Elias\textsuperscript{110}.

![Diagram](image)

Figure 6.3. The reduction of HapenH\textsubscript{2} to [H\textsubscript{4}]HapenH\textsubscript{2}
6.4.1. Preparation of Reduced Ligands

(a) \([H_4]HapenH_2\)

The Schiff base hapenH_2 (4.961 g, 16.73 mmol) was dissolved in methanol (30 cm^3) and cooled in an ice bath. Sodium borohydride (1.270 g, 33.47 mmol) was added slowly with stirring and effervescence was observed. The yellow colour of the Schiff base slowly disappeared and when the reaction was complete, the product was colourless. The white powder which formed was filtered off, washed with ice-cold methanol and dried. Yield, 2.321 g (46%).

Analysis for C_{18}H_{24}N_{2}O_{2}  

Calculated: C, 71.97; H, 8.05; N, 9.33 %  

Found: C, 71.76; H, 8.18; N, 9.37 %

(b) \([H_4]Hap-1,3-pnH_2\)

A similar reduction of hap-1,3-pnH_2 also gave good microanalysis results:

Analysis for C_{19}H_{26}N_{2}O_{2}  

Calculated: C, 72.58; H, 8.33; N, 8.91 %  

Found: C, 72.45; H, 8.41; N, 8.91 %
6.4.2. Preparations of Chromium(II) Complexes

(a) Cr[H₄]hapen

The reduced ligand [H₄]hapenH₂ (1.008 g, 3.356 mmol) was pumped on for two hours before being dissolved in freshly distilled THF and the solution was cooled to -60° in an acetone/dry ice mixture. Butyllithium (2.68 cm³, 2.5 M solution in hexane, 6.710 mmol) was injected into the flask through a septum cap using a pre-dried syringe and needle. The colourless solution became pale yellow and upon the addition of anhydrous chromium(II) acetate (0.571 g, 3.356 mmol), the solution became purple in colour. The acetone/dry ice bath was removed and the reaction mixture was stirred overnight. It was then left in the freezer for 24 hours upon which some purple solid formed. The solid was filtered off and dried under vacuum. Yield, 0.701 g (60%).

Analysis for CrC₁₈H₂₀N₂O₂
Calculated: C, 61.70; H, 6.33; N, 8.00 %
Found: C, 61.72; H, 6.79; N, 7.77 %

(b) Cr[H₄]hap-1,3-pn

A few attempts to synthesise Cr[H₄]hap-1,3-pn were carried out using the butyllithium method above. The preparations were unsuccessful as the microanalysis results obtained for the products were unsatisfactory. A typical set of results is presented below:

Analysis for CrC₁₉H₂₄N₂O₂
Calculated: C, 62.62; H, 6.64; N, 7.69 %
Found: C, 51.19; H, 6.14; N, 4.58 %
Magnetic measurements were carried out on Cr[H₄]hapen.

Table 6.4. Variation of reciprocal susceptibility and effective magnetic moment with temperature for Cr[H₄]hapen.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>10⁻²χ⁻¹ (c.g.s.)</th>
<th>μₑff (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>2.47</td>
<td>3.09</td>
</tr>
<tr>
<td>261</td>
<td>2.28</td>
<td>3.02</td>
</tr>
<tr>
<td>229</td>
<td>2.70</td>
<td>2.91</td>
</tr>
<tr>
<td>197</td>
<td>1.98</td>
<td>2.82</td>
</tr>
<tr>
<td>165</td>
<td>1.73</td>
<td>2.76</td>
</tr>
<tr>
<td>101</td>
<td>1.25</td>
<td>2.54</td>
</tr>
<tr>
<td>87</td>
<td>1.11</td>
<td>2.50</td>
</tr>
</tbody>
</table>

Diamagnetic correction = -195.5 x 10⁻⁶ c.g.s.

θ = 110°

Graph 6.4. Plot of reciprocal susceptibility and effective magnetic moment against temperature.
The complex Cr[H₄]hapen shows a temperature dependent effective magnetic moment which varies from 3.09 B.M. at 295 to 2.50 B.M. at 87 K. It obeys the Curie-Weiss law with a large \( \theta \) value of 110°. It is therefore reasonable to suggest that the complex is antiferromagnetic. Possibly the complex could be a dimer, similar in structure to Cu(salen) (Figure 6.4).
6.5. Complexes of Tertiary Phosphines

The complex \( \text{Cr(depe)}_2 \text{I}_2 \) \(^{111}\) [depe = 1,2-bis(diethylphosphine)ethane] exhibits a sharp spin crossover in the temperature range 175 - 165 K from the high-spin state \( (S=2) \) to the low-spin state \( (S=1) \). This was the first example of such behaviour exhibited by a chromium(II) complex. An X-ray structure determination at room temperature showed that the chromium(II) ion is octahedrally coordinated by two axial iodide ions and two bidentate phosphine ligands. No complexes of chromium(II) with three bidentate tertiary phosphine ligands were known, so salts of the non- or weakly-coordinating anions BF\(_4^-\) and CF\(_3\)SO\(_3^-\) were investigated.

6.5.1. \([\text{Cr(dmpe)}_3][\text{BF}_4]_2\)

Chromium(II) tetrafluoroborate hexahydrate (1.960 g, 5.874 mmol) was dissolved in methanol (40 cm\(^3\)) and 1,2-bis(dimethylphosphino)ethane (3.11 cm\(^3\), 1:3 + 10% excess) was added to the solution via a syringe in a fume cupboard. An orange precipitate rapidly appeared but re-dissolved to give a yellow-brown solution. After leaving the mixture in the freezer for 2 days, some brownish orange semicrystals separated which were filtered off and dried under vacuum. Yield, 1.043 g (26%)

Analysis for \( \text{CrC}_{18}\text{H}_{48}\text{P}_6\text{B}_2\text{F}_8 \)

Calculated: C, 31.98; H, 7.16; N, 0.00 %

Found: C, 32.59; H, 7.67; N, 0.00 %
6.5.2. Attempt to prepare $[\text{Cr(depe)}_3][\text{CF}_3\text{SO}_3]_2$

Chromium(II) triflate tetrahydrate (2.680 g, 5.903 mmol) was dissolved in deoxygenated methanol (40 cm$^3$) to give a light blue solution. 1,2-Bis(diethylphosphino)ethane (2.97 cm$^3$, 1:3 + 5% excess) was syringed into the solution and the solution turned purple. The reaction was left to stir for 5 hours and then taken to near dryness under vacuum leaving a very viscous purple liquid which dissolved very easily in THF, acetone, ethanol and ethyl acetate. It remained a viscous liquid in hexane and diethyl ether. After shaking and stirring in diethyl ether for 4 hours, it slowly solidified and the green ether solution was decanted. The remaining solid was dried under vacuum.

Analysis for $\text{CrC}_3\text{H}_7\text{P}_6\text{F}_6\text{S}_2\text{O}_6$ Calculated: C, 39.67; H, 7.49; N, 0.00 %
Analysis for $\text{Cr(depe)}_{1.5}[\text{CF}_3\text{SO}_3]_2$ Calculated: C, 30.96; H, 5.50; N, 0.00 %

Found: C, 30.38; H, 5.75; N, 0.00 %

Elemental analyses showed that only the $[\text{Cr(dmpe)}_3][\text{BF}_4]_2$ preparation was successful, so magnetic measurements were carried out on this complex. The results are presented in Table 6.5 and Graph 6.5. The effective magnetic moments are essentially independent of temperature and the values ranging (3.05 to 3.08 B.M.) are slightly higher than the spin only value for two unpaired electrons (2.83 B.M.), suggesting that the complex is low spin chromium(II). The plot of reciprocal susceptibility against temperature is a straight line through the origin (Curie law) which shows that there is no interaction between the metal centres.
Table 6.5. Variation of reciprocal susceptibility and effective magnetic moment with temperature of [Cr(dmpe)$_3$][BF$_4$]$_2$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^{-2} \chi^{-1}_A$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>2.45</td>
<td>3.09</td>
</tr>
<tr>
<td>261</td>
<td>2.21</td>
<td>3.07</td>
</tr>
<tr>
<td>229</td>
<td>1.97</td>
<td>3.05</td>
</tr>
<tr>
<td>197</td>
<td>1.66</td>
<td>3.08</td>
</tr>
<tr>
<td>165</td>
<td>1.41</td>
<td>3.06</td>
</tr>
</tbody>
</table>

Diamagnetic correction = -406.4 x 10^{-6} c.g.s.

$\theta = 0$

Graph 6.5. Plot of reciprocal susceptibility and effective magnetic moment against temperature.

![Graph showing reciprocal susceptibility and effective magnetic moment against temperature.](image-url)
6.6. Complexes of Manganese(II) with Schiff Base Anions

The first manganese complex with a tetradeinate Schiff base ligand was reported by Pfeiffer et al.\(^1\) who isolated orange-yellow crystals from the reaction of manganese(II) acetate with \(N,N'\)-ethylenebis(salicylaldimine). Asmussen and Soling\(^1\) then, from detailed preparative and magnetic studies on Mn(salen) concluded that the complex possessed antiferromagnetic interactions and found a discontinuity in the magnetic susceptibility versus temperature curve in the region of 85 - 107 K. Subsequently, Earnshaw et al.\(^1\) reported magnetic studies results comparable to those of Asmussen and Soling at higher temperatures, but, in the region of the reported discontinuity in the plot of reciprocal susceptibility against temperature, they found a smooth curvature away from the Curie-Weiss behaviour, which is characteristic of appreciable antiferromagnetic interactions. This behaviour was accounted for by assuming the Mn(salen) is binuclear and that there is interaction between the spins \(S = 5/2\) of the metal ions. Lewis et al.\(^1\) reported results which were in agreement with those of Earnshaw et al. and their conclusions suggested that Mn(salen) takes up a binuclear structure, similar to that of Cu(salen), in that the X-ray diffraction powder photographs of Mn(salen) and Cu(salen) are very similar.

The copper complex has been shown to consist of dimeric Cu(salen) units,\(^1\) the dimerization occurring via the mutual sharing by the copper atoms of one of the oxygen atoms of each ligand (Figure 6.4); this is a relatively rare stereochemistry for manganese(II).
It is therefore interesting to explore the chemistry of manganese(II) complexes of Schiff bases derived from 2-hydroxyacetophenone.

The manganese(II) Schiff base complexes were prepared using the method of Horwitz.117

6.6.1. \(N,N'-\text{bis}(2\text{-hydroxyacetophenone})\text{ethylenediiminato-manganese(II)} [\text{Mn}(\text{hapen})]\)

The Schiff base hapen\(\text{H}_2\) (1.000 g, 3.374 mmol) and sodium hydroxide pellets (0.269 g, 6.748 mmol) were mixed in methanol (50 cm\(^3\)) and deoxygenated. Anhydrous manganese(II) acetate was added to the mixture against a stream of nitrogen and the system was evacuated and filled with nitrogen.

There was no apparent reaction after stirring for one hour, so the mixture was stirred in a warm water bath (60\(^\circ\)C). Then some pale yellow precipitate appeared and stirring was continued overnight. The solid was filtered off with difficulty because the precipitate was very fine. The solid
was washed with water and then methanol and pumped on for eight hours to dry it. Yield, 0.867 g (73%).

Analysis for MnC\textsubscript{18}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2}  
Calculated: C, 61.90; H, 5.19; N, 8.02 %

Analysis for MnC\textsubscript{18}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2}.1\textsubscript{1/2}H\textsubscript{2}O  
Calculated: C, 57.45; H, 5.62; N, 7.44 %

Found: C, 57.59; H, 5.93; N, 7.54 %

6.6.2. \textit{N,N'-bis(2-hydroxyacetophenone)-1,3-propanediiminato-}

manganese(II) [Mn(hap-1,3-pn)]

The Schiff base hap-1,3-pnH\textsubscript{2} (2.000 g, 6.443 mmol) and potassium hydroxide pellets (72.30 g, 12.88 mmol) were added to absolute ethanol (50 cm\textsuperscript{3}) and the mixture was deoxygenated in the usual manner. Anhydrous manganese(II) acetate (1.115 g, 6.443 mmol) was added to the mixture and the flask was evacuated and filled with nitrogen a few times before being stirred in a warm water bath (80\textdegree C) for one hour until the yellow solution turned orange.

Stirring was continued for a further two hours before the reaction mixture was allowed to cooled slowly to room temperature. A yellow-orange precipitate appeared which was filtered off, washed with deoxygenated water followed by deoxygenated methanol and then dried under vacuum for eight hours. The resultant solid was pale yellow. Yield, 1.365 g (58%).
Analysis for MnC₁₉H₂₀N₂O₂ Calculated: C, 62.81; H, 5.55; N, 7.71 %
Analysis for MnC₁₉H₂₀N₂O₂·2½H₂O
Calculated: C, 55.88; H, 6.17; N, 6.86 %
Found: C, 55.82; H, 5.81; N, 6.51 %

6.6.3. Attempt to prepare Bis(2-hydroxyacetophenone propyliminato)manganese(II) [Mn(happram)₂]

The ligand HappramH (2.000 g, 11.28 mmol) and potassium hydroxide pellets (0.633 g, 11.28 mmol) were dissolved in methanol (50 cm³) and the bright yellow solution was deoxygenated in the usual manner before anhydrous manganese(II) acetate was added against a stream of nitrogen. The reaction was heated under reflux for three hours and the yellow powder obtained after cooling to room temperature was filtered off, washed with ice-cold deoxygenated methanol and dried under vacuum.

Analysis for MnC₂₂H₂₈N₂O₂ Calculated: C, 64.86; H, 6.93; N, 6.88 %
Found: C, 28.79; H, 3.65; N, 0.00 %

From the microanalysis it is clear that the preparation had failed. The Schiff base was probably hydrolysed during the synthesis.

Magnetic measurements were carried out on the complexes Mn(hapen).1½H₂O and Mn(hap-1,3-n).2½H₂O. The results are summarised in Tables 6.6 and 6.7 and the plots of reciprocal susceptibilities and effective magnetic moments against temperature are illustrated in Graphs 6.6 and 6.7.
Table 6.6. Variation of reciprocal susceptibility and effective magnetic moment with temperature of Mn(hapen).1\frac{1}{2}H_2O.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^{-2} \chi_A^{-1}$ (c.g.s.)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>261</td>
<td>0.83</td>
<td>5.02</td>
</tr>
<tr>
<td>229</td>
<td>0.74</td>
<td>4.98</td>
</tr>
<tr>
<td>199</td>
<td>0.66</td>
<td>4.92</td>
</tr>
<tr>
<td>165</td>
<td>0.56</td>
<td>4.87</td>
</tr>
<tr>
<td>133</td>
<td>0.47</td>
<td>4.74</td>
</tr>
<tr>
<td>101</td>
<td>0.39</td>
<td>4.56</td>
</tr>
<tr>
<td>87</td>
<td>0.35</td>
<td>4.48</td>
</tr>
<tr>
<td>81</td>
<td>0.34</td>
<td>4.35</td>
</tr>
</tbody>
</table>

Diamagnetic correction = $-154.2 \times 10^{-6}$ c.g.s.

$\theta = 40^\circ$

Graph 6.6. Plot of reciprocal susceptibility and effective magnetic moment against temperature.
Table 6.7. Variation of reciprocal susceptibility and effective magnetic moment with temperature of Mn(hap-1,3-pn).2\%H₂O

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>10⁻²χ_a⁻¹ (c.g.s.)</th>
<th>μ_eff (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>261</td>
<td>0.59</td>
<td>5.94</td>
</tr>
<tr>
<td>229</td>
<td>0.51</td>
<td>6.01</td>
</tr>
<tr>
<td>197</td>
<td>0.44</td>
<td>6.00</td>
</tr>
<tr>
<td>165</td>
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<td>5.88</td>
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<tr>
<td>133</td>
<td>0.32</td>
<td>5.79</td>
</tr>
<tr>
<td>101</td>
<td>0.25</td>
<td>5.67</td>
</tr>
<tr>
<td>87</td>
<td>0.22</td>
<td>5.62</td>
</tr>
</tbody>
</table>

Diamagnetic correction = -179.0 x 10⁻⁶ c.g.s.
θ = 15°

Graph 6.7. Plot of reciprocal susceptibility and effective magnetic moment against temperature.
Table 6.8. Summary of magnetic behaviour of manganese(II) Schiff base complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\mu_{261}$ (B.M.)</th>
<th>$\mu_{87}$ (B.M.)</th>
<th>$\theta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(Hapen).1½H$_2$O</td>
<td>5.02</td>
<td>4.35</td>
<td>40</td>
</tr>
<tr>
<td>Mn(Hap-1,3-pn).2½H$_2$O</td>
<td>5.94</td>
<td>5.62</td>
<td>15</td>
</tr>
</tbody>
</table>

The complex Mn(hapen).1½H$_2$O has an effective magnetic moment of 5.02 B.M. ($\mu_\infty$ for manganese(II), high-spin, $d^5 = 5.92$ B.M.) at 261 K which slowly decreases with decrease of temperature and at 87 K the $\mu_{\text{eff}}$ is 5.62 B.M. Correspondingly, at this temperature, the $\chi_A^{-1}$ plot shows a slight but definite deviation from straight line behaviour. It is likely that this complex is antiferromagnetic, resembling the salen analogue discussed previously.

A gradual decrease in the effective moment at lower temperatures was found for Mn(hap-1,3-pn).2½H$_2$O, again probably due to antiferromagnetic interactions.


87. F. Umland and D. Thierig, Angew. Chem., 1962, 74, 388.

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