NITROSYLMETALLOPORPHYRIN COMPLEXES AS MODELS FOR CURED MEAT PIGMENTS

A Thesis Presented to the University of Surrey for the Degree of Doctor of Philosophy in the Faculty of Chemical and Biological Sciences

by

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A range of nitrosylmetalloporphyrin complexes, $\text{M(porph)NO} \ [\text{M} = \text{Fe, Co}; \ \text{porph} = \text{TPP, OEP, TpivPP}]$, some labelled with $^{15}\text{NO}$, has been synthesised and investigated as structural and spectroscopic models of the cured meat pigment, nitrosylmyoglobin. The nitrosylmetalloporphyrins were found to be unstable in solution (and some in the solid state) with respect to loss or further reaction of the nitrosyl ligand.

The diamagnetic cobalt(III) porphyrin nitrosyls and a range of other square pyramidal complexes of cobalt(III) with an apical nitrosyl ligand have been further investigated by $^{15}\text{N}$ and $^{59}\text{Co}$ NMR spectroscopy to establish whether the CoNO group is bent or linear and to study nephelauxetic and spectrochemical effects at the metal. In all cases studied the CoNO group is bent ($\text{CoNO} \sim 120^\circ$). The basal ligands were dithiocarbamate, tetradeutate Schiff base, porphyrin, and bidentate diamine and oximate giving $\text{S}_4$, $\text{S}_2\text{N}_2$, $\text{N}_4$, $\text{OONN}$, or $\text{ONON}$ coordination in the equatorial plane. The shielding of both cobalt and nitrogen tends to decrease with decrease in $\text{M(d)}$ to $\pi^*(\text{NO})$ back-bonding as indicated by M-N and N-O bond distances, and the MNO angle and the NO stretching frequencies. The shieldings decrease with electron withdrawal by ring substituents and also in going from sulphur to nitrogen to oxygen coligands, i.e. with decrease in ligand field splitting and in the nephelauxetism of the coligands.

The bent nitrosyls of cobalt can function as oxygen transfer catalysts via a nitrosyl-nitro couple. Consequently, a range of Co(III) porphyrin nitro complexes, $(\text{L})\text{Co(porph)NO}_2$
(porph = TPP, OEP; L = py, 1MeIm) and several nitro complexes containing the other basal ligands have been synthesised and investigated by the $^{15}$N and $^{59}$Co NMR technique. The coordinated nitro ligand is labile and linkage isomerism and ligand exchange have been observed. These observations may be related to the deterioration of cured meat colour which is of importance to the food industry. The crystal structure of (py)Co(TPP)NO$_2$ is presented; the nitro group of which is rotationally disordered. Recrystallisation of (1MeIm)Co(TPP)NO$_2$ gave [Co(TPP)(1MeIm)$_2$]NO$_2$, the crystal structure of which has been determined. Formation of this nitrite is further evidence for the lability of the nitro ligand.

The known complex Fe(salphen)NO was prepared using ascorbic acid for the first time to prevent contamination with the oxo-bridged iron(III) dimer. Variable temperature $^{57}$Fe Mossbauer effect studies of the $S = 1/2$ to $S = 3/2$ spin transition for Fe(salphen)NO show that the crossover is continuous and centred at $T_c \sim 181$ K, and that the electronic transition between the two spin states is rapid on the Mossbauer timescale.

The fluxionality of CoCl$_2$($^{15}$NO)(PPh$_2$Me)$_2$ was studied by variable temperature $^{15}$N and $^{31}$P NMR. An $^{17}$O NMR study of the $\mu$-peroxo complex [(NH$_3$)$_5$Co$^{17}$O$_2$Co(NH$_3$)$_5$](NO$_3$)$_4$·2H$_2$O is presented. An attempt to measure $^{15}$N NMR spectra of the diamagnetic 18 electron species, Fe(porph)($^{14}$NO)($^{15}$NO) (porph = TPP, OEP) presumably containing linear FeNO$^+$ and bent FeNO$^-$ was unsuccessful.
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5.3.1 Introduction

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1.1 Formation and Deterioration of Cured Meat Colour

1.1.1 Meat Colour and the Consumer

An important property of meat, whether fresh or cured is its colour, since it has a major influence on the consumer's decision to buy the food product. Deterioration of colour in meat has long been used as an early warning of meat "going-off", and UK legislation prohibits the use of chemical substances (e.g. ascorbic acid, nicotinic acid) to artificially prolong fresh meat colour. In the case of preserved meats this is not so and the bright pink colour of well-cured bacon and ham has long been used as a selling point, particularly since the development of transparent plastic vacuum packaging. Accompanying this, the fading of cooked cured ham colour under shop lighting has also long been recognised as a problem.

1.1.2 Meat, Muscle, and Myoglobin

The term 'meat' signifies the edible flesh or muscle of the animals which are acceptable for consumption by man. Edible and acceptable have different interpretations according to one's country and religion. Meat (muscle) is a very complex system and a 'typical composition' for meat is shown in Table 1.1. The concentration of myoglobin, the oxygen binding pigment, in the protein varies greatly according to species e.g. rabbit (0.02 % wet weight), sheep (0.35), pig (0.45), ox (0.60), horse (0.70), and sperm whale and seal (up to 8 %). The overall 'redness' of fresh meat is largely
Table 1.1 Composition of a Typical Meat After Rigor Mortis (and drained of blood)

<table>
<thead>
<tr>
<th>Component</th>
<th>% Wet Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>75 %</td>
</tr>
<tr>
<td>Protein</td>
<td>19 %</td>
</tr>
<tr>
<td>Lipid</td>
<td>2.5 %</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>1.2 %</td>
</tr>
<tr>
<td>Nitrogenous Compounds &amp; Inorganics</td>
<td>2.3 %</td>
</tr>
<tr>
<td>Vitamins</td>
<td>Trace</td>
</tr>
</tbody>
</table>

After Lawrie$^6,7$
due to its content of the haem proteins myoglobin (Mb, molecular weight 16700) and haemoglobin (Hb, molecular weight 67000), and the forms in which they exist. The haem proteins are also the principal site of action in curing.\(^8\)

Myoglobin, the oxygen binding pigment, is composed of a 153 residue peptide (the globin), and an iron(II) protoporphyrin IX complex (the haem group) which is held in a cleft in the globin by a coordinate bond between the imidazole nitrogen of the proximal histidine residue (HIS F-8) and iron(II), and by a large number of nonpolar and hydrogen-bonding interactions at the porphyrin periphery\(^9\) (Figures 1.1 and 1.2). The principal biological function of Mb in the living animal is to bind dioxygen.\(^10\) In the purple-red deoxy-form, the five-coordinate Fe(II) is high spin (HS, \(t^4_{2g} e^2_g, S=2\)) with an ionic radius of 78 pm, too large to fit into the porphyrin plane.\(^11\) Consequently, the HS Fe(II) ion projects some 80 pm out of the plane of the porphyrin ring towards the proximal histidine. The vacant oxygen binding site lies on the side of the porphyrin away from the proximal histidine. Cherry-red oxygenated Mb (MbO\(_2\)) is diamagnetic, and the six-coordinate low spin (LS, \(t^6_{2g}, S=0\)) Fe(II) is thought to lie in the plane of the porphyrin ring (LS Fe(II) ionic radius 61 pm) (Figure 1.3). During dioxygen coordination, the iron atom moves into the porphyrin plane pulling the proximal histidine imidazole ring with it.\(^12\) This motion is transferred through the globin chain and is thought in the case of Hb to account for the cooperativity of oxygen binding between the four distant iron porphyrins and is termed the "Perutz Mechanism".\(^13\) The important point here is that these deoxy-haem proteins have a vacant sixth
Figure 1.1 Schematic Representation of the Tertiary Structure of Myoglobin

OVERALL SIZE OF MOLECULE
= 4.4 x 4.4 x 2.5 nm approx.
Figure 1.2 Schematic Representation of the Haem Group

imidazole group of histidine F8

square pyramidal complex of iron(II) protoporphyrin IX
Figure 1.3 Reversible Oxygenation of Myoglobin

\[
\begin{align*}
\text{iron(II)} & \quad \text{iron(II)} \\
\text{HS} & \quad \text{LS} \\
4 \text{ unpaired electrons} & \quad S = 0 \ (\text{DIAMAGNETIC}) \\
\end{align*}
\]
coordination position which can bind many other ligands besides dioxygen, including nitric oxide.

1.1.3 Formation of Cured Meat Colour

The characteristic red-pink colour of cured pork is due to the presence of nitrosylmyoglobin, MbNO, an iron mononitrosyl, present as such in uncooked bacon and in cooked hams as the much more stable nitrosyl haemochrome, in which the globin moiety is denatured by heat (see Section 1.1.4). The pigment MbNO is easily produced by the direct action of nitric oxide gas on a deoxygenated solution of the muscle protein Mb. But in normal curing it arises from the action of nitrite, present in the curing brines to preserve the meat from microbial decomposition, particularly to prevent the growth of Clostridium botulinum, and to develop the characteristic colour and taste of cured meats. The addition of curing salts to preserve meat is an ancient craft, and a typical traditional Wiltshire bacon curing process involves pressurised injection of, and immersion of the carcass in, a freshly prepared salt solution containing NaCl, NaNO₃ or KNO₃, and NaNO₂, followed by draining and long maturation to give bacon, which on cooking produces ham. Nitrate is considered to provide a reservoir from which more nitrite can be formed by enzymatic reduction. Nitrite itself has pH dependent antimicrobial activity, but its mode of inhibition of bacterial growth is complex and is thought to involve inhibition of pyruvate-ferredoxin oxidoreductase (PFO) by nitric oxide produced under the conditions of the cure. PFO is a nonhaem-iron enzyme which catalyses the reversible decarboxylation of pyruvate to acetyl coenzyme A.
using the oxidant ferredoxin. This reaction is an essential step in the glucose metabolism of these organisms. However, the Perigo Effect, which is the greater, almost pH independent inhibition of bacterial growth found even when free NO$_2^-$ is depleted on storage of cured meat, is believed to be due to the formation from sodium nitrite, nitrous acid or other nitrosating agents of more powerful inhibitors called Perigo Type Factors, of unknown composition. Work on the possible role of Fe(II) amino acid nitrosyl complexes in this respect has shown that their formation is likely to be important in NO$_2^-$ depletion and subsequent inhibitor formation in cured meats.

The chemistry of curing is very complex and a number of possible routes of interaction of NO$_2^*$ with the various forms of Mb exist (Figure 1.4). The oxidising ability of NO$_2^-$ under the pH conditions of the cure is clear, but the situation is far from simple. We are particularly interested in reaction at the iron of the haem group, but NO$_2^-$ under acidic conditions can also react with the porphyrin ring, the protein, and all the myriad components of meat, including biological amines to form the various nitrosamines which are potent carcinogens. Despite the good possibility of nitrosamine formation under certain conditions, sodium nitrite is permitted as an additive to meat in most countries. Obviously the antibacterial action and cosmetic effects are thought to outweigh the potential

* Where NO$_2^-$ is written, HNO$_2$ or other reagents derived from NO$_2^-$ may be the actual reactants.
Figure 1.4 Possible Routes of Formation of Nitrosylmyoglobin During Curing

\[
\text{MbO}_2 \rightarrow \text{MetMb} \rightarrow \text{NO} \rightarrow \text{NO MetMb} \rightarrow \text{NO Mb}
\]

\[
\text{HNO}_2 + \text{H}^+ + e^- \rightarrow \text{NO} + \text{H}_2\text{O}
\]

\[
\text{pH} = 6 \text{ (approx.)}
\]
risks. The large literature on nitrosamines is reviewed elsewhere.\textsuperscript{28}

The muscle pigment Mb is oxidised to metMb [Fe(III)] by NO\textsubscript{2} which is itself reduced to nitric oxide. These products can complex under the strictly anaerobic conditions expected inside meat to form metMbNO,\textsuperscript{29} and spectroscopic evidence for its formation as an intermediate has been obtained in model systems involving ascorbate.\textsuperscript{24} MetMbNO is an unstable red pigment which is autoreduced on standing to form the corresponding relatively stable Fe(II) form, MbNO, the cured meat pigment\textsuperscript{30} (and metHbNO is autoreduced to HbNO\textsuperscript{31}). The mechanism of this reduction of metHb and metMb by NO is not known, but Chien\textsuperscript{31} suggests the following possible hydrolytic mechanism:

\begin{align*}
\text{Fe}^{\text{III}}\text{Mb} + \text{NO}^* & \rightarrow \text{Fe}^{\text{III}}\text{MbNO}^* \quad (1.1) \\
\text{Fe}^{\text{III}}\text{MbNO}^* + 2\text{OH}^- & \rightarrow \text{Fe}^{\text{II}}\text{MbNO}_2 + \text{H}_2\text{O} \quad (1.2) \\
\text{Fe}^{\text{II}}\text{MbNO}_2 + \text{NO}^* & \rightarrow \text{Fe}^{\text{II}}\text{MbNO}^* + \text{NO}_2^- \quad (1.3)
\end{align*}

However, Chien gave no evidence for bound nitrite at haem,\textsuperscript{31} and a dissociation mechanism could also be involved:

\begin{align*}
\text{Fe}^{\text{III}}\text{MbNO}^* & \rightarrow \text{Fe}^{\text{II}}\text{Mb} + \text{NO}^+ \quad (1.4) \\
\text{Fe}^{\text{II}}\text{Mb} + \text{NO}^* & \rightarrow \text{Fe}^{\text{II}}\text{MbNO}^* \quad (1.5)
\end{align*}

MetMbNO is also easily reduced by enzyme systems active in muscle mitochondria. In the living animal Mb and Hb are subject to oxidising conditions, and require the action of a suitable biological reducing system to maintain the haem iron in its normal physiologically reduced Fe(II) state. These largely unknown systems are thought to occur in cured meats
as operational post-mortem enzyme systems, since the development of a good cured meat colour clearly requires the operation of a reducing system capable of reducing unstable metMbNO to MbNO (and/or metMb to Mb). Ascorbate, which is widely used as a curing additive, can bring about all the haem changes required \(^8,32\) (Figure 1.5), including the reduction of nitrosamine concentration in cured meats.\(^34\)

Specific biochemical reducing systems which may be important in the development of cured meat colour have been the subject of intensive investigation by Walters et al. since 1964.\(^35-38\) The results described in the literature appeared as a project summary in 1968.\(^39\) Walters et al.\(^39\) suggest that formation of cured meat colour requires partic-

**Figure 1.5 Facile Oxidation of Ascorbic Acid** \(^33\)

\[
\text{Ascorbic acid} \quad \xrightarrow{\text{R} = -\text{CH(OH)}\text{CH}_2\text{OH}} \quad \text{Dehydroascorbic acid} \quad + 2\text{H}^+ + 2\text{e}^- \\
E^0' (\text{pH 7}) = +0.058 \text{ V} \quad 33
\]

pation of cytochrome c from the mitochondrial electron transport chain. Their scheme (Figure 1.6) involves the initial oxidation by NO\(_2^-\) of Mb (present as MbO\(_2\)) to metMb, and of ferrocytochrome c to ferricytochrome c, which complexes with the other reaction product, nitric oxide to form nitrosylferricytochrome c. This may then be reduced using a suitable oxidisable substrate (e.g. succinate) by muscle mitochondria and the reduction releases the NO ligand
Figure 1.6 Formation of Cured Meat Pigment (from Walters et al. 39)
to form a complex with metMb. This metMbNO may then be reduced with NADH (or a NADH generating system of substrate and dehydrogenase enzyme) to the cured meat pigment MbNO. Three metabolites: pyruvate, α-ketoglutarate, and succinate apparently act as substrates for NADH formation, but lactate (present in muscle in large amounts after death) is only effective in this reaction in the presence of lactate dehydrogenase from the sarcoplasm (i.e. it is not a mitochondrial enzyme). Walters et al. in a later publication examining mitochondrial enzyme pathways and their possible role during curing gave further evidence that under anaerobic conditions $\text{NO}_2^-$ can bring about the oxidation of exogenous ferrocytochrome c in the presence of intact mitochondria. Thus $\text{NO}_2^-$ acts as an inefficient electron acceptor to the mammalian respiratory chain. Cytochrome oxidase, the enzyme in the electron transport chain involved in the reduction of $\text{NO}_2^-$, also complexes with NO in the ferrous form, and may also participate in the reduction of metMbNO and metMb.

Dependence upon the tissue respiratory pathways for the formation of cured meat pigment has also been demonstrated by Watts et al. Nevertheless, this by no means excludes alternative and complementary routes of formation of the cured meat pigment. For example, Moehler has proposed that metMb, first formed by the action of $\text{NO}_2^-$ on Mb, is reduced chemically by thiols (RSH), biochemically by NADH, with FMN or FAD acting as redox intermediates, or enzymatically by an NADH-dependent dehydrogenase in the presence of cytochrome c, ultimately to MbNO. Possible enzymatic pathways for aerobic metMb reductase have been reported by other workers. Giddings has suggested that metMb reduction in post-rigor
meat is primarily enzymatic; it may involve mitochondrial and/or sub-mitochondrial particles as generators of reducing equivalents and also as scavengers of residual oxygen on vacuum packaging. Hagler et al.\textsuperscript{46} have reported the occurrence of a specific metMb reductase in beef heart muscle which rapidly and directly reduces metMb \textit{in vitro}.

A number of workers have investigated the effects of endogenous muscle metabolites including peptides, amino acids,\textsuperscript{47} and carbohydrates on the formation of cured meat pigment. Thus Tinbergen\textsuperscript{48} concluded that low molecular weight peptides (e.g. glutathione) and amino acids with free -SH groups were responsible for NO\textsubscript{2}\textsuperscript{-} reduction to NO which subsequently complexed with Mb to produce the cured meat pigment. Similar work\textsuperscript{49} also suggested glutathione and glutamate as being involved in cured colour formation. Various other reductants investigated include hydroquinone and glyceraldehyde,\textsuperscript{50} and in other work the effect of inorganic salts including NaCl, sodium polyphosphates, and FeSO\textsubscript{4} on colour formation in both model and cured meat systems has been studied.\textsuperscript{51} Fransham\textsuperscript{52} has also suggested that thiols such as cysteine or reduced glutathione may be important in cured colour formation, especially in cooked cured meat systems where enzymatic reduction is not possible due to thermal inactivation. The role of thiols in cured colour formation was investigated with a view to lowering levels of NO\textsubscript{2}\textsuperscript{-} in cured meats. Besides reducing metMb and NO\textsubscript{2}\textsuperscript{-}, thiols were implicated as intermediate carriers of NO through formation of S-nitrosothiols which can easily donate their NO to Mb. Nitrite utilisation during colour formation is improved in the presence of thiols and the residual NO\textsubscript{2}
level is lowered; this has implications in nitrosamine formation, and the use of S-nitrosocysteine as a potential curing agent to replace \( \text{NO}_2^- \) is discussed. This compound apparently has none of the hazards associated with \( \text{NO}_2^- \) (such as nitrosamine formation) in the preservation of meat by curing.

It has been demonstrated that NADH or NADPH with FMN, FAD, or riboflavin can in the presence of \( \text{NO}_2^- \) convert Mb to MbNO (and metMb to Mb) without the need for any enzymatic contribution.\(^{53,54}\) In these non-enzymatic reductions, EDTA, flavins, and methylene blue acting as mediators were said to enhance the rate of reduction very greatly, and the rates of reaction were actually faster than any enzyme-catalysed rates thus far reported. Other workers have shown that the reduction of metMb formed in cured meat can be accomplished by reduced NADH, which can be formed from NAD\(^+\) by the action of lactate dehydrogenase in the presence of lactate.\(^{55}\)

Thus there may be many routes to the cured meat pigment MbNO in this very complex system.

1.1.4 Cooked Cured Meat Colour

The colour of fresh cured meat is due to the iron mono-nitrosyl MbNO in which the Fe atom is coordinated to the four N atoms of protoporphyrin IX, one N atom of the proximal histidine of globin and the NO group. The colour of cooked cured meat, however, is due to a heat-denatured globin nitric oxide haemochromogen complex in which it is believed that the iron-imidazole bond has been broken because this pink pigment can be extracted into acetone\(^8\) (Figure 1.7). Bonnett et al. have produced direct ESR evidence for this 5-coordinate
cooked cured meat pigment, and consider uncooked bacon to be a mixture of both 5- and 6-coordinate forms.

Figure 1.7 Formation of Cooked Cured Meat Pigment

Kamerei and Karel obtained ESR spectra for frozen solutions of native bovine MbNO (buffer pH 5.5) with strongly resolved hyperfine splittings (hfs) that resembled the ESR spectrum of HbNO in the presence of inositol hexaphosphate (IHP). IHP, an allosteric effector, converts HbNO from the relaxed (R) to the tense (T) quaternary state. In the T state the bond between the proximal histidine and iron is ruptured in the α-chains of HbNO. The observed hfs were consistent with coupling with the $^{14}$N nucleus (I=1) from bound NO since there were three peaks of equal intensity. No further hfs due to the $^{14}$N nucleus of proximal histidine were detected. This was explained by assuming that the trans-effect of the NO ligand results in such a dramatic stretching of the Fe-N_HIS bond.
iron to $\text{N}_{\text{HIS}}$ occurs; thus native bovine MbNO (uncooked) behaves as pentacoordinate. However, Dickinson and Chien have previously measured the EPR spectra of single crystals of sperm whale Mb$^{14,15}\text{NO}$ (crystallised from pH 6.2 buffer) and observed for the first time clear splittings of resonance lines due to the imidazole nitrogen of histidine F-8, thus providing definite proof of 6-coordination. Clearly pH and other effects are important in determining whether native MbNO and HbNO exist as 5- or 6-coordinate species (see Section 1.1.5.4).

The identity of the ligand in the vacant coordination position in cooked cured meat pigment is uncertain, and it has been suggested, but not established by Tarladgis, from optical and EPR spectroscopy, that the pigment of cooked cured meat is a haem compound (nitric oxide myochrome) containing NO groups at both axial coordination sites (diamagnetic, no ESR signal) rather than the more widely accepted 5-coordinate denatured globin-FeNO haemochrome description of Bonnett et al.. The pigment was easily extracted into acetone but no solution infrared spectra for these extracts were presented. Further evidence for this dinitrosyl cooked cured meat pigment is available from studies in which $^{15}\text{NO}_2^-$ was used to determine the amount of $^{15}\text{NO}$ bound to unheated compared to heated solutions of Mb. Heated samples contained twice as much $^{15}\text{N}$ as unheated samples. It was considered likely that the globin portion was detached from Mb by heating, and two sites for NO binding were therefore made available. This proposed structure received support from Wayland and Olson who provided evidence of a dinitrosyl porphyrinato complex, Fe(TPP)(NO)$_2$, ...
for which the structure in Figure 1.8 was suggested. In this compound the Fe$^{II}$-NO$^{-}$ unit is isoelectronic with FeO$_2$ of oxyhaem proteins$^{65}$ and with the bent Co$^{III}$-NO$^{-}$ unit in Co(TPP)NO.$^{66}$ While the cooked cured meat pigment could have such a structure, especially with the excess of NO (NO$_2^-$) present in the cure, the presence of other 6-coordinate complexes is more likely, these having nitrogenous bases trans- to the NO ligand. Stable 5- and 6-coordinate haem nitrosyls e.g. Fe(TPP)NO,$^{67}$ (1MeIm)Fe(TPP)NO,$^{68}$ and Fe(PP$^{IX}$-DME)NO$^{69}$ are known and will be more fully discussed in Section 1.3 with the dinitrosyl Fe(TPP)(NO)$_2$.

Nitrosylhaem can be selectively extracted from MbNO and HbNO into aqueous acetone by the Hornsey method$^{70}$, which is used to determine these pigments in the food industry. Thus complexation with the strongly trans-directing nitrosyl ligand weakens the coordinate bond linking the haem and the globin. The globin portion is denatured and the nitrosylhaem enters solution. The cured meat pigments alone are cleaved by aqueous acetone, whilst the other haemoprotein derivatives (e.g. MbO$_2$, metMb, MbCO) are denatured intact. However, the Hornsey method is not specific for cooked cured meat pigments.

Figure 1.8 Proposed Structure of Fe(TPP)(NO)$_2$
as Tarladgis\textsuperscript{62} has implied, but it will be more efficient in cases where the Fe-N\textsubscript{HIS} bond is broken as in the cooked cured meat pigment.\textsuperscript{56}

The effect of heat on the quantity of \textsuperscript{15}NO fixed from Na\textsuperscript{15}NO\textsubscript{2} in the purified pigment of bovine muscle has been determined.\textsuperscript{71} 0.75 mol of \textsuperscript{15}NO/mol of pigment was incorporated in the intact (uncooked) pigment, but after heating at 100°C for 1/2 hr the quantity of \textsuperscript{15}NO fixed on the pigment had practically doubled as the globin coagulated. Longer time or higher temperature increased the precipitation of the globin fraction and the fixation of \textsuperscript{15}NO on the pigment. This result explains the better colour stability of cooked versus raw cured products. Moehler\textsuperscript{72} also found the reaction of NO\textsubscript{2} with beef muscle to be enhanced by heating.

1.1.5 Deterioration of Cured Meat Colour

Recognition of the role of reducing agents in the formation of the cured pigment has led to the deliberate addition of such substances during curing to sustain MbNO formation from residual NO\textsubscript{2} (and NO\textsubscript{3}) in the product, thereby replacing that which has been lost in various reactions on long term storage. Perhaps the most widely used reducing agent in cured meats is ascorbic acid or the isomeric erythorobic acid.\textsuperscript{73} In the case of fresh meat products, the maintenance of the attractive red colour (MbO\textsubscript{2}) is very much a matter of careful post-slaughter handling and storage, avoiding elevated temperatures and microbial growth.\textsuperscript{74, 75} For cured meats, the maintenance of a good cured colour is largely a matter of achieving the maximum conversion of the meat pigments to the relatively stable
MbNO, and obtaining a good level of residual NO$_2^-$ in the product. Similar considerations must also apply for cooked cured meats.

Woolford$^76$ in an attempt to rationalise the decreasing concentration of NO$_2^-$ in muscle with respect to time, used aqueous Mb solutions under conditions relevant to the meat curing process (i.e. pH 6.0 under anaerobic reducing conditions with NO$_2^-$, 3 mM, 200 ppm). The rate of loss of NO$_2^-$ from these model cures was studied in order to produce a 'balance sheet' of NO$_2^-$ in formation of nitrosamines. Fujimaki et al.$^77$ have also studied the fate of NO$_2^-$ in meat curing model systems composed of buffered aqueous solutions of Mb, NO$_2^-$, and ascorbate. The added NO$_2^-$ changed to HNO$_2$ under the acidic conditions used and was ultimately oxidised to NO$_3^-$, except for that which was fixed as MbNO and the stable gases N$_2$O and N$_2$. These effects are easily observed in simple systems consisting of Mb in solution, but in the case of cured meat itself, the situation is complicated by the presence of a host of other substances with which NO$_2^-$ and ascorbate can react to cause loss of cured meat colour. Using $^{15}$NO$_2^-$ it was determined$^78$ that only 70-80 % of the $^{15}$N could be recovered from cured meat; 1-5 % was released in a gaseous form, 5-15 % was combined with haem protein, 5-20 % and 1-10 % respectively remained as residual NO$_2^-$ or was converted to NO$_3^-$, 5-15 % was bound to thiols, 1-5 % to lipids, and 20-30 % to other proteins.

In the deterioration of cured meat colour there are many factors to be considered and it is best that these are dealt with individually.
1.1.5.1 Oxidation

Antonini and Brunori\textsuperscript{14} point out, that once formed, MbNO and HbNO are very stable compounds in the absence of oxygen. In the presence of oxygen the stability of the pigments is limited by the rate of dissociation from the haem complex of NO which is then irreversibly oxidised to NO\textsubscript{2} ($t_{1/2}$ for dissociation is several hours at room temperature). It is stated that oxygen does not react directly with the bound NO.\textsuperscript{14} Although the rate of dissociation is slow the complexes are also subject to photodissociation (see Section 1.1.5.). The exclusion of oxygen by vacuum packaging essentially eliminates photo-induced colour fading of cured meats by avoidance of the oxidation of the dissociating NO by oxygen.\textsuperscript{79,80} Singlet oxygen ($^{1}\text{O}_2$) generation would of course also be avoided under anaerobic conditions. Superoxide anion ($\text{O}_2^{-}$) has been implicated in the mechanism of oxidation of Hb by nitrite.\textsuperscript{81} The generation of superoxide anion during curing could have a very destructive effect on cured pigment stability. The reaction between HbNO and \text{O}_2 has been accurately followed by EPR spectroscopy and an oxygen sensitive electrode.\textsuperscript{82} HbNO prepared anaerobically was reacted with dissolved \text{O}_2 in phosphate buffer at pH 7.4, 34°C. HbNO was quantitatively converted to metHb by consuming dissolved \text{O}_2, and NO\textsubscript{3} was produced. The dissociation of HbNO was the rate-limiting step, yielding Hb and NO; and NO in solution was converted to NO\textsubscript{2}\. At higher \text{O}_2 concentrations, HbO\textsubscript{2} was transiently formed, and reacted with NO\textsubscript{2}, yielding metHb and NO\textsubscript{3}. At lower \text{O}_2 concentration, Hb reacted with NO\textsubscript{2}, yielding HbNO, metHb, and NO\textsubscript{3}. Production of NO\textsubscript{3} from NO\textsubscript{2} and \text{O}_2 was catalysed by metHb.
It is known that many haem compounds\textsuperscript{83-4} can catalyse the oxidation of unsaturated fatty acids by oxygen, and that the products of oxidation, the hydroperoxides (ROOH) can bring about the destruction of haem compounds.\textsuperscript{85} The process can be regarded as autocatalytic, and because of this there is a fairly close inter-relationship between the state of the pigments and the state of the lipids in a sample of meat. The primary reaction of the oxidative deterioration of food lipids is the combination of the lipid, principally unsaturated fatty acid residues, with molecular oxygen.\textsuperscript{86} The products of this self-propagating autoxidation reaction are hydroperoxides and the rate of autoxidation is accelerated by UV, visible, and IR light, particularly in the presence of photochemical pigments such as chlorophyll.\textsuperscript{87} Although haemoproteins may catalyse the initial dehydrogenation of a fatty acid residue, their overiding contribution to lipid oxidation is by catalysis of the decomposition of the hydroperoxides once formed. The catalysis of these reactions by haem compounds is inhibited by various antioxidants, particularly phenolic compounds.\textsuperscript{88} The effect of MbNO on lipid oxidation has been studied in linoleate and \(\beta\)-carotene/linoleate aqueous model systems and compared with that of metMb and \(\text{MbO}_2\) in short- and long-term reactions.\textsuperscript{89} Overall, metMb and \(\text{MbO}_2\) have a clear prooxidative effect, whereas under the same conditions MbNO acted as a specific antioxidant whose activity was maintained even in the presence of autoxidation catalysts such as the other haem proteins or lipoxygenase.\textsuperscript{90} MbNO probably acts as a free radical scavenger in this system.\textsuperscript{90} This would lead to destruction of the cured meat pigment with marked colour
fading. In cured meat, the curing brine itself is reported to catalyse oxidation of adipose tissue triglycerides leading to depletion of free NO$_2^-$\textsuperscript{91}. However, contradictory evidence\textsuperscript{92} showed that low concentrations of NO$_2^-$ (20-50 ppm) caused inhibition of lipid oxidation in heated water-extruded pork muscle systems catalysed by metMb or certain metal (Fe$^{2+}$, Cu$^{2+}$, Co$^{2+}$) ions. The cured meat pigment MbNO also exhibited antioxidant effects in these pork muscle systems. Progressive depletion of NO$_2^-$ was found to occur during refrigerated storage of both heated and unheated NO$_2^-$ treated pork muscle, and in model systems. Three cooperative mechanisms for the antioxidative activities in meat were proposed (a) the formation of MbNO which has antioxidant properties, (b) the formation from MbNO on heating, of a stable complex, nitrosyl-haemochrome, in which the catalytic activity of the haem Fe is now blocked and from which nonhaem iron, a highly effective autoxidation catalyst, cannot be released and (c) NO$_2^-$ appears to complex with nonhaem Fe and possibly Cu and Co forming stable complexes, thus inhibiting their catalytic activity.

\textbf{1.1.5.2 Reducing Agents}

Loss of reducing activity in meat \textit{post mortem} is due to a combination of factors including a fall in pH, depletion of required substrates and cofactors, and ultimately complete loss of the necessary structural integrity and functional properties of the mitochondria.\textsuperscript{45} The observation\textsuperscript{93} that thorough mincing destroys the reducing system in meat supports this view.

A better understanding of the interaction of ascorbate
with the cured meat system could permit more effective use of this additive. Other natural reducing agents important in meat have been mentioned in Section 1.1.3 and include cysteine and reduced glutathione (a tripeptide, \( \gamma \)-L-glutamyl-L-cysteiny1-glycine) since glutathione peroxidase, a natural muscle enzyme has these two as substrates. Glutathione peroxidase is thought to decompose fatty acid hydroperoxides \textit{in vivo}, thereby acting as a natural antioxidant.\(^{94}\)

\textbf{1.1.5.3 Radiation and the Role of Light}

Colour changes have been reported in packaged fresh meat exposed to fluorescent light (for its germicidal effect) in supermarket display cases.\(^{95}\) As well as the photochemical effects, a severe surface heating effect leading to colour deterioration was reported. The dissociation of NO from tetrameric HbNO was found to be cooperative,\(^{96,97}\) and the rate constants for dissociation of the first and fourth molecules of NO differed by about 100-fold.\(^{96}\) Normally, the rate of dissociation of NO from haem pigments is very slow, but these complexes are subject to photodissociation, although the quantum yield is very low.\(^{98}\) The haem complexes of \( \text{O}_2 \) and CO are also subject to photodissociation but with significantly higher quantum yields.\(^{98}\) The photosensitivity of haem compounds has been known for a long time.\(^{99}\) Cooked cured meat is particularly susceptible to fading when exposed to light.\(^{5}\) Elevation of temperature was found to increase the quantum efficiency of ligand (NO, \( \text{O}_2 \), CO) photodissociation from protohaem, Hb, and Mb.\(^{100}\) The photosensitivity to flash photolysis of the metal-substituted (Mn, Fe, Co) analogues of Hb, Mb, and peroxidase haemoproteins with CO, NO, and \( \text{O}_2 \) as
The photodissociative reactivity could be classified according to stereochemical and electronic effects: linear formally $d^6$ metal-ligand fragments (e.g. Fe(II)CO, Mn(II)NO) were relatively photolabile, but systems with a bent fragment and higher electron occupancy (e.g. Fe(II)O$_2$, Fe(II)NO, Co(III)NO) were relatively photoinert.$^{101}$

It has been suggested$^{102,103}$ that photo-sensitiser molecules such as riboflavin may be responsible for the initiation of the autoxidation of lipids as previously mentioned (Section 1.1.5.1), but it seems more likely that singlet oxygen may be involved.$^{104}$ Singlet oxygen is a high energy destructive oxidising species with a significant lifetime in certain biological systems, and it can be generated by energy transfer from a variety of photoenergised sensitiser molecules including flavins and certain porphyrins to ordinary ground state oxygen. Coordinated bent NO is probably a good quencher for singlet oxygen which reacts electrophilically rather than in a free radical fashion,$^{105}$ and this may explain the greater susceptibility of cured meats to light induced discoloration. However, the overall process is likely to be of low efficiency, which explains why the enhancement of pigment oxidation by light is fairly small.$^{106}$ As previously stated, one obvious way to prevent much light induced discoloration is to exclude all oxygen from packaged cured meats.

The ligand binding of NO to horse heart Mb (0.05 mM) was studied as a function of $\gamma$-radiation dose.$^{107}$ At 100 krad, the MbNO peaks at 575 and 545 nm decreased by about 50% while the peak at 410 nm decreased by 20%. Formation of MbNO
could not be detected at higher radiation doses. Evidence for conformational changes in the globin moiety caused by irradiation was presented in terms of increased susceptibility to enzymatic (trypptic) hydrolysis and changes in polyacrylamide gel electrophoretic pattern. Radiation sterilisation of cured meats containing low levels of \( \text{NO}_2^- \) induced development of colour changes. This effect was studied in greater detail by Kamerei and Karei who investigated the effects of ionising \( \gamma \)-radiation (40-4000 krad) on aqueous solutions of bovine MbNO (pH 5.5 buffer); the effects on the haem NO moiety were studied using absorption and ESR spectroscopy, and the effects on the globin by circular dichroism, electrophoresis, and isoelectric focussing. Irradiation of MbNO induces changes in the haem as well as the protein, and their results showed the following behavior: the bright red colour of MbNO changes to brown upon irradiation, as MbNO becomes progressively denitrosylated, with metMb as the immediate product. Upon increasing doses of \( \gamma \)-radiation (up to 800 krad) at 0°C, parallel to denitrosylation of MbNO, metMb is converted by water radiolytic products to other compounds including Mb, ferriMbperoxide, and choleglobin type pigments (i.e. destruction of the porphyrin ring at the highest doses). Using thermal energy analysis no NO could be detected over irradiated MbNO solution, indicating rapid reaction of radiation liberated NO with radiolytic products of water (\( \text{e}_{\text{aq}}^- \), 'OH, H'). The changes in the protein include partial denaturation of the \( \alpha \)-helix, preferential scission of the polypeptide chain, destruction of basic amino acid residues by water radiolytic products, and dimerisation of the complete molecule by covalent bonding. Freezing of the
MbNO solutions was found to have a substantial protective effect against the ionising radiation.

1.1.5.4 pH

The susceptibility of cooked hams to photo-induced discoloration was found to be dependent on pH; MbNO being significantly more stable to light irradiation at pH 6.8 than at pH 6.2 in orthophosphate buffer. The chemistry of NO₂⁻ under mildly acidic conditions, which closely resembles the situation in curing, is very complex principally because nitrous acid itself has a very complex chemistry. Treatment of porphyrins and their metal complexes with excess NaNO₂ in aqueous acidic solution (CH₃COOH-H₂SO₄) gives the meso-C-nitration products, 5-nitroporphyrins.

Denaturation of the protein, e.g. by lowering the pH or by increasing the temperature, results in the haem group becoming exposed, and binding by other ligands can then occur. The denatured protein derivatives of Mb are ferrohaemochromes (Fe(II), non oxygen sixth ligand). Several types of amino acid side chain can coordinate to the haem iron following denaturation of Mb. They may be derived from other proteins adjacent to Mb. Ferrohaemochromes readily oxidise causing permanent brown discoloration of the meat. There have been extensive visible absorption, infrared, resonance Raman, EPR, and ¹H NMR spectroscopic investigations of the haemoproteins HbNO (in the presence and absence of IHP), MbNO, and various derivatives concerned with establishing whether the nitrosyl haem group in question is 5- or 6-coordinate. Generally the spectroscopic data at high pH are consistent with 6-coordinate haem-NO, but on lowering
the pH the spectra revert to those characteristic of 5-coordinate haem-NO, consistent with Fe—N\(_{\text{HIS}}\) bond dissociation via protonation of coordinated imidazole. This bond is naturally weakened due to the trans influence of the NO ligand. Bonnett et al.\(^5\) observed ESR spectra for uncooked bacon which indicated the presence of both 5- and 6-coordinated nitrosylhaems, however, the pH conditions of the cure used in their work was not mentioned. Obviously, the pH of the curing process will determine the coordination number of the nitrosylhaem in cured meats.

1.1.5.5 Temperature

The effect of temperature on the rate of most simple chemical reactions is well known.\(^{115}\) However, the effect of temperature on such a complex system as cured meat must lead to a multitude of effects. For instance, at elevated temperatures (well below cooking temperature) there will be an increased chance of microbial spoilage of the product. The thermal history in storage of a cured meat product is going to have a significant affect on its overall quality, including the colour deterioration. The surface heating effect of germicidal UV light leading to marked colour deterioration has already been mentioned. High storage temperatures favour greater oxygen scavenging by residual respiratory enzymes as well as other oxygen consuming processes such as fat oxidation.\(^8\) Low storage temperatures on the other hand would promote increased penetration of oxygen into the surface of the meat, and consequently oxygen solubility in tissue fluids would be enhanced.\(^8\)

The development and stability of NO pigments in pre- and
post-chilled cured pork muscles has been studied. In cold brine, the differences in NO pigment content between pre- and post-chill cured muscles were not significant. The pre-chill cured muscles retained significantly greater amounts of pigments after 24 hr of light exposure. In warm brine, the pre-chill cured muscles possessed significantly higher concentrations of NO pigments than the post-chill cured muscles. The NO pigment retention was significantly greater in the pre-chill cured muscles for the 3-, 5-, and 7-hr exposures to light than in the post-chill cured muscles. The combination of pre-chill and warm brine produced the greatest colour development and stability in all muscles. The rate of formation of cured meat pigment from residual NO$_2^-$ in cured meats held in frozen storage for long periods would also be slower than that at ambient temperatures. Because of the thermal denaturation of enzymatic reducing systems, added reductants such as ascorbate or endogenous -SH compounds etc. are essential to the production and maintenance of a good cooked cured colour. However, the fact of the very destructive nature of the reducing agent ascorbate on the free NO$_2^-$ concentration during cooking should also be noted.

1.1.5.6 Heavy Metal Contamination

The autoxidation of haem pigments (especially MbO$_2$) is very susceptible to catalysis by metal ions; in phosphate buffer solution, copper was found to be the most active species, with iron, zinc, and aluminium much less so. The rate of autoxidation of Hb and Mb is increased by the presence of salt, but part of this increase is destroyed by EDTA addition, and is presumably due to trace metal
contamination of the salt. Heavy metals are also known to catalyse autoxidation of lipids by initiating free radical formation.\textsuperscript{120,121} This would have an effect on the status of the haem pigments as described in Section 1.1.5.1. Metal complexes are well known to promote N-nitrosation reactions.\textsuperscript{122} This has important implications in depletion of cured colour and formation of nitrosamines in meat.

1.1.6 Preservation of the Cured Meat Colour

Since the cured pigment MbNO is fairly stable compared with other Mb derivatives, probably the most important factor in ensuring cured colour stability is the completeness with which the meat pigments are converted to their nitrosyl derivatives. Although the amount of NO\textsubscript{2} required for the conversion of all the haem present in meat is quite low (ca. 5 ppm);\textsuperscript{123} it is essential to have an excess of free NO\textsubscript{2} present after the initial cure to ensure continued colour stability.\textsuperscript{124} Walters\textsuperscript{8} has stated that for development of a good cooked cured colour in bacon from the red uncooked form, the overall change requires a residual NO\textsubscript{2} content of about 30 ppm (0.43 mM), and to ensure a level of this order after long storage, the residual NO\textsubscript{2} content at the time of manufacture may need to be as high as 80 ppm (1.16 mmol). Other workers\textsuperscript{125} considered 100 ppm of NO\textsubscript{2} to be sufficient for the formation and upkeep of a desirable red colour of cured beef. It was considered\textsuperscript{126} that very low NO\textsubscript{2} levels may cause discolouration of cured meats, and that ascorbate is the most efficient reductant for desired pigment formation, followed by cysteine and dithionite. The relationship of added nitrate (50-5000 ppm) to pigment
formation in cured pork sausage over a 10 day storage period has been investigated.\textsuperscript{127} Higher colour stability was obtained with the use of >500 ppm nitrate, the amount of residual nitrate and nitrite being directly proportional to the initial quantity of nitrate added.\textsuperscript{127}

Ascorbate protects cured pigment once it is formed by scavenging oxygen, acting as an antioxidant to prevent lipid peroxide formation, and by generally maintaining a supply of nitric oxide from residual nitrite. But over a period of time it may lead to the destruction of the residual \( \text{NO}_2^- \), and this may impair the cooked cured colour. It was found\textsuperscript{128} that the rate of formation of \( \text{MbNO} \) in systems containing bovine \( \text{Mb} \), \( \text{NO}_2^- \), and ascorbate increases sharply with decreasing \( \text{pH} \) in the range \( \text{pH} 4.5-6.5 \), and so better control of meat \( \text{pH} \) during curing could lead to increased yields of cured colour. Tarladgis\textsuperscript{62} has recommended that colour deterioration in cured meats due to dissociation of NO from the iron porphyrin complex can be delayed by the provision of stronger reducing conditions in the medium, excess \( \text{NO}_2^- \), and by avoiding exposure to any kind of energy which may cause electronic excitation. Curing \textit{in vacuo} was found to increase the percent conversion of \( \text{Mb} \) to \( \text{MbNO} \), and increased the decomposition of \( \text{NO}_2^- \).\textsuperscript{129} Alternate vacuum application and exposure to atmospheric pressure as well as occasional mechanical manipulation further improved the product.

Kemp \textit{et al.}\textsuperscript{130} have stated that for better colour in cured meat, the omission of nitrate from the curing brine would be worthy of investigation, since it was reported that only ham cured with nitrite alone (i.e. without nitrate as a reservoir of nitrite) retained a good colour after one month
storage at 24°C. The use of a slightly more alkaline brine was also thought to give a more stable cured colour for pork. As a consequence of the discovery of nitrosamines in cooked bacon, an extensive survey of substitutes for NO$_2$-(NO) in the generation of cured colour has been conducted. Of some 300 nitrogenous compounds examined only a few gave the required pink colour, and most of these gave colours which faded rapidly. Two compounds which gave fairly stable pink colours were 3-butyroylpyridine and imidazole. Toxicity effects, however, were not mentioned in this work. A number of pyridine derivatives, especially nicotinamides, have been claimed as preservatives of the colour of cured meats by acting as ligands to the haem pigments. Some patents claim improved cured colour from the use of ascorbate and citrate, and ascorbate or the more rapidly dissolving isomeric erythorbate with isocitrate. Other patents claim improved colour intensification and stability in cured meats using glucose oxidase enzyme and chondroitin sulphate (a heteropolysaccharide) as additives to the cure.

The many factors which influence the final quality of a cured meat product especially with respect to cured colour make research in this area most difficult; this is perhaps a consequence of small chemical changes having far reaching effects. The absolute amount of haem pigment involved is very small but the effect on saleability of the product is enormous. It is clear that the essential chemistry of cured meat colour development and deterioration occurs at the haem FeNO group, but the nature, products, and reversibility of the reactions of this nitrosylmetalloporphyrin complex are very intricate.
1.2 Nitrosyl Chemistry

1.2.1 Nitric Oxide and the Coordinated Nitrosyl Group

Nitric oxide is a colourless, monomeric, paramagnetic diatomic gas at room temperature with a low melting point (−163.6°C) and a low boiling point (−151.8°C). The gas is thermodynamically unstable and decomposes into its elements at elevated temperatures (>1100°C). Nitric oxide reacts rapidly with molecular oxygen to give dark brown fumes of NO₂ (Equation 1.6), the normal product of reactions which produce NO if they are carried out in air:

\[
2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \quad (1.6)
\]

The simple LCAO-MO description of the bonding in NO is similar to that in N₂ and CO, but with an extra electron in one of the \(\pi^*\) antibonding orbitals:

**GROUND STATE ELECTRONIC CONFIGURATION OF NITRIC OXIDE**

\[
(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^1
\]

**valence bond**

**structure**

N≡O

**bond length 1.151 Å**

**bond order 2.5, \(V_{\text{NO}} 1876 \text{ cm}^{-1}\)**

This \(\pi^*\) electron effectively reduces the bond order from 3 (in N₂ and CO) to 2.5 (in NO). Nitric oxide is much more reactive than CO because of this \(\pi^*\) electron.
1.2.1.1 Transition Metal Nitrosyl Complexes

The structural, electronic, and catalytic properties of the nitrosyl group coordinated to transition metals have been the subject of numerous comprehensive reviews.\footnote{142-159} Nitric oxide can react directly with many transition metal compounds to give NO complexes, but there are many other preparative methods available.\footnote{153} The nitrosyl group shows a wide range of coordination geometries: linear, bent, doubly bridging,\footnote{160} and triply bridging.\footnote{161} This versatility of NO as a coordinating ligand arises from its unusual electronic structure and free radical nature, and NO may thus be regarded as 'electronically amphoteric'. In this review we shall concern ourselves with the details of the terminal (end-on) bonding modes of nitrosyl ligand i.e. linear and bent nitrosyl coordination.

**LINEAR NITROSYL COORDINATION** (or 3 electron donation)

From the physical data available in the literature,\footnote{149,151,158} the majority of organometallic nitrosyls involve a three electron donation. Ionisation easily removes the antibonding $\pi^*$ electron from nitric oxide (which acts as a reducing agent) to give the nitrosonium cation, $\text{NO}^+$ (Equation 1.7):

$$\text{NO} \rightarrow \text{NO}^+ + e^- \quad (1.7)$$

The ionisation potential for this process is quite low at $\text{IP}_{\text{NO}} = 9.26 \text{ eV}$ as compared to CO (14.01 eV), $\text{N}_2$ (15.58 eV), and $\text{O}_2$ (12.07 eV).\footnote{162} Formation of $\text{NO}^+$ by loss of the antibonding $\pi^*$ electron reinforces the N—O bond so that the
NO$^+$ cation has a shorter bond length,$^{141}$ a greater dissociation energy (251 kcal mol$^{-1}$) and a higher vibrational frequency at 2220 cm$^{-1}$ in HNO$_3$,$^{163}$ (and between 2150 and 2400 cm$^{-1}$ for most nitrosonium compounds$^{164}$) compared with 1876 cm$^{-1}$ for free NO.$^{165}$ In the valence bond description both atoms are sp hybridised to give a triply bonded molecule isoelectronic with CO and N$_2$: 

\[
\text{valence bond structure of NO}^+ \quad \left[ :N\equiv O : \right]^+ \\
\text{bond order 3} \\
\text{bond length 1.06 \AA}^{141}
\]

Thus NO$^+$ and CO are very similar ligands in their coordination behavior. Coordination in this mode can be imagined simply as transfer of the antibonding electron to an empty orbital on the metal, followed by formal coordination as NO$^+$, with donation of the ($\sigma_{2s}^*$)$^2$ sp hybridised lone pair electrons into empty metal orbitals, giving effectively a three electron donation to produce characteristically linear MNO complexes (MNO $\sim$ 180°), with short M—N bond distances. This is indicative of considerable back-bonding into the $\pi^*$ orbitals and is especially favoured in complexes of metal atoms with relatively high electron density, however this process does not remove electrons from the formal valence shell of the metal (Figure 1.9). 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,$^{166}$ therefore maximising $d_\pi - p_\pi$ back-bonding. As well as the short M—N
bond characteristic of good $\pi$-back-bonding the N–O bond is short also; this is nominally a triple bond weakened by the extensive metal nitrogen back-bonding. In these complexes NO acts as a $\sigma$-electron donor (Lewis base) towards transition metals and is considered formally to be NO$^+$.

**BENT NITROSYL COORDINATION** (or 1 electron donation)

In this much rarer alternative coordination mode there is formally one electron donation. This is analogous to the bent organic nitroso functional group, RNO, or in XNO compounds consisting of a doubly bonded NO, a single $\sigma$-bond between N and substituent and a lone pair on N. Using a similar description to that above, coordination in this mode is imagined as transfer of an electron of opposite spin from the metal to nitric oxide to give NO$^-:

valence bond structure $\NO^- \quad \text{bond order 2}$

of NO$^- \quad \text{bond length 1.21 Å}$
Donation of the two electrons \((\sigma_{2s}^*)^2\) from NO\(^-\) to a metal orbital gives the bent nitrosyl group (Figure 1.10).

**Figure 1.10 Schematic Picture of Bent Nitrosyl Coordination**

\[
\begin{align*}
M & \rightarrow \pi^* \\
\text{(1) } M & \rightarrow \pi^*_N \\
\text{sp}^2 \text{ hybridised} & \\
\text{lone pair} & \\
\text{(2) the effectively} & \\
\text{oxidised metal} & \\
\text{coordinates NO}^- &
\end{align*}
\]

Bending of the MNO group splits the degeneracy of the \(\pi^*\) orbitals and \(\pi\)-bonding is reduced in the plane of the bend, and so the M—N bond is somewhat longer than in M—NO\(^+\). In this bonding mode there is a lone pair localised on nitrogen which is formally sp\(^2\) hybridised to give a strongly bent nitrosyl (MNO\(\sim\)120\(^\circ\)). In bent nitrosyl complexes the NO is acting as a \(\sigma\)-electron acceptor (Lewis acid) towards transition metals and is therefore formally considered to be NO\(^-\). However, the electron affinity of NO remains unknown, and the alkali metal nitrosyls (Na,Ba) originally formulated as anionic nitrosyls,\(^{143}\) e.g. Na\(^+\)NO\(^-\), have been shown to contain the hyponitrite ion,\(^{167}\) \(\text{N}_2\text{O}_2\)^\(2^-\). The red isomer of [Co(NH\(_3\))\(_5\)NO]\(^{2+}\) was for long considered\(^{168}\) to be the only derivative of NO\(^-\), but was later found to have a dimeric cationic structure \([\text{Co(NH}_3\text{)}\text{N}_2\text{O}_2]\)^\(4^+\), where the hyponitrite ion is asymmetrically bonded in a trans conformation to the
two cobalt moieties, with IR bands assignable to the \( \text{N}_2\text{O}_2 \) ligand at 1136, 1046, and 923 cm\(^{-1} \). However, it was finally proven with the structure determination of \([\text{Co}(\text{S}_2\text{CNMe}_2)_2\text{NO}]\), though this had to be further refined, and then with the structure determination of \([\text{IrCl(CO)(NO)(PPh}_3)_2\text{BF}_4]\) the nitrosyl tetrafluoroborate oxidative addition product of Vaska's complex, that a bent MNO linkage in a metal nitrosyl complex was possible. The iridium complex is square pyramidal with \( \text{IrNO} = 124^\circ \), a long Ir–N bond of 1.97 Å, much longer than representative M–N bond distances in linear metal nitrosyls, and \( \nu_{\text{NO}} \) 1680 cm\(^{-1} \) in the region where RNO absorb. The criterion of formal oxidation state of coordinated nitric oxide is therefore the bond angle of the MNO group. A linear MNO group with a short M–N distance characterises \( \text{NO}^+ \), whereas a bent MNO group with a longer M–N distance characterises \( \text{NO}^- \). ESR experiments have shown that an intermediate situation may exist in which the unpaired electron is either retained on the NO group (M\( \rightarrow \text{NO} \)) in which nitric oxide bonds by donation of two electrons to the metal from neutral NO\(^*\), or delocalised in a MO extending over the entire complex which then behaves like a free-radical species. But this is thought not to be common.

After a comprehensive investigation of the IR spectra of metal nitrosyls, it was concluded that the coordinated NO groups absorb in the wide range from ca. 1045 to 1980 cm\(^{-1} \), but that the majority of compounds have NO stretching frequencies lying in the range 1580 to 1980 cm\(^{-1} \); it was suggested that in these compounds coordination was of the linear type \( \text{(NO}^+ \)\). The few complexes with NO absorptions in
the range 1045 to 1580 cm\(^{-1}\) were considered to involve bonding of NO\(^-\)\(^{174}\). These earlier \(v_{\text{NO}}\) ranges have been re-classified and it was suggested\(^{175}\) that since ionic NO\(^+\) is isoelectronic with dinitrogen (N\(_2\)), with \(v_{\text{N-N}}\) 2331 cm\(^{-1}\), nitrosyls with \(v_{\text{NO}}\) in the region 1700 to 1900 cm\(^{-1}\) may be regarded as containing NO\(^+\); and since the NO\(^-\) ion is isoelectronic with dioxygen (O\(_2\)) with \(v_{\text{O-O}}\) 1555 cm\(^{-1}\) (Raman active band) nitrosyls with \(v_{\text{NO}}\) in the region 1500 to 1700 cm\(^{-1}\) can be considered to contain NO\(^-\). Gray et al.\(^{176}\) have suggested that all compounds containing coordinated NO\(^+\) have a linear MNO grouping, and complexes containing NO\(^+\) or NO\(^-\) are expected to have a bent MNO group, thereby providing a nondegenerate level for an extra electron to enter. Symons et al.\(^{177}\) have suggested \(v_{\text{NO}}\) ca. 1900 cm\(^{-1}\) for linear MNO and \(v_{\text{NO}}\) ca. 1650 cm\(^{-1}\) for bent MNO groups. It has though been pointed out that a definite distinction between NO\(^+\) and NO\(^-\) in metal complexes is not possible using \(v_{\text{NO}}\) values alone,\(^{178}\) and a direct correlation between \(v_{\text{NO}}\) and M—N bond distance is not possible either.\(^{148}\) The stretching frequency ranges quoted most recently for coordinated nitrosyl overlap and are 2000-1600 cm\(^{-1}\) (linear) and 1725-1525 cm\(^{-1}\) (bent).\(^{179}\) It is this overlap which has limited the usefulness of the IR technique as a structural probe. The use of \(^{15}\)N NMR as a criterion of MNO bond geometry in this context is discussed in Section 2.3.8.2.1. Although the NO group generally occurs as a terminal ligand, bridging NO groups are known (\(v_{\text{NO}}\) 1350-1500 cm\(^{-1}\)) where NO acts as a 3 electron donor.\(^{160-1}\)

Bent nitrosyl (\(\angle\text{MNO} = 120^\circ\)) in ML\(_5\)NO complexes is known to exhibit large structural trans effects, with the trans axial M—L bond being longer than the cis M—L bond. Linear
nitrosyl in such complexes does not exhibit this effect. The bent NO\(^-\) group (M\(^{\wedge}\)NO = 121.3\(^\circ\)) in \([\text{CoCl(\text{en})}_2\text{NO}]^+\) cation exhibits a pronounced structural trans influence (ca. 0.3 Å), as evidenced by the very long Co—Cl distance of 2.576(3) Å. The different trans influences of NO\(^+\) and NO\(^-\) are consistent with the suggestion based on calculated overlap integrals that strong σ-donor and weak π-acceptor ligands will exert a trans bond weakening effect. Detailed IR studies support the idea that NO\(^+\) is the best π-acceptor ligand.

The formal valence bond segregation of transition metal nitrosyls into complexes of NO\(^+\) and NO\(^-\), while useful in the above discussion, is unrealistic, and the bonding in these complexes is better thought of in terms of a MO approach allowing for considerable metal-ligand electron delocalization. In a MO representation the number, symmetry type, and relative energy of the orbitals contributed by the metal and associated ligands as well as the NO group are important. Consequently nitrosyl bonding to transition metals has been described in terms of MO theory by many authors and some of the more important concepts are reviewed in Section 1.2.2.

### 1.2.2 Bonding Theories

As the chemistry of metal nitrosyl compounds progressed, and more experimental data (X-ray structures and spectroscopy) became available, the theories of bonding in these compounds became more fully developed to account for the diversity of structural and electronic types observed.

Gray et al. first presented MO schemes to account for the electronic spectra of linear nitrosyl and carbonyl
compounds such as Fe(S₂CNMe₂)₂NO and Mn(CO)₅X (X = NO⁻, Br⁻, Cl⁻, I⁻). The orbital scheme developed assumed that one strong field NO or CO ligand bonded in a distorted octahedral structure (C₄ᵥ) dominated the overall ligand field, and this was considered correct whether or not a trans axial ligand was present (i.e. for 5- and 6-coordination).

Pierpont and Eisenberg¹⁸⁵ examined nitrosyl bonding in 5- and 6-coordinate tetragonal complexes and presented the first MO explanation of linear versus bent NO bonding using procedures earlier developed by Walsh for triatomic species.¹⁸⁶ The bonding characteristics of some first row transition metal pentacyanonitrosyl complexes (d⁴, d⁵, d⁶) of C₄ᵥ symmetry were examined via MO calculations.¹⁸⁷ A correlation was obtained between the square of the stretching frequency (v² NO) and the electron occupancy of (and therefore back-bonding into) the antibonding 2π orbital of the nitrosyl group.

Mingos reported¹⁸⁸ some MO calculations for [Co(NH₃)₅-NO]²⁺ (CoNO, 180 → 90°) and showed that the energetics of angular distortion of the metal nitrosyl from linearity influenced the stability of only two metal-ligand MO's substantially. The calculations suggested that the a₁(d² z) antibonding metal-ligand σ orbital and the eₓ(π* NO, dₓz) metal-ligand antibonding orbital have the same symmetry and similar energies in the distorted molecule and therefore strongly mix to give rise to a more bonding a'(π* NO, d² z), and a less bonding a'(d² z, π* NO) pair. The energy separation between these orbitals was shown to be approximately proportional to distortion angle, and electron occupation of the more stable a'(π* NO, d² z) would lead to an energetically
favourable distortion. The relative stability of 
[Co(NH₃)₅NO]²⁺ as a function of the angle of the coordinating 
nitrosyl has also been investigated by a series of other MO 
calculations. It was found that the most stable conformer 
is the one in which the nitrosyl bends in such a manner as to 
eclipse an equatorial NH₃ ligand. The preference of an 
eclipsed conformer to its staggered counterpart was 
interpreted as due to enhanced electrostatic interaction 
attendant upon bending of the nitrosyl.

Wayland et al. reported electronic and EPR spectra 
for CoTPP complexes of CO, NO, O₂, RNC, and (RO)₃P and 
proposed a general MO bonding model for Co(II) and Fe(II) 
porphyrin complexes based on the previous methods of 
Mingos and Pierpont and Eisenberg. The model was found 
to be compatible with the available electronic, magnetic, and 
structural data for these metalloporphyrin complexes and 
could consequently be used as a basis for a model of the 
 bonding in MbO₂.

By this time X-ray studies were showing that 
unconstrained 5-coordinate ML₄NO d⁸ metal nitrosyl complexes 
are either square pyramidal with bent apical nitrosyl, 
MNO~120°, or trigonal bipyramidal with linear equatorial 
nitrosyl, MNO~180°, and consequently the bonding models 
being developed had to account readily for this behavior.

Enemark and Feltham published in 1974 perhaps the 
most complete description of the bonding in metal nitrosyl 
complexes which adequately accounts for all their known 
structural, physical, and chemical properties by using the MO 
correlation method originally used by Walsh. This was 
basically the same method as previously used by Pierpont and
Eisenberg and Mingos but was more fully developed to take into account the ambiguities of the orderings of the energy levels of the MO's. The MO correlation diagrams were obtained by treating each $M(NO)_x$ moiety as a covalently bound inorganic functional group which is perturbed by the coordination of the other ligands to the metal and then correlating all reasonable MO orderings of the complex in various geometries. The results presented established that the properties of nitrosyl complexes are determined primarily by the nature of the HOMO. The authors devised the notation $[MNO]^n$ for describing transition metal nitrosyl complexes where $n$ corresponds to the number of d electrons on the metal when the nitrosyl is considered to be formally NO$^+$. In a [CoNO]$^8$ complex there are totally eight electrons in the d shell of the metal and the $\pi^*$ orbitals of the ligating nitrosyl. Complexes with six or fewer electrons in this $d\pi - \pi^*$ manifold are expected to be linear, electrons occupying the nonbonding $xy$ orbital (z axis being that of the nitrosyl), and the symmetric admixtures of the metal orbitals with the nitrosyl $\pi^*$ orbitals. Bent nitrosyls are destabilised in this regime for $[MNO]^n$ when $n < 6$ due to reduced metal-to-ligand back-bonding in the plane defined by the metal nitrosyl linkage. Addition of two more electrons to form $[MNO]^8$ complexes radically changes the picture. The next lowest-lying levels are the $\pi^*$ orbitals of the nitrosyl ligand. If the nitrosyl bends, one of the $\pi^*$ orbitals is allowed to mix with the vacant $d^2$ orbital of the metal thereby stabilising the complex. In linear coordination such interaction is symmetry forbidden. Consequently, on addition of the seventh and eighth electrons to the $d\pi - \pi^*$ manifold,
bending of the nitrosyl is observed (Figure 1.11).

Hoffman et al.\textsuperscript{191} published the other outstanding paper on MO theory of nitrosyls in the same year. The work was concerned solely with pentacoordinate nitrosyls using the frontier orbital approach. The MO model was based on a MNO bonding scheme derived from the interaction of a ML\textsubscript{4} fragment of varying geometry and a NO group, to account for the range of coordination geometries of nitrosyls established crystallographically. The results established an important set of rules and were based on conservation of orbital symmetry arguments combined with extended Huckel calculations on [IrCl\textsubscript{4}NO]\textsuperscript{2-} (square pyramidal, apical NO), IrCl\textsubscript{2}(PH\textsubscript{3})\textsubscript{2}NO (distorted square pyramidal, apical NO), and Mn(CO)\textsubscript{4}NO (TBP, equatorial NO). The concepts\textsuperscript{191} applied to unconstrained [MNO]\textsubscript{8} systems lead to the following conclusions below.

For square pyramidal nitrosyls the better the $\sigma$- or $\pi$-donating capability of the basal ligands, the more likely the nitrosyl is to bend. In compounds of the type ML\textsubscript{2}L\textsubscript{1}NO, L \textit{trans} to L, the nitrosyl group should bend in the plane containing the poorer donors. In a compound of the type ML\textsubscript{2}DA(NO), D = $\pi$-donor \textit{trans} to A = $\pi$-acceptor, if the NO group bends in the DMA plane then it should bend toward the acceptor.

For trigonal bipyramidal nitrosyls the nitrosyl is less likely to bend in the equatorial position of a TBP than in the apical site of a SP. If a nitrosyl in the equatorial position of a TBP bends, then it would prefer to bend in the axial plane rather than the equatorial one. Nitrosyl groups in axial positions in a TBP and in basal sites in a SP prefer to be linearly coordinated. In ML\textsubscript{4}NO species, if L are
Figure 1.11 Bending of the [Co(NO)₈] Moiety: Molecular Orbital Correlation Diagram for Five-coordinate Complexes of the [Co(NO)₈] Group in Ligand Fields of C₅ᵥ, C₄ᵥ, and C₃ᵥ Symmetry. The Orbitals are Occupied by a Total of Eight Electrons.
strong $\pi$-acceptor ligands, a TBP with an equatorial nitrosyl will be preferred. If the ligands are strong $\pi$-donors a range of geometries is possible, from a strongly bent SP to a less bent TBP. A bent nitrosyl will move its nitrogen off the coordination axis in the direction of $\pi$-coordination.

Wayland and Newman$^{192}$ further applied MO theory to complexes of diatomic molecules including NO, CO, and O$_2$ with metalloporphyrins (Cr, Mn, Fe, Co, Ni, Cu). The porphyrin ligand constrains the systems to strict square pyramidal geometry in 5-coordination. Hawkins and Hall$^{193}$ performed MO calculations on some square pyramidal iron nitrosyls of the $[\text{FeNO}]^6$, $[\text{FeNO}]^7$, and $[\text{FeNO}]^8$ configurations and confirmed the earlier reports$^{151}$ for these systems: $[\text{FeNO}]^6$, linear NO; $[\text{FeNO}]^7$, wide variety of geometry; $[\text{FeNO}]^8$, bent NO, and also confirmed for $[\text{Fe(CO)}_2(\text{CN})_2\text{NO}]^-$ that the nitrosyl does bend in the plane of the better $\pi$-acceptor (CO plane) as suggested by Hoffman et al.$^{191}$

Other MO calculations have been reported for the nitrosyl complexes Co(CO)$_3$NO and Mn(CO)$_4$NO,$^{194}$ the linear and bent conformations of the NiNO moiety (Ni 3d$^{10}$ configuration),$^{195}$ and pentacoordinate Fe(S$_2$CRN$_2$)$_2$X (X = NO, Cl, Br, I, NCS) complexes.$^{196}$ In a MO study of $[\text{Fe(CN)}_5\text{NO}]^{2-}$, $[\text{Mn(CN)}_5\text{NO}]^{3-}$, and $[\text{V(CN)}_5\text{NO}]^{3-}$ it has been shown$^{197}$ that the HOMO is an orbital of $\pi$-symmetry localised on the CN$^-$ ligand, and the LUMO is a degenerate $\pi^*$ MNO orbital localised mainly on nitrogen but with varying amounts of metal and cis (but not trans) ligand character. Analysis of the character and energy of the LUMO orbitals as a function of ligand electronegativity, total number of electrons, and nature of metal shows that nucleophilic attack or reduction at the N atom is
favoured over the same reactions at the metal for complexes to the right of the transition series, with high formal charge on the metal. More advanced MO calculations on similar complexes ([M(CN)\textsubscript{5}NO]\textsuperscript{N\textsuperscript{-}}, M = Fe, Cr, Mn) showed the HOMO to be of mixed character.

Experimentally measured nitrogen 1s electron binding energies have been correlated with charges on nitrogen from extended Huckel calculations, and therefore formal oxidation states for various simple inorganic and organic compounds containing nitrogen including nitrates, nitrites, azides, pyridines, and cyano and nitroso compounds. This work was later extended to a study of N\textsubscript{1s} binding energies in relation to electronic structure, bonding, and v\textsubscript{NO} in transition metal nitrosyls (bent and linear). Correlations were found between the N\textsubscript{1s} binding energy of a nitrosyl group and its electron density, and the binding energies were roughly directly proportional to v\textsubscript{NO} (with bent nitrosyls having lower binding energies). A more recent study of charge transfer in back-bonding to coordinated linear nitrosyl and carbonyl groups showed reasonable correlations between N\textsubscript{1s} binding energies versus NO stretching force constants and between O\textsubscript{1s} binding energies versus NO stretching force constants. This indicated that the N and O core binding energies could be taken as measures of d\textsubscript{π} → π\textsuperscript{*} back-bonding in metal nitrosyl compounds, and that in back-bonding to NO similar amounts of charge are transferred to the N and O atoms. The C, N, and O core valence-valence Auger spectra of NO, CO, Co(CO)\textsubscript{3}NO, Fe(CO)\textsubscript{5}, and Mo(CO)\textsubscript{6} have been obtained. These spectra were interpreted qualitatively in terms of ground state MO
descriptions, and of the polarisation of the orbital electron density distribution. The N and O spectra of NO were found to be far more similar than the C and O spectra of CO, reflecting a more equal electron density distribution of the valence Mo's.\textsuperscript{201}

Enemark and Feltham have reviewed the extensive structural data from X-ray, neutron and electron diffraction, and microwave spectroscopy reported up to the end of 1979.\textsuperscript{158} They suggested that the general theoretical base developed above provides a framework for correlating the chemical properties and structural features of transition metal nitrosyls, and that structural data undoubtedly helped to develop the current theories of bonding for metal nitrosyls.\textsuperscript{151,191}

### 1.3 Nitrosylmetalloporphyrins

The structure and bonding of the diatomic molecules O\textsubscript{2}, NO, and CO coordinated to metalloporphyrins have been intensively investigated. Model compounds are obviously important in understanding the stereochemistry of the ligated haem groups of haemoproteins. The stereochemical trends in the coordination geometry of the nitrosylmetalloporphyrins are in reasonable accord with the bonding theories available. Table 1.2 gives structural and spectroscopic data for the coordination sphere of structurally characterised nitrosylmetalloporphyrins.

Reduction by zinc amalgam of Mo(IV)(TTP)Cl\textsubscript{2} (TTP is the dianion of meso-tetra-p-tolylporphyrin) in benzene under NO led to a green solution from which crystals of [cis-Mo(TTP)-(NO)\textsubscript{2}].C\textsubscript{6}H\textsubscript{6} (v\textsubscript{NO} 1740 and 1600 cm\textsuperscript{-1}) were isolated.\textsuperscript{202} When
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\hat{\text{NO}}$</th>
<th>$M-N_p$</th>
<th>$M-\text{NO}$</th>
<th>$N-O$</th>
<th>$M-$porph</th>
<th>$M-X_{\text{AXIAL}}$</th>
<th>$X_{\text{MN}}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(TTP)(NO)(MeOH)</td>
<td>179.8(4)</td>
<td>2.091(4)</td>
<td>1.746(6)</td>
<td>n.g.</td>
<td>0.28</td>
<td>2.284(5)</td>
<td>n.g.</td>
<td>202</td>
</tr>
<tr>
<td>([MNO]$^5$, $v_{\text{NO}}$ 1540 cm$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>cis-Mo(TTP)(NO)$_2$</td>
<td>158.0(8)</td>
<td>2.135(8)</td>
<td>1.70(1)</td>
<td>n.g.</td>
<td>0.99</td>
<td></td>
<td></td>
<td>202</td>
</tr>
<tr>
<td>([M(NO)$<em>2$]$^6$, $v</em>{\text{NO}}$ 1740, 1600 cm$^{-1}$)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Mn(TTP)NO</td>
<td>177.8(3)</td>
<td>2.004(5)</td>
<td>1.641(2)</td>
<td>1.160(3)</td>
<td>0.34</td>
<td></td>
<td></td>
<td>203</td>
</tr>
<tr>
<td>([MNO]$^6$, $v_{\text{NO}}$ 1735 cm$^{-1}$)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Mn(TPP)(NO)(4Mepip)</td>
<td>176.2(5)</td>
<td>2.027(3)</td>
<td>1.644(5)</td>
<td>1.176(7)</td>
<td>0.10</td>
<td>2.206(5)</td>
<td>177.2(2)</td>
<td>203</td>
</tr>
<tr>
<td>([MNO]$^6$, $v_{\text{NO}}$ 1740 cm$^{-1}$)</td>
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<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td><a href="ClO$_4$">Fe(OEP)(NO)</a></td>
<td>176.9(3)</td>
<td>1.9994(1)</td>
<td>1.644(3)</td>
<td>1.112(4)</td>
<td>0.32</td>
<td></td>
<td></td>
<td>207</td>
</tr>
<tr>
<td>([MNO]$^6$, $v_{\text{NO}}$ 1862 cm$^{-1}$)</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
\[
\begin{array}{cccccccc}
\text{Complex} & \text{M—N}_p & \text{M—porph, displace-} & \text{M—N}_p & \text{M—porph, displace-} & \text{M—N}_p & \text{M—porph, displace-} \\
& \text{metry of metal centre from the least squares mean porphyrin plane. n.g. = value not given.} \\
\end{array}
\]
this green solution was chromatographed on alumina using CH₂Cl₂-CH₃OH as eluant it became red and [Mo(TTP)(NO)-(CH₃OH)].2C₆H₆ (v_NO 1540 cm⁻¹) crystallised. Structural data for these two molybdenum complexes ([M(NO)₂]⁶ and [MNO]⁵ respectively) are shown in Table 1.2. The mononitrosyl is linear (MNO 179.8°) as expected for a [MNO]⁵ moiety. The slight bending of the cis-nitrosyl groups in cis-Mo(TTP)(NO)₂ (average MNO 158°) is a common perturbation in polynitrosyl complexes.¹⁵¹,¹⁵₈ The cis-geometry is probably due in part to the large size of the Mo atom relative to the size of the hole in TTP²⁻ and in part to the propensity of the π-accepting nitrosyl ligands to adopt cis-geometry. Under NO the mononitrosyl reverts progressively to the diamagnetic di-nitrosyl; the paramagnetic mononitrosyl behaves as a low spin d⁵ species (S=1/2, ν_eff = 1.71 BM) giving a characteristic 6-line ESR signal with ⁹⁵,⁹⁷Mo (I=5/2) hyperfine splitting, and absence of ¹⁴N hyperfine structure consistent with the localisation of the unpaired electron in the Mo d_xy level.²⁰²

The structural characterisation of [Mn(II)(TTP)NO].C₆H₆ (v_NO 1735 cm⁻¹)²⁰³ and [Mn(II)(TPP)(NO)(4Mepip)] (v_NO 1740 cm⁻¹)²⁰³,²⁰⁴ allows comparison of the stereochemical changes accompanying the addition of a sixth ligand to the [MNO]⁶ coordination sphere. Both complexes have essentially linear MnNO groups (MnNO 177.8(3)° and 176.2(5)° respectively), an expected feature of [MnNO]⁶ systems. The Mn—N_NO bond distances (1.641(2) and 1.644(5) Å respectively) are not much affected by the increase in coordination number, nor is v_NO in these complexes. However, the Mn—N_p bond distance is lengthened, and the addition of a sixth ligand leads to a substantially smaller displacement of Mn from the porphyrin
A similar comparison of the coordination group geometries of the two low spin Fe(II) complexes, Fe(TPP)NO \( (\nu_{NO} 1670 \text{ cm}^{-1}) \) and Fe(TPP)(NO)(1MeIm) \( (\nu_{NO} 1625 \text{ cm}^{-1}) \) displays the stereochemical effects of adding a sixth ligand to the \([\text{MNO}])^7\) coordination sphere. Changes in Fe—N distances are minimal, increasing from 2.001 Å in Fe(TPP)NO to 2.008 Å in the six-coordinate Fe(TPP)(NO)(1MeIm). The Fe—N distance of 1.717 Å for Fe(TPP)NO increases to 1.743 Å upon addition of the sixth ligand, and FeNO decreases by 7°. The axial FeNO groups are decidedly nonlinear with FeNO of 149.2(6)° in Fe(TPP)(NO) and 142.1(6)° in Fe(TPP)(NO)(1MeIm). The displacement of the iron atom out-of-plane of the porphyrinato nitrogens decreases some 0.14 Å to 0.07 Å in Fe(TPP)(NO)(1MeIm). The large out-of-plane displacement for low spin Fe(NO) of 0.21 Å is attributed to non-bonded contact repulsions between the single axial ligand and the N atoms of the porphyrinato core, because low spin Fe(II) porphyrins are expected to have Fe—N bond distances sufficiently short to allow centralisation of the metal ion in the porphyrinato mean plane, unlike high spin 5-coordinate Fe(II) and Fe(III) porphyrins in which the Fe—N distances (>2.07 Å) are too long to permit this centralisation. The 0.03 Å increase in the Fe—N length and the 7° decrease in FeNO in this 6-coordinate versus 5-coordinate complex suggest decreased \(\pi\)-bonding between Fe and NO, the presumed consequence of the trans-1-methylimidazole ligand. The long Fe—N bond of 2.180(4) Å in Fe(TPP)(NO)(1MeIm) was thought to be the result of a structural trans-effect from
the NO of 0.2 Å in magnitude with respect to other 6-coordinate iron porphyrin complexes. This long bond was not attributed to steric interactions but rather to electronic effects and is the consequence of the partial donation of the unpaired electron of NO to the $d_z^2$ orbital of the iron which is an antibonding orbital with respect to the axial Fe—N $\text{MeIm}$ bond. A similar structural trans-effect is seen in [CoCl(en)$_2$(NO)]$^+$. Structural data from X-ray measurements (2.8 Å resolution) are available for horse-heart HbNO. The FeNO was found to be 145±10°, with Fe—N$_{\text{NO}}$ of 1.74 Å and N—O of 1.1 Å. These results are in reasonable agreement with the above data on Fe(TPP) nitrosyls. The significantly different Fe—N$_{\text{AXIAL}}$ bond lengths in the two crystalline forms of (4Mepip)Fe(TPP)NO do not appear to be attributable to steric interaction between atoms of the trans-axial ligand and atoms of the porphyrinato core. The Fe—N$_{\text{4Mepip}}$ bond length in (4Mepip)Fe(TPP)NO.CHCl$_3$ is 2.328(10) Å and in (4Mepip)Fe(TPP)NO is 2.463(7) Å. These data and the comparable data for (1MeIm)Fe(TPP)NO (Table 1.2) provide a remarkably linear correlation between the Fe—N$_{\text{AXIAL}}$ bond distance and $\nu_{\text{NO}}$ in these 6-coordinate [FeNO] complexes.

Fe(TPP)NO is an [FeNO]$^+$ complex and thus has only one electron in an orbital which favours bending of the NO ligand. It is therefore reasonable to expect that the MNO is substantially larger in Fe(TPP)NO than in the [CoNO]$^8$ complex, Co(TPP)NO, which has two such electrons. Diamagnetic Co(TPP)NO crystallises preferentially from CH$_2$Cl$_2$-piperidine solutions in which the 6-coordinate (pip)Co(TPP)NO is presumed to be the most plentiful species. The [CoNO]$^8$...
complex is square pyramidal with a strongly bent CoNO linkage of 135°. The electron configuration for Co(TPP)NO best corresponds to the formulation Co(III)NO⁻.

The preparation and structural characterisation of the two low spin Fe(III), [FeNO]⁶ complexes, [Fe(TPP)(NO)-(H₂O)](ClO₄) and [Fe(OEP)NO](ClO₄), were reported.²⁰⁷ The structural features are distinctly different from those of the [FeNO]⁷ species. A comparison of the axial bonding parameters of the two [FeNO]⁶ complexes with the [FeNO]⁷ complexes and with the isoelectronic [MnNO]⁶ species is seen from Table 1.2. The two [FeNO]⁶ complexes have shorter Fe—N_NO bonds and more linear FeNO groups relative to the [FeNO]⁷ species. But the length of the Fe—N_NO bonds is comparable to that of the [MnNO]⁶ species. The 6-coordinate [FeNO]⁷ complexes all display a significant lengthening of the bond trans- to the NO ligand, this is not expected nor observed in the [FeNO]⁶ complex [Fe(TPP)(NO)(H₂O)](ClO₄). The observed v(NO) of 1862 cm⁻¹ for [Fe(OEP)NO](ClO₄) and 1937 cm⁻¹ for [Fe(TPP)(NO)(H₂O)](ClO₄) are well outside the range of 1625 to 1675 cm⁻¹ observed for the analogous Fe(II) species. The cations of the 6-coordinate [Fe(TPP)(NO)(H₂O)](ClO₄) are well separated in the crystalline lattice. In contrast the 5-coordinate [Fe(OEP)NO](ClO₄) forms a very tight π—π dimer complex with the two planar cores parallel with an interplanar separation of only 3.36 Å.²⁰⁷

Nitric oxide forms 1:1 low spin complexes with M(II)(TPP) and M(III)(TPP)(X) species (M = Cr, Mn; X = Cl⁻, CH₃COO⁻, CN⁻).²⁰⁸ Exposure of toluene solutions of Mn(TPP)(X) (high spin d⁴) to NO leads directly to Mn(TPP)(X)(NO) (v(NO) 1830 cm⁻¹). Reduction by NaBH₄ of green Mn(TPP)(X) solutions
gives violet high spin Mn(II)(TPP) \((\mathbf{d}^5, S=5/2)\) which then reacts with NO to give red-orange solutions of low spin Mn(TPP)NO \([\text{Mn(I)NO}^+, [\text{MnNO}]^6, \nu_{\text{NO}} 1760 \text{ cm}^{-1}]\). In the presence of methanol Cr(III)(TPP)(OMe) reacts with NO to form the red solid Cr(TPP)NO \((\nu_{\text{NO}} 1700 \text{ cm}^{-1})\) via the proposed intermediate Cr(TPP)(OMe)(NO) in a reductive nitrosylation reaction. The isoelectronic \([\text{MNO}]^5\) complexes, Mn(TPP)(X)(NO) and Cr(TPP)NO, have \(S=1/2\) ground states \([\langle \mathbf{d}_{xz}, \mathbf{d}_{yz} \rangle^4, \langle \mathbf{d}_{xy} \rangle^1\]\) and EPR spectral parameters indicative of the odd electron occupying a molecular orbital of predominantly metal \(d_{xy}\) character.\(^{208}\) In the formal sense these linear \([\text{MNO}]^5\) complexes may be described as Mn(II)(TPP)(X~)(NO+) and Cr(I)(TPP)(NO+), although \(d_{xz,yz} \rightarrow \pi^*\) back-bonding reduces the MNO charge separation.

The reversible reaction of solid Fe(TPP)Cl with gaseous nitric oxide to form solid Fe(TPP)(Cl)(NO) \((\nu_{\text{NO}} 1881 \text{ cm}^{-1})\) was reported by Vaska and Nakai.\(^{209}\) The NO uptake by solid Fe(TPP)Cl is slow and equilibration \((P_{\text{NO}} 760 \text{ mmHg at } 25^\circ\text{C})\) is only attained after ca. 7 days in 92 % yield. However, in \(\text{CH}_2\text{Cl}_2\) or \(\text{CHCl}_3\) solution adduct formation is fast. The product Fe(TPP)(Cl)(NO) was found to be unstable with respect to disociation of NO in the solid state and in solution, and the authors claimed the compound to be high spin \((\mu_{\text{eff}} = 4.5 \text{ BM})\). This reaction was studied in more detail by Wayland and Olson\(^{64}\) who found Fe(TPP)(Cl)(NO) to be diamagnetic. The reaction was studied spectroscopically in toluene solution, glass media, and nujol mulls. In the presence of methanol Fe(TPP)Cl (high spin \(S=5/2\)) reacts with excess NO to produce Fe(II)(TPP)NO. This reaction is thought to proceed via the methanolysis of coordinated NO+ in the intermediate
Fe(II)(TPP)(Cl^-)(NO^+) complex. Fe(II)(TPP)NO has a doublet ground state ($S=1/2$) with the odd electron in a molecular orbital with Fe(d$_z^2$) and NO($\sigma_N$) character and exhibits Curie behaviour from 270 to 330 K. Toluene glass EPR spectra show $^{14}$N hyperfine structure from the axial NO. Nitrogen donors add to Fe(II)(TPP)NO in the vacant sixth coordination position, and these complexes have EPR spectra showing $^{14}$N hyperfine structure from both N bonded ligands. A second molecule of NO is reversibly coordinated by Fe(TPP)NO to form diamagnetic Fe(TPP)(NO)$_2$ which on the basis of magnetic and spectroscopic properties is formulated as Fe(II)(TPP)(NO^-)(NO^+) The two nitrosyl stretching frequencies observed at 1690 and 1870 cm$^{-1}$ are consistent with linear Fe(II)NO$^+$ and bent Fe(II)NO$^-$ units. The preparation and characterisation of Ru(II)(MP$_{IX}$DME)(NO)$_2$ (MP$_{IX}$DME = mesoporphyrinato IX dimethylester) has been reported. The infrared spectrum (nujol mull) of this complex exhibited two strong bands at 1786 and 1838 cm$^{-1}$ and although this was originally attributed to a solid state effect, this Ru(II) complex is probably best formulated as containing both coordinated NO$^+$ and NO$^-$ in analogy with the isoelectronic Fe(TPP)(NO)$_2$. Toluene solutions of Co(TPP)NO were found to add nitric oxide sequentially to form first an unstable low spin ($S=1/2$) complex, Co(TPP)(NO)$_2$ at low NO pressures (0.1 to 5 mmHg), and then a diamagnetic species tentatively formulated as [Co(TPP)(NO)(N$_2$O$_2$)] at higher (>20 mmHg) NO pressures. The three species are readily interconverted on changing the equilibrium NO pressure. The dinitrosyl has a single $\nu_{NO}$ at 1696 cm$^{-1}$ characteristic of two bent CoNO units. The single additional electron, which according to preliminary EPR
measurements entered the NO π-system in Co(TPP)(NO)₂ (a formally [Co(NO)₂]⁹ species), was thought to be responsible for the observed equivalency of the NO moieties.²¹¹ The rhodium porphyrins [Rh(OEP)]₂, Rh(OEP)H, and Rh(OEP)Cl all were found on reaction with nitric oxide to yield the same product Rh(OEP)NO (v(NO) 1630 cm⁻¹).²¹² The reactions of Rh(OEP)Cl and Rh(TPP)Cl with NO proceeded through a metastable paramagnetic intermediate ([Rh(III)(porph)]²⁺(Cl⁻)(NO⁻)) which from EPR, electronic spectral, and electrochemical studies was formulated as containing a porphyrin π-cationic radical unit with an ²A₁u ground state caused by intramolecular oxidation (or electron abstraction) of the porphyrin ligand by incoming NO.²¹² Rh(OEP)(NO)(Cl) was found to further associate to form a radical dimer (S=1), but only monomeric Rh(TPP)(NO)(Cl) (S=1/2) was observed and this probably reflects the increased steric requirements of TPP. Rh(OEP)NO and Rh(TPP)NO in toluene or CHCl₃ solution also interact reversibly with NO to form paramagnetic cationic radical (S=1/2) dinitrosyls ([Rh(porph)]²⁺(NO⁻)₂). The earlier reported²¹¹ cobalt dinitrosyl Co(TPP)(NO)₂ may be reformulated as a porphyrin cationic radical species ([Co(TPP)]²⁺(NO⁻)₂) with the odd electron occupying an ²A₂u molecular orbital.²¹²

The quantum yield 𝛿 = 0.08 to 0.1 for NO photodissociation from Fe(PP°IX)(1MeIm)(NO) in the presence of excess 1MeIm is wavelength independent,²¹³ but for Fe(PP°IX)NO 𝛿 = 0.05 to 0.08. The results are important in understanding haem-ligand photodissociation. In contrast, for Mb and T- and R-state Hb, 𝛿 = 10⁻³. The NO binding rate for the 5-coordinate model complex, Fe(PP°IX)(1MeIm) was found to be
an order of magnitude greater than for the haemoproteins. Comparisons between results for model compounds and those for haemoproteins are useful in examining the mechanisms by which the properties of the haem group are modulated by a protein environment. The above observations were thought to arise because a ligand can only enter or exit the haem pocket through a restricted pathway.\textsuperscript{213}

The adducts of Co(TPP) with the axial ligands CO, \textsuperscript{13}CO, NO, \textsuperscript{16}O\textsubscript{2}, \textsuperscript{16}O\textsubscript{18}O, and \textsuperscript{18}O\textsubscript{2} have been studied in Ar and/or Kr matrices by infrared spectroscopy.\textsuperscript{214} Co(TPP)NO was found to have \textit{v}_{\text{NO}} at 1690 cm\textsuperscript{-1} in a Kr matrix and 1693 cm\textsuperscript{-1} in Ar. Formation of the mixed ligand adduct Co(TPP)(CO)(NO) with \textit{v}_{\text{NO}} at 1683 cm\textsuperscript{-1} in Ar was also confirmed.\textsuperscript{214}

The action of NO on the $\beta$-crystalline forms of metal phthalocyanines of the first transition series from Cr to Cu and on VO(Pc) has been investigated.\textsuperscript{215} Cr(II)(Pc), Mn(II)(Pc), Fe(II)(Pc), and Co(II)(Pc) all react with NO to form the mononitrosyl derivatives which have \textit{v}_{\text{NO}} at 1690, 1685, and 1705 cm\textsuperscript{-1} respectively for Cr(Pc)NO, Fe(Pc)NO, and Co(Pc)NO. The IR spectrum of Mn(Pc)NO is dependent upon sample preparation and exhibits two forms; form A with \textit{v}_{\text{NO}} at 1631 and 1753 cm\textsuperscript{-1}, and form B at 1763 cm\textsuperscript{-1}. The other complexes Ni(II)(Pc), Cu(II)(Pc), and VO(Pc) do not react with NO. The 5-coordinate complexes Cr(Pc)NO and Mn(Pc)NO react with pyridine to form the corresponding 6-coordinate complexes Cr(Pc)(NO)(py) ($\textit{v}_{\text{NO}}$ 1680 cm\textsuperscript{-1}) and Mn(Pc)(NO)(py) ($\textit{v}_{\text{NO}}$ 1737 cm\textsuperscript{-1}). In the presence of pyridine Co(Pc)NO and Fe(Pc)NO decompose with loss of NO to form M(Pc)(py)$_2$. Otherwise, the air-stable Co(Pc)NO and Fe(Pc)NO derivatives are very robust compounds and dissolve in concentrated H$_2$SO$_4$. 
to be precipitated unchanged on dilution with water. The air-sensitive Cr(Pc)NO and Mn(Pc)NO are stable only under an inert atmosphere.\textsuperscript{215} In later work it was found that the $\alpha$-forms of Cr(II)(Pc), Fe(II)(Pc), and Co(II)(Pc) do not react with NO.\textsuperscript{216} The different behaviour of the $\alpha$-forms from that of the $\beta$-forms may be accounted for on the basis of their different crystal structure. Detailed IR studies suggested that steric factors associated with the arrangement of the molecules in the crystal lattice are as important in determining the manner of metal-NO binding as the structure of the molecule and the central metal ion.\textsuperscript{216} An X-ray photoelectron spectroscopic study of nitrosyl metal (Fe, Co, Mn) phthalocyanines showed the metal 2p and 3s binding energies to change considerably on coordination, consistent with electron transfer from metal to NO in Fe and Co and from NO to Mn in the complexes.\textsuperscript{217} The observed shifts are qualitatively consistent with the assumed MNO configurations ($M^{-}NO^{+}$ for Mn(Pc)NO and $M^{+}NO^{-}$ for Fe(Pc)NO and Co(Pc)NO).\textsuperscript{217}

The preparation of a nitrosyl haem Fe(OAPMe$_2$)$_2$NO ($v_{NO}$ 1685 cm$^{-1}$) has been briefly described (OAPMe$_2$ = $\alpha,\gamma$-dimethyl-$\alpha,\gamma$-dihydro-octaethylporphyrinato).\textsuperscript{218}

The electrochemically reversible one-electron oxidation and facile one-electron reduction of Fe(porph)NO (porph = TPP, OEP) to yield [Fe(porph)NO]$^{+}$ and [Fe(porph)NO]$^{-}$ respectively in CH$_2$Cl$_2$ and pyridine was reported.\textsuperscript{219} Both mononitrosyls were stable in CH$_2$Cl$_2$; while in pyridine partial dissociation of NO occurred both before and after oxidation. Oxidation of Fe(porph)NO greatly increases the lability of the nitrosyl ligand. However electrolysis under NO produces the dinitrosyl [Fe(porph)(NO)$_2$]$^{+}$ (S=1/2) with $v_{NO}$
at 1940 and 1860 cm$^{-1}$ for the TPP derivative. The odd electron in Fe(porph)NO is known from ESR studies to occupy a bonding orbital with Fe $d_z^2$ and $\sigma_N$ character.\textsuperscript{64} One-electron reduction of Fe(porph)NO should place an electron in this $\sigma$-bonding orbital, which will be substantially delocalised onto the NO ligand. The relative ease of reduction of Fe(TPP)NO (-0.93 V in CH$_2$Cl$_2$) is consistent with the electron going into a bonding orbital. Oxidation of Fe(porph)NO removes the single bonding electron with a consequent labilisation of the nitrosyl ligand. Addition of a second NO molecule results in a low spin complex, with occupation of the Fe $d_z^2$ orbital as required by the appearance of hyperfine splitting in the ESR spectrum from the two axial nitrogens.

The electrochemistry of Fe(II)(porph)NO (porph = TPP, OEP) was further investigated in nine nonaqueous solvents.\textsuperscript{220} In weakly coordinating solvents such as CH$_2$Cl$_2$ or PhCN, five diffusion-controlled one-electron transfer reactions were observed. Three of these reactions were oxidations, the remaining two reactions involved reversible electro-reductions, either at the Fe(II) centre or at the porphyrin ring. In strongly coordinating solvents such as DMSO or pyridine, similar redox reactions were observed, but coupled to some of the electron transfer steps were a number of chemical reactions such as NO displacement by solvent coordination. The data provide evidence for the stabilisation of the Fe(II) oxidation state with respect to Fe(III) in Fe(TPP)NO. The electrochemistry of Fe(porph)NO is however greatly dependent upon the solvent binding ability. Binding of one or two nitrosyl ligands to Fe(porph) generates dramatic shifts of redox potentials for oxidation and
reduction of the relatively stable Fe(II), the magnitude of the shifts being larger for the dinitrosyl complexes. The spectrophotometric and electrochemical characterisation of Cr(TPP)NO in eleven nonaqueous solvents was reported. Cr(TPP)NO exhibits two reversible one-electron reductions. The metal-centred rapid one-electron oxidation of Cr(TPP)NO to [Cr(TPP)NO]⁺ is irreversible in all solvents studied because after reduction [Cr(TPP)NO]⁺ decomposes to [Cr(TPP)]⁺ and NO (an EC mechanism). Nitrosylation was found to stabilise the divalent state of chromium. The electron-transfer and ligand-addition of Mn(TPP)NO and Co(TPP)NO were studied in nine nonaqueous solvents. In all solvents, stable complexes of [Co(TPP)NO]⁻, [Co(TPP)NO]⁺, [Mn(TPP)NO]⁻, and [Mn(TPP)NO]²⁻ could be generated at the electrode surface. In contrast [Mn(TPP)NO]⁺ was not stable and rapidly decomposed to yield [Mn(TPP)]⁺ and NO. The investigations in mixed-solvent systems provide clear evidence for the presence of [Co(TPP)(NO)(L)]⁺ and [Mn(TPP)(NO)(L)] in solution where L = DMF, DMSO, and pyridine.

The synthesis, characterisation, and electrochemical properties in nonaqueous media under various NO pressures of the twelve neutral diamagnetic Fe(II)(porph)(NO)(R) complexes (where porph = TPP, OEP and R = CH₃⁻, n-C₄H₉⁻, C₆H₅⁻, p-CH₃C₆H₄⁻, p-CH₃OC₆H₄⁻, and C₆F₉⁻) have been presented. Air-stable Fe(porph)NO complexes contain Fe(II) which depending on the porphyrin ring is oxidised to Fe(III) in a range of potential between 0.6 and 0.8 V (versus SCE). In contrast, 5-coordinate σ-bonded alkyl- or aryl-ironporphyrins contain Fe(III) in stable form, and these complexes may be reduced to Fe(II) in the range -0.7 to -1.0 V depending on
the porphyrin ring and the type of bound alkyl- or aryl-group. However, in the 6-coordinate complexes it appears from the electrochemical evidence that the effect of an NO molecule in stabilising the Fe(II)porphyrin oxidation state is greater than that of the σ-bonded aryl group in producing the Fe(III) species because there is more than 1.5 V difference between electrooxidation and electroreduction of Fe(porph)(NO)(C₆H₅) and Fe(porph)(C₆H₅) in the same solvent and electrolyte. Values of $v_{NO}$ for each of the Fe(porph)-(NO)(R) complexes range between 1764 and 1850 cm⁻¹ depending upon the nature of the porphyrin ligand and the specific alkyl- or aryl-ligand. The $v_{NO}$ of the 6-coordinate complexes correlate quite well with the electron donor properties of the alkyl- or aryl-group; the more electron donating the R group the lower the nitrosyl stretching frequency.

The effects of the fifth ligand on NO nitrogen hyperfine interactions in Fe(OEP)(NO)(B) and Fe(TPP)(NO)(B) (B = axial nitrogenous base) was investigated by ENDOR spectroscopy (which is a useful technique for resolving hyperfine coupling data hidden beneath wide lines in EPR spectra). The results showed the FeNO conformation in these model complexes to vary with axial base, and it was implied that changes of the MbFeNO angle with temperature, accompanying changes of the spin density on the nitrogen orbitals in the NO ligand reported previously in EPR spectra of single crystals of MbNO, may relate to changes in the strength of the interaction between the Fe and the fifth ligand His F8.

Fe(II)(PpΙXDME)NO ($v_{NO}$ 1655 cm⁻¹) was synthesised and characterised by IR and EPR spectra in a variety of solvents. The EPR spectra suggested a bending of the FeNO
unit, and that the unpaired electron of the nitrosyl group is considerably delocalised to the iron $d_{z^2}$ orbital. The EPR parameters of the 5-coordinate Fe(PP$^{IX}$DME)NO in the glass state were nearly identical to those of IHP treated HbNO$^{227}$ suggesting that the Fe–$N_{\text{HIS}}$ bond in IHP treated HbNO is stretched or cleaved.$^{59,60}$

It has been found that the EPR and IR spectroscopic parameters of Fe(PP$^{IX}$DME)NO complex are very sensitive to changes in the trans-axial base and to polarity and hydrogen bonding ability of the solvent.$^{69,226,228}$ The IR spectra of Fe(PP$^{IX}$DME)(NO)(B) complexes (B = various nitrogenous axial bases including imidazoles, pyridines, cyclic secondary amines, and aliphatic amines) were measured in benzene or 1,2-dichloroethane solution.$^{229}$ The nitrosyl stretching frequencies of these complexes decreased and the equilibrium constant for $[\text{Fe(PP}^{IX}\text{DME)NO}] + B \rightleftharpoons [\text{Fe(PP}^{IX}\text{DME)(NO)(B)}]$ increased respectively with an increase in the ligand basicity $[pK_a(B^+)]$ ($v_{\text{NO}}$ was found to decrease in the order: cyclic amines > aliphatic amines > pyridines > imidazoles, and the equilibrium constants for imidazoles were larger than for pyridines). Similar variations with $pK_a(B^+)$ of axial base were observed for previously determined EPR spectral parameters of Fe(PP$^{IX}$DME)(NO)(B)$^{228}$ The results indicate that the extra stabilisation of the Fe–$N_{\text{HIS}}$ bond arises from the $d_{\pi} -- p_{\pi}$ bonding involving the destabilisation of the $\pi^*$ NO orbital, and imidazoles have greater $\pi$-bonding ability than pyridines.$^{229}$

Further studies on 5-coordinate Fe(PP$^{IX}$DME)NO have shown the EPR spectra of the frozen toluene solution to be sensitive to sample preparation.$^{230}$ The EPR spectra of the
slowly frozen (opaque glass) and the rapidly frozen (transparent glass) samples differed in line shape and the absorptions were assigned to different concentrations of the dimer and the monomer of the nitrosyl in each case. A previous report had shown that [Fe(OEP)NO]ClO_4 in the solid state forms a π-π dimer in which both nitrosyl groups are oriented outwards. The EPR intensity of the dimer absorption in opaque glass state was found to be much lower than that in the transparent glass state, especially with lower concentrations of Fe(PPDME)NO. These EPR parameters of the transparent toluene glass were found to be quite similar to those of HbNO denatured by sodium dodecyl sulphate detergent.

EPR and electronic spectra at room temperature and 77 K of Fe(PPDME)(NO)(B) have suggested that azolate (deprot- onated imidazole, Im^-) complexes have a weaker iron to NO bond and a stronger iron to trans-axial ligand bond than azole (ImH) complexes, and that overall azolate, Im^-, has a much greater σ-donor ability (or basicity) than ImH. This weakening of the Fe-NO bond may facilitate the dissociation of the nitrosyl ligand. Accordingly, it was suggested that complete deprotonation to Im^- or fractional deprotonation by hydrogen bonding of proximal histidine imidazole NH to amino acid residues of the polypeptide chain in haemoproteins could enhance the reactivity of the trans-axial NO ligand. Other work has reported EPR, IR, and electronic spectroscopic studies of Fe(PPDME)NO adducts with various N-, O-, and S-donor bases as axial ligands trans- to the nitrosyl group. In all cases the spectral parameters were dependent upon the electronic and stereochemical properties.
of the axial ligands.

Ultimately in the reactions of NO with the haemoproteins Mb and Hb, the only stable product observed is the [FeNO]\(^7\) species, irrespective of whether the haem group was originally in the Fe(II) or Fe(III) state.\(^31,61\) Other haemoproteins including horseradish peroxidase, cytochrome c peroxidase,\(^234\) and cytochrome c\(^235\) react to yield stable low spin ferric nitrosyl complexes, which do not possess an EPR spectrum.\(^234\) The susceptibility of these ferric haem proteins to reduction by nitric oxide appears to be related to the magnitude of their oxidation-reduction potentials.\(^234\) The related ferrous nitrosyl species of peroxidases and cytochrome c can also be prepared; these derivatives are low spin (S=1/2) compounds.\(^234\) Both the Fe(III) and Fe(II) haems of nitrite reductases have been detected.\(^236\) These enzymes catalyse the one-electron reduction of NO\(^2^-\) to NO. In comparison the reaction of Fe(II) and Fe(III) porphyrinato complexes with NO normally yields 5- and 6-coordinate [FeNO]\(^7\) species as detailed above. The ferric reactant is reduced in an apparently facile process called reductive nitrosylation in the presence of base.\(^64\)

Space constraints have prevented a survey of nitrosyl-haemoprotein chemistry, but the range of bonding and stereochemistry in nitrosylmetalloporphyrin chemistry has been presented.
CHAPTER 2. EXPERIMENTAL TECHNIQUES AND BACKGROUND TO
SPECTROSCOPIC INVESTIGATIONS

2.1 Preparative Methods

2.1.1 Technique for Manipulation of Air-Sensitive Compounds

Some compounds prepared in this work are extremely sensitive to atmospheric oxidation, particularly in solution. Consequently, where it was necessary preparations and subsequent manipulations were carried out under dinitrogen using techniques similar to those described by Larkworthy. The apparatus used is shown in Figure 2.1 and consists of an all-glass manifold with a mercury manometer, M, which can be connected via socket V to an Edwards high vacuum pump, and via port N to a supply of commercial 'whitespot' oxygen-free nitrogen. The nitrogen was further purified before entry into the line by passage through a column C of oxygen-scavenging solid and a column D of drying agent (anhydrous magnesium perchlorate). The solid in C is prepared from CrO$_3$ and SiO$_2$ gel heated to 500°C under CO gas; this gives a self-indicating blue powder (Cr(II) adsorbed on SiO$_2$) which can be used at room temperature. Excess nitrogen pressure in the line could be vented via the bubblers B. There are two main positions on the apparatus to which reaction vessels can be attached: P$_1$, which is used in conjunction with the trap assembly, T, for drying, and P$_2$, which allows the reaction vessel to be connected via flexible tubing for ease of manipulation.

The methods used were very similar to conventional
Figure 2.1 Nitrogen Line Apparatus

Catalyst Column C

Drying Agent Column D

N₂ Supply In, N

N₂ Sweep

N₂ Out

Bubblers B

Traps T

To Vacuum Pump, V

Position P₁

Mercury Manometer M

Position P₂
Schlenk techniques except that the purity of the nitrogen was exceptional (the apparatus was designed for study of the coordination chemistry of extremely air-sensitive Fe(II), Cr(II), and V(II) complexes), and the system is entirely anaerobic with no opening of the flasks to the atmosphere when joining apparatus together. Glass 3-tap reaction vessels of the detachable type (Figures 2.2(a), (b), (c)) or the complete type (Figure 2.3) could be used thoroughly greased (Apiezon L, M, or T) and held together by steel springs. Flasks equipped with greaseless taps were also available. The reaction apparatus was deoxygenated thoroughly by evacuation and nitrogen flushing (three times).

Air-sensitive products could be isolated by filtration through wide-bore (6 mm) glass taps onto sintered glass filters. A schematic diagram of a typical filtration assembly is shown in Figure 2.4(a) with a typical glass filter shown in Figure 2.4(b). The filters have taps at the top and bottom to ensure total exclusion of air instead of at the side as in Schlenkware. After adequate drying of products under vacuum, the opening of the filter unit or reaction vessel could be performed in a nitrogen atmosphere glove box, and characterisation could be undertaken. Excess sample was stored either under nitrogen in tubes of the type shown in Figure 2.5(a) with well-fitting caps (Figure 2.5(b)), greased and held together with steel springs, or under vacuum in flame-sealed glass tubes.
Figure 2.2 Detachable 3 Tap Apparatus

Quickfit B34 Joints

(a)  (b)  (c)

Figure 2.3 Complete 3 Tap Flask (greased or greaseless (PTFE) taps can be used)
2.1.2 General Method for Synthesis of Metal Nitrosyl Complexes

2.1.2.1 Preparation and Purification of Nitric Oxide

The apparatus used for generation of pure nitric oxide for use in synthesis of nitrosyl complexes is shown in Figure 2.6. Nitric oxide gas was produced according to Blanchard.\textsuperscript{238} Equal volumes of aqueous iron(II) sulphate heptahydrate (1 M solution, acidified with 55 ml 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 screwclips SC closed, to remove any traces of NO\textsubscript{2} or H\textsubscript{2}O present). This produces a large "brown-ring" reaction,\textsuperscript{173} and thermal decomposition of the brown-ring complex gives nitric oxide according to Equation 2.1:

\[
2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}
\]

Previous IR analysis of the reaction gases showed that nitric oxide generated from the decomposition of the brown ring complex contained very little impurities, with mainly unreactive N\textsubscript{2}O, and some NO\textsubscript{2} present, although no quantitative estimates were made.\textsuperscript{23} The nitric oxide generated filled vessel C, and the excess 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
Figure 2.6 Apparatus for Generation of Nitric Oxide and Preparation of Nitrosyl Complexes
was purified first by passage through the dry ice-acetone trap E and then through column F containing solid KOH pellets and column G containing 4Å type molecular sieves (to remove any residual traces of NO₂ or moisture present). The pressure of nitric oxide in the line apparatus compared to atmospheric was measured using the mercury manometer M. More nitric oxide could be generated as required during the preparations by draining off the spent reaction mixture tap T in the bottom of flask C and then allowing more reactants to mix in C.

2.1.2.2 Use of the Nitric Oxide Line in Preparation of Nitrosyl Complexes

In the preparation of nitrosyl complexes the two-neck reaction vessel L was normally used. Depending on the preparation either the sidearm N, a stopper, or a subaseal could be used (Figure 2.7). The solid reactant(s) were accurately weighed into the reaction vessel, and the appropriate amount of solvent and a magnetic follower were added. The reaction vessel was then attached to the NO line at tap Z, via a short length of rubber tubing, and mounted just clear (ca. 2 cm) of the magnetic stirrer S to prevent any undesirable heating of the flask during the reaction.

With taps H, Y, V, and R closed and X and Z open (Figures 2.6 and 2.7), the apparatus was evacuated up to the manometer M via tap W, and then the reaction vessel and contents were very carefully evacuated using tap R. Taps R and W were then closed and the apparatus was filled with nitrogen from tap V. Nitrogen was carefully admitted into the reaction flask using tap R, and the pressure was equalised to atmospheric. The entire process was repeated twice more to
Figure 2.7 Reaction Flask Assembly
For Preparation of Nitrosyl Complexes

Figure 2.8 Transfer of $^{15}$NO Gas to Gas Burette J
remove any air present in the system and thoroughly deoxygenate the solvent. The reaction flask and rubber connecting tube were left under vacuum with taps R and Z closed until the reaction was initiated. With care low boiling solvents could be prevented from bumping under low pressure by cooling the reaction vessel in liquid nitrogen and then continuing the evacuation-nitrogen flushing procedure as above, warming each time to room temperature when flushing with nitrogen to deoxygenate the solvent.

The gas burette J was evacuated, care being taken not to let mercury pass through the tap Y, and filled with nitrogen three times as above, and left filled with mercury with Y closed. Then the apparatus was evacuated with taps H, Y, Z and R closed. Tap W was closed and the nitric oxide from vessel D was allowed to enter the evacuated apparatus by adjusting D'. The gas was drawn into the burette J by lowering the mercury storage reservoir J' after carefully opening tap Y. When sufficient nitric oxide had entered burette J, tap Y was closed and J' adjusted until the levels of mercury in the two arms of the burette were equal. Tap Z was now opened followed by tap R, thus admitting nitric oxide into the evacuated reaction vessel, the pressure being equalised to atmospheric very quickly. The flask was gently swirled to allow the solvent to equilibrate with the gas and then the burette was opened to the reaction flask by opening tap Y. The levels in J were quickly adjusted and the initial volume was noted at the start of the reaction. Taps H and X had been closed to isolate the reaction assembly from the rest of the apparatus. The stirrer S was started and the uptake of nitric oxide followed with the gas burette J. The
room temperature from the thermometer attached to the gas burette and the atmospheric pressure were noted.

If it was necessary to refill J during the reaction, taps Y, Z, and R were closed and the gas burette refilled by opening H, and then taps X and Y. When the burette contained sufficient nitric oxide, taps H, X, and Y were closed, the new level in J was noted, taps Y, Z, and R were reopened, and the reaction continued. If the reaction was particularly slow and required stirring under nitric oxide overnight or longer, tap R was closed since rubber tubing absorbs nitric oxide over extended periods of time. At the end of the required time, the temperature, pressure, and burette readings immediately before and after opening tap R were noted, indicating any changes in gas volume which could be taken into account when calculating the volume uptake of the reaction at STP. Any further gas uptake during reaction was followed by burette J. The moles of nitric oxide combined per mole of complex were calculated from the volume uptake of gas. No correction was made for the vapour pressure of the solvent. The reaction flask was evacuated and filled with nitrogen before work-up of the reaction mixture.

2.1.3 Synthesis of $^{15}$N Nitrosyl Complexes

2.1.3.1 From Gaseous $^{15}$NO

In the earlier part of the work 99% labelled $^{15}$N nitric oxide gas in 100 ml flasks was kindly supplied by Dr Joan Mason of the Open University. The flasks were joined by the glassblower to a short B14 cone and attached at tap Q to the apparatus shown in Figure 2.8 which was connected to the
nitric oxide line at tap Z. The $^{15}$NO was transferred to the gas burette J in the following manner. The apparatus was degassed as usual up to capillary bulb K' with tap Q open. Tap Q was closed. Burette J was evacuated and filled with mercury. Taps X, Y, and Z were closed, and the apparatus above X was filled with nitrogen to atmospheric pressure. The glass seal on flask K was broken with the iron rod I using a small magnet. Taps Q and Z were opened to release the $^{15}$NO and then tap Y was opened with care to allow the $^{15}$NO into the gas burette J in suitable quantity. To remove all the $^{15}$NO from bulb K, taps Y and Z were closed and tap Q was opened. Bulb K' was immersed in liquid nitrogen, and the remaining $^{15}$NO condensed into bulb K', leaving K essentially empty. Tap Q was then closed and K' allowed to warm up to room temperature. As the solid $^{15}$NO evaporated, taps Z and Y were opened, allowing the gas into burette J. Tap Y was closed and the pressure in the burette was equalised to atmospheric. To recover any $^{15}$NO in the apparatus including the burette and bulb K', bulb K was immersed in liquid nitrogen to condense the gas back, and then taps Q and Z were closed. Thus $^{15}$NO could be transferred to and from the gas burette J with minimum loss. Flask K and K' were then removed from tap Z and the reaction vessel attached.

2.1.3.2 Synthesis of $^{15}$NO from Na$^{15}$NO$_2$

In later work gaseous $^{15}$NO became unavailable and it was necessary to generate the gas from 99 % labelled Na$^{15}$NO$_2$ (also supplied by Dr Joan Mason) according to methods in Brauer, modified for small quantities. The gas was generated in the apparatus shown in Figure 2.9, which
Figure 2.9 Apparatus for Preparation of $^{15}$N Nitric Oxide from $^{15}$NO$_2$.
consists of a 3-tap bulb apparatus with capillary tubing to lessen dead-space connected via a right-angled bend to a two-neck 100 ml pear-shape flask, F, equipped with a glass vacuum tap, D on the side arm with a subaseal wired on.

In a typical experiment AnalaR FeSO$_4$.7H$_2$O (0.6375 g, 2.3 mmol), NaBr (0.6375 g, 6.25 mmol), and Na$^{15}$NO$_2$ (0.3 g, 4.3 mmol) were layered alternately in the pear-shape flask F and a small stirring bar was placed carefully on top of the undisturbed reaction mixture. The apparatus was carefully deoxygenated, placed under nitrogen, and the dry reaction mixture frozen in liquid nitrogen. Deoxygenated water (0.5 ml) was injected via the subaseal through the side arm tap D onto the top of the reaction mixture and tap D was closed. The reaction flask F and frozen contents were then evacuated of nitrogen, and tap A was closed. With taps B and C open, the Dewar was removed from under flask F and placed under bulb E to allow the nitric oxide formed during the reaction to condense in the capillary bulb (the level of the liquid nitrogen was not too high, so that the NO condensed in the bulb and did not block the capillary tube). Flask F was allowed to warm to room temperature with stirring to initiate the reaction. The colour changed to brown, with vigorous effervescence of nitric oxide which condensed in bulb E. After reaction was complete (ca. 30 min with warming), tap B was closed and as the Dewar was removed from bulb E, tap A and the tap Y on the burette were quickly opened to allow the rapidly evaporating $^{15}$NO into the burette.

The above method was thoroughly tested with unlabelled sodium nitrite before the $^{15}$N labelled salt was used. Yields of nitric oxide ranging from 55 to 63 % were obtained.
2.2 Purification of Solvents and Reagents

Unless otherwise stated solvents and reagents were purchased from Aldrich or BDH and used as received. However, during the work certain solvents and reagents were purified according to literature methods. 240

2.2.1 Reagents

Acetylacetone was washed with 2M NaOH until the aqueous layer remained alkaline, and then with water; after drying over Na$_2$SO$_4$ it was fractionally distilled under nitrogen immediately before use.

Benzaldehyde was washed with 10% Na$_2$CO$_3$ solution until no more CO$_2$ was evolved, and then with water. After drying over MgSO$_4$ it was fractionally distilled under nitrogen at reduced pressure, and stored under nitrogen.

Ethyl cyanoacetate was washed with 10% Na$_2$CO$_3$ solution, and then with water. After drying over Na$_2$SO$_4$ it was fractionally distilled under reduced nitrogen pressure immediately before use.

Pyrrole was predried with solid NaOH, then fractionally distilled under reduced nitrogen pressure from sodium wire, and stored under nitrogen in the dark.

Pyridine and 2,6-lutidine were purified by refluxing over solid KOH for 2 hr, followed by fractional distillation.

1-Methylimidazole was distilled under reduced nitrogen pressure from solid KOH.

2.2.2 Solvents

Acetone was purified by addition of successive small portions of KMnO$_4$ at reflux, until the violet colour per-
sisted, and, after drying over activated 4Å Linde molecular sieves, it was distilled.

'Ethanol-free' chloroform was prepared by washing commercial CHCl₃ (containing 1% ethanol as stabiliser) thoroughly with water, predrying over CaCl₂, then refluxing from P₂O₅ under N₂. It was stored in the dark.

Benzene and toluene were each shaken with cold concentrated H₂SO₄ (to remove thiophens), then water, dilute NaOH, then water again. After predrying over CaCl₂ they were distilled from sodium or P₂O₅.

N,N'-Dimethylformamide was stored over activated 4Å Linde molecular sieves and distilled under reduced nitrogen pressure immediately before use.

Dichloromethane was washed with cold concentrated H₂SO₄ until the acid layer remained colourless, then with water, dilute Na₂CO₃, then water again. After predrying over CaCl₂, it was distilled from P₂O₅ into brown glass reagent bottles containing 4Å molecular sieves and kept in the dark.

Tetrahydrofuran was distilled under N₂ after refluxing over LiAlH₄ and was stored in the dark.

1,2-Dimethoxyethane was distilled from sodium wire.

2.2.3 Chromatographic Materials

Silica gel (Merck grades 60-120 mesh and 230-400 mesh, 500 m²g⁻¹) and alumina (standard grades neutral and basic) supplied by BDH were stored in an oven at 180°C until required. The activity of the alumina for column chromatography was standardised by the Brockmann method of measuring the adsorption behaviour of a number of azo-dyes on a small column of dry alumina. Silica gel and alumina
preparative TLC plates (1 mm thick, 200 mm x 200 mm or 76 mm x 52 mm size) were prepared by Mr Vic Zettel of the Chemistry Department using silica kieselgel 150G/LS 254 (Schleicher and Schull) supplied by Anderman and Co, and aluminium oxide 60 GF\textsubscript{254} neutral (type E) catalogue number 1092, Merck supplied by BDH, respectively.

2.3 Experimental Methods

2.3.1 Microanalyses

Microanalyses of stable and air-sensitive compounds were performed by Mr Errol Hopwood and Miss Nicola Watts of the Chemistry Department.

2.3.2 Mass Spectrometry

Mass spectra were recorded by Mr Jim Delderfield of the Chemistry Department on the MS12 mass spectrometer.

2.3.3 Magnetochemistry

Room temperature magnetic susceptibility measurements were recorded on the Johnson Matthey Equipment magnetic susceptibility balance model number MSB 1. Variable temperature magnetic susceptibility measurements were recorded on the Newport Instruments variable temperature Gouy balance. A full treatment of magnetochemistry is in the literature\textsuperscript{242} and is not considered in detail here.

2.3.4 Single Crystal X-Ray Crystallography

Crystallographic data were collected on the Enraf-Nonius CAD4 X-ray diffractometer and the structure solution was
carried out by Mr Glen Smith of the Chemistry Department.

2.3.5 Mossbauer Spectroscopy

The Mossbauer measurements were performed by Prof E Konig and colleagues at the University of Erlangen-Nurnberg, West Germany.

2.3.6 Infrared spectroscopy

IR spectra of compounds prepared in this work were recorded on a Perkin Elmer PE577 IR grating spectrometer either as pressed KBr discs (1 cm dia) or as nujol mulls between KBr plates in the range 4000 to 200 cm\(^{-1}\).

2.3.6.1 IR Spectroscopy of Nitrosyls and Coordinated Nitrite

The vibrational spectroscopy of porphyrins and metallo-porphyrins is adequately covered in two reviews\textsuperscript{243} and is not considered in detail here.

IR spectroscopy has been the accepted method for characterising transition metal nitrosyl complexes.\textsuperscript{244} The skeletal vibrations of MNO groups are found in two distinct regions: 1500-2000 cm\(^{-1}\) (\(v_{\text{NO}}\)) and below 650 cm\(^{-1}\) (\(v_{\text{M-N}}\) and \(\delta_{\text{MNO}}\)).\textsuperscript{245} The N-O stretching frequency is usually the major peak in the entire IR spectrum which shifts ca. 25-40 cm\(^{-1}\) to lower wavenumber upon \(^{15}\)N substitution. The strong bands identified as \(v_{\text{NO}}\) are usually very broad and frequently have shoulders or are split by as much as 30 cm\(^{-1}\). It is now widely accepted that \(v_{\text{NO}}\) alone is of limited use for distinguishing between linear and bent MNO geometry since IR regions characteristic of linear (2000-1600 cm\(^{-1}\)) and bent
Values of $v_{M-N}$ and $\delta_{MNO}$ are not often reported due to difficulties in distinguishing these relatively weak bands [$\delta_{MNO}$ 500-650 cm$^{-1}$; $v_{M-N}$ 280-650 cm$^{-1}$] from the many strong bands arising from the other ligands. However, $^{15}$N substitution has made unequivocal assignment possible in some NO (and NO$_2^-$) complexes.

The nitrite ion, NO$_2^-$ coordinates to metal ions in many ways. As a monodentate ligand it may bond either through nitrogen to form the well-known nitro complexes or through one oxygen atom to give the less common nitrito complexes. It may chelate through both oxygen atoms, and it may also function as a bridging ligand with either nitrogen and oxygen or both oxygen atoms acting as donors (Figure 2.10). Vibrational spectroscopy is very useful in distinguishing between these structures. The normal vibrations of the monodentate N-bonded nitro ligand may be approximated by those of a planar ZXY$_2$ molecule (Figure 2.11). Typical values for Group VIII MNO$_2^-$ complexes are given in Table 2.1.

Since the asymmetric ($v_{as}$) and symmetric ($v_s$) NO$_2$ stretches and NO$_2$ deformations ($\delta$) of NO$_2^-$ are nondegenerate modes, the number of IR bands arising from these does not change on coordination. However, shifts of $v_{as}$ and $v_s$ from the free ion values (e.g. NaN$_2$: $v_{as}$ 1250 cm$^{-1}$ and $v_s$ 1335 cm$^{-1}$) have proved useful in determining the mode of coordination of the nitrite ion. It can be seen from Table 2.1 that in nitro complexes both $v_{as}$ and $v_s$ are raised in frequency, but in monodentate nitrito complexes (M-O-N=O) $v_{as}$ is increased while $v_s$ is lowered, and the two $v$(NO$_2$) of
nitrito complexes become well separated, $v_{\text{N-O}}$ and $v(\text{NO})$ being at 1400-1485 and 1050-1110 cm\(^{-1}\) respectively. Nitrito complexes also lack wagging modes ($\nu_w$ NO\(_2\) ca. 620 cm\(^{-1}\)) which appear in all nitro complexes. For NO\(_2^-\) bridges $v_{\text{as}}$ is raised appreciably while $v_s$ is lowered by a smaller amount. If the nitro group is chelating, both $v_{\text{as}}$ and $v_s$ are lower.
Figure 2.11 Vibrational Modes for Planar MNO₂ Molecule
(Coordinated NO₂⁻)

\[ \text{key} \]

- \( v_{\text{as}} \) asymmetric stretching
- \( v_{\text{s}} \) symmetric stretching
- \( \delta_{\text{ONO}} \) in-plane deformation (bending)
- \( \phi_{r} \) rocking, \( \phi_{w} \) wagging
Table 2.1 Typical Values for Group VIII MNO₂ Vibrational Modes

<table>
<thead>
<tr>
<th>mode</th>
<th>Nakamoto *¹</th>
<th>Adams *²</th>
</tr>
</thead>
<tbody>
<tr>
<td>v_\text{as}NO₂</td>
<td>1370-1470</td>
<td>1363-1497</td>
</tr>
<tr>
<td>v_\text{s}NO₂</td>
<td>1320-1340</td>
<td>1300-1373</td>
</tr>
<tr>
<td>δ ONO</td>
<td>820-850</td>
<td>800-850</td>
</tr>
<tr>
<td>ϕ_wNO₂</td>
<td>430-640</td>
<td>585-650</td>
</tr>
<tr>
<td>v_M-N</td>
<td>290-450</td>
<td></td>
</tr>
<tr>
<td>ϕ_rNO₂</td>
<td>250-310</td>
<td></td>
</tr>
</tbody>
</table>

*¹ for Co(III), Ni(II), Ir(III), Rh(III), Pt(II), Pt(IV), Pd(II) complexes

*² for Pt(II), Pt(IV), Pd(II) complexes

and δ ONO is higher than those of the monodentate N-bonded nitro complexes. The asymmetric stretching frequency v_\text{as} depends on the degree of asymmetry of the coordinated chelated nitro group, it is lowest when the two N—O bonds are equivalent and becomes higher as the degree of asymmetry increases.!

In many nitro complexes, several types of nitro coordination are mixed, and the existence of nitro-nitrito equilibria is well understood.
2.3.7 Visible Absorption Spectroscopy

Visible absorption spectra of the compounds in solution were recorded under nitrogen on a Pye-Unicam SP18-100 spectrophotometer in the range 350-750 nm.

2.3.7.1 Visible Absorption Spectroscopy of Porphyrins and Metalloporphyrins

The electronic spectrum of a complex molecule can provide a great deal of chemical information about ligand field strength, oxidation state, symmetry etc. following the correct assignment of the bands.\textsuperscript{249}

Studies of metal-ligand interactions in natural products and their synthetic models are complicated. The porphyrin nucleus consists of four pyrrole rings joined by four methine bridges to give a macrocycle.\textsuperscript{250} This aromatic tetrapyrrolic structure with its extensive $\pi$-delocalisation is a powerful chromophore. The colours of the various haemoprotein derivatives arises primarily from the $\pi$-system of this organic chromophore. In electronic spectra of metal complexes of porphyrins, d-d transitions are hidden under the intense absorptions of the ligand; thus one of the most important sources of information about the metal-ligand interactions is unavailable. However, the porphyrin spectra have their own important individual characteristics.

The theoretical basis of the electronic absorption and emission spectra of the porphyrins and their derivatives has been extensively dealt with elsewhere,\textsuperscript{251} and only the main qualitative features will be given in this discussion. The leading optical phenomena are ground state absorption and excited state emission. We are concerned with absorption
spectra in the visible-near UV region. The electronic heart of a porphyrin is the inner 16-membered ring with its 18 \( \pi \)-electrons. The porphyrin macrocycle is highly conjugated and a number of resonance forms can be written. There are nominally 22 \( \pi \)-electrons, but only 18 of these are included in any one delocalisation pathway and this conforms with the Hückel \( 4n + 2 \) rule for aromaticity.\(^{250,252}\) The ring is structured with a basic fourfold symmetry, including four N atoms directed towards the centre. This electronic heart is responsible for porphyrin-type optical spectra which are then perturbed to a greater or lesser extent by various chemical modifications to the basic structure e.g. external substitution, changes in conjugation pathway as in chlorins, phlorins, chlorophylls etc., and changes in central substituent.

Porphyrins are highly coloured, their main absorption bands having very high extinction coefficients (\( \varepsilon \)). The Soret band around 400 nm is the most intense band in the spectra of porphyrins and their derivatives,\(^{253}\) with \( \varepsilon \) about 400,000 L mol\(^{-1}\) cm\(^{-1}\). The Soret band is found in all tetrapyrroles in which the nucleus is fully conjugated; it can therefore be regarded as a characteristic of this macrocyclic conjugation since it is less intense in chlorins (reduced porphyrins) and metallochlorins, and totally absent in porphyrinogens (porphyrin precursors in which the ring is not fully closed) and biliverdins (bile pigments) where rupture of the macrocycle has occurred.

In neutral solvents, there are four satellite bands, numbered I to IV. The free base synthetic porphyrins \( \text{TPP}H_2 \),\(^{254} \) \( \text{OEP}H_2 \),\(^{255} \) and the picket fence porphyrin,
exhibit the most common 'etio-type' visible spectrum [where \( \varepsilon_{IV} > \varepsilon_{III} > \varepsilon_{II} > \varepsilon_{I} \), see Figure 2.12(a)], as do all naturally occurring porphyrins. Correlations also occur between the nature of the side chains on porphyrins and the positions and intensities of their visible absorption bands.²⁵⁰

The visible absorption spectrum is a sensitive probe of the metalation of porphyrins.²⁵⁷ On metalation the four-band spectrum changes to give two visible bands (the Q bands) between 500 and 600 nm, separated by about 30-40 nm [Figure 2.12(b)].²⁵¹ The lower energy or \( \alpha \)-band, is due to a transition to the lowest excited singlet state, while the higher energy or \( \beta \)-band is due to a merging of many vibrational excitations (the vibronic excitation envelope). For each band \( \varepsilon \sim 1-2 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1} \). The two visible bands which are labelled \( \alpha \) and \( \beta \), parallel bands I and III in the free base spectra. The intense Soret band (or B band) between 380 and 420 nm is due to the second excited singlet state and has \( \varepsilon \sim 2-4 \times 10^5 \text{ mol}^{-1} \text{ cm}^{-1} \). The difference between free-base and metal-type porphyrin spectra (i.e. spectra shown by most metal complexes and by the acid dication) arises from the fact that the two free-base hydrogen atoms in the centre lower the conjugated ring symmetry from square (\( D_{4h} \)) to rectangular (\( D_{2h} \)) symmetry. Generally, with metalloporphyrins there is little change with metal in optical absorption, but substantial change in optical emission.²⁵¹

The spectra of metalloporphyrins are grouped into regular and irregular porphyrin types. A definition²⁵¹ of a regular porphyrin is one whose optical absorption and fluorescence emission spectra are determined essentially by
Figure 2.12 Typical Visible Absorption Spectra for Porphyrin Derivatives

(a) Typical 'Etio-Type' Porphyrin Spectrum

(b) Typical Metalloporphyrin Spectrum
the π-electrons of the porphyrin ring, with only minor perturbations from the electrons of the central substituent e.g. from electrons in metal p_z or d_{xz}, d_{yz} orbitals. Thus the normal spectrum is observed with all d^0 or d^{10} ions. The irregular metalloporphyrins differ from the regular in emission properties, and in most cases in absorption properties also. Practically all transition metal ions with open shells produce abnormal porphyrin spectra. The irregular absorption types are further characterised as hypso and hyper. These are defined as follows: \(^{251}\)

(1) hypso-type absorption spectra follow the regular absorption pattern but are blue-shifted ( \(\alpha < 570 \text{ nm}\) ) due to filled metal d_π to porphyrin e_g (π*) back donation. Such spectra are shown by transition metal porphyrins of Groups VIII and IB with low spin d^{5-9} metal configurations. Important metals within this class are Fe(II), S = 0 and Co(III), S = 0. Whether an iron(II) porphyrin is hypso strongly depends on the axial ligands which influence the spin state. Only the S = 0 case is hypso with S = 1 or S = 2 being hyper. Cobalt(III), the other metal oxidation state of interest in this class, is rather inert to effects by fifth and sixth ligands and Co(III) porphyrins show hypso spectra. Lower cobalt oxidation states of II and I are also hypso in porphyrins.

(2) d-type hyper absorption spectra show prominent extra absorption bands (\(\varepsilon > 1000\) mol\(^{-1}\) cm\(^{-1}\)) in the region >320 nm in addition to significant shifts of the porphyrin (π — π*) bands, and are found with high oxidation state transition metal ions of Groups VIA, VIIA and certain of Group VIII in configurations d^{1-6}. The extra bands are attributed to charge
transfer (CT) transitions arising from the possible vacancies in the d shell. All Fe(III) [S = 1/2, 3/2, and 5/2] and Fe(II) [S ≠ 0] porphyrins show hyper spectra. Fe(I) and Fe(IV) porphyrin spectra also appear to be hyper. Because of the proximity of the metal d and porphyrin HOMO and LUMO levels, the iron porphyrin absorption spectra are thus variable and more complicated than any other metalloporphyrin spectra.

Various theories accounting for hypso/hyper effects are given in Gouterman's reviews, and these invariably involve mixing of metal orbitals and ring orbitals causing the various effects. Coupling between transition metal and p orbitals occurs because of the proximity in energy of the various levels and favourable symmetry character. Axial ligands may affect the energy levels further as well as introducing their own MO's capable of mixing. A unified theory for the electronic structure of some 13 six-coordinate osmium porphyrins, Os$^{II/IV}$(OEP)(L)(L') [L, L' = neutral or ionic ligands including NH$_3$, py, N$_2$, CO, CS, NO, methoxide, nitride, oxide, and perchlorate] based on the absorption and emission spectra and on the results of iterative extended Huckel calculations has been presented. The wide variation in electronic properties of these 13 complexes was explained in terms of competition between equatorial back-bonding (delocalisation from metal d$_\pi$ to ring e$_g$($\pi^*$) orbitals) and axial back-bonding (delocalisation from metal d$_\pi$ to ligand $\pi^*$ orbitals) depending on axial ligands and oxidation state of osmium. Coordination of $\sigma$-donor ligands with no $\pi$-acceptor capacity (e.g. NH$_3$) causes high metal d$_\pi$ ($= d_{xz}, d_{yz}$) energy, and as a result equatorial back-bonding is strong and
dominates, so back-bonding repulsions of $d_{\pi}$ to ring $e_g(\pi^*)$ cause a strong hypsochromic (blue) shift to the ($\pi$, $\pi^*$) spectrum. There are also low energy CT ($d_{\pi}$, $\pi^*$) transitions and the metal is easily oxidised. With $\pi$-acceptor ligands, axial back-bonding dominates and lowers the energy of the $d$ levels and reduces equatorial back-bonding, so that the energy of the $e_g(\pi^*)$ levels is not so affected and as a result the ($\pi$, $\pi^*$) spectrum is less hypsochromic. That the hypsochromic shift as compared with the normal absorption diminishes with increasing $\pi$-acceptor capacity of the axial ligand(s) is illustrated by the observation that the wavelength of the $\alpha$-band shows a progressive bathochromic (red) shift in the series $\text{Os(OEP)(py)}_2 < \text{Os(OEP)(N}_2\text{(THF)} < \text{Os(OEP)(CO)(py)} < \text{Os(OEP)(NO)(OMe)}$.\textsuperscript{258}

The interaction of Co(TPP) with CO, NO, and O$_2$ ligands has been studied spectroscopically.\textsuperscript{190} In toluene glass electronic spectra of the CO and NO complexes there is a doubling of the Soret band in which it was suggested could be due either to CT bands or to a ligand field effect.

2.3.8 Nuclear Magnetic Resonance Spectroscopy

Routine $^1$H NMR spectra were recorded by Mr Jim Bloxsidge of the Chemistry Department on a Bruker WH90 spectrometer. N, Co, O, P, and some $^1$H NMR spectra were recorded by Drs Oliver Howarth, Eirian Curzon, and Aidan Harrison on the SERC high field (400 MHz) NMR facility at Warwick University.

2.3.8.1 Sealed NMR Tube Experiments

In later work sealed NMR tubes were required. Tubes 225 mm (9") long, precision diameter 10 mm with a 2 mm
constriction 25 mm (1") from the open end to facilitate sealing, were purchased from the Wilmad Company. They were glassblown to a Quickfit B14 cone or joined to it by a short length of PVC tubing secured by Araldite epoxy resin. The required quantities of solid reagents were weighed into the tube and a small subaseal was wired securely onto the joint. The contents of the tube were deoxygenated through the subaseal via a syringe needle. Using a nitrogen bleed to the atmosphere through a second syringe needle inserted through the subaseal, the required amounts of deoxygenated deuterated solvent and other reactants (e.g. pyridine) were then added through the subaseal under nitrogen from a third syringe. The subaseal was then removed and the tube quickly attached to the nitric oxide line at tap Q on the capillary apparatus similar to that used to transfer $^{15}$NO into the gas burette as shown in Figure 2.8. The contents of the NMR tube were protected by the nitrogen blanket during the rapid transfer. The tube contents were frozen in liquid nitrogen and the tube evacuated. By careful opening of the burette tap the required amount of $^{15}$NO was condensed directly into the NMR tube. After $^{15}$NO transfer, the NMR tube was flame-sealed at the constriction with a small blowtorch and the seal was protected with wax.

2.3.8.2 NMR Nuclei ($^{15}$N, $^{59}$Co, $^{17}$O)

The theory of the NMR experiment is covered in detail elsewhere. Each NMR nucleus used in this work ($^{15}$N, $^{59}$Co, $^{17}$O) is considered briefly. Table 2.2 gives the NMR properties of the relevant nuclei. The ground state nuclear spin quantum number $I$ is a fundamental property and can be zero or
Table 2.2 NMR Properties of Relevant Nuclei

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Nuclear Spin</th>
<th>Natural Abundance</th>
<th>Magnetogyric Ratio</th>
<th>NMR Frequency</th>
<th>Reference Standard</th>
<th>Relative Receptivity to proton, D&lt;sup&gt;p&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>^1H</td>
<td>1/2</td>
<td>99.985</td>
<td>26.7510</td>
<td>100.000</td>
<td>Me₄Si</td>
<td>1.000</td>
</tr>
<tr>
<td>^1H</td>
<td>1</td>
<td>99.635</td>
<td>1.9324</td>
<td>7.224</td>
<td>MeNO&lt;sub&gt;2&lt;/sub&gt; or NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1.0 x 10⁻³</td>
</tr>
<tr>
<td>^15N</td>
<td>1/2</td>
<td>0.365</td>
<td>-2.7107</td>
<td>10.136783</td>
<td></td>
<td>3.85 x 10⁻⁶</td>
</tr>
<tr>
<td>^17O</td>
<td>5/2</td>
<td>0.037</td>
<td>-3.6266</td>
<td>13.557</td>
<td>H₂O</td>
<td>1.08 x 10⁻⁵</td>
</tr>
<tr>
<td>^31P</td>
<td>1/2</td>
<td>100</td>
<td>10.829</td>
<td>40.48072</td>
<td>H₃PO₄</td>
<td>0.0663</td>
</tr>
<tr>
<td>^59Co</td>
<td>7/2</td>
<td>100</td>
<td>6.3171</td>
<td>23.614</td>
<td>[Co(CN)₆]&lt;sup&gt;3-&lt;/sup&gt;</td>
<td>0.277</td>
</tr>
</tbody>
</table>
take positive integral or half-integral values such that the associated angular momentum of the nucleus is $\hbar[I(I+1)]^{1/2}$. Nuclei with $I = 0$ cannot give NMR spectra, but when $I$ is non-zero the nucleus has a magnetic moment $\mu_I$, where $\mu_I = \gamma I[I(I+1)]^{1/2}$ (in units of the nuclear magneton, $\mu_N$). The magnetogyric ratio $\gamma$ is another fundamental property and it may be positive or negative depending on whether the magnetic moment is parallel or antiparallel to the angular momentum vector. $^{260}\gamma$ is important since it affects the frequency and intensity of the resonance. When a nucleus of non-zero spin $I$ is placed in a strong magnetic field ($B_0 = 1-10$ T) the orientation of its spin axis becomes quantised, i.e. each permitted orientation has a certain energy. Irradiation with a suitable radiofrequency causes transitions between the different orientations which can be detected to provide the NMR spectrum. The NMR frequency, $\omega$ is set on the scale of the $^1H$ resonance of Me$_4$Si = 100 MHz, and the values quoted in Table 2.2 are the resonances of the reference standards listed in the next column. The relative shift between the two reference standards for nitrogen NMR (MeNO$_2$ and NO$_3^-$) is negligible for all practical purposes. $^{260}$ The receptivity $D^P$ of a nucleus at natural abundance is a rough guide of the ease of obtaining an observable signal for the nucleus relative to $^1H$ at the same concentration. The sensitivity of a nucleus $X$ relative to the proton is directly proportional to the cube of its magnetogyric ratio, and the receptivity (or absolute sensitivity) is found by multiplying relative sensitivity by the natural abundance, $N$, i.e. $D^P = [\gamma_X^3 N_X I_X (I_X+1)/\gamma_P^3 N_P I_P (I_P+1)]$ at constant magnetic field, $B_0$. $^{260}$
Nitrogen NMR has been extensively studied.\(^ {261-3} \) The element possesses two magnetically active isotopes: \(^ {14}\text{N} \) and \(^ {15}\text{N} \) with the properties in Table 2.2. \(^ {14}\text{N} \) signals are generally easily detected but the associated nuclear electric quadrupole moment leads to short relaxation times and linewidths that are usually quite broad (100-1000 Hz). \(^ {15}\text{N} \) NMR spectroscopy has the advantage of high resolution since \( I = \frac{1}{2} \) and the quadrupole moment zero so that the lines are narrow. However, the low abundance and receptivity of this isotope (Table 2.2) present practical problems in measurement. One solution is to use \(^ {15}\text{N} \) isotopic enrichment as here, and another is to use widebore superconducting magnets to measure \(^ {15}\text{N} \) in natural abundance.\(^ {263} \)

The \(^ {15}\text{N} \) chemical shifts are the same as those for \(^ {14}\text{N} \) in the same environment since the electronic shielding mechanism is the same for all nitrogen nuclei. There is some disagreement over the reference standard for \(^ {15}\text{N} \) NMR, although \( \text{CH}_3\text{NO}_2 \) is usually used. The chemical shift range for nitrogen nuclei is quite large (ca. 1100 ppm); however, the range for a given class of compound (nitrosyls excepted) is often only ca. 50 ppm. \(^ {15}\text{N} \) NMR spectroscopy therefore has great promise as a structural tool since \( I = \frac{1}{2} \), there is a large chemical shift range, the line widths are narrow, and the spectra are simple because there are usually few nitrogen atoms in any molecule. The quadrupolar relaxation behaviour of \(^ {14}\text{N} \) is used to study molecular dynamics.\(^ {260} \) Major disadvantages are that \(^ {14}\text{N} \) and \(^ {15}\text{N} \) both suffer from low magnetogyric ratios resulting in low NMR frequencies and small spin-spin coupling constants. In addition, the long
relaxation times for $^{15}\text{N}$ and its low natural abundance make $^{15}\text{N}$ NMR signals even more difficult to detect. Often a relaxation reagent e.g. Cr(acac)$_3$ is necessary for reasonable acquisition times for $^{15}\text{N}$ NMR. However, new techniques and larger superconducting magnets are making $^{15}\text{N}$ (and $^{14}\text{N}$) NMR spectroscopy much more accessible.

Nitrogen chemical shifts and coupling constants are particularly sensitive to the disposition of lone pairs and $\pi$-electrons which are important in the structure and reactivity of nitrogen compounds. In the following discussion of the factors which determine the range of $^{15}\text{N}$ chemical shifts the emphasis is placed on ligands such as NO and NO$_2^-$ relevant to this work. It is interesting to note that there are many parallels between the patterns of $^{14}\text{N}$, $^{15}\text{N}$ and $^{13}\text{C}$ chemical shifts in functional groups that are electronically similar e.g. -C≡C- and -C≡N.

2.3.8.2.1.1 Simplified Theory of Nuclear Magnetic Shielding for Nitrogen Nuclei

The nuclear magnetic shielding ($\sigma_A$) of an atom A is usually given as the algebraic sum of a diamagnetic term, $\sigma_D^A$, a paramagnetic term, $\sigma_P^A$, arising from electronic circulations on A, and a third term, $\sigma^{AB}$, which sums the contributions from all other atoms B (Equation 2.2)

$$\sigma_A = \sigma_D^A + \sigma_P^A + \sigma^{AB}$$

The parameter $\sigma_A$ is the shielding (screening) constant of nucleus A (a dimensionless number usually quoted in ppm), which depends upon the electronic environment of A.\cite{259-260}
is not normally feasible to measure shielding constants directly, but changes in shielding may be found. These lead to chemical shifts ($\delta$) in the resonance frequency, which are generally reported in ppm relative to the resonance of some suitable reference compound. The chemical shift for nucleus $A$, $\delta_A \propto -\sigma_A$ at constant field strength, so increase in the chemical shift implies decrease in shielding. The main contribution to the chemical shift of nuclei is the variation in the paramagnetic term, $\sigma_p^A$. This is because usually the variation in the diamagnetic term, $\sigma_d^A$, is small for a given element, and the third term $\sigma^{AB}$ is also small because contributions from other atoms tend to cancel each other out. For a second row element like nitrogen the variation in the paramagnetic term is given by Equation 2.3, which is a simplified version of a more rigorous treatment:

$$\sigma_p^A = -\mu_0 \mu_B^2 \langle r^{-3} \rangle_{2p} \Sigma Q$$

$$\frac{2\pi \Delta E}{\mu_0 \mu_B^2 \langle r^{-3} \rangle_{2p} \Sigma Q}$$

or

$$\sigma_p^A \propto -\langle r^{-3} \rangle_{2p} \cdot \Sigma Q$$

$$\frac{\Delta E}{\mu_0 \mu_B^2 \langle r^{-3} \rangle_{2p} \Sigma Q}$$

where $\mu_0$ is the permeability of free space, $\mu_B = e\hbar/2m$, the Bohr magneton, the radial factor $\langle r^{-3} \rangle_{2p}$ is the mean inverse cube of the $2p$ electron radius, the $\Sigma Q$ terms express the imbalance or asymmetry of charge in the valence shell of $A$, and $\Delta E$ is an effective excitation energy. This is all a drastic approximation of a more rigorous treatment which sums
over all excited states in the molecule, but it has been found to be quite valid.263

The three terms in the above equation with the biggest influence on the chemical shift are the radial factor $\langle r^{-3}\rangle_{2p}$, the energy difference $\Delta E$, and the asymmetry of charge $\Sigma Q$. The downfield shift (deshielding) is the larger, the closer the paramagnetic circulation is to the nucleus (i.e. the larger is $\langle r^{-3}\rangle_{2p}$), the greater the asymmetry of the valence electrons (i.e. the larger the $\Sigma Q$ term), and the easier the excitation (i.e. the smaller the $\Delta E$). However, these three factors are not independent. With electronegative substituents nitrogen becomes more positive, $r$ decreases, and $\langle r^{-3}\rangle_{2p}$ and the deshielding increases. The asymmetry factor, $\Sigma Q$, alone can account for the sequence of N shifts in the series:

\[
\begin{align*}
\text{N} & \equiv X \\
\text{lowest field} & \quad \text{highest field} \\
(\text{deshielded}) & \quad X = O, N, \text{etc.} \quad (\text{shielded})
\end{align*}
\]

The order is that of increasing asymmetry of nitrogen charge from highest field to lowest field. The $\Delta E$ and $\Sigma Q$ terms are related; $\Delta E$ tends to decrease as $\Sigma Q$ increases. Qualitative arguments of nitrogen shielding are often based on changes in $\Delta E$(HOMO - LUMO), the frontier orbital separation energy for rotation of electronic charge in the magnetic field. This is especially so for nitrogen nuclei that have a lone pair e.g. nitroso, R-N=O. This is because nitrogen carrying a lone pair in a delocalised system is strongly deshielded by low energy $n_N \rightarrow \pi^*$ circulations in a
magnetic field (these act to reinforce the applied field and hence are termed 'paramagnetic circulations'). Strongest deshieldings are observed for -N=N-, -N=0, and M—N=NR etc., all of which have a low-lying $n_N \rightarrow \pi^*$ state. The paramagnetic term which dominates the chemical shift will then express the deshielding due to circulation of electrons in the magnetic field between the HOMO and LUMO frontier orbitals of which the $n_N \rightarrow \pi^*$ circulation is the example. The nitrogen line moves farther downfield (low frequency) the smaller is the virtual excitation energy $\Delta E$ which is thus envisaged as the frontier orbital separation $\Delta E(\text{HOMO} - \text{LUMO})$ for rotation of charge in the magnetic field. The $n_N \rightarrow \pi^*$ excitation in a nitroso group involves rotation of charge about the nitrogen (Figure 2.13). So patterns in chemical shift can also be well interpreted by variations in this effective excitation energy as well as the other terms in Equation 2.3.

Figure 2.14 gives the chemical shifts of some representative nitrogen compounds on the scale $\text{CH}_3\text{NO}_2 \delta_N = 0$ ppm. Nitrogen in NH$_4^+$ resonates at high field because of high local symmetry ($\Sigma Q$ small) and because $\Delta E$ is the large separation between $\sigma$ and $\sigma^*$ orbitals; consequently $\sigma^p_p$ is small and the nitrogen nucleus is shielded. Nitrogen bearing a lone pair is deshielded and resonates somewhat downfield. NO$_3^-$ resonates at medium field because both $\Sigma Q$ and $\langle r^{-3} \rangle_{2p}$ are large.$^{264-5}$ Azo (XN=NX) and nitroso (XN=0) compounds resonate at very low field because $\Sigma Q$ is large due to the lone pair, and $\Delta E$ is very small. The nitrogen resonance moves downfield for nitroso compounds as the $n_N \rightarrow \pi^*$ band moves to longer wavelengths in the electronic spectrum.$^{266-7}$ This
Figure 2.13 $n_N \rightarrow \pi^*$ Circulation in Nitroso Group (RNO) Expressed as a Rotation of Charge About Nitrogen

(The nitrogen 2s and 2p$_x$ electrons have lone-pair character. The nitrogen 2p$_x$ orbital which lies in the RNO plane is shown horizontal in the diagram and the NO(\(\pi^*_y\)) orbital which is perpendicular to the RNO plane is shown vertical. The arrows show that the $n_N \rightarrow \pi^*$ excitation involves rotation of charge (2p$_z \rightarrow 2p_y$)).
Figure 2.14 Range of Nitrogen Shifts in Various Compounds

- Bent Nitrosyl, $\text{NO}^-$, $\text{M} = \text{H}$
- Linear Nitrosyl, $\text{NO}^+$, $\text{M} = \text{H}$
- Dinitrosyls, $\text{M} = \text{H}$
- Deshielded (Low Field)
- Shielded (High Field)
- Various Nitrogen Shifts and Compounds
is illustrated by the series of compounds: FNO (colourless) → alkyl nitrosamines, \( R_2 N\text{-NO} \), alkyl nitrites, RONO (yellow) → thionitrites, RSNO (red) → C-nitroso compounds, \( R_3 C\text{-NO} \) (blue) which are in order of increasing deshielding or decreasing \( \Delta E \propto \Delta E^{-1} \). \( NO_2^- \) is an ambidentate ligand with a large difference in nitrogen shift dependent upon the mode of linkage. Nitro compounds \( (RNO_2) \) resonate at medium field close to \( NO_3^- \), and nitrites \( (RONO) \) are shifted downfield (δ 200 ppm) because of the bent two-coordinate nitrogen bearing a lone pair. Such medium field resonances for nitro ligands were reported in \( ^{14}N \) NMR for square planar \([M(NO_2)_4]^{2-} \) \( (M = \text{Pd, Pt}) \) and octahedral \([\text{Co(NO}_2)_6]^{3-} \). But the resonance assigned to complexed nitrite in \([\text{Co(NO}_2)_6]^{3-} \) was later correctly assigned to free nitrate formed by oxidation of dissociated \( NO_2^- \) by Co(III). This work on the hexanitrocobaltate(III) anion was extended in a detailed study of \( ^{14}N, ^{59}\text{Co}, \) and \( ^{17}O \) NMR in a later investigation of the crystal field strength of the coordinated nitro ligand.

The first \( ^{15}N \) NMR study of Co(III) complexes containing \( ^{15}NO_2^- \) (nitro) has appeared. Relative to \( ^{15}NO_2^- \), cis- and trans-[Co(\( ^{15}NO_2 \))\(_2\)(en)\(_2\)]\(^+\) gave sharp singlet resonances at 85.0 and 95.0 ppm, and cis- and trans-[CoCl(\( ^{15}NO_2 \))(en)\(_2\)]\(^+\) gave resonances at 71.0 and 65.5 ppm respectively. A study of non-aqueous solutions of some diamagnetic covalent metal-nitrato compounds gave \( ^{14}N \) NMR shifts of ca. 25 ppm upfield of free nitrate ion, but the method failed to distinguish between the various bonding modes available to nitrate: unidentate, MONO\(_2\), bidentate, MO\(_2\)NO, bridging bidentate, MON(OM)OM or bridging terdentate, MON(OM)OM, due to
the similar nitrogen shielding obtained in most cases because the coordination linkage is through oxygen.

The free nitrosonium ion, \( \text{NO}^+ \) (in \( \text{NO}^+\text{HSO}_4^- \)) resonates at -5 ppm quite close to \( \text{NO}_3^- \) at -20 ppm (MeNO\(_2\), \( \delta_N = 0 \) ppm). Coordination shifts of about +50 ppm have been reported for linear \( \text{M}-\text{NO} \) in tetrahedral and octahedral complexes of Fe, Co, and Ru. The line at ca. 50 ppm in the \( ^{14}\text{N} \) NMR spectra of the Co, Ru, and Os nitrosylpentammines was assigned to the nitrosyl group.

The first \( ^{15}\text{N} \) NMR study of some Group VIB organometallic nitrosyl complexes extended this range downfield. Eight "piano-stool" type (\( \eta^5 \)-cyclopentadienyl)nitrosyl derivatives of Cr, Mo, and W were measured in natural abundance. The single nitrosyl lines in the mononitrosyls [(\( \eta^5 \)-Cp)M(CO)-(NO)] resonate at about +50 ppm downfield of NO\(^+\) whereas the dinitrosyls [(\( \eta^5 \)-Cp)M(NO\(_2\))Cl] have single resonances about +150 ppm further downfield from the mononitrosyl resonances. Since \( ^{14}\text{N} \) is quadrupolar, the linewidth increases with molecular size and with local \( \Sigma Q \), so that linear nitrosyls give rather broad lines (\( W_{1/2} \) 500 Hz). No \( ^{14}\text{N} \) resonances have been identified for bent nitrosyls for similar reasons.

Studies on \( ^{15}\text{N} \)-enriched diazenido (M-N=NR) complexes have shown that rhodium complexes with a bent M-N\(_\alpha\)=N\(_\beta\)--Ar group (Rh-N=N, \( \angle \approx 125^\circ \)) have \( ^{15}\text{N} \) resonances ca. 350 ppm downfield of the nitrogen of linear diazenido complexes of Mo, W, Re, and Ru. This deshielding is due to the low-energy \( n_N \longrightarrow \pi^* \) electronic circulations in the magnetic field which arise when the conjugated \( \alpha \)-nitrogen atoms carry a lone pair. This intrinsic property of -N=X compounds was
Further used in nitrosyl chemistry by Mason et al. who reported deshieldings of 350 to 700 ppm for nitrogen in strongly bent metal-nitrosyl groups (MNO ca. 120°) in enriched complexes of Rh or Co compared with linear nitrosyl groups in certain complexes of Fe, Co, and Ru. This established the 15N NMR criterion of bond angle in nitrosyl complexes. The nitrogen shielding of the strongly bent apical nitrosyl groups in the square pyramidal [MNO]8 cobalt complexes is the lowest yet observed for diamagnetic compounds. This 15N NMR work was extended to 95 % enriched bent (360 to 500 ppm) and linear (-50 to 150 ppm) nitrosyl groups in 4-, 5-, and 6-coordinate complexes of platinum group metals (Ru, Rh, Pt). In addition, the range of 15N resonances for coordinated nitro (at ca. 45 ppm) and hypo-nitrito (at ca. 35 ppm) ligands were established to facilitate the observation of these intermediates in reactions of nitrosyl complexes.

The strongly bent CoNO group was studied further by 15N and 59Co NMR in some non-fluxional, five-coordinate Co(III) complexes with Schiff base or dithiocarbamato basal ligands and bent apical nitrosyl ligands. The 15N and 59Co shieldings tend to decrease with a decrease in MNO angle, and in the energy of the longer wavelength absorption. The trend of the cobalt shielding resembles that of the 15N shielding reflecting the interdependence of the frontier orbital gap for charge rotation at the two nuclei. However, the cobalt shifts in the bent nitrosyl complexes are also strongly dependent on the nature of the basal ligands, and the relatively low cobalt shielding is also consistent with the thought that the strongly bent nitrosyl is a weaker ligand.
than linear nitrosyl. Nitrogen deshielding on bending increases with decrease in ligand field splitting and is shown by greater deshielding for Co complexes than for Ru, Rh, Os, and Ir, because ligand field splitting increases from the first to the second or third transition series. Also higher $^{15}\text{NO}$ shielding in the dithiocarbamato relative to the Schiff base complexes correlates with higher $^{59}\text{Co}$ shielding (i.e. greater splitting of the ligand field). Correlations of increased shielding of a transition metal nucleus with increased ligand field strength and nephelauxetic ability of ligands are discussed in the next section on $^{59}\text{Co}$ NMR.

Nitrogen-15 NMR (99 % enriched samples) has shown that the Roussin esters $\text{Fe}_2(\text{SR})_2(\text{NO})_4\ (R = \text{Me}, \text{Pr}^1)$ exist as an equimolar mixture of two conformers of $C_{2v}$ and $C_{2h}$ symmetry respectively [Figure 2.15(a)]. The same study demonstrated that for the Roussin-type salts $[\text{Fe}_4X_3(\text{NO})_7^-\ (X = S, Se)$, the solid state structure for $X = S$ persists in aqueous solution and that the anion for $X = Se$ is isostructural in solution [Figure 2.15(b)]. The same was shown to be true for the cubane-type clusters, $[\text{Fe}_4X_4(\text{NO})_4]\ (X = S, Se)$. Nitrogen-15 NMR (90 % enriched samples) was used in the characterisation of the novel clusters $[\text{M}_3(\text{CO})_{10}(\text{NO})]^-\ (M = \text{Ru}, \text{Os})$ where the NO doubly bridges one edge of the metal triangle, and for $[\text{Ru}_6\text{C}(\text{CO})_{15}(\text{NO})]^-\$ which contains a terminal nitrosyl ligand [Figure 2.16]. The doubly bridging nitrosyl resonates some 400 ppm downfield of the terminal mononitrosyl (at ca. 411 ppm).

An X-ray crystallographic study of 5-coordinate $[\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2]\text{BF}_4$ has shown the cation to be square pyramidal with bent apical and linear basal nitrosyl ligands.
Figure 2.15(a) The Two Conformers \( (C_{2h}, C_{2v}) \) of the Roussin Esters, \( \text{Fe}_2(\text{SR})_2(\text{NO})_4 \) (\( R = \text{Me}, \text{Pr}^i \))

\[
\begin{array}{c}
\text{Fe} \\
\text{S} \\
\text{R} \\
\text{S} \\
\text{Fe} \\
\text{NO} \\
\text{NO} \\
\text{ON} \\
\text{ON} \\
\end{array}
\]

\( C_{2h} \)

\[
\begin{array}{c}
\text{Fe} \\
\text{S} \\
\text{R} \\
\text{S} \\
\text{Fe} \\
\text{NO} \\
\text{NO} \\
\text{ON} \\
\text{ON} \\
\end{array}
\]

\( C_{2v} \)

Figure 2.15(b) The Structure of the Roussin Salt \( [\text{Fe}_4\text{S}_3(\text{NO})_7]^- \)
Figure 2.16 Framework Structure of the Cluster Anions $[M_3(\text{CO})_{10}(\text{NO})]^- \ (M = \text{Ru}, \text{Os})$ and $[\text{Ru}_6(\text{CO})_{15}(\text{NO})]^-$

![Diagram of Cluster Anion Structure](image)

Figure 2.17(a) Crystal Structure of the Complex Cation $[\text{RuCl(NO)}_2(\text{PPh}_3)_2]^+$ (an example of a $[\text{M(NO)}_2]^8$ complex with both a linear and a bent MNO group)

![Diagram of Complex Cation Structure](image)

Figure 2.17(b) Intramolecular Interconversion of Bent and Linear Nitrosyl Ligands in $[\text{RuCl}^{14}\text{NO})(^{15}\text{NO})(\text{PPh}_3)_2]^+$

![Diagram of Intramolecular Interconversion](image)
The labelled compound gave a single $^{15}$N NMR resonance ($\delta_N \text{ ca. } 130$ ppm, triplet, $^{2}J(^{31}P-^{15}N)$ 2.5 Hz) in solution over the temperature range 183 to 300 K, and this is further evidence for the rapid intramolecular interconversion of bent and linear nitrosyl ligands proposed earlier from the complexity of the IR spectrum [Figure 2.17(b)]. Consistent with this proposal, a $^{14,15}$N equilibrium isotope effect in the fluxionality was observed with semi-$^{15}$N enrichment in the molecule. This ruthenium nitrosyl and others were further studied in the solid state by high resolution cross-polarisation magic-angle-spinning (CP/MAS) $^{15}$N NMR spectroscopy. Solid $[\text{RuCl}^{14}\text{NO})(^{15}\text{NO})(\text{PPh}_3)_2]\text{BF}_4$ shows a large chemical shift anisotropy for the bent as compared with the linear nitrosyl ligand, in comparison to the solution $^{15}$N NMR results which showed bent-linear fluxionality. The CP/MAS spectra clearly establish that $[\text{RuCl}^{14}\text{NO})(^{15}\text{NO})(\text{PPh}_3)_2]\text{BF}_4$ is not fluxional in the solid state at ambient temperatures with two shifts being obtained. $^{15}$N CP/MAS NMR spectroscopy has proved to be a sensitive alternative to single crystal X-ray crystallography for distinguishing bent, linear, and intermediate geometries in the solid state. However, more work is required.

2.3.8.2.2 Cobalt ($^{59}$Co) NMR Spectroscopy

Cobalt-$^{59}$ NMR spectroscopy is a very useful method of investigating diamagnetic cobalt compounds. Cobalt(II) is paramagnetic and is therefore difficult to investigate by NMR methods. Although low-spin $d^6$ complexes of Co(III) have provided most of the samples for $^{59}$Co NMR study, spectra can be obtained from diamagnetic Co complexes of formal oxidation
states $+1$, $0$, and $-1$ (here oxidation state Co(0) is formally $3d^{10}$ in the diamagnetic cobalt carbonyl complexes and not paramagnetic $3d^9$).

The $^{59}$Co nucleus is 100% abundant with nuclear spin $I = \frac{7}{2}$, an intermediate value quadrupole moment ($0.4 \times 10^{-28}$ cm$^2$), and a reasonable detection sensitivity (receptivity) of 0.277 (versus $^1$H). The quadrupole moment makes $^{59}$Co line-widths particularly sensitive to electric field gradients at Co, and therefore to the symmetry about the cobalt atom. The chemical shift range for the cobalt nucleus in its various chemical environments is 18000 ppm (Figure 2.18) with reported linewidths from 175 Hz to 40 kHz in some instances. $^{260}$[Co(CN)$_6$]$^{3-}$ ($\delta ^{59}$Co 0 ppm) is the most popular reference, although [Co(en)$_3$]$^{3+}$ (7120 ppm), [Co(NH$_3$)$_6$]$^{3+}$ (8150 ppm), and [Co(acac)$_3$] (12500 ppm) have been used.

From the chemical shift diagram (Figure 2.18) a number of structural correlations are recognisable. Empirically the shielding of the nucleus roughly correlates with the oxidation state of the metal atom. Except for the cyano complexes, Co(III) compounds resonate in the high frequency region from 3000 to 14000 ppm, and lower oxidation state cobalt complexes are found in the lower frequency region (-4000 to 2000 ppm). The cyano complexes resonate between 0 and 1800 ppm. Also, in octahedral Co(III) complexes the shielding of the $^{59}$Co nucleus increases from O- to N-, S-, Se-, As-, or C-donor ligands, but the shift ranges in some cases overlap considerably.

Oxygen donor ligands provide the least shielded environment for cobalt(III) because of their large paramagnetic contribution to the chemical shift; consequently
Figure 2.18 $^{59}$Co Chemical Shift Ranges for Different Chemical Environments

- $\text{CoO}_6$
- $\text{CoO}_4\text{XY}$
- $\text{CoN}_3\text{XYZ}$
- $\text{CoN}_4\text{XY}$
- $\text{CoN}_6$
- $\text{CoN}_5\text{X}$
- $\text{CoS}_6$
- $\text{CoSe}_6$
- $\text{CoAs}_6$
- [Co$^{\text{III}}$(NO)$_2$X(PR$_3$)]
- Co(CN)$_5$X
- [Co$^{\text{III}}$(η$^3$-allyl)(η$^5$-Cp)R]
- Co$^0$ carbonyls
- [Co$^{-1}$($\pi$-L)$_2$(η$^5$-Cp)]
- Co$^{-1}$ carbonyls
- [Co$^{-1}$(PF$_3$)$_4$]
Co\textsuperscript{III}\textsubscript{6} complexes resonate between 12000 and 14000 ppm. Nitrogen donor ligands cause higher shielding so Co\textsuperscript{III}\textsubscript{N\textsubscript{6}} resonances occur between 5000 and 10000 ppm, while carbon donor ligands cause the highest cobalt shielding with [Co(CN)\textsubscript{6}]\textsuperscript{3-} resonating at 0 ppm. Ligands containing S-, Se-, and As-donor atoms cause intermediate shieldings giving cobalt shifts from 5000 to 7000 ppm.

\textsuperscript{59}Co NMR spectroscopy may be seen to be very well suited for the study of diamagnetic Co(III) complexes. A practical advantage lies in the fact that the \textsuperscript{59}Co chemical shifts are very sensitive to changes within a complex. Therefore it has been important to establish regularities applicable to \textsuperscript{59}Co chemical shifts.

2.3.8.2.2.1 Theoretical Basis for Nuclear Magnetic Shieldings in Cobalt(III) Complexes

The Ramsey general theory of chemical shielding\textsuperscript{286} may be successfully extended to \textsuperscript{59}Co chemical shifts in octahedral Co(III) complexes, and this was first shown by Griffith and Orgel,\textsuperscript{287} and then Freeman, Murray, and Richards (FMR).\textsuperscript{288} According to Ramsey\textsuperscript{286} the shielding constant of a nucleus may be expressed as the sum of two terms, a diamagnetic and a paramagnetic term ($\sigma = \sigma_\text{D} + \sigma_\text{P}$ as in nitrogen shielding discussed above). In diamagnetic compounds of transition metals in which there are excited electronic states energetically close to the ground state, the chemical shift depends mainly on the paramagnetic term. The diamagnetic term is almost invariant in all Co(III) complex compounds because its value is largely determined by core electrons whose wavefunctions are practically uninfluenced by
Consequently the major factor in determining cobalt chemical shifts is temperature-independent paramagnetism (TIP) arising from the d—d splitting. An increase in the paramagnetic term causes decreased shielding of the nucleus and results in resonance at lower fields and hence increased chemical shifts. For Co(III) complexes it can be assumed that only the lowest d—d electronic transition makes a contribution to the paramagnetic term. In an octahedral ligand field the spin-allowed excited states are \( 1\text{T}_{1g}(t_{2g}^5e_g^1) \) and \( 1\text{T}_{2g}(t_{2g}^5e_g^1) \) which correspond to the first and second absorption bands respectively in the visible spectrum. However, only the \( 1\text{T}_{1g} \) state may interact with the ground state \( (1\text{A}_{1g}(t_{2g}^6e_g^0) \) in octahedral symmetry) through its angular momentum under the influence of the magnetic field.

Within the framework of the crystal field theory the paramagnetic shielding of the central ion for Co(III) complexes of octahedral symmetry may be written as Equation 2.4:

\[
\sigma_p = -32 \mu_B^2 \langle r^{-3} \rangle_{3d} k'^2 \tag{2.4}
\]

\[
\Delta E(1\text{A}_{1g} \rightarrow 1\text{T}_{1g})
\]

where \( \mu_B \) is the Bohr magneton, \( k' \) is the orbital reduction factor of the d orbitals, \( r \) is the distance of the d electrons from the nucleus, and \( \Delta E \) is the energy of the first spin-allowed transition. Many classical NMR spectroscopic investigations of octahedral Co(III) complexes have shown that \(^{59}\text{Co} \) NMR shifts are dominated by the \( 1/ \Delta E \) term of the
paramagnetic shielding and therefore the frontier orbitals of the complexes. Equation 2.4 predicts a linear dependence between cobalt shift and the wavelength of the first absorption maximum in the visible spectrum, and this was proved by Griffith and Orgel, and FMR who demonstrated this correlation to hold experimentally. This regularity has been derived for complex compounds with octahedral ligand field symmetry on the assumption that the orbital reduction factor of d orbitals does not vary from complex to complex. But in subsequent investigations, deviations have been found in complexes with ligands from different periods as well as in complexes of low ligand field symmetry e.g. trans-CoX$_2$Y$_4$ complexes of tetragonal (D$_{4h}$) symmetry. Griffith and Orgel, FMR, and others all analysed their $^{59}$Co data by establishing a linear dependence upon $\Delta E^{-1}$. Six-coordinate Co$^{III}$O$_6$ and Co$^{III}$N$_6$ type complexes were thus the first to be studied by $^{59}$Co NMR and their chemical shifts showed a very good correlation with the wavelengths of their characteristic d$\rightarrow$d bands in the visible spectrum.

The theory was further developed by Fujiwara et al. who made allowance for variation of both the orbital reduction factor $k'$, and radial factor $\langle r^{-3}\rangle_3d$ from complex to complex. Indeed Fujiwara et al., Martin and White, and Kanekar et al. all observed deviations from the above correlation for complexes with S-, Se-, and As-donor ligands. Complexes containing first row donor atoms C-, N-, O- lie fairly close to the same correlation line, but complexes with S-, Se-, and As-donors establish a new correlation line having a lower slope (Figure 2.19). This can be explained in terms of varying effects which different ligands have upon
Figure 2.19. $^{59}\text{Co}$ Chemical Shift Dependence upon $1/\Delta E$ for Octahedral Cobalt(III) Complexes. Data from reference 290 (●); data from reference 298 (○).
\( <r^{-3}>_{3d} \) for the 3d orbitals of the cobalt atom. All ligands increase the radial size of the 3d valence orbitals of a metal beyond that which occurs in the uncomplexed ion and some ligands cause a greater cloud expansion or 'nephelauxetic effect' than others.\(^ {300} \) Yamasaki et al.\(^ {301} \) were the first to realise the non-constancy of the radial factor and the significance of the relative magnitude of the electron cloud or nephelauxetic effect as being important in the magnitude of \( \sigma_p \). Any ligand-induced expansion of the Co 3d orbitals causes a reduction in \( <r^{-3}>_{3d} \) which is reflected in a lower slope for \( {}^{59}\text{Co} \) vs \( \Delta E^{-1} \).

However, although some of the above workers discuss this nephelauxetic effect, others have invoked a change in the orbital reduction factor of d-orbitals, \( k' \), as being responsible for the deviations mentioned. The orbital reduction factor is an empirical constant\(^ {260} \) which describes the extent to which the orbital angular momentum for a metal atom in a complex is reduced below its free ion value as a result of covalent bond formation (combined \( \sigma \) and \( \pi \) effects), and can be taken as a measure of deviation from pure 3d orbitals i.e. mixing of metal-ligand orbitals. However, it is extremely difficult to separate these two effects which are thought to occur simultaneously, and it is best to regard any effects on the product \( k'^2 <r^{-3}>_{3d} \) as a whole.\(^ {260} \)

Juranic\(^ {302} \) believes that an investigation into the extent of covalent bonding (extension and deformation of d-orbitals) may be achieved on the basis of the nephelauxetic ratio (\( \beta \)) of complexes under investigation and the corrected slope given by \( 32 \mu_B^2 <r^{-3}>_{3d} k'^2 / \beta \) appears to give a better correlation (\( \beta = \frac{B_{\text{RACAH complex}}}{B_{\text{RACAH free ion}}} \)), where
B = Racah interelectronic repulsion parameter. If $\beta$ is small, the nephelauxetic effect or cloud expansion is large. However, it is expected that d-electron delocalisation is manifested by a uniform decrease of the parameters and $k'$ as well as $\langle r^{-3}\rangle_3$. As a consequence of this more general correlation, Juranic further proposed that there is a magnetochemical series of ligands in transition metal complexes that is independent of the central ion (i.e. ligands arranged according to increasing magnetic shielding of the cobalt nucleus). Juranic in later work invoked a new term, the 'paramagnetic circulation-removing ratio', $\eta_{\sigma\pi}$, closely related to donor atom electronegativity to explain metal-ligand bond covalency effects in nuclear magnetic shielding of Co(III) complexes. However, this just seemed to describe the combined variation of the previous quantities mentioned. Bramley et al. also commented on the involvement of nephelauxetism in $^{59}$Co NMR chemical shifts and proposed the introduction of the nephelauxetic ratio $\beta$ into the Ramsey shielding equation for Co(III) complexes. A good fit to the shielding equation was obtained for orthoaxial complexes in which the ligands lie on the cartesian axes. However, chelating ligands with distorted geometries gave irregular correlation.

$^{59}$Co NMR parameters of various organo-Co(I) and -Co(III) complexes with $\pi$-ligands have been determined. It was shown that despite the large line width, the chemical shifts in organo-Co(I) complexes with $\pi$-ligands (CpCo$^I$L, L = olefin) seem to be governed by the paramagnetic shielding term and its $1/\Delta E$ dependence. The $^{59}$Co shielding can then be rationalised by changes in the energy gap (HOMO - LUMO)
between the frontier MO levels of the complexes when olefins of variable donor and acceptor properties are bound to ($\eta^5$-Cp)Co(I).

2.3.8.2.2.2 Other Relevant $^{59}$Co NMR Studies

The first $^{59}$Co NMR spectra for various Co(III) porphyrin complexes, $[\text{Co(porph)}L_2]^+$ ($\text{porph} = \text{TPP, OEP}$; $L = \text{Im, MeIm, py, NH}_3$), were recorded$^{307}$ in a study of hydrogen bonding in the axial ligands of these complexes. Hydrogen bonding by axial imidazole in $[\text{Co(porph)}(\text{Im})_2]^+$ to solvent or external base was found to influence the chemical shift and line width. The $^{59}$Co chemical shifts could be used to determine d–d transition energies when they are otherwise obscured by other more intense (allowed) bands, as in these metallo-porphyrins.

In the study of $^{59}$Co and $^{14}$N NMR relaxation in $[\text{Co(NO}_2)_6]^{3-}$, mentioned above,$^{269}$ scalar relaxation of the second kind was shown to make a substantial contribution to the $^{59}$Co relaxation, thereby accounting for the large cobalt linewidth in this symmetrical complex. The scalar coupling in this case is between the Co nucleus and the six equivalent directly bonded nitrogens which relax efficiently by a nuclear electronic quadrupole mechanism. The single $^{59}$Co line was found to decrease in intensity with time. In recent and much more detailed work, Eaton and coworkers$^{270}$ found at least 10 different species present in the $^{59}$Co spectra of aged solutions of this hexanitrocobaltate(III) anion. These were assigned to mixed nitro/nitrito/aqua ions. The crystal field strength of the nitro ligand in this type of complex was found to vary according to the number of nitro groups in
the complex. If only one NO$_2^-$ is present in a complex then it is a strong field ligand. By the time the [Co(NO$_2_2$)$_6$]$^{3-}$ ion is reached (i.e. six NO$_2^-$ ligands), it is a significantly weaker ligand and the reported spectroscopic and chemical properties reflect this change. The facile ligand exchange, slow irreversible reduction to Co(II), and changes in crystal field strength were easily detected by $^{59}$Co NMR in this work.$^{270}$

The use of $^{59}$Co NMR spectroscopy to study ligand field effects in five-coordinate bent (15N labelled) nitrosyl complexes of Co(III) is discussed in Chapter 5.

2.3.8.2.3 Oxygen ($^{17}$O) NMR Spectroscopy

Of the naturally occurring oxygen isotopes, only $^{17}$O possesses a nuclear spin (I = 5/2). Due to its very low natural abundance (0.037 %) and its electric quadrupole moment ($Q = -2.6 \times 10^{-26}$ cm$^2$), coupled to its moderate magnetogyric ratio, the $^{17}$O nucleus is one of the more difficult nuclei to observe by NMR spectroscopy and its receptivity is ca. $10^{-5}$ relative to the $^1$H nucleus. For diamagnetic species quadrupole relaxation dominates and can lead to large linewidths. However, because oxygen is so important chemically the potential importance of $^{17}$O NMR as a structural tool is very great. There has been much work in this area and $^{17}$O NMR has been very well reviewed.$^{260,308}$
3.1 Introduction

The procedures detailed below include the extensive organic ligand syntheses that were indispensable before studying the coordination chemistry of the nitrosylmetalloporphyrin complexes.

3.1.1 Porphyrin Synthesis

The porphyrin ligands chosen for this work were 5,10,15,20-meso-tetraphenyl-21H,23H-porphyrin (TPPH$_2$), 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin (OEPH$_2$), and 5,10,15,20-meso-tetrakis[α$^4$-2-(2,2-dimethylpropionamido)phenyl]-21H,23H-porphyrin, trivial name 5,10,15,20-meso-tetrakis(α$^4$-2-pivalamidophenyl)-21H,23H-porphyrin (α$^4$-T$_{PIV}$PPH$_2$) shown in Figures 3.1, 3.2, and 3.3 respectively.

meso-Tetraphenylporphyrin is probably the most widely used porphyrin because of ease of synthesis. TPPH$_2$ is the parent compound of a variety of porphyrins not structurally related to the naturally occurring porphyrins because of the meso-substitution pattern. Crude TPPH$_2$ was prepared in this work by the Rothemund reaction; this condensation of pyrrole and benzaldehyde has been thoroughly studied with respect to synthesis and mechanism of reaction. The crude TPPH$_2$ prepared in this work was typically contaminated with ca. 2% of meso-tetraphenylchlorin (a chlorin or reduced porphyrin) and was purified by the methods of Barnett et al. which involve treatment of the TPPH$_2$-TPCH$_2$ mixture with excess of a high potential quinone in refluxing CHCl$_3$ to oxidise TPCH$_2$ impurity back to TPPH$_2$. After chromatographic
Figure 3.1

meso - Tetraphenylporphyrin (TPPH₂)

Figure 3.2

Octaethylporphyrin (OEPH₂)
Figure 3.3

\[
\alpha^4-\text{Tetrakis(2-pivalamidophenyl)porphyrin},
\]

\[
(\alpha^4-_{TPIV}PPH_2)
\]
workup the chlorin-free $\text{TPPH}_2$ was isolated in good yield.

**Octaethylporphyrin** is perhaps one of the more important and widely used model compounds for structural studies related to naturally occurring porphyrins due to its similar substitution pattern and high symmetry. The synthetic methods used in this work are illustrated in Figure 3.4. Ethyl 3-oxopentanoate was prepared by Grignard synthesis from ethyl cyanoacetate (Figure 3.4, step 1).\(^{312}\) This starting material was eventually converted by modification of several reported routes\(^{255,313}\) into the monopyrrole precursor, IV (Figure 3.4 step 2a to 5), before self-condensation and oxidation to the OEPH\(_2\) ligand (Figure 3.4, step 6).

meso-Tetrakis(\(\alpha^4\)-2-pivalamidophenyl)porphyrin was the first of the picket fence type porphyrins. The concept of picket fence porphyrins was developed by Collman *et al.*\(^{256}\) in an attempt to mimic the chemistry of the active site of Mb. Such porphyrins have great steric bulk on one side of the porphyrin plane creating a non-protic cavity whilst leaving the other side unencumbered (Figure 3.5). A bulky ligand such as N-alkyl imidazole will coordinate only on the unhindered side of the porphyrin, thus leaving a hydrophobic pocket for complexation of small molecules, e.g. O\(_2\).

The synthetic procedure is outlined in Figure 3.6.\(^{256,314}\) Condensation of 2-nitrobenzaldehyde and pyrrole followed by reduction of the $T^\text{NITRO}$PPH\(_2\) product led to a satisfactory yield of $T^\text{AMINO}$PPH\(_2\) which is a mixture of four atropisomers in statistical abundance (Figure 3.7). This biphenyl-type atropisomerism was first shown to occur by Ullman in ortho-substituted meso-tetraphenylporphyrins.\(^{315}\) These porphyrins have the phenyl group oriented nearly normal
Figure 3.4
Reaction Scheme for Octaethylporphyrin (OEPH₂)

(1) EtMgI
(2) H₂O⁺

N≡CCH₂CO₂Et → Ethyl cyanocacetate

1. Ethyl 3-oxopentanoate → CH₃COOH NaNO₂ → Oxime

IV, 98% → CH₃COOH [Fe(CN)₆]³⁻ △ → OEPH₂

2a. 6. (1) CH₃OH, KOH, △
(2) H₂O⁺

5. III, 35 - 38% → CH₃COOH (CH₃CO₂)₄Pb

IV. 98% → THF NaBH₄ BF₃·OEt₂ (B₂H₆) → I, 61%
Figure 3.5
THE "PICKET FENCE" CONCEPT

hydrophobic pocket for ligand binding

porphyrin ring

bulky axial base prevents dioxygen, nitric oxide coordination on the unhindered side

bulky R group disfavours coordination of base on picket fence side
Figure 3.6

Reaction Scheme for $\alpha^4$-Tetrakis(2-pivalamidophenyl)porphyrin, ( $\alpha^4$-T$_{PIV}$PPH$_2$ )

Where $X = COC(CH_3)_3$

Statistical Mixture of Four Atropisomers
Figure 3.7
Interconversion of the Four Atropisomers of meso-Tetrakis(o-substituted phenyl) porphyrin Depicted Schematically

X = NO₂  \[ T_{\text{NITROPPH}_2} \]
X = NH₂  \[ T_{\text{AMINOPOPH}_2} \]
X = NHCO(CH₃)₃  \[ T_{\text{PTVPPH}_2} \]

<table>
<thead>
<tr>
<th>STATISTICAL ABUNDANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha^4_- )</td>
</tr>
<tr>
<td>1/8</td>
</tr>
</tbody>
</table>
to the porphyrin plane, projecting the o-substituent above or below the plane. In such cases the four atropisomers can be interconverted, and thermal equilibration gives the expected statistical ratio of abundance ($\alpha^4:\alpha^3:\alpha^2$-cis-:\alpha^2-trans-, 1:4:2:1). The atropisomeric interconversion and temperature required for equilibration depends on the ortho-phenyl substituents. The $\alpha^4$-atropisomer is seen to represent the essence of the PFP (Figure 3.5).

In Collman's original work and later reports the separation of the $\alpha^4$-isomer was achieved by exhaustive column chromatography. This method was used initially, but it gave low yields. A better method is a modification of two approaches involving isolation of the $\alpha^4$-isomer by equilibrium displacement on binding to silica gel. Immediately after separation, solutions of the $\alpha^4$-$\text{AMINO}$PPH$_2$ were derivatised (N-acylation) with pivaloyl chloride to give, after subsequent workup, moderate yields (ca. 50%) of pure $\alpha^4$-$\text{PIV}$PPH$_2$ as judged by $^1$H NMR.

3.1.2 Metalloporphyrin Complexes

Heat-stable metalloporphyrins (TPP/OEP) were prepared from boiling DMF. The heat and light sensitive $\alpha^4$-$\text{PIV}$PPH$_2$ was metallated using modifications of published methods for Fe($\text{PIV}$PP)Br$^{256,314}$ and Co($\text{PIV}$PP).$^{317,319-320}$

3.1.3 Nitrosyl Complexes

The nitrosyls were prepared from purified nitric oxide ($^{14}$NO and $^{15}$NO, see Chapter 2 Section 2.2) in two ways:

(a) Reaction of preformed metal complex with NO in a suitable solvent. This method was generally used for
M(porph)NO complexes (M = Fe, Co) (see Figure 3.8 for complete synthetic route to Co(TPP)NO), and for Fe(salphen)NO and CoCl₂(NO)(PPh₂Me)₂ (see Chapter 5, Sections 5.3 and 5.1.2.3 respectively for results and discussion). Fe(porph)NO complexes also required alcohol in the reaction mixture for 'reductive nitrosylation' to occur.¹⁵³,³²¹

(b) Reaction of metal salt (cobalt (II) acetate tetrahydrate), ligand, and nitric oxide in a suitable solvent to give the desired nitrosyl complex. This method was generally used for the Co(III) nitrosyls discussed in Chapter 5.

3.1.4 Nitro Complexes

The 6-coordinate nitro complexes were prepared from the 5-coordinate nitrosyls ¹⁴,¹⁵N) by reaction with oxygen at room temperature in the presence of axial base in a suitable solvent (Equation 3.1):³²²

\[
(L)_4\text{Co—NO} + B + \frac{1}{2} \text{O}_2 \rightarrow B(L)_4\text{Co—NO}_2
\]  

(3.1)

L = equatorial ligand, B = axial base

3.1.5 μ-Peroxo Complexes

These were prepared by literature methods³²³ using ¹⁷O₂ and ¹⁶O₂. They are discussed more fully in Chapter 5.

3.2 Ligand Synthesis

3.2.1 meso-Tetraphenylporphyrin, TPPH₂

3.2.1.1 Crude meso-TPPH₂

Benzaldehyde (66.5 ml, 0.653 mol) and pyrrole (46.5 ml,
Figure 3.8

REACTION SCHEME FOR TETRAPHENYLPORPHYRIN (TPPH)

- **Propionic acid**
- **DDQ** in **CHCl₃**
- **CoCl₂** in **DMF**
- **N₂** in **Piperidine**

**Yield:**
- 2 = 10% of total yield = TPPH₂
- Up to 20% yield
- 82% yield
- 88% yield

**Purity:**
- 75% = 90%
0.672 mol) were added simultaneously to refluxing propionic acid (2.5 l). After complete addition, the resulting mixture was refluxed for a further 30 min before cooling to room temperature. The product was filtered off, washed thoroughly with boiling water (500 ml) and then methanol (200 ml) until the washings were colourless. The resulting lustrous purple crystals were dried under vacuum for several hours to remove traces of adsorbed propionic acid (yield 17.9 g, 17.3 %). Concentration of the propionic acid filtrate by distillation to ca. 500 ml afforded a second crop of TPPH₂ crystals (4.7 g, total yield 22.6 g, 22 %). The visible absorption spectrum of the crude TPPH₂ in AnalaR benzene [λₘₐₓ. 483sh, 515, 548, 592, 646 nm] indicated ca. 2-3 % contamination with meso-tetraphenylchlorin (TPCH₂). The propionic acid filtrate was collected separately from the washing liquors and after refluxing with KMnO₄ (50 g) for 2 hr, the solvent was distilled before reuse.

3.2.1.2 'Chlorin-free' meso-TPPH₂

Crude TPPH₂ (20 g, 32.5 mmol) was dissolved in ethanol-free chloroform (2.5 l) and the solution brought to reflux. 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ, 5 g, 22 mmol) dissolved in dry benzene (150 ml) was slowly added dropwise and the mixture was refluxed for a further 3 hr before filtration of the hot yellow-green solution under suction through a sintered glass column (4 cm dia x 18 cm long) containing neutral alumina (300 g, Brockmann grade I). When dry the alumina was washed with CH₂Cl₂ (400 ml) and the combined dark red filtrates were concentrated to ca. 200 ml on a rotary evaporator. Methanol (200 ml) was added and the
chilled mixture filtered to give well-formed glistening purple crystals which were washed well with methanol and dried thoroughly at 100°C. (yield 17 g, 85 %). (Found: C, 85.61; H, 4.92; N, 9.17. Calc for C₄₄H₃₀N₄: C, 85.97; H, 4.92; N, 9.11 %); m/z 614 (M⁺); ¹H NMR δH (90 MHz, CDCl₃, standard Me₄Si) -2.76[2H, br s, 2NH], 7.74[12H, m, 12 m- and p-phenyl H], 8.21[8H, m, 8 o-phenyl H], 8.84[8H, s, 8 β-pyrrolic H]; λmax (benzene) 372sh (ε 24900 l mol⁻¹ cm⁻¹), 418 (435000), 483sh (3630), 515 (19440), 548 (8050), 592 (5590), 646 nm (3800).

3.2.2 Octaethylporphyrin, OEPH₂, (Figure 3.4)

3.2.2.1 Grignard Preparation of Ethyl 3-Oxopentanoate, (Figure 3.4, step 1)

Dry magnesium turnings (38.9 g, 1.6 mol) were placed in a 2 l round bottom flask equipped with a mechanical stirrer, dropping funnel, nitrogen inlet, thermometer, and efficient condenser. The flask was placed under nitrogen and a small crystal of iodine was sublimed onto the metal surface to help initiate the reaction. Iodoethane (272 g, 1.74 mol) in anhydrous diethyl ether (250 ml) was carefully added over 5 hr with stirring whilst the reaction temperature was kept at ca. 30°C using an ice-water bath. The prepared EtMgI solution was vigorously stirred and maintained at 25°C while purified ethyl cyanoacetate (66 ml, 72 g, 0.62 mol) in anhydrous diethyl ether (100 ml) was added over 2-5 hr. The resulting dark blue-green viscous mixture was then left to stand for 1 week at room temperature protected from atmospheric moisture to allow the reaction to reach completion. The vigorously
stirred reaction mixture was then cooled and slowly decomposed by addition of cold saturated NH₄Cl solution (250 ml). Distilled water (250 ml) and concentrated hydrochloric acid (200 ml) were then added to clarify the aqueous layer. The ether layer was separated and the aqueous layer was ether extracted (3 x 50 ml). Concentrated hydrochloric acid (50 ml) was added to clarify totally the aqueous layer which was again ether extracted (7 x 50 ml). A further portion of concentrated hydrochloric acid (50 ml) was added to the aqueous layer which was finally ether extracted (5 x 50 ml). The combined ether extracts were vigorously stirred with 10 % (2.7 M) hydrochloric acid (200 ml) to hydrolyse any β-imino ester present, and the aqueous layer was separated and ether extracted (2 x 50 ml). The combined ether layers were washed with water (3 x 100 ml), saturated NaHCO₃ solution (2 x 200 ml), and finally again with water (3 x 100 ml), and then dried over anhydrous Na₂SO₄ (200 g). After filtration the solvent was removed on a rotary evaporator. Distillation of this crude product under reduced nitrogen pressure yielded a yellowish fraction boiling at 109-112°C, 6 mmHg (yield 54.82 g, 61 %). ¹H NMR δH (90 MHz, CDCl₃, Me₄Si) [K = keto and E = enol tautomers] 1.08[3H, t, J=7 Hz, CH₃CH₂CO, K+E], 1.28[3H, t, J=7 Hz, OCH₂CH₃, K+E], 2.20[2H, q, J=7 Hz, CH₃CH₂C(OH), E], 2.58[2H, q, J=7 Hz, CH₃CH₂CO, K], 3.40[2H, s, COCH₂COO, K], 4.19[2H, q, J=7 Hz, OCH₂CH₃, K+E], 5.00[1H, s, C(OH)=CHCOO, E] (the concentration of the enol form is low, and the enol OH proton was not detected under the experimental conditions); v_max. (thin film) 1730s and 1710s (C=O), 1650m (−OH---O=C−, β-keto ester H bonding enol form) 1630 cm⁻¹ (C=C, enol form).
Knorr Synthesis of 2-Ethoxycarbonyl-3-ethyl-4-acetyl-5-methyl-pyrrole, Pyrrole I, (Figure 3.4, step 2a,b)

Into an ice cooled 500 ml round bottom flask equipped with a magnetic stirring bar, thermometer, and dropping funnel were placed ethyl 3-oxopentanoate (100 g, 0.7 mol) and glacial acetic acid (200 ml). A solution of NaNO₂ (69 g, 1 mol) in water (110 ml) was added dropwise to the stirred solution keeping the temperature <45°C. The oximino precursor solution was ready for the Knorr reaction as soon as the nitrite addition was complete. 2,4-Pentanedione (100 g, 1 mol), zinc dust (175 g, 2.67 mol), sodium acetate (100 g, 1.2 mol), and glacial acetic acid (150 ml) were placed into a 1 l three neck round bottom flask equipped with a mechanical stirrer, thermometer, dropping funnel, and efficient condenser. The ethyl 2-oximino-3-oxopentanoate solution was added dropwise with vigorous stirring so the mixture refluxed steadily. After the initial reaction had ceased, the mixture was boiled under reflux for 4 hr, and before the temperature fell <100°C, the solution was decanted from the excess zinc which was then washed well with glacial acetic acid. The combined washings were diluted (X4) with cold water, and the product oiled out and crystallised. The product was filtered off, washed thoroughly with water, dissolved in CH₂Cl₂ (600 ml), and the solution filtered to remove residual zinc. The solution was washed with water (200 ml) and reduced in volume to ca. 300 ml on a rotary evaporator and placed on a steam bath. As the CH₂Cl₂ distilled off, hot hexane was added and the boiling continued until the remaining hexane barely covered the crystallised solid. After cooling the off-white
product was collected by filtration, washed with cold hexane and dried. (yield 95.6 g, 61 %). MP 117.5-118°C (from EtOH) (lit. 255 115°C); \( ^1H \) NMR \( \delta \) \( H \) (90 MHz, CDCl\(_3\), Me\(_4\)Si) 1.18[3H, t, J=7.5 Hz, CH\(_3\)CH\(_2\)-], 1.37[3H, t, J=7.5 Hz, CH\(_3\)CH\(_2\)O-], 2.47[3H, s, CH\(_3\)-], 2.55[3H, s, CH\(_3\)CO-], 3.09[2H, q, J=7.5 Hz, CH\(_3\)CH\(_2\)-], 4.35[2H, q, J=7.5 Hz, CH\(_3\)CH\(_2\)O-], 9.80[1H, br s, NH]; \( \nu \) (KBr disc) 1700s and 1620s (C=O), 3200br s cm\(^{-1}\) (N-H).

3.2.2.3 2-Ethoxycarbonyl-3,4-diethyl-5-methylpyrrole, Pyrrole II, (Figure 3.4, step 3)

The pyrrole I (94.2 g, 0.422 mol) was dissolved in dry THF (1 l) in a 3 l round bottom flask equipped with a mechanical stirrer, pressure equalised dropping funnel fitted with a subaseal, condenser, nitrogen inlet, and thermometer. The solution was cooled to 5°C and solid NaBH\(_4\) (39.0 g, 1.03 mol) was added and completely dispersed by stirring before addition of BF\(_3\).OEt\(_2\) (200 g, 173.3 ml, 1.41 mol) at a rate which kept the reaction temperature at 10°C. After complete addition the mixture was warmed to 25°C and stirred for 1 hr. Cold 5 % (1.35 M) hydrochloric acid was cautiously added to the chilled (15°C) mixture which was then poured into a 2 l separatory funnel containing water (500 ml). The organic phase was separated and the aqueous phase was ether extracted (5 x 150 ml). The combined THF/ether phase was washed with saturated NaCl solution (200 ml), then with water (200 ml) before reduction in volume to ca. 500 ml and drying over anhydrous K\(_2\)CO\(_3\) (200 g). After filtration the solvent was removed to give a pale green-yellow product. (yield 88.3 g, 100 %). MP 75.0, 75.5°C (from 96 % EtOH) (lit. 313 75.5°C); \( ^1H \)
NMR $\delta_H$ (90 MHz, CDCl$_3$, Me$_4$Si) 1.06[3H, t, J=7.5 Hz, CH$_3$CH$_2$-],
1.14[3H, t, J=7.5 Hz, CH$_3$CH$_2$-], 1.33[3H, t, J=7.5 Hz,
CH$_3$CH$_2$O-], 2.20[3H, s, CH$_3$-], 2.38[2H, q, J=7.5 Hz, CH$_3$CH$_2$-],
2.72[2H, q, J=7.5 Hz, CH$_3$CH$_2$-], 4.29[2H, q, J=7.5 Hz,
CH$_3$CH$_2$O-], 8.78[1H, br s, NH]; (KBr disc) 1670s (C=O),
and 3010s cm$^{-1}$ (N-H).

3.2.2.4 2-Ethoxycarbonyl-3,4-diethyl-5-acetoxyethyl-
pyrrole, Pyrrole III, (Figure 3.4, step 4)

Pyrrole II (17.7 g, 84.6 mmol) in glacial acetic acid
(490 ml) was stirred during the addition of lead tetra-
acetate (37.5 g, 84.6 mmol) in small portions to give an
orange-red mixture. After complete addition the mixture was
stirred for 2 hr at room temperature before removal of
solvent on a rotary evaporator at 30°C. The red residue was
dissolved in CHCl$_3$ (250 ml) to give a crimson solution which
was washed with water (5 x 100 ml) and then dried over
anhydrous Na$_2$SO$_4$ (100 g). After filtration the solvent was
removed and the crude product was recrystallised from AnalaR
methanol. (yield 7.88-8.49 g, 35-37.5 %). MP 87°C (lit. 91°C);
$^1$H NMR $\delta_H$ (90 MHz, CDCl$_3$, Me$_4$Si) 1.10[3H, t, J=7.5 Hz,
CH$_3$CH$_2$-], 1.14[3H, t, J=7.5 Hz, CH$_3$CH$_2$-], 1.35[3H, t, J=7.5
Hz, CH$_3$CH$_2$O-], 2.07[3H, s, CH$_3$COOCH$_2$-], 2.47[2H, q, J=7.5 Hz,
CH$_3$CH$_2$-], 2.73[2H, q, J=7.5 Hz, CH$_3$CH$_2$-], 4.31[2H, q, J=7.5
Hz, CH$_3$CH$_2$O-], 5.02[2H, s, CH$_3$COOCH$_2$-], 9.03[1H, br s, NH];
$\nu_{\max}$. (KBr disc) 1735s and 1650s (C=O), 3410s cm$^{-1}$ (N-H).

3.2.2.5 3,4-Diethyl-5-hydroxymethyl-pyrrole 2-carboxylic
acid, Pyrrole IV, (Figure 3.4, step 5)

Pyrrole III (15 g, 56 mmol) and solid KOH 30 g, 0.535
mol) were refluxed in methanol (210 ml) for 4 hr. After cooling the solution was filtered and the filtrate and methanol washings were evaporated to dryness before addition of water (150 ml). The aqueous phase was ether extracted (3 x 50 ml) before stirring and cooling to 0°C. The aqueous phase was then acidified dropwise slowly with 3M hydrochloric acid (350 ml), and the sandy-brown precipitate was filtered off and washed with 20 % w/v sodium acetate solution (100 ml), then water, and dried thoroughly under vacuum. (yield 10.87 g, 98 %). MP 132°C (lit. 313 120°C); $^1$H NMR $\delta_H$ (90 MHz, CDCl$_3$, Me$_4$Si) 1.09[3H, t, J=7 Hz, CH$_3$CH$_2$-], 1.16[3H, t, J=7 Hz, CH$_3$CH$_2$-], 2.43[2H, q, J=7 Hz, CH$_3$CH$_2$-], 2.76[2H, q, J=7 Hz, CH$_3$CH$_2$-], 3.8[2H, s, HOCH$_2$-], 4.43[1H, s, HOCH$_2$-], 7.7[1H, vbr s, -COOH], 9.09[1H, br s, NH]; v$_{\text{max}}$ (KBr disc) 1655s (C=O) and 3430s cm$^{-1}$ (N-H).

3.2.2.6 Octaethylporphyrin, (Figure 3.4, step 6)

Pyrrole IV (10 g, 50.7 mmol) in glacial acetic acid (40 ml) containing K$_3$[Fe(CN)$_6$] (1.0 g, 3.04 mmol) was heated at 100°C with magnetic stirring for 1 hr. After standing overnight at room temperature the mixture was filtered to yield crude OEPH$_2$, which was washed well with methanol, and recrystallised from toluene using a Soxhlet extractor to yield fine lustrous purple crystals of pure OEPH$_2$ which were dried under vacuum at 75°C for several hours. (yield 2.81 g, 42 %). (found: C,81.13; H,8.93; N,10.56. Calc. for C$_{36}$H$_{46}$N$_4$: C,80.85; H,8.67; N,10.48 %); m/z 534 (M$^+$); $^1$H NMR $\delta_H$ (90 MHz, CDCl$_3$, Me$_4$Si) -3.73[2H, s, 2NH], 1.92[24H, t, J=7.5 Hz, 8 $\beta$-pyrrolic CH$_3$CH$_2$-], 4.10[16H, q, J=7.5 Hz, 8 $\beta$-pyrrolic CH$_3$CH$_2$-], 10.10[4H, s, 4 methine H]; $\lambda_{\text{max}}$. (benzene) 378sh
3.2.3 meso-Tetrakis(α^4-2-pivalamidophenyl)porphyrin,
\[ \alpha^4-\text{TPivPPH}_2 \]

3.2.3.1 meso-Tetrakis(2-nitrophenyl)porphyrin,
\[ \text{T}_{\text{NITRO}}\text{PPH}_2 \]

2-Nitrobenzaldehyde (100 g, 0.66 mol) was dissolved in glacial acetic acid (1700 ml) in a 3 l round bottom flask equipped with a mechanical stirrer, dropping funnel, and efficient condenser. The solution was brought to reflux, and distilled pyrrole (46 ml, 47.6 g, 0.71 mol) was added slowly to the reaction mixture so as to keep it vigorously refluxing. The resulting black mixture was refluxed for a further 30 min and then cooled in an ice-bath to ca. 30°C. During the cooling CHCl\(_3\) (250 ml) was gradually added to prevent the formation of intractable tars. The bright purple crystalline product was collected by filtration and washed with CHCl\(_3\) (5 x 100 ml), and dried at 100°C overnight. (yield 16.11-16.79 g, 12.3-12.8 %). \( \lambda_{\text{max}} \) (DMF) 419, 480, 515, 549, 593, 649 nm; \( \nu_{\text{max}} \) (KBr disc) 1525 (\( \nu_{\text{as}}\)NO\(_2\)) and 1345 cm\(^{-1}\) (\( \nu_{\text{s}}\)NO\(_2\)).

3.2.3.2 meso-Tetrakis(2-aminophenyl)porphyrin,
\[ \text{T}_{\text{AMINO}}\text{PPH}_2, \text{ A Statistical Mixture of Four Atropisomers} \]

\[ \text{T}_{\text{NITRO}}\text{PPH}_2 \] (12.0 g, 15 mmol) was dissolved in concentrated hydrochloric acid (600 ml) in a 5 l beaker. SnCl\(_2\).2H\(_2\)O (50 g, 0.22 mol) dissolved in concentrated hydrochloric acid (50 ml) was added, and the solution was stirred at room
temperature for 1.5 hr. The beaker was then placed in a hot water bath atop a hotplate-stirrer, making sure that the bottom of the beaker was not in contact with the bottom of the heating bath, and a thermometer was suspended such that it touched neither the bottom nor the sides of the beaker. The temperature of the reaction mixture was raised to 65°C in a 25 min period and was kept at 65-70°C for 25 min with good mechanical stirring (heating the solution above 75°C results in a low yield of impure product). After this time the beaker was placed in an ice bath and swirled to bring the contents to room temperature, and then the solution was very carefully neutralised by the slow addition (ca. 30 min) of concentrated aqueous ammonia (>600 ml) keeping the mixture at room temperature. Chloroform (1 l) was added and the highly basic solution (pH>10) was stirred for 18 hr before transfer to a 5 l separatory funnel. The organic phase was separated and water (1500 ml) was added to the aqueous phase and the mixture was extracted with CHCl₃ (5 x 150 ml). The combined CHCl₃ extracts were returned to the funnel and washed with 2M aqueous ammonia (1 l). The CHCl₃ layer was separated and the aqueous layer was further extracted with CHCl₃ (3 x 50 ml). The combined organic phase was reduced to ca. 600 ml and filtered, and the filtrate and washings were reduced to ca. 250 ml, before 96 % ethanol (150 ml) and concentrated ammonia (10 ml) were added and the solvent mixture was slowly evaporated to ca. 200 ml. The sides of the Buchi flask were washed down with the minimum of CHCl₃ and absolute ethanol (100 ml) was added and the volume was slowly reduced to ca. 75 ml. The resulting almost black microcrystalline product was collected by filtration, washed thoroughly with 96 %
ethanol (5 x 10 ml), and dried in an oven at 100°C for several hours. (yield 7.53 g, 74 %). $^1$H NMR $\delta_H$ (90 MHz, CDCl$_3$, Me$_4$Si) -2.69[2H, br s, 2 NH], 3.42[8H, br s, 4 NH$_2$], 6.94-7.84[16H, m, 16 phenyl substituted H], 8.86[8H, br s, $\beta$-pyrrolic H]; $\lambda_{max}$. (CHCl$_3$) 370sh, 419, 480, 515, 548, 588, 649 nm.

3.2.3.3 Equilibrium Displacement of $\alpha^4$-TAMINO$^{PPH2}$ on Binding to Silica Gel

AnalaR benzene (85 ml) and silica gel (36 g, Merck grade 230-400 mesh, 500 m$^2$g$^{-1}$) were added to a 250 ml three neck round bottom flask fitted with a mechanical stirrer, dry nitrogen inlet, thermometer, condenser, and nitrogen bubbler outlet. The flask was immersed in an oil bath and maintained at 75-80°C with stirring and a steady flow of benzene-saturated dry nitrogen gas. After two hours equilibration, TAMINO$^{PPH2}$ (1.0 g, 1.48 mmol) was added to the flask, and after an additional 20 hr equilibration, the dark red slurry with clear supernatant was cooled to room temperature and poured complete with benzene washings into a glass chromatography column (4 cm id x 8 cm long). The residual undesired atropisomers ($\alpha^3$, cis-$\alpha^2$, trans-$\alpha^2$) were eluted from the column with dry benzene-ether (1:1) until the column effluent became very pale red (ca. 500 ml). AnalaR acetone-ether (1:1) was then used to elute the desired $\alpha^4$-atropisomer from the column (ca. 250 ml). This solution was then immediately used in the derivatisation reaction following. The column effluent was carefully monitored by silica gel TLC (benzene-ether, 1:1) throughout the column chromatographic separation.
3.2.3.4 Derivatisation of $\alpha^4$-TAMINO$\text{PPH}_2$ to $\alpha^4$-TPIV$\text{PPH}_2$

The acetone-ether solution of $\alpha^4$-TAMINO$\text{PPH}_2$ was carefully reduced in volume on a rotary evaporator at ambient temperature to ca. 100 ml, and dry pyridine (1.0 ml, 12.4 mmol) and pivaloyl chloride (1.0 ml, 8.12 mmol) were added in that order, and the solution was stirred at room temperature for 3 hr, protected from atmospheric moisture. After this time, the mixture was stripped to dryness, the residue redissolved in CHCl$_3$ (200 ml), filtered to remove any silica gel, and washed with 2M aqueous ammonia (3 x 100 ml), then water (2 x 100 ml), and dried over anhydrous Na$_2$SO$_4$ (100 g). After filtration, the CHCl$_3$ was removed, and the dark purple residue was dried thoroughly under vacuum before further purification by silica gel column chromatography (Merck grade 60-120 mesh, 2 cm id x 30 cm long, 60 g, CHCl$_3$) by elution with dry CHCl$_3$-Et$_2$O (4:1). The intermediate red fluorescent fraction (at 366 nm) was eluted from the column (ca. 250 ml), and the solvent was removed on a rotary evaporator. The residue was redissolved in CHCl$_3$ (100 ml) and n-heptane (100 ml) and absolute ethanol (100 ml) were added and the volume of the solvent mixture was reduced very slowly at room temperature (to ca. 50 ml) to effect crystallisation. The purple-red crystalline product was collected by filtration, washed with a little ice-cold ethanol and dried thoroughly under vacuum. (yield 0.50-0.74 g, 33-50 %). (Found: C, 72.88; H, 6.19; N, 10.52. Calc for C$_{64}$H$_{66}$N$_{8}$O$_{4}$·1/2 CHCl$_3$: C, 72.34; H, 6.26; N, 10.46 %. Found: C, 73.59; H, 6.80; N, 10.35. Calc for C$_{64}$H$_{66}$N$_{8}$O$_{4}$·1/3 CHCl$_3$: C, 73.52; H, 6.36; N, 10.66 %; found: C, 74.38; H, 6.61; N, 10.08. Calc for C$_{64}$H$_{66}$N$_{8}$O$_{4}$·1/4 CHCl$_3$: C, 74.12; H, 6.41; N, 10.76 %; $^1$H NMR $\delta$$_H$ (90 MHz, CDCl$_3$, Me$_4$Si)
0.074[36H, s, 4-NHCO(CH₃)₃], 7.41-7.94[16H, m, 16 phenyl substituted H], 8.77[4H, s, 4-NHCO(CH₃)₃], 8.83[8H, s, 8 β-pyrrolic H]; λ_max. (CHCl₃) 370sh (ε 3080 1 mol⁻¹ cm⁻¹), 418 (276100), 480sh (3100), 512 (19050), 544 (4070), 588 (5920), 644 nm (1590); v_max. (KBr disc) 1685 cm⁻¹ (C=O).

3.3 Preparation of Metalloporphyrin Complexes

3.3.1 Iron Porphyrin Complexes

3.3.1.1 Chloro-meso-tetraphenylporphyrinato-iron(III), Fe(TPP)Cl

Dry DMF (250 ml) and TPPH₂ (2.0 g, 3.25 mmol) were placed in a round bottom flask equipped with magnetic stirring bar and efficient condenser and the mixture was brought to reflux using an oilbath and stirrer-hotplate. Reflux was allowed for 15 min to enable complete dissolution to occur, then FeCl₂·4H₂O (1.0 g, 5.03 mmol) was added and vigorous reflux was continued. After 15 min, completion of reaction was checked for by loss of the red fluorescence of the porphyrin free base at 366 nm. A further portion of FeCl₂·4H₂O (1.0 g, 5.03 mmol) was then added and the reaction allowed to proceed at a vigorous rate for a further 15 min, after which time it was judged to have gone to completion. The oilbath was replaced by an ice-water bath and the reaction mixture was chilled before the addition of ice-cold water (250 ml) with swirling to precipitate the metalloporphyrin. The partially crystalline purple-brown product was collected by filtration, washed with water (ca. 250 ml) until the washings were colourless, and dried under vacuum at 50°C.
in a drying pistol charged with \( \text{P}_2\text{O}_5 \), and recrystallised from \( \text{CH}_3\text{OH-CHCl}_3 \). (yield 2.20-2.30 g, 96-100 %). (found: C,70.69; H,3.69; N,7.44. Calc for \( \text{FeC}_{44}\text{H}_{28}\text{N}_4\text{Cl.1/2CHCl}_3 \): C,70.22; H,3.73; N,7.27 %; found: C,72.71; H,3.94; N,7.74 calc for \( \text{FeC}_{44}\text{H}_{28}\text{N}_4\text{Cl.1/4CHCl}_3 \): C,72.42; H,3.88; N,7.63 %); \( \lambda_{\text{max}} \) (\( \text{CHCl}_3 \)) 378sh (\( \varepsilon 58670 \) 1 mol\(^{-1}\) cm\(^{-1}\)), 415 (107950), 510 (12970), 578 (3440), 657 (2800), 691 nm (3170); \( \lambda_{\text{max}} \) (pyridine) 418 (119400), 509 (10600), 530 (10200), 655 (2200), 698 nm (2700).

3.3.1.2 Chlorooctaethylporphyrinatoiron(III), \( \text{Fe(OEP)}\text{Cl} \)

\( \text{Fe(OEP)}\text{Cl} \) was prepared in an analogous fashion to \( \text{Fe(TPP)}\text{Cl} \) using OEPH\(_2\) (1.0 g, 1.87 mmol), dry DMF (100 ml), and \( \text{FeCl}_2 \cdot 4\text{H}_2\text{O} \) (1.5 g, 7.5 mmol, in 2 portions). The cocoa brown-purple microcrystalline product collected by filtration was dried under vacuum at 75°C for several hours. (yield 0.968 g, 83 %). (found: C,68.94, H,7.20; N,9.02. Calc for \( \text{FeC}_{36}\text{H}_{44}\text{N}_4\text{Cl} \): C,69.29; H,7.11; N,8.98 %); \( \lambda_{\text{max}} \) (\( \text{CHCl}_3 \)) 379 (\( \varepsilon 88160 \) 1 mol\(^{-1}\) cm\(^{-1}\)), 507 (8210), 536 (8540), 576 (2770), 637 nm (4250).

3.3.1.3 Bromo-meso-tetrakis(\( \alpha^4\)-2-pivalamidophenyl)-porphyrinatoiron(III), \( \text{Fe(T_{PIV}PP)}\text{Br} \)

Anhydrous \( \text{FeBr}_2 \) (3.0 g, 14 mmol), \( \alpha^4\)-\( \text{T_{PIV}PPH}_2 \) (3.0 g, 3 mmol), and dry pyridine (1.0 ml, 12.4 mmol) were dissolved in 1,2-dimethoxyethane (200 ml) under vigorously oxygen-free conditions. The mixture was refluxed under nitrogen and completion of reaction was checked for by alumina TLC (\( \text{CHCl}_3 \)) and spectroscopically by observing the absorption spectrum in the Soret region of small aliquots of the solution that had
been exposed to air and then treated with dilute HBr. The 445 nm absorption, attributed to $\alpha^4_{\text{TPIVPPH}_4}^{2+}$, decreased in intensity and the 417 nm absorption, due to Fe(TPIVPP)Br, increased in intensity as the reaction proceeded. After 4 hr reflux the reaction was considered to be complete and the mixture was stripped to dryness. The residue was taken up in CHCl$_3$ (100 ml) and chromatographed on a column of basic alumina, grade I (3 cm id x 35 cm long, CHCl$_3$, 278 g). All the porphyrinic material (first and second fractions eluting, Fe(TPIVPP)Br and [Fe(TPIVPP)]$_2$O respectively) was removed from the column leaving a single orange band of iron bromide complexes at the top of the column. Concentrated HBr (1 ml) was added and the mixture was dried overnight (Na$_2$SO$_4$), filtered and evaporated to dryness. The purple residue was redissolved in CH$_2$Cl$_2$, methanol and heptane were added and the mixture was very slowly reduced in volume to give dark purple microcrystals which were collected by filtration, washed with methanol, and dried under vacuum. (yield 2.4 g, 71 %). (found: C, 69.36; H, 6.74; N, 8.50. Calc for FeC$_{64}$H$_{64}$N$_8$O$_4$Br.1.5C$_7$H$_{16}$: C, 69.08; H, 6.85; N, 8.65 %); $\lambda_{\text{max.}}$ (CHCl$_3$) 360sh (ε 48900 1 mol$^{-1}$ cm$^{-1}$), 390 (64500), 417 (88770), 508 (13740), 584 (3810), 654 (3300), 680 nm (3100); $v_{\text{max.}}$ (KBr disc) 1680 cm$^{-1}$ (C=O).

3.3.2 Cobalt Porphyrin Complexes

3.3.2.1 meso-Tetraphenylporphyrinatocobalt(II), Co(TPP)

Co(TPP) was prepared in the same way as Fe(TPP)Cl using TPPH$_2$ (2.0 g, 3.25 mmol), dry DMF (250 ml), and CoCl$_2$ (1.0 g, 7.66 mmol, in two portions). The brick red-brown complex was
collected by filtration, washed with water and thoroughly
dried under vacuum. (yield 1.80 g, 82 %). (found: C, 78.71;
H, 4.23; N, 8.17. Calc for CoC_{44}H_{28}N_{4}: C, 78.68; H, 4.20; N, 8.34%
); \( \lambda_{\text{max.}} \) (CHCl\(_3\)) 410 (\( \varepsilon = 231000 \) 1 mol\(^{-1}\) cm\(^{-1}\)), 529 (14800),
642 sh nm (260).

3.3.2.2 Octaethylporphyrinatocobalt(II), Co(OEP)

Co(OEP) was prepared in an analogous manner to Co(TPP)
using OEPH\(_2\) (1.0 g, 1.87 mmol), dry DMF (100 ml), and CoCl\(_2\)
(1.0 g, 7.66 mmol, in two portions). The resulting dark red
needle-like crystals were collected by filtration, washed
thoroughly with water, and dried under vacuum. (yield 0.92 g,
84 %). (found: C, 72.33; H, 7.29; N, 9.27. Calc for CoC\(_{36}\)H\(_{44}\)N\(_4\):
C, 73.07; H, 7.50; N, 9.47 %); \( \lambda_{\text{max.}} \) (CHCl\(_3\)) 392 (\( \varepsilon = 210080 \) 1 mol\(^{-1}\) cm\(^{-1}\)), 518 (10680), 553 nm (22080).

3.3.2.3 meso-Tetrakis(\( \alpha^{4}\)-2-pivalamidophenyl)porphyrinatocobalt(II), \( \alpha^{4}\)-Co(TPPP)

The ligand \( \alpha^{4}\)-TPPPH\(_2\) (0.635 g, 0.63 mmol) was
dissolved in dry THF (50 ml) under nitrogen and 2,6-lutidine
(0.2 ml, 1.7 mmol) added. The solution was heated to 50\(^{\circ}\)C,
CoCl\(_2\) (0.647 g, 5 mmol) was added, and heating continued for
1 hr, with a colour change from wine red to red brown. Metal
insertion was followed by measurement of the visible spectrum
(THF) of small aliquots during the reaction (i.e. disappearance of the characteristic visible spectrum of free base \( \alpha^{4}\)-TPPPH\(_2\) [418, 512, 544, 588, and 644 nm] and the
corresponding appearance of bands due to Co(TPPP) [409, 528, and 555sh]). After complete reaction, the mixture was
allowed to cool, the solvent was removed, and the residue was
taken up in benzene/2M aqueous ammonia (1:1, 500 ml) in a separatory funnel. The organic layer was separated, washed with 2M aqueous ammonia and dried over Na₂SO₄. The solution was filtered and chromatographed on a column of activity grade IV neutral alumina (2.5 cm dia x 60 cm long, 500 g, benzene), eluting with benzene-Et₂O (9:1). Two fractions were collected separately (the first fraction contained rotational isomers, and the second major fraction contained pure α₄-Co(TpvPP); 6500 ml was required to elute the second fraction in 15.5 hr, ca. 7 ml min⁻¹), and evaporated to dryness. The residue from the second fraction was redissolved in CHCl₃, filtered to remove any alumina, evaporated to dryness and dried thoroughly under vacuum at 30°C for 60 min to give a red-purple product containing only the single isomer α₄-Co(TpvPP). (yield 0.3524 g, 52.5 %). (found: C, 68.26; H, 6.16; N, 9.63. Calc for CoC₆₄H₆₄N₈O₄·1/2 CHCl₃: C, 68.69; H, 5.76; N, 9.93 %); H NMR δH (90 MHz, CDCl₃, Me₄Si) -5.85[36H, vbr s, 4 -NHCOC(CH₃)₃], 0.88-4.5[28H, complex m]; λmax. (CHCl₃) 409 (ε 194300 l mol⁻¹ cm⁻¹), 528 (14100), 555sh nm (6980); vmax. (KBr disc) 1690 cm⁻¹ (C=O); μeff = 2.19 BM (20.7°C).

3.4 Preparation of Nitrosyl Metalloporphyrin Complexes

3.4.1 Cobalt Nitrosyl Porphyrin Complexes

3.4.1.1 Nitrosyl-meso-tetraphenylporphyrinatocobalt-(III), Co(TPP)NO

Co(TPP) (1.50 g, 2.33 mmol) and piperidine (10 ml, 100 mmol) in CH₂Cl₂ (60 ml) were carefully deoxygenated and stirred overnight under excess nitric oxide to give a dark
blood-red solution. Accurate measurement of gas uptake during the experiment was not possible due to the large vapour pressure of the solvent at room temperature. After completion of reaction, the excess of NO was replaced by nitrogen. The solution was transferred to a 250 ml beaker and heated to boiling and stirred whilst hot methanol (60 ml) was slowly added. Fine purple-red crystals appeared on continued heating; the mixture was slowly cooled to room temperature, and the product was filtered off. After washing thoroughly with cold methanol the product was dried at the pump. (yield 1.38 g, 88%). (found: C,75.77; H,4.10; N,9.76. Calc for CoC$_4$H$_{28}$N$_5$O: C,75.32; H,4.02; N,9.98 %); m/z 671(CoTPP$^+$), 30(NO$^+$); $\lambda_{\text{max}}$. (CHCl$_3$) 417 ($\varepsilon$ 154170 l mol$^{-1}$ cm$^{-1}$), 539 (13400), 586 (2550), 645 nm (604); $\nu_{\text{max}}$. (KBr disc) 1690 cm$^{-1}$ (NO).

3.4.1.2 Nitrosyloctaethylporphyrinatocobalt(III), Co(OEP)NO

Co(OEP) (0.50 g, 0.845 mmol) and piperidine (5 ml, 50 mmol) in CH$_2$Cl$_2$ (15 ml) were carefully deoxygenated and stirred under excess nitric oxide. The bright scarlet solution changed over the course of the reaction (3 hr) to a deep red-purple colour (uptake of nitric oxide = 18 ml at STP, 0.8 mmol). After completion of reaction, excess NO was removed and the product was worked up as for Co(TPP)NO by addition of hot methanol (25 ml) to the boiling reaction mixture. (yield 0.3022 g, 58%). (found: C,69.80; H,7.32; N,10.86. Calc for CoC$_{36}$H$_{44}$N$_5$O: C,69.55; H,7.13; N,11.26 %); $\lambda_{\text{max}}$. (CHCl$_3$) 383 ($\varepsilon$ 87200 l mol$^{-1}$ cm$^{-1}$), 527 (11260), 559 nm (19400); $\nu_{\text{max}}$. (KBr disc) 1675 cm$^{-1}$ (NO).
3.4.1.3 Nitrosyl-meso-tetrakis(α4-2-pivalamidophenyl)-
porphyrinatocobalt(III), α4-Co(TPIVPP)

Co(TPIVPP) (0.3524 g, 0.33 mmol) and 2,6-lutidine (0.2
ml, 1.7 mmol) in toluene (7 ml) were carefully deoxygenated
and stirred under excess nitric oxide. The orange-red
solution changed colour over the course of the reaction (1
hr) to give a bright red-brown solution (uptake of nitric
oxide = 7.4 ml at STP, 0.33 mmol). After completion of
reaction, the excess NO was removed and replaced with nitro-
gen. Dry deoxygenated n-heptane (40 ml) was carefully added
via syringe through a subaseal in 4 portions to form a layer
on the top of the reaction mixture, which was left overnight
in complete darkness (covered in aluminium foil) to crystal-
lise out. The product was collected by filtration as fragile
dark orange-red crystals, which were washed thoroughly with
heptane and dried at the pump. (yield 0.1744 g, 48 %).
(found: C,68.85; H,5.92; N,11.29. Calc for CoC₆₄H₆₄N₉O₅:
C,69.99; H,5.87; N,11.48 %); λ max. (CHCl₃) 385sh, 412, 423,
537 nm; ν max. (KBr disc) 1665 (NO) and 1690 cm⁻¹ (C=O).

3.4.2 Iron Nitrosyl Porphyrin Complexes

3.4.2.1 Nitrosyl-meso-tetraphenylporphyrinatoiron(III),
Fe(TPP)NO

Fe(TPP)Cl1/4 CHCl₃ (0.2012 g, 0.27 mmol) dissolved in
AnalaR CHCl₃ (30 ml) was carefully deoxygenated, and dry
pyridine (1.0 ml, 12.4 mmol) was added anaerobically by
syringe. The mixture was stirred under excess nitric oxide
for 5 hr (apparent nitric oxide uptake = 16.8 ml at STP, 0.75
mmol), with no apparent colour change. AnalaR methanol (30
ml) was injected in to crystallise the purple product totally, and after the NO atmosphere had been replaced with nitrogen the crystals were collected by filtration, washed thoroughly with methanol and air dried. (yield 0.1831 g, 96 %). (found: C,74.92; H,4.02; N,9.72. Calc for FeC_{44}H_{28}N_{5}O: C,75.65; H,4.04; N,10.02 %). The product was unstable and smelled strongly of NO\textsubscript{2} fumes. The compound was therefore vacuum dried and presented again for analysis. (found: C,75.07; H,4.09; N,9.84 %); \( \lambda_{\text{max}} \). (CHCl\textsubscript{3}) 406, 470sh, 537, 607 nm; \( \nu_{\text{max}} \). (KBr disc) 1690 cm\textsuperscript{-1} (NO).

### 3.4.2.2 Bis(nitrosyl)-meso-tetraphenylporphyrinato-iron(II), Fe(TPP)(NO)\textsubscript{2}

Fe(TPP)Cl (1.0 g, 1.42 mmol), distilled pyridine (5 ml, 62 mmol) and methanol (10 ml) in CH\textsubscript{2}Cl\textsubscript{2} (60 ml) were carefully deoxygenated and stirred for 3 hr under excess NO. Accurate measurement of gas uptake during the experiment was not possible due to the large vapour pressure of the solvent at room temperature. On reaction the deep red solution became red-brown in colour and small crystals appeared. Excess NO was replaced with nitrogen and the product was collected by filtration as small purple crystals which were washed with methanol and dried. (yield 0.8276 g, 80 % for dinitrosyl, 83 % for mononitrosyl). (found: C,74.12; H,3.91; N,9.65. Calc for Fe(TPP)NO, FeC_{44}H_{28}N_{5}O: C,75.65; H,4.04; N,10.02. Calc for Fe(TPP)(NO)\textsubscript{2}, FeC_{44}H_{28}N_{6}O_{2}: C,72.54; H,3.87; N,11.54 %); \( \lambda_{\text{max}} \). (CHCl\textsubscript{3}) 380sh, 416, 509, 578, 650, 690 nm; \( \nu_{\text{max}} \). (KBr disc) 1690 and 1870 cm\textsuperscript{-1} (NO). The product was unstable and smelled strongly of NO\textsubscript{2} fumes and gave two \( \nu_{\text{NO}} \) in the IR spectrum. A portion was recrystallised (CH\textsubscript{2}Cl\textsubscript{2}-MeOH) under
nitric oxide (found: C, 74.17; H, 4.23; N, 9.44 %).

3.4.2.3 Nitrosyloctaethylporphyrinatoiron(II), Fe(OEP)NO

Fe(OEP)Cl (0.1823 g, 0.3 mmol) dissolved in CHCl₃ (12 ml) was carefully deoxygenated. Dry deoxygenated pyridine (1.0 ml, 12.4 mmol) was added anaerobically via syringe and the mixture was stirred under an excess of nitric oxide for 3 hr. The reaction proceeded smoothly with a colour change to a burgundy-red solution under NO (uptake of NO = 8 ml at STP, 0.35 mmol). After the reaction was finished, methanol (30 ml) was injected in under NO to crystallise the product, which was collected as purple-black microcrystals by filtration, washed with methanol and air dried. (yield 0.1507 g, 83 %). (found: C, 68.61; H, 7.24; N, 10.40. Calc for FeOEPNO, FeC₃₆H₄₄N₅O: C, 69.90; H, 7.17; N, 11.32. Calc for FeOEP(NO)₂, FeC₃₆H₄₄N₆O₂: C, 66.60; H, 6.84; N, 12.96. Calc for FeOEPNO.1/10 CHCl₃: C, 68.76; H, 7.05; N, 11.10 %); λₘₐₓ. (CHCl₃) 389, 479, 533, 557 nm; νₘₐₓ. (KBr disc) 1670 cm⁻¹ (NO).

3.4.2.4 Nitrosyl-meso-tetrakis(α₄-2-pivalamidophenyl)porphyrinatoiron(II), Fe(TPIVPP)NO

Fe(TPIVPP)Br.1.5 C₇H₁₆ (0.2022 g, 0.16 mmol) was dissolved in CHCl₃ (10 ml) and carefully deoxygenated. 2,6-Lutidine (1.0 ml, 8.6 mmol) was added under nitrogen and the orange mixture was stirred for 30 min under excess nitric oxide to give a red-brown solution almost instantaneously (apparent NO uptake 10.2 ml at STP, 0.45 mmol). Methanol (10 ml) was added, and then heptane (30 ml). No crystallisation occurred even on cooling in dry ice-acetone mixture. The mixture was carefully reduced under vacuum to half volume, and the
product crystallised. The mixture was again stirred under excess NO with no apparent uptake. The excess NO was removed and replaced with nitrogen. It was observed that the reaction mixture was effervescing slightly (reversible binding of NO). The dark red crystalline precipitate was collected by filtration, washed with heptane, and dried thoroughly. (yield 0.1258 g, 74 %). (found: C, 67.76; H, 5.59; N, 10.75. Calc for FeC₆₄H₆₄N₉O₅·1/2 CHCl₃: C, 67.09; H, 5.63; N, 10.90 %); λₘₐₓ (CHCl₃) 409, 470sh, 539, 600sh nm; vₘₐₓ (KBr disc) 1670 (NO) and 1690 cm⁻¹ (C=O).

3.5 μ-Oxo-bis[porphyrinato iron(III)] Complexes

3.5.1 μ-Oxo-bis[meso-tetraphenylporphyrinato iron(III)], [Fe(TPP)]₂O

Crude Fe(TPP)Cl (1.82 g, 2.6 mmol), dissolved in CHCl₃ (100 ml) in a separatory funnel, was shaken with 2M sodium hydroxide (3 x 100 ml) to effect μ-oxo conversion. The CHCl₃ layer was separated, washed with water (100 ml), separated again, and chromatographed on a column of dry neutral alumina (4 cm id x 30 cm, Brockmann grade I, 570 g) using CHCl₃ as eluant. The progress of the chromatographic separation was monitored by measurement of the visible spectrum. The leading broad red-brown fraction containing unreacted Fe(TPP)Cl was discarded. The second sharp dark brown band containing μ-oxo dimer was collected and evaporated to dryness. The residue was further purified by chromatography on a smaller column of dry activated alumina as before (2 cm id x 30 cm, 115 g) using CHCl₃ and collecting the narrow dark brown band. The solvent was removed and the residue was recrystallised from
CHCl₃-heptane (1:1). The dark purple product was collected by filtration, washed with heptane and dried thoroughly under vacuum. (yield 0.1147 g, 6.2 %). (found: C, 73.66; H, 3.81; N, 7.89. Calc for Fe₂C₈₈H₅₆N₈O.3/4 CHCl₃: C, 73.88; H, 3.96; N, 7.77; found: C, 76.15; H, 3.87; N, 8.06. Calc for Fe₂C₈₈H₅₆N₈O.1/3 CHCl₃: C, 76.16; H, 4.07; N, 8.04 %); λ max. (benzene) 414 (ε 184000 l mol⁻¹ cm⁻¹), 505sh (16600), 572 (13310), 612 nm (6460); ν max (KBr disc) 875m, 892w (ν as Fe-O-Fe).

3.5.2 μ-Oxo-bis{octaethylporphyrinatoiron(III)}, [Fe(OEP)]₂O

[Fe(OEP)]₂O was prepared in an analogous manner to [Fe(TPP)]₂O using Fe(OEP)Cl (0.19 g, 0.3 mmol). The narrow purple-brown band produced on a column of dry neutral activated alumina (grade I, 2 cm id x 30 cm long, 99 g) on elution with CHCl₃ was collected and evaporated to dryness. (yield 0.1631 g, 90 %). (found: C, 72.06; H, 7.92; N, 8.96. Calc for Fe₂C₇₂H₈₈N₈O: C, 72.47; H, 7.43; N, 9.39 %); λ max. (CHCl₃) 393 (ε 159000 l mol⁻¹ cm⁻¹), 460sh (25000), 581 nm (16200); ν as Fe-O-Fe not assignable due to OEP ligand interference.

3.6 Preparation of Cobalt(III) Nitro Complexes

3.6.1 Nitro(pyridine)-meso-tetraphenylporphyrinato-cobalt(III), (py)Co(TPP)NO₂

Co(TPP)NO (0.6 g, 0.86 mmol) was dissolved in CH₂Cl₂ (30 ml) and dry pyridine (1.2 ml, 15 mmol) was added. Dry oxygen gas was vigorously bubbled through the solution for ca. 4 hr. The volume of the reaction mixture was kept approximately constant throughout the experiment by addition of CH₂Cl₂ at
regular intervals. The purple product was crystallised by addition of 60-80°C petroleum spirit-hexane (1:1, 100 ml) with cooling in an ice bath, and was collected by filtration, washed well with hexane (5 x 10 ml) and dried thoroughly under vacuum for several hours. (yield 0.4808 g, 71 %). (found: C, 73.54; H, 4.34; N, 10.14. Calc for Co₄₉H₃₃N₆O₂: C, 73.87; H, 4.17; N, 10.55 %; λ max. (CHCl₃) 433 (ε 204170 1 mol⁻¹ cm⁻¹), 548 (13300), 586 sh (4600), 644 nm (765); υ max. (KBr disc) 1435 (υ asNO₂), 1310 (υ sNO₂), 820 (δ ONO), 640 (ρ wNO₂), and 370 cm⁻¹ (υ M-N).

3.6.2 Nitro(1-methylimidazole)-meso-tetraphenylporphyrinato cobalt(III), (1MeIm)Co(TPP)NO₂

(1MeIm)Co(TPP)NO₂ was prepared in a similar way to (py)Co(TPP)NO₂ using Co(TPP)NO (0.6 g, 0.86 mmol) and 1-methylimidazole (1.2 ml, 15 mmol) in CH₂Cl₂ (30 ml). Dry oxygen gas was bubbled through the mixture for 4 hr, and the purple product was crystallised with 80-100°C petroleum spirit-hexane (1:1, 200 ml), collected by filtration, washed with hexane (5 x 10 ml) and dried thoroughly under vacuum at 50°C for several hours. (yield 0.2786 g, 41 %). (found: C, 71.02; H, 4.71; N, 11.66. Calc for Co₄₈H₃₄N₇N₂.1/5 CH₂Cl₂: C, 70.88; H, 4.25; N, 12.00 %; λ max. (CHCl₃) 433 (ε 169000 1 mol⁻¹ cm⁻¹), 548 (8800), 580 sh nm (3360); υ max. (KBr disc) 1410 (υ asNO₂), 1315 (υ sNO₂), 820 (δ ONO), 620 (ρ wNO₂), and 375 cm⁻¹ (υ M-N).

3.6.3 Nitro(pyridine)octaethylporphyrinatocobalt(III), (py)Co(OEP)NO₂

(Py)Co(OEP)NO₂ was prepared in the same way as for
(py)Co(TPP)NO₂ by bubbling dry oxygen gas through Co(OEP)NO (0.04337 g, 0.07 mmol) and pyridine (1.0 ml, 12.4 mmol) in CH₂Cl₂ (20 ml) for 4 hr. The purple product was crystallised by the addition of 80-100°C petroleum spirit (200 ml), filtered off, washed with petroleum spirit and dried thoroughly under vacuum at 60°C for several hours. (yield 0.0247 g, 50 %). (found: C, 66.90; H, 6.85; N, 11.23. Calc for Co₄₁H₄₉N₆O₂·1/₄ CH₂Cl₂: C, 67.13; H, 6.76; N, 11.38 %); λ max. (CHCl₃) 417 (ε 71700 l mol⁻¹ cm⁻¹), 529 (10600), 561 nm (11200); v max. (KBr disc) 1435sh (v as NO₂), 1345 (v s NO₂), 648 (φ w NO₂), and 385 (v M-N). [δ ONO was not observed in this spectrum].

3,6.4 Nitro(1-methylimidazole)octaethylporphyrinato-cobalt(III), (1MeIm)Co(OEP)NO₂

(1MeIm)Co(OEP)NO₂ was prepared in the same way as (py)Co(TPP)NO₂ by bubbling dry oxygen gas through Co(OEP)NO (0.0632 g, 0.102 mmol) and 1-methylimidazole (1.0 ml, 12.5 mmol) in CH₂Cl₂ (25 ml) for 4 hr. The purple product was crystallised by addition of 80-100°C petroleum spirit (200 ml) with cooling, and was filtered off and dried under vacuum at 90°C for several hours. (yield 0.0677 g, 92.5 %). (found: C, 65.29; H, 7.07; N, 13.26. Calc for Co₄₀H₅₀N₇O₂·1/₄ CH₂Cl₂: C, 65.24; H, 6.87; N, 13.23 %); λ max. (CHCl₃) 417 (ε 94300 l mol⁻¹ cm⁻¹), 528 (10200), 560 nm (9850); v max. (KBr disc) 1460 (v as NO₂), 1345 (v s NO₂), 845 (δ ONO), 620 (φ w NO₂), and 403 cm⁻¹ (v M-N).
3.7 Preparation of $^{15}$N Labelled Cobalt Porphyrin Complexes

3.7.1 $^{15}$N Nitrosyl Cobalt Porphyrin Complexes

3.7.1.1 Co(TPP)$_{15}$NO

Co(TPP)$_{15}$NO was prepared in the same way as Co(TPP)NO from Co(TPP) (0.5996 g, 0.893 mmol) and piperidine (5 ml, 50 mmol) dissolved in CH$_2$Cl$_2$ (50 ml). The mixture was stirred under a slight excess of $^{15}$NO (25 ml at STP, 1.1 mmol) for 3 hr. The deep red reaction mixture was heated to boiling and hot methanol (50 ml) was added. On cooling to room temperature the purple crystalline product was collected by filtration, washed with methanol and thoroughly dried. (yield 0.2803 g, 45 %). $v_{\text{max.}}$ (KBr disc) 1665 cm$^{-1}$ ($^{15}$NO).

3.7.1.2 Co(OEP)$_{15}$NO

Co(OEP)$_{15}$NO was prepared in the same way as Co(OEP)NO from Co(OEP) (0.40 g, 0.68 mmol) and piperidine (1.0 ml, 10 mmol) dissolved in CH$_2$Cl$_2$ (5 ml). The mixture was stirred under $^{15}$NO (15.5 ml at STP, 0.69 mmol) for 1 hr. The deep red reaction mixture was heated to boiling, hot methanol (5 ml) was added, and after cooling to room temperature, the small dark purple lustrous crystals were collected by filtration, washed with methanol and dried thoroughly. (yield 0.3411 g, 81 %). $v_{\text{max.}}$ (KBr disc) 1645 cm$^{-1}$ ($^{15}$NO).

3.7.1.3 Co($\alpha^4$-T$_\text{PIVPP}$)$_{15}$NO

Co($\alpha^4$-T$_\text{PIVPP}$)$_{15}$NO was prepared in the same way as Co(T$_\text{PIVPP}$)NO from $\alpha^4$-Co(T$_\text{PIVPP}$) (0.1813 g, 0.17 mmol) and
2,6-lutidine (0.2 ml, 1.7 mmol) in purified toluene (5 ml). After stirring under $^{15}$NO (4.2 ml at STP, 0.18 mmol) for 1 hr, n-heptane (40 ml) was added under nitrogen and the mixture was cooled to -77°C (dry ice-acetone) and the orange-red product was quickly filtered off, washed with cold (-77°C) heptane and dried thoroughly. (yield 0.0633 g, 34 %). $v_{\text{max}}$. (KBr disc) 1645 ($^{15}$NO) and 1690 cm$^{-1}$ (C=O).

3.7.2 $^{15}$N Nitro Cobalt Porphyrin Complexes

3.7.2.1 (py)Co(TPP)$^{15}$NO$_2$

Dry oxygen was bubbled through Co(TPP)$^{15}$NO (0.15 g, 0.214 mmol), dry pyridine (0.5 ml, 6.2 mmol) and CH$_2$Cl$_2$ (20 ml) for 4 hr. The product was crystallised by addition of 80-100°C petroleum spirit-hexane (3:1, 400 ml), collected by filtration, washed with hexane and dried to give lustrous purple crystals. (yield 0.1306 g, 76 %). $v_{\text{max}}$. (KBr disc) 1405 ($v_{\text{as}}^{15}$NO$_2$), 1295 ($v_{\text{s}}^{15}$NO$_2$), 813 ($\delta^{15}$NO), 640 ($\rho^{15}$NO$_2$), and 370 cm$^{-1}$ ($v_{M-15N}$).

3.7.2.2 (1MeIm)Co(TPP)$^{15}$NO$_2$

Dry oxygen was bubbled through Co(TPP)$^{15}$NO (0.0688 g, 0.098 mmol), 1-methylimidazole (0.50 ml, 6 mmol) in CH$_2$Cl$_2$ (20 ml) for 4 hr. The purple product was crystallised by addition of 80-100°C petroleum spirit-hexane (1:1, 200 ml), collected by filtration, washed with hexane and dried under vacuum at 50°C for several hours. (yield 0.0749 g, 95 %). $v_{\text{max}}$. (KBr disc) 1405 ($v_{\text{as}}^{15}$NO$_2$), 1295 ($v_{\text{s}}^{15}$NO$_2$), 811 ($\delta^{15}$NO), 620 ($\rho^{15}$NO$_2$), and 375 cm$^{-1}$ ($v_{M-15N}$).
3.7.2.3 (py)Co(OEP)\(^{15}\text{NO}_2\)

Dry oxygen was bubbled into Co(OEP)\(^{15}\text{NO}\) (0.0998 g, 0.160 mmol), dry pyridine (1.0 ml, 12.4 mmol) and CH\(_2\text{Cl}_2\) (20 ml) for 4 hr. The purple product was precipitated by addition of 80-100\(^\circ\text{C}\) petroleum spirit (150 ml), with cooling to -77\(^\circ\text{C}\) (dry ice-acetone), as a dark red powder, and collected by filtration, washed with cold (-77\(^\circ\text{C}\)) 80-100\(^\circ\text{C}\) petrol and dried thoroughly. (yield 0.0441 g, 38 \%). \(v\)\(_{\text{max}}\) (KBr disc) 1405 (\(v_{\text{as}}\)\(^{15}\text{NO}_2\)), 1310 (\(v_{\text{s}}\)\(^{15}\text{NO}_2\)), 810 (\(\delta_{\text{0}}^{15}\text{NO}\)), 648 (\(\rho_{\text{w}}^{15}\text{NO}_2\)), and 385 cm\(^{-1}\) (\(v_{\text{M-15N}}\)).

3.7.2.4 (1MeIm)Co(OEP)\(^{15}\text{NO}_2\)

Dry oxygen was bubbled through Co(OEP)\(^{15}\text{NO}\) (0.1012 g, 0.163 mmol), 1-methylimidazole (1.0 ml, 12 mmol), and CH\(_2\text{Cl}_2\) (20 ml) for 5 hr. After attempted crystallisation from petroleum spirit at -77\(^\circ\text{C}\), the purple product oiled out and eventually solidified. This was dried thoroughly under vacuum at 95\(^\circ\text{C}\) for several hours. (yield 0.1101 g, 94 \%). \(v\)\(_{\text{max}}\) (KBr disc) 1445 (\(v_{\text{as}}\)\(^{15}\text{NO}_2\)), 1315sh (\(v_{\text{s}}\)\(^{15}\text{NO}_2\)), 830 (\(\delta_{\text{0}}^{15}\text{NO}\)), 620 (\(\rho_{\text{w}}^{15}\text{NO}_2\)), and 388 cm\(^{-1}\) (\(v_{\text{M-15N}}\)).

3.8 Miscellaneous Work

3.8.1 Miscellaneous Cobalt(III) Nitrosyls

3.8.1.1 Co(5-\text{NO}_2\text{-salen})\(^{15}\text{NO}\)

5-NitrosalenH\(_2\) (0.2400 g, 0.67 mmol) in dry DMF (5 ml) and \((\text{CH}_3\text{COO})_2\text{Co.4H}_2\text{O}\) (0.1667 g, 0.67 mmol) in dry DMF (3 ml) were mixed together under an atmosphere of \(^{15}\text{NO}\) (16 ml at STP, 0.71 mmol) with an immediate colour change to dark...
red-brown. On stirring for 1 hr the brown product crystallised out and was collected by filtration, washed with absolute ethanol and thoroughly dried. (yield 0.2282 g, 77 %). $v_{\text{max}}$ (KBr disc) 1665 cm$^{-1}$ ($^{15}\text{NO}$).

3.8.1.2 Co(N-Ph-salim)$_2^{15}\text{NO}$

N-Phenylsalicylaldimine (0.2643 g, 1.338 mmol) in methanol (2 ml) and (CH$_3$COO)$_2$Co.4H$_2$O (0.1668 g, 0.669 mmol) in methanol (3 ml) were mixed together under an atmosphere of $^{15}\text{NO}$ (15.35 ml at STP, 0.685 mmol) with a colour change to dark green. After stirring for 1 hr the dark green solid was collected by filtration, washed with methanol and dried thoroughly. (yield 0.1443 g, 45 %). $v_{\text{max}}$ (KBr disc) 1605 cm$^{-1}$ ($^{15}\text{NO}$).

3.8.1.3 CoCl$_2$(NO)(PPh$_2$Me)$_2$

CoCl$_2$(PPh$_2$Me)$_2$ (0.25 g, 0.47 mmol) was suspended in absolute ethanol (7 ml) and CH$_2$Cl$_2$ was added dropwise with stirring until the blue crystals just dissolved (ca. 10 ml). The solution was deoxygenated, placed under nitric oxide and quickly cooled to -77°C (dry ice-acetone) to give a dark brown solution. Cold (-77°C) deoxygenated hexane (40 ml) was syringed in the side arm through a subaseal and the mixture was gently stirred to give a light brown crystalline mass. The uptake of NO at STP was not measured in this experiment because the burette contained $^{15}\text{NO}$ and was therefore bypassed for this preparation. The excess NO was removed, and nitrogen admitted. The brown product was rapidly collected by filtration in the air, washed with cold (-77°C) deoxygenated ethanol, followed by cold hexane, and quickly dried at room
temperature under vacuum. (yield 0.1403 g, 53 %). (found: C, 55.87; H, 4.66; N, 2.42. Calc for CoC_{26}H_{26}NP_{2}Cl_{2}O: C, 55.75; H, 4.70; N, 2.50 %). \(^1\)H NMR \(\delta_H\) (90 MHz, CDCl\(_3\), Me\(_4\)Si) 2.39[6H, t, \(J_{P-H} = 5\) Hz, 2 \(\text{trans-PCH}_{3}(C_6H_5)_2\)], 7.42-7.68[20H, m, 2 \(\text{trans-PCH}_{3}(C_6H_5)_2\)]; \(v_{\text{max}}\) (KBr disc) 1740 and 1630 cm\(^{-1}\) (NO).

3.8.1.4 CoCl\(_2\)(\(^{15}\)NO)(PPh\(_2\)Me)\(_2\)

This was prepared as for the unlabelled complex using CoCl\(_2\)(PPh\(_2\)Me)\(_2\) (0.2347 g, 0.44 mmol) in EtOH (10 ml) and CH\(_2\)Cl\(_2\) (ca. 13 ml), stirred under \(^{15}\)NO (11 ml at STP, 0.49 mmol) and worked up in the same way. (yield 0.0689 g, 28 %). \(v_{\text{max}}\) (KBr disc) 1710 and 1605 cm\(^{-1}\) (\(^{15}\)NO).

3.8.2 Miscellaneous Cobalt 14,15 N Nitro Complexes

3.8.2.1 (py)Co(salen)NO\(_2\)

Co(salen)NO (0.2502 g, 0.7 mmol) was dissolved in CHCl\(_3\) (20 ml) and dry pyridine (2.0 ml, 25 mmol) added. Air was vigorously drawn through the solution for 4.5 hr, during which time an orange-brown product precipitated. This was collected by filtration, washed well with pentane and dried. (yield 0.1866 g, 59 %). \(v_{\text{max}}\) (KBr disc) 1415 (\(v_{\text{as}}\)NO\(_2\)), 1315 (\(v_{\text{s}}\)NO\(_2\)), 820 (\(\delta_{\text{ONO}}\)), 588 (\(\varphi_{\text{w}}\)NO\(_2\)), and 435 cm\(^{-1}\) (\(v_{\text{M-N}}\)).

3.8.2.2 (py)Co(salen)\(^{15}\)NO\(_2\)

Co(salen)\(^{15}\)NO (0.0692 g, 0.195 mmol) was dissolved in CHCl\(_3\) (5 ml) and dry pyridine (1.0 ml, 12.4 mmol) was added. Dry oxygen was bubbled through the solution for 2 hr, during which time an orange-brown product had precipitated. The solid was filtered off, washed with n-pentane, and dried.
thoroughly at the pump. (yield 0.0407 g, 46 %). $v_{\text{max}}$ (KBr disc) 1380 ($v_{\text{as}}^{15}\text{NO}_2$), 1290 ($v_{\text{s}}^{15}\text{NO}_2$), 810 ($\delta^{15}\text{NO}$), 575 ($\rho^{15}\text{NO}_2$), and 430 cm$^{-1}$ ($v_{\text{M-15N}}$).

3.8.2.3 (py)Co(7-Mesalen)$^{15}\text{NO}_2$

Co(7-Mesalen)$^{15}\text{NO}$ (0.0541 g, 0.141 mmol) was dissolved in CHCl$_3$ (5 ml) and dry pyridine (1.0 ml, 12.4 mmol) added. Dry oxygen was vigorously bubbled through the solution for 1.5 hr, during which time an orange-brown product had precipitated. The product was filtered off, washed with n-pentane, and dried thoroughly at the pump. (yield 0.0395 g, 58.5 %). $v_{\text{max}}$ (KBr disc) 1375 ($v_{\text{as}}^{15}\text{NO}_2$), 1295 ($v_{\text{s}}^{15}\text{NO}_2$), 810 ($\delta^{15}\text{NO}$), 565 ($\rho^{15}\text{NO}_2$), and 385 cm$^{-1}$ ($v_{\text{M-15N}}$).

3.8.2.4 (py)Co(S$_2$CNPr$_2^i$)$_2^{15}\text{NO}_2$

Co(S$_2$CNPr$_2^i$)$_2^{15}\text{NO}$ (0.1329 g, 0.3 mmol) was suspended in dry acetone (5 ml) and dry pyridine (1.0 ml, 12.4 mmol) was added. Dry oxygen gas was bubbled through the mixture for several hours. The volume of the reaction mixture was kept constant at ca. 5 ml throughout the experiment by topping up with acetone at regular intervals. The product was isolated as a dark green residue after allowing the solvent to evaporate, and was washed with a small amount of diethyl ether and then dried (yield 0.0388 g, 24 %). $v_{\text{max}}$ (KBr disc) 804 cm$^{-1}$ ($\delta^{15}\text{NO}$), the other characteristic IR bands could not be assigned due to ligand interference.

3.8.2.5 (py)Co(S$_2$CNMe$_2$)$_2^{15}\text{NO}_2$

Co(S$_2$CNMe$_2$)$_2^{15}\text{NO}$ (0.025 g, 0.076 mmol) was suspended in dry acetone (5 ml) and dry pyridine (1.0 ml, 12.4 mmol) was
added. Air was passed through the mixture for several hours, the reaction mixture volume being kept constant as above. The product was isolated as a dark green residue after the solvent had evaporated, washed with a small amount of Et₂O and then dried. The characteristic IR bands could not be assigned due to ligand interference.

3.8.3 Preparation of Nitrosyl-\(N,N'\)-o-Phenylenebis-(salicylideneiminato)iron, \(\text{Fe(salphen)NO}\)

3.8.3.1 \(\text{Fe(salphen)}\cdot \text{H}_2\text{O}\)

\(\text{Fe(O}_2\text{CCH}_3\text{)}_2\cdot \text{H}_2\text{O} \) (1.89 g, 9 mmol) was dissolved in deoxygenated 1:1 aqueous DMF (20 ml) in a 3 tap flask, and to this was added slowly a slight excess of \(\text{salphenH}_2\) (3.0 g, 9.48 mmol) dissolved in DMF (30 ml). An olive-green product immediately precipitated, and the mixture was boiled under \(\text{N}_2\) for 10 min. After the reaction mixture had cooled to room temperature, 1:1 aqueous DMF (100 ml) was added, and the product was filtered off, washed with acetone, and dried thoroughly under vacuum. (yield 2.17 g, 62%).

3.8.3.2 \(\text{Fe(salphen)NO}\)

\(\text{Fe(salphen)}\cdot \text{H}_2\text{O} \) (1.12 g, 2.89 mmol) was suspended in deoxygenated 96 % ethanol (100 ml) and stirred with occasional shaking under excess nitric oxide. The olive-green suspension on reaction changed to a dark brown crystalline suspension (nitric oxide uptake = 67.9 ml at STP, 3.03 mmol). Excess nitric oxide was removed and the dark brown complex was filtered off under nitrogen, washed with a small amount of acetone, and dried thoroughly under vacuum. (yield 1.06 g,
90%). (found: C,60.85; H,4.19; N,9.96. Calc for FeC_{20}H_{14-N_3}O_3: C,60.03; H,3.53; N,10.50 %); v_{max}. (nujol mull) 1720 cm^{-1} (NO).

3.8.3.3 Preparation of Fe(salphen)NO Using Ascorbic Acid to Prevent Formation of μ-Oxo Bridged Impurities

The product was prepared in a similar fashion using Fe(salphen),H_2O (0.89 g, 2.3 mmol) and L-ascorbic acid (1.0 g, 5.7 mmol) in 96 % ethanol (75 ml) under excess NO. (yield 0.79 g, 86 %). (found: C,60.04; H,3.75; N,10.01 calc for FeC_{20}H_{14-N_3}O_3: C,60.03; H,3.53; N,10.50 %); v_{max}. (nujol mull) 1720 cm^{-1} (NO).

3.8.4 μ-Peroxo Bridged Binuclear Cobalt(III) Complexes

3.8.4.1 (^{17}O)-μ-Peroxo-bis(pentaamminecobalt(III)) (4+)

Tetranitrate Dihydrate, [(NH_3)_5Co^{17}O_2Co(NH_3)_5]^{4-}\cdot(NO_3)_4\cdot2H_2O

Into a 100 ml two neck round bottom flask equipped with a magnetic stirring bar and wired on subaseal was placed, under nitrogen, Co(NO_3)_2\cdot6H_2O (0.3914 g, 1.345 mmol) dissolved in water (2 ml). The solution was placed under an atmosphere of ^{17}O_2 (15 ml at STP, 0.67 mmol) by carefully condensing the labelled gas into the evacuated reaction vessel which was immersed in liquid nitrogen. On warming up to room temperature, deoxygenated 17M aqueous ammonia (5 ml) was injected in through the subaseal and the mixture was stirred at room temperature for 1 hr. Reaction was virtually instantaneous passing from the red colour of the cobalt nitrate solution, through a bright blue intermediate solution
state to a brown solution, the colour of which gradually
darkened throughout the reaction time. NaNO₃ (0.25 g, 2.93
mmol) in deoxygenated water (1 ml) was added through the
serum cap to facilitate crystallisation of the very soluble
complex, and the mixture was cooled in an ice bath. The dark
brown crystalline product was collected by filtration, washed
with a little aqueous ammonia, then with absolute ethanol and
dried thoroughly. (yield 0.0661 g, 16 %). A second crop of
product was obtained from the filtrate by concentration and
precipitation with ethanol. (0.1561 g, total yield 0.2222 g,
55 %). vₓₓ (KBr disc) 540 cm⁻¹ (vₐₓ Co-O).

3.8.4.2 [(NH₃)₅CoO₂Co(NH₃)₅](NO₃)₄·2H₂O

The unlabelled compound was prepared in a similar
fashion using Co(NO₃)₂·6H₂O (2.6 g, 8.93 mmol) in water (4
ml) and 17M aqueous ammonia (10 ml) under excess oxygen.
Crystallisation was effected using NaNO₃ (1.04 g, 12.24 mmol)
in water (2 ml) to give a brown crystalline solid. (yield
1.6625 g, 62 %). vₓₓ (KBr disc) 560 cm⁻¹ (vₓₓ Co-O).

3.8.5 Starting Materials

3.8.5.1 Anhydrous Iron(II) Bromide, FeBr₂

A mixture of iron wire and filings (10 g, 0.18 mol),
concentrated HBr (45 ml of a 48 % solution, 0.27 mol) and
AnalaR methanol (100 ml) were placed in a 3 tap flask and
warmed to 60°C (water bath) under of nitrogen for 7 hr until
the evolution of H₂ subsided. The pale green solution was
filtered from iron through a porosity 3 filter into a clean
dry deoxygenated 3 tap flask. The solvent was removed under
vacuum to give the product as a green crystalline hexa-
methanol solvate, this was heated at 160°C under vacuum to
give first the white dimethanol solvate, and then the final
anhydrous FeBr₂ product as a very moisture sensitive bright
green-yellow free-running powder. (yield 20 g, 52 %).

3.8.5.1 Bis(acetato)iron(II) Dihydrate, Fe(O₂CCCH₃)₂₂H₂O
Iron wire (30 g, 0.54 mol) was heated (110°C) with 50 %
v/v glacial acetic acid (50 ml) under nitrogen for approxi-
mately 30 hr until the H₂ gas evolution slowed appreciably.
The reaction mixture was allowed to cool to room temperature
and was then diluted with deoxygenated water (100 ml). The
pale green solution was then filtered through celite powder
on a sinter into a clean 250 ml round bottom 3 tap flask
containing a large magnetic stirring bar, and the solvent was
removed to give a white finely crystalline product (crude
yield 33 g). The compound was then slurried with deoxygenated
distilled purified acetone (100 ml) by vigorous shaking of
the flask with a nitrogen bleed to the atmosphere to prevent
any pressure buildup. The compound was then filtered under
nitrogen and washed with acetone and dried thoroughly under
vacuum to give a very air-sensitive white microcrystalline
free-running powder which was stored under nitrogen. (yield
26.42 g, 30 %).
CHAPTER 4. RESULTS AND DISCUSSION

4.1 Starting Materials: Porphyrins and Metalloporphyrins

The porphyrin ligands \( \text{TPPH}_2 \), \( \text{OEPH}_2 \), and \( \alpha^4-\text{TPIVPPH}_2 \) and the corresponding cobalt and iron complexes were successfully synthesised in comparable yields to the literature methods. Table 4.1 illustrates the yield and analytical data for the starting materials, and Table 4.2 lists the visible absorption spectroscopic data for these compounds. A most useful and convenient criterion of purity and stability of these porphyrinic materials is their visible and near-ultraviolet absorption spectra, and the results obtained show good agreement with the literature values for \( \text{TPPH}_2 \), \( \text{OEPH}_2 \), \( \alpha^4-\text{TPIVPPH}_2 \), \( \text{Co(TPP)} \), \( \text{Co(OEP)} \), \( \text{Co(\alpha^4-\text{TPIVPP})} \), \( \text{Fe(TPP)Cl} \) and \( \text{Fe(\alpha^4-\text{TPIVPP})Br} \).

The picket fence porphyrins and complexes tend to form solvates or otherwise occlude molecules of solvent. From the microanalytical data presented in Table 4.1 for the picket fence porphyrin and complexes, it would appear that these compounds are solvated in the solid state. This is probably because the sensitivity of the solid compounds to heat used in drying precluded any vigorous heating, to avoid thermal atropisomerisation of the porphyrin.

The \(^1H\) NMR data for the porphyrin ligands are shown in Table 4.3 and in Figure 4.1. The observation of an intense singlet at 0.074 ppm due to 36 equivalent protons in the \(^1H\) NMR of picket fence porphyrin is consistent with the successful synthesis of the all \( \text{cis-} \alpha^4-\text{TPIVPPH}_2 \) isomer [Figure 4.2(a)]. Apparent differences among the possible
Table 4.1 Yield and Analytical Data for Starting Materials

<table>
<thead>
<tr>
<th>Compound</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>Overall Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found</td>
<td>Found</td>
<td>Found</td>
<td>Y</td>
</tr>
<tr>
<td>(colour, form)</td>
<td>(theor.)</td>
<td>(theor.)</td>
<td>(theor.)</td>
<td></td>
</tr>
<tr>
<td>meso-TPPH$_2$</td>
<td>85.61</td>
<td>4.92</td>
<td>9.17</td>
<td>85 %</td>
</tr>
<tr>
<td>(purple crystals)</td>
<td>(85.97)</td>
<td>(4.92)</td>
<td>(9.11)</td>
<td></td>
</tr>
<tr>
<td>OEPH$_2$</td>
<td>81.13</td>
<td>8.93</td>
<td>10.56</td>
<td>42 %</td>
</tr>
<tr>
<td>(purple crystals)</td>
<td>(80.85)</td>
<td>(8.67)</td>
<td>(10.48)</td>
<td></td>
</tr>
<tr>
<td>T$_{PIV}$PPH$_2$.1/2$CHCl_3$</td>
<td>73.59</td>
<td>6.80</td>
<td>10.35</td>
<td>33-50 %</td>
</tr>
<tr>
<td>(purple crystals)</td>
<td>(73.52)</td>
<td>(6.36)</td>
<td>(10.66)</td>
<td></td>
</tr>
<tr>
<td>Co(TPP)</td>
<td>78.71</td>
<td>4.23</td>
<td>8.17</td>
<td>82 %</td>
</tr>
<tr>
<td>(brick-red precipitate)</td>
<td>(78.68)</td>
<td>(4.20)</td>
<td>(8.34)</td>
<td></td>
</tr>
<tr>
<td>Co(OEP)</td>
<td>72.33</td>
<td>7.29</td>
<td>9.27</td>
<td>84 %</td>
</tr>
<tr>
<td>(dark-red needles)</td>
<td>(73.07)</td>
<td>(7.50)</td>
<td>(9.47)</td>
<td></td>
</tr>
<tr>
<td>Co(T$_{PIV}$PP).1/2$CHCl_3$</td>
<td>68.26</td>
<td>6.16</td>
<td>9.63</td>
<td>52.5 %</td>
</tr>
<tr>
<td>(red-purple solid)</td>
<td>(68.69)</td>
<td>(5.76)</td>
<td>(9.93)</td>
<td></td>
</tr>
<tr>
<td>Fe(TPP)Cl.1/2$CHCl_3$</td>
<td>70.69</td>
<td>3.69</td>
<td>7.44</td>
<td>96-100 %</td>
</tr>
<tr>
<td>(purple-brown precipitate)</td>
<td>(70.22)</td>
<td>(3.73)</td>
<td>(7.27)</td>
<td></td>
</tr>
<tr>
<td>Fe(OEP)Cl</td>
<td>68.94</td>
<td>7.20</td>
<td>9.02</td>
<td>83 %</td>
</tr>
<tr>
<td>(purple-brown microcrystals)</td>
<td>(69.29)</td>
<td>(7.11)</td>
<td>(8.98)</td>
<td></td>
</tr>
<tr>
<td>Fe(T$_{PIV}$PP)Br 1.5 C$<em>7$H$</em>{16}$</td>
<td>69.36</td>
<td>6.74</td>
<td>8.50</td>
<td>71 %</td>
</tr>
<tr>
<td>(dark-purple microcrystals)</td>
<td>(69.08)</td>
<td>(6.85)</td>
<td>(8.65)</td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\varepsilon$ (10$^{-3}$ mol$^{-1}$ cm$^{-1}$)</td>
<td>solvent</td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-----------------------------</td>
<td>-----------------------------------------------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>$\bullet$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPPH$_2$</td>
<td>372sh (24.90) 418 (435.00) 483sh (3.63) 515 (19.44) 548 (8.05) 592 (5.59) 646 (3.80)</td>
<td>benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OEPH$_2$</td>
<td>378sh (87.63) 400 (159.96) 498 (10.62) 531 (6.95) 569 (1.50) 597 (6.50) 623 (6.50)</td>
<td>benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha^4$-TPPP+1/2CHCl$_3$</td>
<td>370sh (30.83) 418 (276.10) 480sh (3.10) 512 (19.05) 544 (4.07) 588 (5.92) 644 (1.59)</td>
<td>CHCl$_3$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (10$^{-3}$ mol$^{-1}$ cm$^{-1}$)</th>
<th>solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(TPP)</td>
<td>410 (231.00) 529 (14.80) 642sh (0.26)</td>
<td>CHCl$_3$</td>
<td></td>
</tr>
<tr>
<td>Co(OEP)</td>
<td>392 (210.08) 518 (10.68) 553 (22.08)</td>
<td>CHCl$_3$</td>
<td></td>
</tr>
<tr>
<td>Co($\alpha^4$-TPP+1/2CHCl$_3$)</td>
<td>409 (194.30) 528 (14.10) 555sh (6.98)</td>
<td>CHCl$_3$</td>
<td></td>
</tr>
<tr>
<td>Fe(TPP)Cl.1/4CHCl$_3$</td>
<td>378 (58.67) 415 (107.95) 510 (12.97) 578 (3.44) 657 (2.80) 691 (3.17)</td>
<td>CHCl$_3$</td>
<td></td>
</tr>
<tr>
<td>Fe(OEP)Cl</td>
<td>379 (88.16) 507 (8.21) 536 (8.54) 576sh (2.77) 637 (4.25)</td>
<td>CHCl$_3$</td>
<td></td>
</tr>
<tr>
<td>Fe($\alpha^4$-TPPP)Br.1.5C$_7$H$_6$</td>
<td>360sh (48.90) 390sh (64.50) 417 (88.77) 508 (13.74) 584 (3.81) 654 (3.30) 680 (3.10)</td>
<td>CHCl$_3$</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.3 $^1$H NMR Data for Porphyrin Ligands ($\delta_\text{H} 90 \text{ MHz, CDCl}_3, \text{Me}_4\text{Si}$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta^1$H ppm [integral, multiplicity, coupling constant]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>meso-TPPH$_2$</td>
<td>-2.76[2H, br s]</td>
<td>2NH</td>
</tr>
<tr>
<td></td>
<td>7.74[12H, m]</td>
<td>12 m- and p-phenyl H</td>
</tr>
<tr>
<td></td>
<td>8.21[8H, m]</td>
<td>8 o-phenyl H</td>
</tr>
<tr>
<td></td>
<td>8.84[8H, s]</td>
<td>8$\beta$-pyrrolic H</td>
</tr>
<tr>
<td>OEPH$_2$</td>
<td>-3.73[2H, s]</td>
<td>2NH</td>
</tr>
<tr>
<td></td>
<td>1.92[24H, t, J=7.5 Hz]</td>
<td>8$\beta$-pyrrolic CH$_3$CH$_2$-</td>
</tr>
<tr>
<td></td>
<td>4.10[16H, q, J=7.5 Hz]</td>
<td>8$\beta$-pyrrolic CH$_3$CH$_2$-</td>
</tr>
<tr>
<td></td>
<td>10.10[4H, s]</td>
<td>4 methine H</td>
</tr>
<tr>
<td>$\alpha^4$-T$_\text{PIV}$PPH$_2$</td>
<td>0.074[36H, s]</td>
<td>4 -NHCOC(CH$_3$)$_3$</td>
</tr>
<tr>
<td></td>
<td>7.41-7.74[16H, m]</td>
<td>16 phenyl H</td>
</tr>
<tr>
<td></td>
<td>8.77[4H, s]</td>
<td>4 -NHCOC(CH$_3$)$_3$</td>
</tr>
<tr>
<td></td>
<td>8.83[8H, s]</td>
<td>8$\beta$-pyrrolic H</td>
</tr>
</tbody>
</table>

Figure 4.1 Substitution Pattern for Porphyrin Ring

X = H, TPPH$_2$
X = -NHCOC(CH$_3$)$_3$, $\alpha^4$-T$_\text{PIV}$PPH$_2$
Figure 4.2(a) $^1$H NMR spectrum of $\alpha^4$-Tp^PPP^H$_2$ (the single isomer)

Figure 4.2(b) $^1$H NMR Spectrum of Co($\alpha^4$-TpvPP) (the single isomer)
atropisomers of the picket fence porphyrins can be observed from their $^1\text{H}$ NMR spectra. The chemical shifts of their methyl protons (of the four t-butyl groups) in CDCl$_3$ are as follows: 0.07 ($\alpha^4$-TPIVPPH$_2$); 0.10, 0.16, and 0.23 ($\alpha^3$-TPIVPPH$_2$); 0.14 ($\alpha^2$-cis-TPIVPPH$_2$) and 0.25 ppm ($\alpha^2$-trans-TPIVPPH$_2$).

The paramagnetic Co(II) nucleus in Co($\alpha^4$-TPIVPP) shifts the resonances of the 36 equivalent protons of the four -NHCOC(CH$_3$)$_3$ groups upfield to give a very broad singlet at ca. -5.85 ppm relative to TMS [Figure 4.2(b)]. Relative intensities could not be estimated because of paramagnetic line broadening of the signals. $^1\text{H}$ NMR was therefore the analytical method of choice for identifying the isomers present in the column eluants during the chromatographic separation of the single isomer Co($\alpha^4$-TPIVPP) from its isomeric mixtures. Analytical thin layer chromatography was also used in this respect. The paramagnetic shifts of the protons in the corresponding Fe($\alpha^4$-TPIVPP)Br were not measured.

Freitag et al. have investigated the photoinduced and thermally induced atropisomerisation of these picket fence porphyrin compounds as the free base, the diacid (TPIVPPH$_4^{2+}$) and the Ni(II) complexes. The isomerisation process involves rotation of a single phenyl ring through a coplanar transition state and requires substantial distortion from planarity of the porphyrin core. The relative thermal isomerisation rates and the photo-isomerisation efficiencies were found to depend on the size of the ortho-substituent as well as the atom(s) coordinated to the central core. Thermally induced interconversion of picket fence porphyrin free base and metal complexes is unimportant at room temperature, but
slight heating of solutions may result in interconversion of atropisomers, and photoatropisomerisation is easily able to occur at room temperatures. For these reasons solutions of the picket fence porphyrin and complexes were generally handled in subdued lighting and care was taken to avoid heating wherever possible.

4.1.1 Magnetochemistry of Co($\alpha^4$-T$_{PIV}$PP) and Fe(OEP)Cl

The room temperature magnetic moment of Co($\alpha^4$-T$_{PIV}$PP) was determined to be 2.19 BM at 20.7°C using the Johnson Matthey susceptibility balance. This is in good agreement with the literature value [2.2 BM at 25°C]$^{319}$ and is consistent with a low spin Co(II), d$^7$ ion in a square planar environment with one unpaired electron ($t_{2g}^6 e_g^1$). In a strongly tetragonally distorted octahedral environment, the square planar four coordinate complex being the extreme case (Figure 4.3), the large energy separation between the two highest energy orbitals means that for a d$^7$ ion only the low spin state with one unpaired electron should occur experimentally. The experimentally determined moments of square planar spin paired Co(II), d$^7$ complexes are generally higher than the spin only value of 1.73 BM ($\mu_{SO} = [n(n+2)]^{1/2}$). The increase in moment is thought to be due to considerable orbital contribution,$^{328}$ or to the existence of some high spin species in the complex.$^{329}$

The variable temperature magnetic data for Fe(OEP)Cl are given in Table 4.4 and illustrated in Figure 4.4 as plots of $1/\chi_A$ versus T and $\mu_{eff}$ versus T. The reciprocal molar susceptibility, $\chi_A^{-1}$ follows Curie-Weiss law behaviour with a $\sigma$ value of 12.7 K, indicating a small degree of antiferro-
Figure 4.3 Distortion of Octahedral Complex (a) Through Tetragonal Symmetry (b) to Square Planar Limit (c) (the $z^2$ orbital may lie below the $xz$ and $yz$ in the square planar complex)
<table>
<thead>
<tr>
<th>T(K)</th>
<th>$\chi_A$ ($10^6$ cgau)</th>
<th>$1/\chi_A$ (cm$^{-1}$)</th>
<th>$\mu_{\text{eff}}$ (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>294.7</td>
<td>16972.6</td>
<td>58.92</td>
<td>6.32</td>
</tr>
<tr>
<td>263.0</td>
<td>18892.5</td>
<td>52.93</td>
<td>6.30</td>
</tr>
<tr>
<td>230.5</td>
<td>21264.2</td>
<td>47.03</td>
<td>6.26</td>
</tr>
<tr>
<td>197.7</td>
<td>24587.7</td>
<td>40.67</td>
<td>6.24</td>
</tr>
<tr>
<td>166.3</td>
<td>28669.6</td>
<td>34.88</td>
<td>6.17</td>
</tr>
<tr>
<td>135.3</td>
<td>34897.2</td>
<td>28.66</td>
<td>6.15</td>
</tr>
<tr>
<td>104.8</td>
<td>44593.6</td>
<td>22.42</td>
<td>6.11</td>
</tr>
<tr>
<td>90.2</td>
<td>51289.2</td>
<td>19.50</td>
<td>6.08</td>
</tr>
</tbody>
</table>

Diamagnetic correction $= -322.5 \times 10^6$ cgau determined by Pascal's constants

Figure 4.4 Temperature Dependence of the Effective Magnetic Moment ($\mu_{\text{eff}}$) and the Reciprocal Magnetic Susceptibility ($\chi_A^{-1}$) of Fe(OEP)Cl
magnetism. The plot gives an excellent straight line relationship (Figure 4.4) as determined by linear regression method giving \( r = 0.999 \). The effective magnetic moment, \( \mu_{\text{eff}} \) of 6.32 BM at 295 K decreased slightly to 6.08 BM at 90.2 K. These values are rather higher than the spin only value of 5.92 BM for a high spin \( d^5 \) ion and could be due to some minor antiferromagnetic interaction.

4.2 Nitrosyl(porphyrinato)cobalt(III) Complexes

Table 4.5 illustrates the yield, analytical, and infrared data for the nitrosyl(porphyrinato)cobalt(III) complexes of TPP, OEP, and \( \alpha^4-\text{TPIVPP} \). There have apparently been no previous reports in the literature for Co(OEP)NO which is therefore a new nitrosyl compound, and although the resonance Raman spectrum of Co(TPIVPP)(NO)(1MeIm) has been reported, there has been no report concerning the synthesis and characterisation of the solid 5-coordinate Co(\( \alpha^4\text{-TPIVPP})\)NO complex. There is reasonably good agreement between the observed and theoretical analytical results. The reactions gave reasonable yields of product, with the uptake of nitric oxide of about one equivalent. The lower yields of Co(\( \alpha^4\text{-TPIVPP})\)NO reflect its high solubility in the reaction solvent.

The nitrosyl stretching frequencies for Co(TPP)NO (1690 cm\(^{-1}\)), Co(OEP)NO (1675 cm\(^{-1}\)), and Co(\( \alpha^4\text{-TPIVPP})\)NO (1665 cm\(^{-1}\)) are all in the region for a bent nitrosyl group with Co(III)NO\(^-\), [CoNO]\(^8\) electronic structure. On \(^{15}\text{NO}\) substitution the nitrosyl stretching frequency shifts ca. 20-30 cm\(^{-1}\) to lower wavenumber to 1665, 1645, and 1645 cm\(^{-1}\) respectively. Correlations of observed isotopic shifts in the
Table 4.5 Analytical and Infrared Data for the Nitrosyl(porphyrinato)cobalt(III) Complexes

<table>
<thead>
<tr>
<th>Compound (colour, form)</th>
<th>%C found</th>
<th>%H found</th>
<th>%N found</th>
<th>Reaction solvent</th>
<th>Yield</th>
<th>v$<em>{14\text{NO}}$ (v$</em>{15\text{NO}}$) (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(TPP)NO (purple-red crystals)</td>
<td>75.77</td>
<td>4.10</td>
<td>9.76</td>
<td>CH$_2$Cl$_2$/piperidine</td>
<td>88%</td>
<td>1690</td>
</tr>
<tr>
<td>Co(OEP)NO (purple crystals)</td>
<td>69.80</td>
<td>7.32</td>
<td>10.86</td>
<td>CH$_2$Cl$_2$/piperidine</td>
<td>58%</td>
<td>1675</td>
</tr>
<tr>
<td>Co(T$_{PIV}$PP)NO (orange-red crystals)</td>
<td>68.85</td>
<td>5.92</td>
<td>11.29</td>
<td>toluene/2,6-lutidine</td>
<td>48%</td>
<td>1665</td>
</tr>
</tbody>
</table>
IR spectra of some transition metal (Fe, Co, Ru, Ir) nitrosyl \( ^{14}\text{NO} \) and \( ^{15}\text{NO} \) complexes has led to definite assignments of \( v_{\text{NO}} \) and skeletal vibrations between metal and NO group. However, deviation of the MNO bond angle from linearity causes a decrease in the isotopic shifts of the NO stretching vibration. Further work reported that the oxidation states of metal atom and NO group significantly influence the isotopic shifts of the vibrational bands upon \( ^{15}\text{NO} \) substitution, and from a comparison of the observed isotopic shifts with the calculated ones the following general rules were established: The observed isotopic shift of the NO stretching vibration for \( \text{NO}^+ \) complex is \( 36-44 \text{ cm}^{-1} \), while that for the \( \text{NO}^- \) is \( 25-28 \text{ cm}^{-1} \); the MNO bending vibration (\( \delta_{\text{MNO}} \)) is observed in the region 450-650 cm\(^{-1}\) and its isotopic shift is \( 10-15 \text{ cm}^{-1} \) for both \( \text{NO}^+ \) and \( \text{NO}^- \) complexes; the MNO stretching vibration (\( v_{\text{M-NO}} \)) for \( \text{NO}^+ \) complexes is observed in the region 500-650 cm\(^{-1}\), while that for the \( \text{NO}^- \) is seen in the region ca. 300 cm\(^{-1}\) and their isotopic shifts are 2-6 cm\(^{-1}\). The magnitude of the isotopic shifts for Co(TPP)NO (25 cm\(^{-1}\)), Co(OEP)NO (30 cm\(^{-1}\)), and Co(\( \alpha^4\)-TPIVPP)NO (20 cm\(^{-1}\)) upon \( ^{15}\text{NO} \) substitution in this work are found to conform with the above empirical rule for \( \text{NO}^- \) isotopic shifts. Assignment of \( \delta_{\text{MNO}} \) and \( v_{\text{M-NO}} \) for these complexes was not possible due to interference by porphyrin ligand absorptions.

Table 4.6 lists the visible absorption spectroscopic data for the nitrosyl(porphyrinato)cobalt(III) complexes. The visible spectrum of Co(TPP)NO in dichloroethane has been reported previously [413 (\( \epsilon 1.4 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1} \)), 538 (1.68 \times 10^4) and 584sh nm (2.81 \times 10^3)], and is in excellent...
Table 4.6 Visible Absorption Spectral Data for Nitrosyl(porphyrinato)cobalt(III) Complexes\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max.}}$ (10\textsuperscript{-3} $\varepsilon$) / nm (1 mol\textsuperscript{-1} cm\textsuperscript{-1})</th>
<th>Soret</th>
<th>$\beta$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(TPP)NO</td>
<td>417 539 586 645 \textsuperscript{(154.17) (13.40) (2.55) (0.60)}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(OEP)NO</td>
<td>383 527 559 \textsuperscript{(87.20) (11.26) (19.40)}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co($\alpha^4$-TPIVPP)NO</td>
<td>385sh 412 537 \textsuperscript{423}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} measured in chloroform solution.
agreement with the result recorded in Table 4.6 in CHCl₃ solution. A discussion of the data in Table 4.6 is best considered along with that for the porphyrin free base and Co(II) complexes. The four band visible spectra of TPPh₂, OEPH₂, and α₄-T_PIVPPH₂ are altered on complexation to give spectra showing two bands in the visible region, and the UV (Soret) band is retained. The Soret band is electronically allowed and is an order of magnitude more intense than the visible band which acquires its intensity from a vibronic mechanism.²⁵¹,³³⁴ The two visible bands are labelled α and β, and parallel bands I and III in the free base. The two bands in Co(II) porphyrins are considered to arise from transitions from the ground ²A₁g to two excited ²Eₜ states which are heavily mixed.¹⁸⁹,³³⁵ From Table 4.2 it can be observed that the Co(II) porphyrins are hypsochromically (blue) shifted compared to the normal spectrum of the respective free base porphyrins. This is best seen by the higher energy shifts in the Soret region in TPPh₂ from 418 nm to 410 nm in Co(TPP), in OEPH₂ from 400 nm to 392 nm in Co(OEP), and in α₄-T_PIVPPH₂ from 418 nm to 409 nm in Co(α₄-T_PIVPP). Cobalt(II), d⁷ and other d⁶ to d⁹ ions have in common a filled d subshell where the dₓz and dᵧz orbitals are apt to overlap (back-bond equatorially) with the empty π* levels of the porphyrin, which are thereby raised up in energy thus causing a hypsochromic shift of the porphyrin (π - π*) transitions with respect to the normal (d⁰, d¹⁰ metalloporphyrin or free base) spectrum.

It is seen from Table 4.6 that the general trend on complex formation with nitric oxide is of bathochromic (red) shifts of the Co(II) porphyrin Soret and visible bands. But
overall the spectra of the nitrosyl(porphyrinato)cobalt(III) complexes are still hypsochromically (blue) shifted with respect to the spectra of the free base porphyrins. In Co(TPP)NO the Soret and $\beta$ bands of Co(TPP) are red shifted (Soret: 410 to 417 nm and $\beta$: 529 to 539 nm). There is the appearance of a new ($\alpha$) band at 586 nm which is not present in the spectrum of Co(TPP), and the low intensity shoulder at 642 nm in Co(TPP) is hardly changed in Co(TPP)NO at 645 nm. In Co(OEP)NO the Soret band is actually blue shifted even further (392 nm in Co(OEP) to 383 nm in Co(OEP)NO), whilst the visible bands are red shifted ($\beta$: 518 to 527 nm and $\alpha$: 553 to 559 nm) compared to Co(OEP). In Co($\alpha^4$-TPivPP) the Soret band at 409 nm is split to lower energy into two lower intensity peaks at 412 nm and 423 nm in Co($\alpha^4$-TPivPP)NO, and a low intensity shoulder appears at 385 nm. The band at 528 nm in Co($\alpha^4$-TPivPP) is also red shifted to 537 nm in Co($\alpha^4$-TPivPP)NO and the shoulder at 555 nm in Co($\alpha^4$-TPivPP) disappears in the nitrosyl.

Substantial broadening or splitting of Soret bands and the appearance of new visible bands is known to occur in porphyrin complexes with potentially $\pi$-acceptor ligands (CO, NO, O$_2$, CH$_3$NC),$^{189}$ and a splitting of the Soret region to lower energy was observed for Co(TPP)NO at 77 K in toluene glass to give two well-defined lower intensity bands,$^{189}$ as observed for Co($\alpha^4$-TPivPP)NO at room temperature in CHCl$_3$ in this work. Furthermore, this splitting in the Soret region of Co(TPP)NO at 77 K$^{189}$ was not observed in the room temperature chloroform solution spectra measured here.

Axial ligands introduce molecular orbitals capable of mixing with the already interacted metal and porphyrin ring
orbitals, and the presence of an axially coordinated ligand could introduce new charge transfer bands such as the e(d_{xz},d_{yz}) \rightarrow b_1(\pi^*)[2A_1 \rightarrow 2E] transition or shift existing M \rightarrow L or L \rightarrow M bands into the Soret region.\textsuperscript{189,251,335} Another possibility is that the Soret (2E) state is split by a ligand field or Jahn-Teller mechanism.\textsuperscript{189} Because the porphyrinato ligand competes in \pi-acceptance with an axial ligand it is expected that the hypsochromic (blue) shift as compared with the normal absorption will diminish with increasing \pi-acceptor capacity of an axial ligand.\textsuperscript{251} In 4-coordinate Co(II) porphyrins there is only equatorial back-bonding into the porphyrin ring, but on coordination of nitric oxide to give the pentacoordinate Co(porphyrin)NO, this back-bonding no longer dominates and some axial back-bonding into NO \pi^* can occur to give (\pi,\pi^*) bands shifted to lower energy giving less hypsochromic spectra (Table 4.6).

It is also seen from Tables 4.2 and 4.6 that the Soret region of the meso-substituted porphyrins TPP and \alpha^4-T_{PIV}PP is red shifted in the cobalt nitrosyls compared to the cobalt porphyrin (from 410 nm to 417 nm in Co(TPP)NO and from 409 nm to 412 and 423 nm in Co(\alpha^4-T_{PIV}PP)NO) but in OEP, which has a different substitution pattern, the Soret is blue shifted from 392 to 383 nm in Co(OEP)NO. This could be a manifestation of the greater electron density of the OEP\textsuperscript{2-} ring pushing up the porphyrin \pi^* orbital energies. However, the nature of the electron removed, whether d_{z^2} or d_{x^2-y^2} would determine whether oxidation from Co(II) to Co(III) causes a red or blue shift because ultimately it would affect d_{\pi} back-bonding into porphyrin ring orbitals, thereby altering the energy gap of the (\pi,\pi^*) transition. The
effective oxidation state of cobalt in the bent nitric oxide complex depends on how the pair of covalent bonding electrons is distributed between cobalt and nitric oxide and also on the extent of \( d_\pi \rightarrow p_\pi \) back-bonding. Axial back-bonding decreases with bending and is also related to the charge distribution in the \( \sigma \)-orbitals. In the limiting case of \( \text{Co(III)NO}^- \), axial back-bonding will be relatively insignificant. Bending the nitrosyl should also affect the equatorial back-bonding and therefore raise the energy of the porphyrin \( \pi^* \) orbitals and hence the degree of hypso shift. However, this would be difficult to quantify.

4.2.1 \( ^{15}\text{N} \) and \( ^{59}\text{Co} \) NMR Investigations of \( ^{15}\text{N} \)-Nitrosyl-(porphyrinato)cobalt(III) Complexes

The chemical shifts and linewidths \( w_{1/2} \) (full width at half-height) of the cobalt(III) nitrosyl porphyrin complexes were measured in \( \text{CD}_2\text{Cl}_2 \) solution. The relevant spectroscopic and structural data for these complexes are illustrated in Table 4.7. A detailed discussion of the \( ^{15}\text{N} \) and \( ^{59}\text{Co} \) NMR results for these complexes and other square-pyramidal apical bent nitrosyls in terms of ligand field effects in the nuclear magnetic shielding of the \( ^{15}\text{N} \) and \( ^{59}\text{Co} \) nuclei is given in Chapter 5, Section 5.1.2.1.

The discussion here will involve the importance of the porphyrin ligand in these results. Since the NMR spectra for these complexes were all recorded in the same solvent, we may examine the effects of the porphyrin ligand. In the \( ^1\text{H} \) NMR of diamagnetic porphyrins the long-range diamagnetic contribution of the aromatic macrocyclic system to the chemical shift is the most important single factor that distinguishes
Table 4.7 Spectroscopic and Structural Data for Square Pyramidal Nitrosyl(porphyrinato)cobalt(III) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \delta^{(15)N} )^{a}</th>
<th>M–N</th>
<th>N–O</th>
<th>M–N</th>
<th>( v^{14}\text{NO} )^{b}</th>
<th>( v^{15}\text{NO} )^{b}</th>
<th>( \delta^{59}\text{Co} )^{a}</th>
<th>( W_{1/2} )^{a}</th>
<th>Relative ( 59\text{Co} ) peak Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(TPP)NO</td>
<td>770.7</td>
<td>135^{d}</td>
<td>1.01^{d}</td>
<td>1.83^{d}</td>
<td>1690</td>
<td>1665</td>
<td>7909</td>
<td>4250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>disordered</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(OEP)NO</td>
<td>760.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1675</td>
<td>1645</td>
<td>8113</td>
<td>3200</td>
<td></td>
</tr>
<tr>
<td>Co(T\text{PIVPP})NO</td>
<td>536.7^{w^{c}}</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1665</td>
<td>1645</td>
<td>7900</td>
<td>280</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7996</td>
<td>3800</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7842</td>
<td>250</td>
</tr>
</tbody>
</table>

a) NMR spectra measured in CD\text{2}Cl\text{2} at room temperature. \( ^{15}N \) shifts relative to neat liquid nitromethane and \( ^{59}\text{Co} \) shifts relative to aqueous K\text{3}[Co(CN)\text{6}], high frequency positive. \( W_{1/2} \) is the \( ^{59}\text{Co} \) line width at half height.

b) KBr disc.

c) Overnight run without Cr(acac)\text{3}, therefore low intensity \( ^{15}N \) resonance is dubious. No other promising peaks were observed within range +1000 to -230 ppm. This is indicative of extensive decomposition.

d) Reference 66.
porphyrins from similar non-aromatic structures. If a closed loop of electrons is subjected to an external magnetic field, a Larmor precession of the entire $\pi$-cloud is induced. The circulation of the electrons (ring current) gives rise to a secondary magnetic field. The effect is strongly anisotropic, it does not average out to zero by random tumbling of the molecule and thus the ring current gives rise to an anisotropic shielding effect on protons within the range of the ring current, which functions as a built-in shift reagent and accounts for the large $^1H$ shift range of porphyrins. In porphyrins the deshielding effect of electron-withdrawal is usually overcompensated by the simultaneous decrease in ring current that results from lowering of the electron density of the $\pi$-system (and this can cause upfield proton shifts). However, the ring current has a much smaller effect on heavier nuclei and it seems probable that the change in $^{59}$Co chemical shift due to this interaction will be of much smaller magnitude than the temperature-independent paramagnetism influence arising from the d-d splitting in the ligand field.

The $^{15}N$ resonances for Co(TPP)$^{15}NO$ and Co(OEP)$^{15}NO$ are at 770.7 and 760.1 ppm respectively, and are typical values for bent CoNO strongly deshielded by paramagnetic $n_{N} \rightarrow \pi^*$ circulations in the bent CoNO unit. The $^{15}N$ shift for Co(TPP)$^{15}NO$ is at lower field than for Co(OEP)$^{15}NO$, however, the reverse is true for the values of $^{59}$Co with Co(TPP)$^{15}NO$ resonating at 7909 ppm and Co(OEP)$^{15}NO$ at 8113 ppm. The higher $v_{NO}$ for Co(TPP)NO (more linear NO) does not correlate with its higher nitrogen shift, nor does the lower $v_{NO}$ of Co(OEP)NO correlate with its lower nitrogen shift. The change
from TPP to OEP is one of increased electron-release to cobalt ion. Phenyl groups are electron-withdrawing when non-coplanar and the ethyl groups of OEP are electron-releasing. The nitrogen shielding for the OEP and TPP complexes is in line with the trends reported in Chapter 5, where shielding of N and Co is decreased (i.e. higher chemical shift) by introduction of electron-withdrawing substituents (here the phenyl groups of TPP) but electron-releasing substituents have the opposite effect and increase the Co and N shielding. In Co(TPP)NO and Co(OEP)NO however, the trend in cobalt shift is reversed and the electron-releasing OEP gives a decreased Co shielding (i.e. higher cobalt shift) compared to the electron-releasing TPP. In agreement with our data is the report that $^{59}$Co shifts for OEP complexes were found to be larger than for similar complexes of TPP [Co(porph)(B)$_2$]$^+$ (B = Im, 1MeIm) species. Although this is not thought to be a ring current effect, the reason for this trend could be a property of the porphyrin ligand. The porphyrin orbitals will interact with the filled d$_\pi$(xz, yz) orbitals of cobalt. Electron-releasing groups will raise the energy of these overlapping orbitals, therefore decreasing the shielding. According to the Ramsey equation the chemical shift values for Co(III) compounds are dominated by an inverse correlation with $\Delta E (^{1}A_{1g} \rightarrow ^{1}T_{1g})$, where $\Delta E$ approximates to the separation between the t$_{2g}$ and e$_g$ orbitals. Electron-release by a ligand substituent will raise the energy of the d$_\pi$ and decrease $\Delta E$ with a consequent increase in Co shift. However, this is also more likely to make the nitrosyl ligand bend, but this is not apparent from the reduced $^{15}$N shift for Co(OEP)$^{15}$NO versus
Co(TPP)\textsuperscript{15}NO. However, selective influences could operate in these cobalt nitrosyls where the porphyrin ligand may have a larger effect on the cobalt shielding than on the nitrogen shielding. The direct effect on cobalt shielding, but not on nitrogen shielding is of the d-d circulations in the basal plane, just as direct effects on the nitrosyl ligand are less important to the cobalt shielding since the coordination geometry is unchanged. Correlations of increased shielding of a transition metal nucleus with increase in ligand field strength\textsuperscript{338} suggest that since TPP has a more shielded Co nucleus here then it is a stronger field ligand than OEP.

There are many factors that influence the linewidth of a $^{59}$Co resonance. Because of its quadrupole moment, the cobalt will couple with the electric field gradient at the nucleus, and the relaxation of $^{59}$Co among different nuclear spin states is generally dominated by the quadrupolar mechanism.\textsuperscript{260} A number of other relaxation mechanisms besides quadrupolar coupling can be considered for porphyrin complexes with axial ligands;\textsuperscript{307} chemical exchange mechanisms for these nitrosyls are unlikely in the timeframe of the NMR experiment. Dipolar broadening should not be a problem at these low concentrations (ca. 50 mg compound in 3 ml solvent), and scalar coupling will be small.\textsuperscript{260} The linewidth of Co(OEP)\textsuperscript{15}NO is about three-quarters that of Co(TPP)\textsuperscript{15}NO, and although the reason for this is not clear it may have to do with the smaller OEP ligand being a more highly symmetric molecule. Linewidths may also be correlated with viscosity; molecular tumbling times are important, and solvent type and structure of compound also play a role.\textsuperscript{260}

The OEP and TPP nitrosyl complexes appear to be reason-
ably stable under nitrogen during the acquisition of spectroscopic data. The $^{59}$Co NMR spectrum of Co(OEP)$_{15}$NO was measured two days before measurement of the $^{15}$N spectrum, but there was no evidence of decomposition as the nitrogen spectrum revealed just one strong peak. The $^{15}$N and $^{59}$Co NMR spectra of Co(TPP)$_{15}$NO were measured on two separate samples on different days, and no decomposition is apparent. However, lack of a strong low field $^{15}$N resonance, plus the appearance of three $^{59}$Co resonances is suggestive of extensive decomposition of Co(TPypPP)$_{15}$NO in solution. The $^{59}$Co NMR spectrum of this compound was measured one day before the $^{15}$N spectrum was recorded, during which time obvious decomposition had taken place to give a spectrum containing the very weak (and therefore dubious) peak at 536.7 ppm, which was collected overnight without the use of a relaxation agent (Cr(acac)$_3$). No other likely $^{15}$N resonances were found within the large chemical shift range +1000 to -230 ppm. Addition of Cr(acac)$_3$ and faster pulsing did not improve the quality of the spectrum. Picket-fence porphyrin complexes are known to be very susceptible to light-induced isomerisation. It is therefore quite possible that the three peaks seen in the $^{59}$Co NMR spectrum are due to three of the four possible isomers of this compound. However, it is heartening to see that the major peak at 7900 ppm for Co(TPypPP)$_{15}$NO is similar to the only peak at 7909 ppm in the $^{59}$Co NMR spectrum of Co(TPP)$_{15}$NO, a porphyrin which is similarly meso-substituted. This could therefore be the $^{59}$Co peak corresponding to the nitrosyl species. If the low intensity $^{15}$N resonance at 536.7 ppm is real, it is between the usual ranges for bent and linear CoNO groups. This could
mean that this CoNO group is less strongly bent than those in Co(TPP)NO and Co(OEP)NO, possibly because the picket-fence interacts with the nitrosyl ligand. However, the $^{59}$Co NMR data suggest extensive decomposition and the $^{15}$N assignment is uncertain.

Iron picket-fence porphyrin complexes place dioxygen in a hydrophobic pocket protected from chemical reaction and are therefore reversible oxygen carriers in solution and in the solid state. Reversible combination of Co(T$_{PIV}$PP) with nitric oxide in solution was suspected in this work since during the preparation, solutions of the nitrosyl were observed to effervesce gently. The reversibility of this reaction was investigated spectroscopically; however, there was only minor spectroscopic change on placing chloroform solutions of Co(T$_{PIV}$PP)NO under vacuum, although on readmission of NO the intensity of the peaks grew. More experiments are necessary since the $^{59}$Co and $^{15}$N NMR spectra clearly show decomposition with time. Consequently, measurement of the $^{15}$N and $^{59}$Co NMR spectra of a CDCl$_3$ solution of Co(T$_{PIV}$PP)$^{15}$NO in a sealed NMR tube under $^{15}$NO was attempted. The results are in Section 4.6.

It was not possible to follow the disappearance of $v_{NO}$ by infrared spectroscopy on solid Co(T$_{PIV}$PP)NO because insufficient compound was available. However, the solid does not change colour on storage, nor did fumes of nitrogen oxides develop above the sample in a closed container. The behavior of this diamagnetic myoglobin model compound with NO needs to be more thoroughly investigated by electronic, IR and NMR spectroscopic techniques. It is, however, apparent that $^{15}$N and $^{59}$Co NMR measurements used in conjunction are a
sensitive method for studying the decomposition of
diamagnetic bent cobalt nitrosyls.

4.3 Oxidation of Cobalt Nitrosyl Complexes to Cobalt Nitro
Complexes

During the long acquisition times necessary to observe the $^{15}$N spectra of the enriched nitrosyls (see Chapter 5) it became apparent that some decomposed to other diamagnetic species thought to be the corresponding nitro complexes. To investigate this some enriched nitrosyls were oxidised with dioxygen in the presence of base to the nitro complexes. From the 5-coordinate porphyrin nitrosyl complexes 6-coordinate cobalt porphyrin nitro complexes containing coordinated axial base (py or 1MeIm) were prepared in reasonable yields in both the $^{14}$N and $^{15}$N labelled forms, and there is quite good agreement between theoretical and observed analytical data (Table 4.8). Some nitro complexes were found to be solvated, and the solvent proved extremely difficult to remove even on extended heating under high vacuum. In the infrared spectra there was a small broad peak at ca. 750 cm$^{-1}$ which could be indicative of $v_{C\cdot\cdot\cdotCl}$ of CH$_2$Cl$_2$.

The NMR data presented in Chapter 5 for these and similar cobalt nitro complexes in solution do not show definitely the presence of a coordinated nitro group in all complexes. Nevertheless, the two TPP complexes give very similar visible spectra as do the two OEP complexes. Substitution of pyridine for 1-methylimidazole seems to produce little effect on band position, and similar Soret and visible bands are seen with only minor changes in intensity (Table 4.9). The visible spectrum reported for
Table 4.8 Yield and Analytical Data for Nitro(axial base)(porphyrinato)cobalt(III)complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>%C found (theor.)</th>
<th>%H found (theor.)</th>
<th>%N found (theor.)</th>
<th>Overall Yield 14N (15N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(py)Co(TPP)NO₂ (purple crystals)</td>
<td>73.54</td>
<td>4.34</td>
<td>10.14</td>
<td>71%</td>
</tr>
<tr>
<td>(1MeIM)Co(TPP)NO₂·1/5CH₂Cl₂ (purple crystals)</td>
<td>(73.87)</td>
<td>(4.17)</td>
<td>(10.55)</td>
<td>(76%)</td>
</tr>
<tr>
<td>(py)Co(OEP)NO₂·1/4CH₂Cl₂ (purple crystals)</td>
<td>66.90</td>
<td>6.85</td>
<td>11.23</td>
<td>50%</td>
</tr>
<tr>
<td>(1MeIm)Co(OEP)NO₂·1/4CH₂Cl₂ (purple solid)</td>
<td>(65.24)</td>
<td>(6.87)</td>
<td>(13.23)</td>
<td>(94%)</td>
</tr>
<tr>
<td>Compound</td>
<td>$\lambda_{\text{max}}$ ($10^{-3} \varepsilon$) nm</td>
<td>$\beta$ mol$^{-1}$ cm$^{-1}$</td>
<td>$\alpha$ mol$^{-1}$ cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td>--------------------------------------------------</td>
<td>-------------------------------</td>
<td>-------------------------------</td>
<td></td>
</tr>
<tr>
<td>(py)Co(TPP)NO$_2$</td>
<td>433 548 586sh 644</td>
<td>(204.17) (13.30) (4.60) (0.765)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1MeIm)Co(TPP)NO$_2$</td>
<td>433 548 580sh</td>
<td>(169.0) (8.80) (3.36)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(py)Co(OEP)NO$_2$</td>
<td>417 529 561</td>
<td>(71.70) (10.60) (4.2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1MeIm)Co(OEP)NO$_2$</td>
<td>417 528 560</td>
<td>(94.30) (10.20) (9.85)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) measured in chloroform solution.
Co(TPP)NO\(_2\) in dichloroethane of 433 (\(\epsilon \, 3.35 \times 10^5 \) 1 mol\(^{-1}\) cm\(^{-1}\)), 512sh (5.58 x 10\(^3\)), 549 (1.51 x 10\(^4\)), and 588sh nm (5.98 x 10\(^3\)) is in excellent agreement with the spectrum reported here for the same compound in chloroform.

In the TPP nitro complexes the Soret band has undergone a shift from 417 nm in Co(TPP)NO to 433 nm in both pyridine and 1-methylimidazole derivatives, with an increase in extinction coefficient. The \(\beta\)-band at 539 nm in Co(TPP)NO is similarly red-shifted to 548 nm in both TPP nitro derivatives. The intensity of absorption has remained roughly the same. The \(\alpha\)-band which appears as a shoulder in Co(TPP)NO has remained in roughly the same position in both nitro complexes and has the same overall intensity. For both the OEP nitro complexes the Soret band has red-shifted 34 nm from 383 nm in the nitrosyl to 417 nm, with an increase in intensity. Both the \(\alpha\)- and \(\beta\)-bands have stayed largely the same in the nitro complexes compared to the nitrosyl. However, the \(\alpha\)-band has dropped in intensity.

All cobalt porphyrins exhibit hypso-type spectra.\(^{251}\) The above spectra for the 6-coordinate nitro complexes can be seen to be hypso in character because they do not show any prominent extra absorptions in the region >320 nm. However, the spectra for the nitro complexes are not blue-shifted compared to the parent porphyrin spectra. The optical spectra of hypso porphyrin complexes can be rationalised for \(d^6\) metals, and the main factors at play are: (1) the energy difference (ligand field splittings) between the filled orbitals \((d_{xy})^2(d_\pi)^4\) and the empty orbitals \(d_z^2, d_{x^2-y^2}\) of the metal, (2) the energy for charge transfer transitions from metal to ring or vice versa, and (3) the mixing of the
filled $d_\pi$ of the metal with the empty $\pi^*$ orbitals of the ring i.e. equatorial back-bonding. The $\pi^*$ levels are pushed up to higher energy giving rise to the hypsochromic effect. Factors (1) and (2) are of major importance to porphyrin emission spectra, and factor (3) is the most important in the absorption spectra of porphyrins. There also exists the 'rule of bathochromism' where in a metalloporphyrin containing filled $d_\pi$ orbitals capable of back-bonding, a bathochromic or red shift of the $\alpha$-band results if a given axial ligand is replaced by a new one with a larger $\pi$-acceptor capacity. This is applicable to all porphyrin spectral types and is useful for identifying porphyrin complexes in which coordination of a certain axial ligand with known $\pi$-acceptor capacity is suspected. For axial ligands which are predominantly $\sigma$-donor (e.g. NH$_3$) with no $\pi$-acceptor capacity the energy of the $d_\pi$ orbitals is raised and as a result equatorial back-bonding is strong. Back-bonding repulsions of $d_\pi$ to $\pi^*$ porphyrin causes a strong hypsochromic shift to the $\pi, \pi^*$ spectrum. Such is the case for the bent CoNO$^-$ complexes in the previous section. But NO$^-$ as well as being a strong $\sigma$-donor also has weak to moderate $\pi$-acceptor capacity which will reduce $d_\pi$ energy so the hypsochromism is reduced compared to only $\sigma$-donors. In the 6-coordinate complexes we had thought to have changed the axial ligand NO$^-$ in the 5-coordinate nitrosyls to NO$_2^-$ and axial base (py or 1MeIm). However, the $^{15}$N and $^{59}$Co NMR data presented in Chapter 5 for solutions of these nitro complexes suggest that in noncoordinating solvents, either the 6-coordinate NO$_2^-$/axial base or possibly bis(axial base), [Co(porph)(B)$_2$(NO$_3$)] (B = py, 1MeIm) species could exist.
N-Bonded nitrite is a strong $\sigma$- and $\pi$-bonding ligand high in the spectrochemical series. Pyridine and imidazole are weaker $\pi$-acceptors than NO$_2^-$, but interaction of axial base ligand $\pi^*$ orbitals with metal $d_{\pi}$ orbitals is still significant. The axial back-bonding of the replacement ligands NO$_2^-$, py, MeIm lowers the energy of $d_{\pi}$ and also reduces equatorial back-bonding. As a result the $\pi, \pi^*$ spectra are much less hypsochromic. The increased $\pi$-bonding character of the replacement (NO$_2^-$ for NO$^-$) and extra ligand (py, 1MeIm) must be responsible for the decreased hypsochromism of the 'nitro' complexes compared to the nitrosyls and parent porphyrin spectra. The fact that 1-methylimidazole and pyridine seem to have much the same effect here on visible band shifts suggests nearly identical $\pi$-bonding character in these systems.

NMR and IR spectroscopic data for the nitro cobalt porphyrin complexes are presented in Table 4.10. Only in the instance where the corresponding cobalt nitrosyl was stable and fully characterised was the oxidation reaction in the presence of base attempted. The infrared band assignments for the nitro complexes were determined from their $^{15}$N substitution isotopic shifts and are believed to be correct in light of previous reports (see Chapter 5, Section 5.1.2.2 for complete discussion). On $^{15}$N substitution, isotopic shifts of about 15-20 cm$^{-1}$ to lower wavenumber occur in the symmetric and asymmetric stretching absorptions, with smaller differences in the other characteristic absorptions. These assignments give definite proof for the existence of the N-bonded nitro group in the solid state (KBr disc).

The $^{15}$N and $^{59}$Co NMR spectra of these porphyrin nitro complexes are discussed in Chapter 5, Section 5.1.2.2 along
Table 4.10 NMR and IR Spectroscopic Data for Nitro(axial base)(porphyrinato)cobalt(III) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\delta^{15\text{N}}$ (ppm)</th>
<th>$\delta^{59\text{Co}}$ (ppm)</th>
<th>$W_{1/2}$ (Hz)</th>
<th>Relative Intensity</th>
<th>$v_{\text{as NO}_2}$ (cm$^{-1}$)</th>
<th>$v_{\text{s NO}_2}$ (cm$^{-1}$)</th>
<th>$\delta_{\text{NO}}$ (cm$^{-1}$)</th>
<th>$\varphi_{\text{w NO}_2}$ (cm$^{-1}$)</th>
<th>$v_{\text{M-N}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(py)Co(TPP)$^{15\text{NO}_2}$</td>
<td>CDCl$_3$</td>
<td>-2.5</td>
<td>7902</td>
<td>2500</td>
<td></td>
<td>1435</td>
<td>1310</td>
<td>820</td>
<td>640</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1405)</td>
<td>(1295)</td>
<td>(813)</td>
<td>(640)</td>
<td>(370)</td>
</tr>
<tr>
<td>(1MeIm)Co(TPP)$^{15\text{NO}_2}$</td>
<td>CDCl$_3$</td>
<td>-2.9</td>
<td>8077</td>
<td>170</td>
<td>1</td>
<td>1410</td>
<td>1315</td>
<td>820</td>
<td>620</td>
<td>375</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1405)</td>
<td>(1295)</td>
<td>(811)</td>
<td>(620)</td>
<td>(375)</td>
</tr>
<tr>
<td>(py)Co(OEP)$^{15\text{NO}_2}$</td>
<td>CD$_2$Cl$_2$</td>
<td>-2.4</td>
<td>8204</td>
<td>1300</td>
<td>1.6</td>
<td>1435sh</td>
<td>1435</td>
<td>n.o.</td>
<td>648</td>
<td>385</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1405)</td>
<td>(1310)</td>
<td>(810)</td>
<td>(648)</td>
<td>(385)</td>
</tr>
<tr>
<td>(1MeIm)Co(OEP)$^{15\text{NO}_2}$</td>
<td>CD$_2$Cl$_2$</td>
<td>-2.4</td>
<td>8307</td>
<td>140</td>
<td>1.3</td>
<td>1460</td>
<td>1345</td>
<td>845</td>
<td>620</td>
<td>400</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1445)</td>
<td>(1315sh)</td>
<td>(830)</td>
<td>(620)</td>
<td>(390)</td>
</tr>
</tbody>
</table>

a) Measured at 25°C. $^{15\text{N}}$ shift relative to neat liquid nitromethane and $^{59\text{Co}}$ shift relative to aqueous $K_3[\text{Co(CN)}_6]$, high frequency positive. $W_{1/2}$ is the $^{59\text{Co}}$ line width at half height.

b) KBr disc.
with similar 6-coordinate cobalt nitro complexes. From the discussion in Chapter 5 on the lability of these cobalt nitro compounds, it appears that the nitro compounds are mostly decomposing in solution to form other cobalt complexes and uncoordinated nitrate. One such possibility which has already been mentioned for these porphyrins in noncoordinating solvents is \([\text{Co(porph)}(\text{B})_2]^+\text{NO}_3^-\) (B = py or 1MeIm). It is interesting to note that in the $^{59}$Co NMR study of \([\text{Co(porph)}(\text{B})_2]^+\text{X}^-\) (where porph = TPP, OEP; B = Im, 1MeIm; X$^- = \text{ClO}_4^-, \text{BPh}_4^-, \text{BF}_4^-\) the chemical shift range for these species varied between 8300 and 8800 ppm. The chemical shifts reported for the complexes in Table 4.10 fall within the same range. However, our results are also substantiated by the $^{15}$N assignment of free NO$_3^-$ in solution. It is therefore feasible that such species are present in the solutions of the nitro cobalt porphyrins (and for further discussion of possible mechanism of formation of such species see Section 5.1.2.2). Within the limited data set here it may be seen that OEP gives larger cobalt shifts than TPP, and within each porphyrin class, 1MeIm gives higher cobalt shift than py. The increase in cobalt shift is in the direction of electron-release to cobalt from TPP to OEP and from py to 1MeIm.

From the NMR data in Section 4.2.1 it is seen that Co(TPP)NO and Co(OEP)NO are reasonably stable in solution in the absence of air, as are the other 5-coordinate square-pyramidal bent nitrosyls presented in Section 5.1. On oxidation to the 6-coordinate nitro complexes the situation changes, and from the solution NMR results the coordinated nitro group is an extremely labile ligand. In the following section the crystal structure of one of the nitro complexes,
(py)Co(TPP)NO₂, is presented. This structural determination is definitive proof of the stability of these nitro complexes in the solid state, and of the correct assignment of the IR spectroscopic data. Apparently though, these nitro derivatives are not stable for long periods in solution since repeated recrystallisation of the analogous (1MeIm)Co(TPP)NO₂ led to decomposition to [Co(TPP)(1MeIm)₂]NO₂, but this became evident only after the crystal structure had been solved.

4.3.1 Single Crystal X-Ray Structure Determinations of (py)Co(TPP)NO₂ and [Co(TPP)(1MeIm)₂]NO₂

4.3.1.1 Molecular Structure of Nitro(pyridine)(tetraphenylporphyrinato)cobalt(III), (py)Co(TPP)NO₂

Small purple crystalline blocks of (py)Co(TPP)NO₂ were grown by slow diffusion of excess 80-100°C petrol into a CH₂Cl₂ solution of the complex (0.1 g in 5 ml solvent).

Crystal Data. Co₄₉H₃₃N₆O₂, Monoclinic, a = 14.461(4), b = 23.435(8), c = 13.227(4) Å, β = 100.77(1)°, V = 4403.4 Å³. Space group P2₁/n, Z = 4, FW = 796.78, F(000) = 1648, DCALC = 1.202 g cm⁻³, absorption coefficient (MoKα) = 4.296 cm⁻¹, wavelength λ(MoKα) = 0.71073 Å.

Data Collection and Processing. The unit cell parameters were derived from 25 accurately centred reflections on an Enraf-Nonius CAD4 diffractometer using MoKα radiation. Crystal size was approximately 0.2 x 0.1 x 0.3 mm. Intensity data were measured with MoKα radiation in the range 1° - 26° with a standard reflection monitored hourly. After data reduction the reflection data list contained 9221 reflections of which 5983 were used. An analysis of the
standard reflections indicated a loss of intensity of 15.4 % over the data collection period which was corrected for.

**Structure Determination and Refinement.** From a Patterson map the position of the Co atom was derived, whilst the program MULTAN revealed a further 28 atoms of the structure. Refinement of these atoms converged at $R = 0.37$ and a calculated electron density map showed up the remaining atoms of the structure. Inclusion of these extra atoms together with the H atoms in calculated positions converged at $R = 0.15$. At this stage it was found that the pair of oxygen atoms of the NO$_2$ group were occupying two possible sites. A refinement of the occupancy factors gave values in the range 0.79 to 0.44 with correspondingly high temperature factors. In view of the correlation that occurs between these parameters the site occupancy was fixed at 0.5 for all four atom sites. Application of the empirical absorption correction by the program DIFABS reduced $R$ to 0.11. Anisotropic refinement, initially for Co alone, then for all non-H atoms converged at $R = 0.08$.

**Description of Molecular Structure.** The molecular structure of (py)Co(TPP)NO$_2$ is shown in Figure 4.5 in ORTEP form, where each atom is represented by a 50 % thermal ellipsoid with the relative size and orientation required by crystallographically determined thermal parameters. Only the pertinent bond lengths within the coordination sphere of the cobalt atom are given in Table 4.11, with the relevant bond angles in Table 4.12.

The symmetry of the coordination sphere of the cobalt is approximately $D_{2d}$ ($ar{4}2m$) with the Co—N(1)(pyridine) bond distance of 2.020(4) Å being significantly longer than the
Figure 4.5 Ortep Drawing of (py)Co(TPP)NO₂ with the Atom Numbering Scheme
Table 4.11 Bond Lengths Within the Coordination Sphere of (py)Co(TPP)NO₂

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co—N(21)</td>
<td>1.963(4)</td>
</tr>
<tr>
<td>Co—N(22)</td>
<td>1.958(4)</td>
</tr>
<tr>
<td>Co—N(23)</td>
<td>1.956(4)</td>
</tr>
<tr>
<td>Co—N(24)</td>
<td>1.956(4)</td>
</tr>
<tr>
<td>(Co—Nₚ)ₚ̅ AV</td>
<td>1.958(3)</td>
</tr>
<tr>
<td>Co—N(1)(py)</td>
<td>2.020(4)</td>
</tr>
<tr>
<td>Co—N(2)(nitro)</td>
<td>1.963(4)</td>
</tr>
</tbody>
</table>

(Numbers in parentheses are estimated standard deviation in least significant digits)

Table 4.12 Bond Angles Within the Coordination Sphere of (py)Co(TPP)NO₂

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(21)—Co—N(22)</td>
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<tr>
<td>N(21)—Co—N(23)</td>
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<td>N(21)—Co—N(24)</td>
<td>89.6</td>
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<tr>
<td>N(22)—Co—N(23)</td>
<td>89.5</td>
</tr>
<tr>
<td>N(22)—Co—N(24)</td>
<td>179.5</td>
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<tr>
<td>N(23)—Co—N(24)</td>
<td>90.5</td>
</tr>
<tr>
<td>N(1)—Co—N(2)</td>
<td>179.0</td>
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<tr>
<td>N(1)—Co—N(21)</td>
<td>88.6</td>
</tr>
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<td>N(1)—Co—N(22)</td>
<td>89.9</td>
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<td>N(1)—Co—N(23)</td>
<td>89.8</td>
</tr>
<tr>
<td>N(1)—Co—N(24)</td>
<td>90.0</td>
</tr>
<tr>
<td>N(2)—Co—N(21)</td>
<td>91.4</td>
</tr>
<tr>
<td>N(2)—Co—N(22)</td>
<td>89.1</td>
</tr>
<tr>
<td>N(2)—Co—N(23)</td>
<td>90.3</td>
</tr>
<tr>
<td>N(2)—Co—N(24)</td>
<td>90.4</td>
</tr>
</tbody>
</table>
other Co—N distances, which are Co—N(2)(nitro) = 1.963(4) Å and averaged equatorial distance, (Co—Np)AV = 1.958(3) Å. The Co—N\textsubscript{NITRO} distance of 1.963(4) Å is a slightly longer than normal Co—N\textsubscript{NITRO} bond length when compared to structural data for [Co(NH\textsubscript{3})\textsubscript{5}(NO\textsubscript{2})\textsuperscript{2+}; Co—N\textsubscript{NITRO} = 1.921(21) Å, \textsuperscript{341} [Co(NH\textsubscript{3})\textsubscript{3}(NO\textsubscript{2})\textsubscript{3}]; (Co—N\textsubscript{NITRO})AV = 1.92(1) Å, \textsuperscript{342} and to (3,5-lut)Co(TPP)NO\textsubscript{2} with Co—N\textsubscript{NITRO} = 1.948(4) Å. \textsuperscript{343} If bond distance is related to bond strength and then to kinetic and thermodynamic stability, then this long bond implies that decomposition or rearrangement is possible. The multiple signals in the $^{15}$N NMR spectra of these nitro compounds substantiates this idea.

The so-called dihedral angle $\phi$ is 42.6° and is therefore close to the expected 45°. The dihedral angle $\phi$ is defined as the angle between the plane of the axial aromatic base and a plane passing through an idealised Co—N\textsubscript{AXIAL} bond and one of the porphyrin nitrogen atoms. \textsuperscript{344} Steric interactions between the adjacent H atoms of the coordinated axial base and the porphyrin core N atoms are at a maximum for $\phi = 0$ or 90° and a minimum for $\phi = 45°$. The axial base can be positioned away from the sterically least-active bisecting position, $\phi = 45°$ by crystal packing effects. As the value of $\phi$ deviates further from 45°, ligand porphyrin contacts increase and these may be relieved by elongation of the M-L bond.

The cobalt and porphyrin ring nitrogens are practically planar with N(23) most out of plane. The rest of the porphyrin ring is far from flat and the distances above and below the plane of the cobalt atom are shown in Figure 4.6. The porphyrin ring nitrogens therefore form a slight saddle with the cobalt atom in the centre, and this ruffling of the
Figure 4.6 Relative Planarity of the Porphyrin Ring in \((\text{py})\text{Co(TPP)NO}_2\)

Positive and negative displacements from the metalloporphyrin mean plane are given in Å.
core corresponds to that required by the point group $D_{2d}$ with the complexing Co—$N_p$ equatorial bonds on the twofold axes and the methine carbon atoms ($C_m$) in the dihedral mirror planes of $D_{2d}$. Deviations from planarity arise from distortions induced by axial ligands and from ill-defined crystal packing influences. When M—$N_p$ bonds shorter than 1.96 Å are desired by the metal centre, then a strong ruffling of the porphyrinato skeleton is conducive to shrinking the central hole (this is discussed in Section 4.3.2).

The oxygens of the coordinated nitro group are disordered and have been fixed into their most favourable positions which are nearly at right angles ($83.3^\circ$) to each other. The absolute geometry of the $N$-bonded disordered $NO_2^-$ group is shown in Figure 4.7, along with a schematic diagram depicting the angles between relevant planes in the molecule. This disorder is probably because of some unusually short contacts that the oxygen atoms of the nitro group make with the carbon atoms of a pyridine ring and a phenyl ring of the next nearest neighbouring porphyrin complex in the crystal lattice. A 4.0 Å search around each atom in the structure revealed some unusually short contact distances which are given in Table 4.13.

The bond lengths and angles in the TPP skeleton and the rest of the complex molecule are not significantly different from previously reported values (see Table 4.16 in Section 4.3.2 for references).

4.3.1.2 Molecular Structure of [Bis(1-methylimidazole)(porphyrinato)cobalt(III)(1+)] Nitrite, [Co(TPP)(1MeIm)$_2$]NO$_2$

(1MeIm)Co(TPP)NO$_2$ was recrystallised twice for X-ray
Figure 4.7(b) Schematic Diagram Illustrating the Important Planes Within the Coordination Sphere of (py)Co(TPP)NO_2

Dihedral angle, $\phi$

$= 42.6^\circ$

Planes are defined as:

1. Co, N(1), C(501), C(502), C(503), C(504), C(505)
2. Co, N(2), O(1A), O(2A)
3. Co, N(2), O(1B), O(2B)
4. Co, N(21), N(1), N(23)
5. Co, N(22), N(1), N(24)
6. Co, N(21), N(2), N(23)
7. Co, N(22), N(2), N(24)

Angles between planes:

1)-(2) 89.3°  (2)-(4) 46.7°  (3)-(7) 127.0°
1)-(3) 6.0°  (2)-(5) 43.8°  (4)-(5) 90.5°
1)-(4) 42.6°  (2)-(6) 46.7°  (4)-(6) 1.0°
1)-(5) 132.9°  (2)-(7) 43.8°  (4)-(7) 90.5°
1)-(6) 42.6°  (3)-(4) 36.6°  (5)-(6) 90.4°
1)-(7) 132.9°  (3)-(5) 127.0°  (5)-(7) 0.1°
(2)-(3) 83.3°  (3)-(6) 36.7°  (6)-(7) 90.4°
<table>
<thead>
<tr>
<th>Atoms</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
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<td>pyridine ring</td>
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<tr>
<td>O(1A)----C(504')</td>
<td>3.25</td>
</tr>
<tr>
<td>O(1B)----C(503')</td>
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<tr>
<td>O(1B)----C(504')</td>
<td>3.00</td>
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<tr>
<td>phenyl ring</td>
<td></td>
</tr>
<tr>
<td>O(1B)----C(305')</td>
<td>3.37</td>
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<tr>
<td>O(2A)----C(305')</td>
<td>2.97</td>
</tr>
<tr>
<td>O(2A)----C(304')</td>
<td>3.22</td>
</tr>
</tbody>
</table>

(Prime notation indicates atoms of an equivalent 'nearest neighbour' molecule in unit cell)
crystallography, and in doing so decomposed to the above complex. The compound (1MeIm)Co(TPP)NO₂ was first crystallised by slow diffusion of excess 80-100°C petrol into a CH₂Cl₂ solution (0.2 g in 8 ml) of the complex to give extensively twinned crystals that were unsuitable for X-ray work. The compound was again recrystallised in the same way using CHCl₃-petrol to give a mixture of crystals (blocks, plates, and needles). The blocks were suitable for X-ray work and the crystal structure was solved as [Co(TPP)(1MeIm)₂]NO₂. The result corroborates the lability of the coordinated nitro group as also deduced from the ¹⁵N and ⁵⁹Co NMR work.

Crystal Data. CoC₅₂H₄₀N₉O₂, Monoclinic, a = 27.257(18), b = 16.482(30), c = 23.067(19) Å, β = 107.95(07)°, V = 9858.9 Å³, Space group C2/c, Z = 8, FW = 881.89, F(000) = 3664, DCALC = 1.188 g cm⁻³, Absorption coefficient (MoKα) = 3.911 cm⁻¹, wavelength λ(MoKα) = 0.71073 Å.

Data Collection and Processing. The C-centred monoclinic unit cell parameters were determined from 25 accurately centred reflections on an Enraf-Nonius CAD4 diffractometer from a block-shaped crystal of approximate size 0.3 x 0.2 x 0.2 mm. Intensity data were collected using MoKα radiation in the range 1 to 22°, with a standard reflection monitored hourly. After data reduction from a total of 6020 unique reflections some 3506 were used. Analysis of the standard reflections showed an intensity loss of only 0-1 % which was considered insignificant.

Structure Determination and Refinement. From the Patterson map the position of the Co atom was deduced, whilst the program MULTAN yielded not only the same position of this atom but also 24 other atoms of the structure. A limited
structural refinement of these 25 atoms converged at $R = 0.42$ and from subsequent analysis the remainder of the structure was obtained, which was now found to contain two imidazole groups coordinated to Co. An absorption correction by the program DIFABS reduced $R$ to 0.14. Anisotropic refinement was started first with Co alone, then for all non-H atoms and reached convergence at $R = 0.112$. A difference map revealed small extra peaks which could be a counterion in the structure. Considerable difficulty was experienced in obtaining the correct disposition and orientation of this group which was taken to be a $\text{NO}_2^-$ ion, and which could only be refined isotropically. Even so the geometry of the bonds and O-N-O angle is highly distorted. $R$ finally converged at 0.096.

Description of the Molecular Structure. The ORTEP plot for the complex cation giving 50 % thermal ellipsoids is shown in Figure 4.8. Only the bond lengths and angles within the coordination sphere of the cobalt ion are shown in Tables 4.14 and 4.15 respectively. Again, as in the previous molecular structure, the porphyrin ring is far from flat and displacements of the carbon atoms of the porphyrin skeleton out of plane vary $\pm 0.35 \text{ Å}$. The imidazole planes are roughly at right angles to each other (78°) giving dihedral angles for each IMelm of $\phi_1 = 60^\circ$, $\phi_2 = 18^\circ$ with independent bond lengths of 1.946(4) and 1.971(11) Å respectively. The porphyrin nitrogens, N(21) to N(24) are in a slight saddle form as in the previous structure with the cobalt ion exactly in the centre (Figure 4.9). However, the geometry around the cobalt is close to a regular octahedron with angles 90 $\pm 1^\circ$ and with bond lengths 1.96 $\pm 0.02 \text{ Å}$.

The crystal structure includes an $\text{NO}_2^-$ molecule as a
Figure 4.8 Ortep Drawing of the Complex Cation \([\text{Co(TPP)-(1MeIm)}_2]\text{NO}_2\) with the Atom Numbering Scheme
Table 4.14 Bond Lengths Within the Coordination Sphere of \([\text{Co}(\text{TPP})(\text{1MeIm})_2\text{NO}_2]\)

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co—N(21)</td>
<td>1.960(10)</td>
</tr>
<tr>
<td>Co—N(22)</td>
<td>1.979(9)</td>
</tr>
<tr>
<td>Co—N(23)</td>
<td>1.967(10)</td>
</tr>
<tr>
<td>Co—N(24)</td>
<td>1.950(10)</td>
</tr>
<tr>
<td>(Co—Np)_{AV}</td>
<td>1.977(9)</td>
</tr>
<tr>
<td>Co—N(1)</td>
<td>1.946(4)</td>
</tr>
<tr>
<td>Co—N(2)</td>
<td>1.971(11)</td>
</tr>
</tbody>
</table>

Table 4.15 Bond Angles Within the Coordination Sphere of \([\text{Co}(\text{TPP})(\text{1MeIm})_2\text{NO}_2]\)

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(21)—Co—N(22)</td>
<td>89.0(4)</td>
</tr>
<tr>
<td>N(21)—Co—N(23)</td>
<td>177.6(5)</td>
</tr>
<tr>
<td>N(21)—Co—N(24)</td>
<td>90.2(4)</td>
</tr>
<tr>
<td>N(22)—Co—N(23)</td>
<td>91.0(4)</td>
</tr>
<tr>
<td>N(22)—Co—N(24)</td>
<td>177.7(5)</td>
</tr>
<tr>
<td>N(23)—Co—N(24)</td>
<td>89.9(4)</td>
</tr>
<tr>
<td>N(1)—Co—N(2)</td>
<td>177.4(4)</td>
</tr>
<tr>
<td>N(1)—Co—N(21)</td>
<td>92.6(5)</td>
</tr>
<tr>
<td>N(1)—Co—N(22)</td>
<td>89.7(4)</td>
</tr>
<tr>
<td>N(1)—Co—N(23)</td>
<td>89.8(4)</td>
</tr>
<tr>
<td>N(1)—Co—N(24)</td>
<td>88.2(4)</td>
</tr>
<tr>
<td>N(2)—Co—N(21)</td>
<td>88.4(5)</td>
</tr>
<tr>
<td>N(2)—Co—N(22)</td>
<td>92.8(4)</td>
</tr>
<tr>
<td>N(2)—Co—N(23)</td>
<td>89.2(5)</td>
</tr>
<tr>
<td>N(2)—Co—N(24)</td>
<td>89.4(4)</td>
</tr>
</tbody>
</table>
[Co(TPP)(MeIm)_2]NO_2 and the Slight Saddle Form of the Central Cobalt Atom With Respect to the Porphyrin Ring Nitrogen Atoms

$\phi$ is the dihedral angle (and is described in the text)

Positive and negative displacements of the nitrogen atoms from the cobalt atom mean plane are given in $\AA$. 

is the plane of the aromatic axial base
counterion. However, this anion did not refine at all well and finished up as a very distorted group with \( N(5)-O(1) = 1.17 \text{ Å}, N(5)-O(2) = 1.40 \text{ Å}, \) and \( O(1)-N(5)-O(2) = 76° \). There were no other peaks in the electron density map to suggest that there were other possible sites for this group; however, the poor refinement may mean that some may not have been found. Decomposition of \((1\text{MeIm})\text{Co(TPP)NO}_2\) to \([\text{Co(TPP)-(1MeIm)}_2\text{]}\text{NO}_2\) has thus occurred in solution on extended recrystallisation. The fact that three different crystalline types were observed suggests that at least three species formed on recrystallisation, but no further work was carried out.

4.3.2 Relationship of the Molecular Structures of \((\text{py})\text{Co(TPP)}\text{NO}_2\) and \([\text{Co(TPP)(1MeIm)}_2\text{]}\text{NO}_2\) to Other Structures of Cobalt Porphyrin Complexes Containing Axially Coordinated Nitrogenous Bases

Unlike iron porphyrins the cobalt porphyrins are insensitive to the presence of fifth and sixth axial ligands and remain low spin in both \( \text{Co(II)} \left( d^7, S = \frac{1}{2} \right) \) and \( \text{Co(III)} \left( d^6, S = 0 \right) \) oxidation states. Crystallographic data for cobalt porphyrins obtained from a search of the Cambridge Crystallographic Data Base, are shown in Table 4.16 giving bond lengths in the coordination sphere, dihedral angles, and a qualitative estimate of porphyrin planarity. The data for the six-coordinate complexes are more relevant to the two structures reported in this work, but the data for the five-coordinate structures are included in order to compare \( \text{Co(II)}-N_{AXIAL}^{\text{AV}} \), \( \text{Co(II)}-N_p^{\text{AV}} \) and analogous \( \text{Co(III)}-N \) bond lengths, and to consider the influence of a single electron in the \( 3d_z^2 \) orbital on bond lengths.
Table 4.16 Structural Data for Cobalt Porphyrinato Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>((\text{Co-N})_{P}^a) (Å)</th>
<th>(\text{Co-N}^b_{AX}) (Å)</th>
<th>(\text{Co-X}^c_{AX}) (Å)</th>
<th>Planarity</th>
<th>(\phi^d) (°)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(III), d^6, S=0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-coordinate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Co(TPP)(pip)_2]^+</td>
<td>1.978(3)</td>
<td>2.060(3)</td>
<td></td>
<td>unruffled</td>
<td></td>
<td>347</td>
</tr>
<tr>
<td>(3,5lut)Co(TPP)NO_2</td>
<td>1.954(2)</td>
<td></td>
<td></td>
<td>ruffled</td>
<td>36.4</td>
<td>343</td>
</tr>
<tr>
<td></td>
<td>2.036(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Co—N(lut)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.948(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Co(TPP)(Im)_2]^+</td>
<td>1.98(2)</td>
<td>1.93(2)</td>
<td></td>
<td>unruffled</td>
<td>45</td>
<td>345</td>
</tr>
<tr>
<td>Compound</td>
<td>Co(II), $d^7$, $S = 1/2$</td>
<td>Co(II), $d^7$, $S = 3/2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>----------------</td>
<td>-----------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(py)Co(TPP)Cl</td>
<td>1.976(9)</td>
<td>1.978(8)</td>
<td>2.251(3)</td>
<td>ruffled</td>
<td>43</td>
<td>350</td>
</tr>
<tr>
<td>(py)Co(TPP)(OMe)</td>
<td>1.96(1)</td>
<td>1.99</td>
<td>1.92</td>
<td>ruffled</td>
<td>32</td>
<td>351</td>
</tr>
<tr>
<td>Co(TPP)(pip)$_2$</td>
<td>1.987(2)</td>
<td>2.436(2)</td>
<td>unruffled</td>
<td>346</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(OEP)(3Mepy)$_2$</td>
<td>1.992(1)</td>
<td>2.386(2)</td>
<td>unruffled</td>
<td>10</td>
<td>352</td>
<td></td>
</tr>
<tr>
<td>Co(Pc)(4Mepy)$_2^e$</td>
<td>1.930(4)</td>
<td>2.322(5)</td>
<td>ruffled</td>
<td>45</td>
<td>353</td>
<td></td>
</tr>
<tr>
<td>Co(TPP)(1MeIm)</td>
<td>1.977(3)</td>
<td>2.157(3)</td>
<td>ruffled</td>
<td>0</td>
<td>349</td>
<td></td>
</tr>
<tr>
<td>Co(OEP)(1MeIm)</td>
<td>1.96(1)</td>
<td>2.15(1)</td>
<td>ruffled</td>
<td>10</td>
<td>354</td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Co—N(py)</td>
<td>Co—N(nitro)</td>
<td>Bond Length</td>
<td>Ruffling</td>
<td>Temperature</td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------</td>
<td>-------------</td>
<td>--------------</td>
<td>----------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>Co(TPP)(1,2Me₂Im)</td>
<td>1.985(2)</td>
<td></td>
<td>2.216(2)</td>
<td>unruffled</td>
<td>20</td>
<td>355</td>
</tr>
<tr>
<td>Co(TPP)(3,5lut)</td>
<td>2.000(5)</td>
<td></td>
<td>2.161(5)</td>
<td>unruffled</td>
<td>41.1</td>
<td>348</td>
</tr>
<tr>
<td>(py)Co(TPP)NO₂</td>
<td>1.958(3)</td>
<td></td>
<td></td>
<td>ruffled</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>[Co(TPP)(1MeIm)₂]NO₂</td>
<td>1.977(9)</td>
<td></td>
<td>1.946(4)</td>
<td>ruffled</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.971(11)</td>
<td></td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>

- a) Averaged Co—N(pyrole) equatorial bond length.
- b) Co—N bond length is averaged if the axial bases are identical.
- c) Qualitative estimate of porphyrin core planarity (see individual reference).
- d) Φ is the dihedral angle and is defined in the text.
- e) Pc = phthalocyanine.
The crystal structure of (3,5-lut)Co(TPP)NO₂ (where 3,5-lut is 3,5-dimethylpyridine) resembles that of (py)Co(TPP)NO₂. In the crystal (3,5-lut)Co(TPP)NO₂ has a required twofold axis of symmetry and the porphyrin core is strongly ruffled in approximate agreement with D₂d symmetry. The methine carbon atoms are displaced by +0.56 and -0.64 Å from the mean plane of the core. The magnitude of this ruffling is much larger than needed to allow the equatorial Co—Nₚ bonds to take the value of 1.95 to 1.96 Å which is generally preferred with nitrogen of monodentate ligands, and consequently this ruffling was attributed primarily to packing effects. The N-bonded nitro group displayed high thermal motion and the oxygen atoms suffered some unspecified positional disorder with an N—O bond length of 1.155 Å and O—N—O of 115.4°, however, the nitro group in our work was much more disordered (Figure 4.7). The other bond lengths are (Co—Nₚ)_{AV} = 1.954(2) Å, Co—N_{NITRO} = 1.948(4) Å, and Co—N_{LUT} = 2.036(4) Å, very similar to those obtained for (py)Co(TPP)NO₂ [(Co—Nₚ)_{AV} = 1.958(3) Å, Co—N_{NITRO} = 1.963(4) Å, and Co—N_{PY} = 2.020(4) Å]. The departure of the dihedral angle (φ = 35.4°) from the sterically most favourable value of 45° presumably also arises from the steric bulk of the 3,5-dimethyl groups since pyridine in (py)Co(TPP)NO₂, with φ = 43°, is aligned close to the preferred value of 45°. The differences in the two sets of axial bond lengths may also reflect differing steric requirements of the nitro ligand and even a moderately oriented substituted pyridine ligand (φ = 35.4°) versus a well oriented unsubstituted pyridine ligand (φ = 43°) respectively.

A further example of the importance of steric interact-
ions in determining axial bond lengths is illustrated by the molecular structures of the two structurally independent but centrosymmetric \([\text{Co(TPP)}(\text{Im})_2]^+\) cations in \([\text{Co(TPP)}(\text{Im})_2]-(\text{O}_2\text{CCH}_3).\text{H}_2\text{O}.\text{CHCl}_3\). Here the smaller steric requirements of the coplanar imidazole ligands and a favourable orientation of \(\phi = 43^\circ\) lead to bond lengths of \((\text{Co—N}_\text{Im})_{\text{AV}} = 1.93(2)\ \AA\) and \((\text{Co—N}_p)_{\text{AV}} = 1.98(2)\ \AA\). These bond lengths correspond closely to those in the coordination sphere of \([\text{Co(TPP)}-(1\text{MeIm})_2]\text{NO}_2\) (Table 4.14), the major structural difference being that the two bulkier 1-methylimidazole ligands in \([\text{Co(TPP)}(1\text{MeIm})_2]\text{NO}_2\) are disposed almost at right angles to each other.

The rest of Table 4.16 gives data on crystal structures of 5- and 6-coordinate complexes with substituted pyridines, imidazoles, and the cyclic aliphatic amine piperidine in both the \(\text{Co(II)}\) and \(\text{Co(III)}\) oxidation states. Low spin \((S=1/2)\) 6-coordinate \(\text{Co(II)}\) porphyrins with electronic configuration \((d_{xz}, d_{yz}, d_{xy})^6 (d_{z^2})^1\) have one more \(d\) electron than \(\text{Co(III)}\) porphyrins. The effect of this electron in the \(d_{z^2}\) orbital on the stereochemistry of these molecules is seen by comparison of the bonding parameters of the neutral \([\text{Co(TPP)}(\text{pip})_2]\) molecule with that of the \([\text{Co(TPP)}(\text{pip})_2]^+\) cation. In the \(\text{Co(II)}\) derivative, the \((\text{Co—N}_p)_{\text{AV}}\) distance of 1.987(2) \(\AA\) is only slightly longer than in the \(\text{Co(III)}\) derivative with \((\text{Co—N}_p)_{\text{AV}} = 1.978(3)\ \AA\). The porphyrinato cores in both derivatives are essentially planar. However, the axial \(\text{Co—N}\) bond lengths are quite different with \((\text{Co—N}_{\text{AX}})\) in \([\text{Co(TPP)}(\text{pip})_2]^{\text{+}}\) being 2.436(2) and 2.060(3) \(\AA\) respectively. This increase of 0.4 \(\AA\) is required by the presence of the odd electron in the \(d_{z^2}\) orbital of the
The same pattern is seen for other bis(axial base) Co(II) porphyrins in Table 4.16. The effect of the unpaired electron on the stereochemistry of 5-coordinate LS Co(II) porphyrins is not so pronounced as in 6-coordinate complexes, but it is still important. It is also apparent from Table 4.16 that equatorial Co—N_p bond lengths are much the same in both Co(II) and Co(III) porphyrin complexes. In a LS Co(III) (and Fe(II), Fe(III) also) metalloporphyrin the pairing of electron spins in the d_{xy}, d_{yz}, and d_{xz} orbitals of the metal ion allows the full utilisation of the unoccupied d_{x^2-y^2} and d_{z^2} orbitals for complexing the quadridentate porphyrinato macrocycle and two axial ligands. In a LS 5-coordinate Co(II) metalloporphyrin the unoccupied d_{x^2-y^2} orbital in the metal ion is fully available for complexing with the porphyrinato macrocycle and the singly occupied d_{z^2} orbital is adaptable to a somewhat weaker complexing of one axial ligand. The stability of Co(II) 6-coordinate species is also limited by the presence of the unpaired electron in the d_{z^2} orbital.

During the structure determination of [Co(TPP)(1MeIm)2]−NO_2^−, the structure first arrived at by analysis was Co(TPP)−(1MeIm)2. However, from a comparison of the Co—NAx distances of this complex with data for Co(II)− and Co(III)−porphyrins in Table 4.16 it was decided that the structure could not be a cobalt(II) complex but must contain cobalt(III), and thus an anion, either NO_3^- or NO_2^- must be present. The difference electron density map revealed very small extra peaks thought originally to be solvent of crystallisation. However, on closer examination the structure was seen to be [Co(TPP)−(1MeIm)2]^+ with the extra peaks a NO_2^- counterion, highly
distorted in the structure.

In complexes containing coordinated imidazole the 2,4 hydrogen atoms of each ligand have steric requirements with the porphyrin nitrogen atoms, though not with the porphyrin carbon atoms. The same is true for the 2,6 hydrogen atoms of coordinated pyridines. The steric requirements of imidazoles are substantially less demanding than those of pyridines because of the differing geometries of 5- and 6-membered rings. From Table 4.16 it is seen that in the 5-coordinate complexes Co(TPP)(3,5-lut)$^{348}$ and Co(TPP)(1MeIm)$^{349}$ in the absence of significant steric constraints (i.e. bulky R groups in the sterically active positions of coordinated imidazole and pyridine), the bases behave almost identically with Co—N$_{AX}$ bond lengths of 2.161(5) and 2.157(3) Å respectively. When discussing the coordination of aromatic nitrogenous ligands, the dihedral angle, $\phi$, is a fundamental orientation parameter of the coordination group. From Table 4.16 it is difficult to see any direct correlation between core ruffling and $\phi$ in this series of cobalt complexes. Deviations from planarity exist in each structure as a consequence of the ill-defined packing constraints that are exclusive to each structure in question. The earlier mentioned phenomenon where the desire for the (Co—N$_p$)$_{AV}$ distance to be 1.96 Å or less is accommodated by a shrinking (with concomitant ruffling) of the porphyrin core, is probably the reason for the ruffling in (py)Co(TPP)NO$_2$ and [Co(TPP)(1MeIm)$_2$]NO$_2$. The structural parameters of the two Co(III)porphyrins determined in this work fit in very well with previous X-ray data for Co(III)porphyrins.
4.4 Nitrosyl(porphyrinato)iron(II) Complexes

The iron nitrosyls shown in Table 4.17 were all prepared in reasonable yield, and the analyses are fairly good for the mononitrosyls although it is necessary to assume that Fe(OEP)-NO and Fe(TpivPP)NO contain some chloroform of solvation. There is a weak absorption in the IR of Fe(OEP)NO at ca. 750 cm\(^{-1}\) which may be assigned to \(\nu_{C-Cl}\) of chloroform. The C, H, N percentages for the "dinitrosyl" Fe(TPP)(NO)\(_2\) lie between the theoretical values for mononitrosyl and dinitrosyl. This reflects the instability of the dinitrosyl in the solid state; on standing it smelled of nitrogen oxides. Fe(TpivPP)-NO is apparently a new compound. In the majority of preparations the reaction mixtures appeared to absorb more than one molar equivalent of nitric oxide (Table 4.17). However, since none of the other iron porphyrins apart from Fe(TPP)-(NO)\(_2\) formed a dinitrosyl complex, then vapour pressure errors because of volatile solvents may have caused this.

The electronic spectra of the iron nitrosyls in CHCl\(_3\) solution are recorded in Table 4.18. The visible spectra for Fe(TPP)NO and Fe(OEP)NO agree reasonably well with literature values.\(^{25-6,67,220}\) The spectrum of the dinitrosyl Fe(TPP)-(NO)\(_2\) is reminiscent of the spectrum\(^{220}\) (415, 513, 662 and 690 nm) generated by introduction of a low pressure of NO gas into a solution of Fe(TPP)NO. From Table 4.2 and Table 4.18 it may be seen that generally on going from porphyrin to iron porphyrin halide and then to iron porphyrin nitrosyl that the Soret band undergoes a progressive blue shift: for TPPH\(_2\) (418) to Fe(TPP)Cl (415) to Fe(TPP)NO (406); for OEPH\(_2\) (400) to Fe(OEP)Cl (379) to Fe(OEP)NO (389); and for TpivPPH\(_2\) (418) to Fe(TpivPP)Br (417) to Fe(TpivPP)NO (409), whereas the two
Table 4.17 Analytical, Yield, and Infrared Data for Nitrosyl(porphyrinato)iron Complexes

<table>
<thead>
<tr>
<th>Compound (colour, form)</th>
<th>%C found (theor.)</th>
<th>%H found (theor.)</th>
<th>%N found (theor.)</th>
<th>Reaction Solvent, NO uptake at STP (molar equiv.)</th>
<th>Yield (%)</th>
<th>v(NO) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(TPP)NO (purple crystals)</td>
<td>75.07</td>
<td>4.09</td>
<td>9.54</td>
<td>CHCl(_3)/pyridine/MeOH</td>
<td>96</td>
<td>1690</td>
</tr>
<tr>
<td>Fe(OEP)NO (purple-black microcrystals)</td>
<td>(75.65)</td>
<td>(4.04)</td>
<td>(10.02)</td>
<td></td>
<td></td>
<td>2.78</td>
</tr>
<tr>
<td></td>
<td>(68.61)</td>
<td>(7.24)</td>
<td>(10.40)</td>
<td>CHCl(_3)/pyridine/MeOH</td>
<td>83</td>
<td>1670</td>
</tr>
<tr>
<td>Fe(T(_{PIV}))PP)NO.1/2CHCl(_3) (dark-red crystals)</td>
<td>(67.76)(^a)</td>
<td>(5.59)</td>
<td>(10.75)</td>
<td>CHCl(_3)/2,6-lutidine/MeOH</td>
<td>74</td>
<td>1670</td>
</tr>
<tr>
<td>Fe(TPP)(NO)(_2) (purple crystals)</td>
<td>74.12(^b)</td>
<td>3.91(^b)</td>
<td>9.65(^b)</td>
<td>CH(_2)Cl(_2)/pyridine/MeOH</td>
<td>80(^c)</td>
<td>1690</td>
</tr>
<tr>
<td></td>
<td>(72.54)(^a)</td>
<td>(3.57)</td>
<td>(11.54)</td>
<td></td>
<td></td>
<td>1870</td>
</tr>
</tbody>
</table>

\(^a\) C, H, N values given for Fe(OEP)NO.1/10CHCl\(_3\). \(^b\) Intermediate C, H, N values are between mononitrosyl and dinitrosyl and reflect the instability of the dinitrosyl in the solid state. \(^c\) Yield given is for dinitrosyl, calculated yield for mononitrosyl is 83 \%. 
Table 4.18 Visible Absorption Spectral Data for Nitrosyl (porphyrinato)iron Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max.}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Soret ( \beta ) ( \alpha )</td>
</tr>
<tr>
<td>Fe(TPP)NO</td>
<td>406 470sh 537 607</td>
</tr>
<tr>
<td>Fe(OEP)NO</td>
<td>389 479 533 557</td>
</tr>
<tr>
<td>Fe(TpivPP)NO</td>
<td>409 470sh 539 600sh</td>
</tr>
<tr>
<td>Fe(TPP)(NO)(_2)</td>
<td>380sh 416 509 578 650 690</td>
</tr>
</tbody>
</table>

\(^{a}\) measured in chloroform solution.
bands in the visible region normally undergo a red shift on going from halide to nitrosyl: for Fe(TPP)Cl to Fe(TPP)NO ($\beta$: 510 to 537, $\alpha$: 578 to 607); for Fe(OEP)Cl to Fe(OEP)NO ($\beta$: 507 to 533, $\alpha$: 536 to 557); and for Fe(TPIVPP)Br to Fe(TPIVPP)NO ($\beta$: 508 to 539, $\alpha$: 584 to 600).

The absorption spectra of these iron porphyrins are defined as hyper-type spectra since they show variable hypso/hyper shifts, and prominent extra bands. The extra bands seen as shoulders (Table 4.18) are possibly charge transfer transitions from porphyrin ring $\pi$-orbitals to metal d-orbitals. The levels responsible for the optical spectra of iron porphyrins are very complicated owing to the presence of filled and empty d-levels in the same energy region as the HOMO and LUMO of the porphyrin ligand. Spectra of these iron porphyrins may therefore be strongly perturbed by very small shifts in d-levels. Strictly speaking these iron nitrosyls have filled subshells (ground state $S = 1/2$ for Fe(TPP)NO, the odd electron which originates on NO becoming highly delocalised into the iron $d^2$ orbital), and charge transfer bands should be limited. However, other iron porphyrins with filled subshells, e.g. Fe(II)(porph)(py)$_2$ and Fe(I) porphyrins have charge transfer hyper-type spectra.

It is interesting to compare the visible spectra of these iron nitrosyls with metalloprotein nitrosyls and with the cured meat system to see if the iron nitrosyls are good spectroscopic models of the haem protein nitrosyls. Tarladgis determined the absorption spectra of various cured meat pigments and these are shown in Table 4.19.

It should be expected that the absorption spectrum of Fe(OEP)NO is the most similar to cured meat spectra because
Table 4.19 Absorption Spectra of Various Cured Meat Pigments

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Band Positions (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soret</td>
<td>[\beta \quad \alpha]</td>
</tr>
<tr>
<td>Absorption Spectra (acetone)</td>
<td></td>
</tr>
<tr>
<td>HbNO</td>
<td>412, 492, 552, 572</td>
</tr>
<tr>
<td>Fresh Cured Ham</td>
<td>412, 492, 552, 572</td>
</tr>
<tr>
<td>Heat Denatured HbNO</td>
<td>482, 535, 583</td>
</tr>
<tr>
<td>Cooked Cured Ham</td>
<td>482, 548, 576</td>
</tr>
<tr>
<td>Reflectance Spectra</td>
<td></td>
</tr>
<tr>
<td>HbNO</td>
<td>490, 561, 576</td>
</tr>
<tr>
<td>Fresh Cured Ham</td>
<td>422, 496, 565, 582</td>
</tr>
<tr>
<td>Heat Denatured HbNO</td>
<td>486, 553, 574</td>
</tr>
<tr>
<td>Cooked Cured Ham</td>
<td>414, 484, 552, 576</td>
</tr>
</tbody>
</table>

of the similar substitution pattern of OEP to natural porphyrins. From Tables 4.18 and 4.19 the solution spectrum of 5-coordinate Fe(OEP)NO is reasonably similar to the solution and reflectance spectra of heat-denatured HbNO and cooked cured meat, where the iron nitrosyl is also believed to be 5-coordinate. The same Fe(OEP)NO spectrum is quite dissimilar to the spectrum of native HbNO and fresh cured ham where the iron nitrosyl is thought to be 6-coordinate. Visible spectra of native HbNO from many different species place the characteristic band positions at Soret (412 to 418), \(\beta\): (530 to 550), and \(\alpha\): (560 to 580). The spectra of the iron nitrosyls of the meso-substituted TPP and T_{PIV}PP are
also reasonably similar to the denatured (5-coordinate) haemoprotein nitrosyl systems, allowing for the different substitution pattern. Tarladgis claims that the cooked cured ham spectra are indicative of the dinitrosyl species Fe(porph)(NO)₂. However, the spectra of these extracts bear no reasonable resemblance to the spectrum of Fe(TPP)(NO)₂ shown in Table 4.18, though this may be an effect of the different type of porphyrin chromophore in the two systems.

4.5 μ-Oxo-bis[(porphyrinato)iron(III)] Dimers

The analytical and spectroscopic data for the two μ-oxo compounds [Fe(TPP)]₂O and [Fe(OEP)]₂O are shown in Table 4.20. The compounds were prepared as an aid to characterisation of decomposition products of the nitrosyl(porphyrinato)iron complexes in reaction with dioxygen. Unfortunately, the stability of the NO group coordinated to iron porphyrin was not investigated. More work is needed and the characterisation of these two complexes may be of use in future investigations.

4.6 Sealed NMR Tube Experiments

From the earlier results the reaction of Co(T₃IVPP) with NO was suspected to be reversible. The NMR evidence suggested that the cobalt nitrosyl decomposed rapidly in solution with loss of ¹⁵NO before or during data acquisition. The compound Fe(TPP)Cl is known to react reversibly with NO to form Fe(II)(TPP)(Cl⁻)(NO⁺) in solution and in the solid state. In the presence of methanol, Fe(TPP)Cl reacts with excess NO to produce Fe(TPP)NO. In solution and in the solid state a second molecule of NO is reversibly coordinated by Fe(TPP)NO.
Table 4.20 Analytical, Infrared, and Visible Absorption Spectral Data for μ-Oxo Porphyrins

<table>
<thead>
<tr>
<th>Compound</th>
<th>%C found</th>
<th>%H found</th>
<th>%N found</th>
<th>λ_{max.} (ε) / nm (1 mol^{-1} cm^{-1})</th>
<th>IR bands(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(TPP)](_2)O.1/3CHCl(_3)</td>
<td>76.15</td>
<td>3.87</td>
<td>8.06</td>
<td>(benzene) 414 (184000), 505sh</td>
<td>892m</td>
</tr>
<tr>
<td></td>
<td>(76.16)</td>
<td>(4.07)</td>
<td>(8.04)</td>
<td>(16600), 572 (13310), 878s</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>612 (6460)</td>
<td></td>
</tr>
<tr>
<td>[Fe(OEP)](_2)O</td>
<td>72.06</td>
<td>7.92</td>
<td>8.96</td>
<td>(CHCl(_3)) 393 (159000), 460sh</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(72.47)</td>
<td>(7.43)</td>
<td>(9.39)</td>
<td>(25000), 581 (16200)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) KBr disc
to form the dinitrosyl Fe(TPP)(NO)₂. The two nitrosyl stretching frequencies are consistent with linear Fe\(^{II}\)NO\(^+\) and bent Fe\(^{II}\)NO\(^-\) units, and the diamagnetic complex is formulated as an 18 electron species Fe\(^{II}\)(TPP)(NO\(^-\))(NO\(^+\)).\(^{64}\) The above observations suggested that if these unstable diamagnetic nitrosyl solutions were sealed in an NMR tube under an atmosphere of excess \(^{15}\)NO, then it might be possible to detect signals from the coordinated \(^{15}\)NO group(s). In closed systems loss of \(^{15}\)NO from solution would be prevented. Consequently, the reaction mixtures (I) to (III) in Table 4.21 were sealed in 10 mm id NMR tubes and \(^{15}\)N NMR spectra recorded. The \(^{59}\)Co and \(^{1}\)H NMR spectra of (I) were also recorded.

The \(^{15}\)N NMR spectrum of solution (I) was disappointing. It was very noisy, and no obvious peaks due to coordinated \(^{15}\)NO (or to \(^{15}\)NO\(^2\)\(^-\) or \(^{15}\)NO\(^3\)\(^-\)) were observed between +1000 ppm and -100 ppm. In the \(^{59}\)Co NMR spectrum four peaks were observed at 7865, 7929, 7979, and 8045 ppm, with the peak at 7979 ppm having the highest intensity. These peaks closely correspond to the \(^{59}\)Co NMR spectrum of Co(TpivPP)\(^{15}\)NO with resonances at 7842, 7900, and 7996 ppm reported in Table 4.7. These results suggest the presence of a mixture of the four different isomers of picket fence porphyrin. In the \(^{1}\)H NMR of solution (I) there is a singlet at 2.55 ppm from the dimethyl groups of 2,6-lutidine, and a complex multiplet at 6.9-7.6 ppm indicative of the phenyl protons of lutidine and the porphyrin. Peaks at 0.14 (major species) and 0.15 ppm (minor species) indicated that isomerisation of the picket fence porphyrin had occurred, as did a slight doubling of the peaks at ca. 8.7 (NH) and ca. 9.0 ppm (β-pyrrolic H). Unfortunately, the \(^{1}\)H NMR spectrum was only measured upfield to
-0.4 ppm and not to ca. -6 ppm to see any evidence of paramagnetic Co(II)(TpIVPP). But these $^1$H NMR data show that the major species in solution are diamagnetic. This could arise from the diamagnetic nitrosyl or a lutidine species. However, as this base is noncoordinating due to the steric effect of the 2,6-dimethyl groups, the diamagnetic species in solution could be the nitrosyl complex. The analytical data presented earlier suggest that Co(TpIVPP)NO exists in the solid state. The lack of a $^{15}$N NMR signal could then possibly be due to fast exchange of coordinated and free $^{15}$NO in this complex.

The $^{15}$N NMR spectrum of solution (II) was very noisy; however, two peaks were observed at 794.15 and 8.46 ppm. The intensities of these peaks were similar to the spectrum noise, but they may correspond to the bent and linear FeNO groups of Fe(TPP)(NO)$_2$. The result is by no means conclusive and much more work is needed. Degassed solutions of the similar dinitrosyl $^{210}$Ru(II)(porph)(NO)$_2$ were reported to lose NO slowly in the dark.$^{357}$ For solutions of Ru(OEP)(NO)$_2$ this process is accelerated by irradiation into either the visible or Soret bands.$^{357}$ The iron and ruthenium porphyrin nitrosyls might be expected to behave similarly with respect to ligand photoejection, and this process may have been a contributory factor in the failure to observe a strong $^{15}$N resonance in this work. There was no evidence in the $^{15}$N NMR spectrum for MeO$^{15}$NO, the species supposed to form in the reductive nitrosylation of Fe(TPP)Cl to iron porphyrin nitrosyls.$^{64,153,321}$ Similarly, no resonances were observed in the spectra of solution (III) even though Fe(OEP)Cl also forms a diamagnetic dinitrosyl.$^{220}$ In retrospect it may have been
Table 4.21 Reaction Mixtures Sealed in NMR Tubes

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td></td>
</tr>
<tr>
<td>Co(TPIVPP)$_{15}$NO</td>
<td>16.7 mg, 0.015 mmol</td>
</tr>
<tr>
<td>2,6-Lutidine</td>
<td>0.01 ml, 0.085 mmol</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>2 ml</td>
</tr>
<tr>
<td>$^{15}$NO</td>
<td>3 ml, 0.13 mmol</td>
</tr>
<tr>
<td>(II)</td>
<td></td>
</tr>
<tr>
<td>Fe(TPP)Cl.1/4 CHCl$_3$</td>
<td>25 mg, 0.034 mmol</td>
</tr>
<tr>
<td>pyridine</td>
<td>0.05 ml, 0.62 mmol</td>
</tr>
<tr>
<td>methanol</td>
<td>0.25 ml</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>2 ml</td>
</tr>
<tr>
<td>$^{15}$NO</td>
<td>4.2 ml, 0.19 mmol</td>
</tr>
<tr>
<td>(III)</td>
<td></td>
</tr>
<tr>
<td>Fe(OEP)Cl</td>
<td>25 mg, 0.041 mmol</td>
</tr>
<tr>
<td>pyridine</td>
<td>0.1 ml, 1.24 mmol</td>
</tr>
<tr>
<td>methanol</td>
<td>0.25 ml</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>2 ml</td>
</tr>
<tr>
<td>$^{15}$NO</td>
<td>4 ml, 0.18 mmol</td>
</tr>
</tbody>
</table>

better not to include methanol in the NMR tubes since in the presence of methanol and excess NO, Fe(TPP)Cl forms Fe(TPP)NO eventually.\(^{64}\) If methanol had been omitted the $^{15}$N NMR spectrum of diamagnetic Fe(TPP)(Cl$^-$)(NO$^+$)$^{64}$ might have been observed. This might be a suitable starting point for a more thorough investigation of these 'unstable' nitrosyls in sealed NMR tubes.
5.1 A $^{15}\text{N}$ and $^{59}\text{Co}$ NMR Study of Some Cobalt Nitrosyl and Nitro Complexes

5.1.1 Chemical Transformations of Coordinated Nitrosyl and Nitro Groups: The Nitrosyl-Nitro Couple

The chemistry of the coordinated nitrosyl ligand has been well reviewed. In this context the NO+/NO$^-$ formalism, representative of electron donor or acceptor property of coordinated nitrosyl, is useful for correlation with, and prediction of, reactivity. For example, the coordinated nitrosyl cation NO$^+$ is electrophilic and can be attacked by various nucleophiles e.g. $\text{NO}_\text{coord}^+ + 2\text{OH}^- \rightarrow \text{NO}_\text{coord}^- + \text{H}_2\text{O}$. Likewise the formal bonding mode M(NO$^-$) may be categorised as being susceptible to attack by electrophiles at nitrogen. However, where nitric oxide is $\mu_2$-bridging, for example in the Ru and Os cluster cations, [M$_3$(CO)$_{10}$NO]$^+$, reaction with electrophiles at oxygen can lead to O-methylation and O-protonation of coordinated NO to give coordinated $\mu_3$-NOR groups. Also, in the absence of any strong base trans- to the NO group in [Co(en)$_2$NO]$^{2+}$, electrophilic attack was found to occur at the oxygen atom. Both of these findings are in contrast to the previous contention that electrophilic attack should occur at the nitrogen atom. Other characteristic reactions of coordinated nitrosyl ligand such as reduction, disproportionation, and various insertion processes are not so readily correlated with bonding modes.

Following arguments about the susceptibility of coordi-
inated NO⁺ (i.e. complexes with high \( v_{\text{NO}} \)) to nucleophilic attack,\(^{155,359}\) nitrosyl complexes having low \( v_{\text{NO}} \) values should be liable to attack by electrophiles. However, such low \( v_{\text{NO}} \) values are usually associated with 'electron-rich' metals (to the right of the periodic table),\(^{157}\) commonly in low oxidation states with various degrees of coordinative unsaturation. Consequently, reactions involving attack at the metal (e.g. oxidative addition) will compete with any reactions involving the bent NO⁻ group. As well as reactions at the coordinated group, nitrosyl complexes are also catalytically active in various organic transformations\(^{362}\) including polymerisation of olefins, selective homogeneous hydrogenations, isomerisations, and metathesis reactions; they also have potential in pollution control for removal of NO\(_x\) species and CO from the atmosphere.\(^{152,157,358,362-3}\)

In this work we are especially concerned with the reactivity of the coordinated bent nitrosyl group, NO⁻ with molecular oxygen. Clarkson and Basolo\(^{322}\) found that several 5-coordinate cobalt(III) nitrosyl complexes Co(L₄)NO combined with dioxygen at room temperature in the presence of nitrogen and phosphorus donors B to give the corresponding cobalt(III) nitro complexes \((B)\text{Co}(L₄)\text{NO}_₂\), where \( L₄ \) is a tetradeutate Schiff base ligand or two bidentate dithiocarbamate or diamine ligands, e.g.

\[
\text{Co(salen)NO} + \text{py} + 1/2 \text{O}_2 \rightarrow (\text{py})\text{Co(salen)NO}_₂ \quad (5.1)
\]

\[
[\text{Co(en)}_2\text{NO}]^{2+} + \text{MeCN} + 1/2 \text{O}_2 \rightarrow [\text{Co(en)}_2(\text{NO}_₂)\text{(MeCN)}]^{2+} \quad (5.2)
\]

The reaction mechanism suggested\(^{322}\) is given in Figure 5.1.
where rapid formation of the electron-rich (20 electron) intermediate (B)Co(L₄)NO (II) is the initial reaction (eqn 5.3). The rate-determining step (eqn 5.4) is electrophilic attack by oxygen on the nitrosyl nitrogen to give the peroxy-nitrate intermediate (III) which is rapidly attacked by another molecule of (B)Co(L₄)NO giving the dimer (IV), which
may be formally described as containing peroxy-bridged dinitrogen tetroxide bonded to two cobalt(II) moieties. Fast homolytic fission of the peroxy link affords the nitro product (V). In the rate-determining step (eqn 5.4), the greater the basicity of the coordinated axial base, the greater the electron density on the nitrosyl nitrogen, and the more rapid the reaction.322

Tovrog et al.364-5 have investigated selective and catalytic oxidations of organic compounds by these nitro complexes, [(B)Co(L₄)NO₂]. Their approach is outlined in Figure 5.2.

Figure 5.2 Idealised Oxygen Transfer Reactions

\[
\begin{align*}
\text{ML} + \frac{1}{2} \text{O}_2 & \rightarrow \text{MLO} \quad (5.8) \\
\text{MLO} + S & \rightarrow \text{ML} + \text{SO} \quad (5.9) \\
S + \frac{1}{2} \text{O}_2 & \rightarrow \text{SO} \quad (5.10)
\end{align*}
\]

alternatively,

\[
\begin{align*}
\text{ML} + \frac{1}{2} \text{O}_2 & \rightarrow \text{MLO} \\
\text{MLO} + S'H_2 & \rightarrow S' + \text{ML} + \text{H}_2\text{O} \quad (5.11) \\
S'H_2 + \frac{1}{2} \text{O}_2 & \rightarrow S' + \text{H}_2\text{O} \quad (5.12)
\end{align*}
\]

where \( L = \text{NO} \) and \( S, S' = \text{substrate} \)

The approach is based on the splitting of molecular oxygen on a ligand of a transition metal complex (eqn 5.8) to form two equivalents of a complex with an oxidised ligand. An oxygen atom from the oxidised ligand is then transferred to the
substrate (eqns 5.9 and 5.11) in a reaction which regenerates the original complex (the metal nitrosyl) and completes the catalytic cycle.

Representative reactions\textsuperscript{364-5} using the cobalt nitro complexes include oxidation of phosphines to phosphine oxides, primary and secondary alcohols to aldehydes and ketones respectively, olefins to ketones, thioethers to sulphoxides, and also the epoxidation of olefins. These specific oxygenation reactions do not suffer from the low selectivity of normal free radical oxidations. The initial studies by these workers focussed on the coordinatively saturated cobalt nitro complexes, (B)Co(L\textsubscript{4})NO\textsubscript{2} similar to those studied by Clarkson and Basolo\textsuperscript{322} in order to establish the oxidation power of the unactivated nitro ligand toward unactivated substrates in a catalytic system; and the nitro ligand was soon found to be a very weak oxidant. Fortunately its ability to transfer an oxygen atom to an organic substrate can be enhanced either by activation of the nitro ligand or by activation of the substrate,\textsuperscript{364-5} as discussed below. The preliminary work studied the stoichiometric oxidation of PPh\textsubscript{3} by (py)Co(salphen)NO\textsubscript{2} at 60°C in 1,2-dichloroethane.\textsuperscript{366} This oxidation can be carried out catalytically (Figure 5.3) by exposing a solution of (py)Co(salphen)NO\textsubscript{2}, PPh\textsubscript{3}, and excess pyridine to molecular oxygen. The nitro complex (py)Co(salphen)NO\textsubscript{2} was also found to oxidise Mo(IV)O(S\textsubscript{2}CNR\textsubscript{2})\textsubscript{2} to Mo(VI)O\textsubscript{2}(S\textsubscript{2}CNR\textsubscript{2})\textsubscript{2} with concomitant formation of the nitrosyl complex Co(salphen)NO. Dioxo complexes of Mo(VI) are able to oxidise PPh\textsubscript{3} to OPPh\textsubscript{3}.\textsuperscript{367} Therefore the cobalt nitro complex was thought to be a stronger oxidant than the Mo(VI) complex. Later work\textsuperscript{368} found
the rate of catalytic oxidation in Figure 5.3 to be strongly dependent on the solvent. Only solvents which are capable of hydrogen bonding to the nitro group such as acetic acid, CHCl₃, or 1,2-dichloroethane lead to successful oxidation. Despite this, attempts to oxidise other organic substrates such as thioethers, alcohols, and olefins without additional activation failed.

Based on the above observation that oxidation of phosphines was promoted by hydrogen bonding solvents, these workers sought to amplify this mild solvent effect by employing stronger Lewis acids which serve to activate the nitro ligand and allow the extension of this chemistry to less easily oxidisable substrates. Thus in deoxygenated media the combination of the Lewis acids BF₃·Et₂O or LiPF₆ with the cobalt nitro complexes (py)Co(salphen)NO₂ and (py)Co(PPP)NO₂ readily oxidises primary and secondary alcohols to the corresponding aldehydes or ketones, according to the mechanism in Figure 5.4. The Lewis acids coordinate to the oxygen of the nitro group in an equilibrium process, as
Figure 5.4 Mechanism of Alcohol Oxidation by a Combination of a Cobalt Nitro Complex with a Lewis Acid (A)

\[
(py)(L_4)CoNO_2 + A \xrightleftharpoons{} (py)(L_4)CoN\quad \text{(I)}
\]

\[
(py)(L_4)CoNO_A \xrightarrow{} (py)(L_4)CoN\quad \text{(II)}
\]

\[
+ \quad \text{C} = \text{O} + \text{H}_2\text{O} \quad \text{(III)}
\]

well as to the other bases (e.g. alcohols) present in the reaction mixture. Coordination to the nitro ligand decreases the electron density at the nitrogen atom and makes it more susceptible to nucleophilic attack by alcohols. The inability of the activated cobalt nitro complexes to oxidise ethers under identical conditions supports an ester intermediate (III). The mechanism of the catalytic oxidation of alcohols is illustrated in Figure 5.5 where the stoichiometric oxidation step is followed by reoxidation of the nitrosyl complex by \(O_2\). An important aspect of this nitrosyl/nitro coupled oxidation of alcohols is that the facile reoxidation
Figure 5.5 Catalytic Oxidation of Alcohols by Cobalt Nitro Complexes

Figure 5.6(a) Mechanism of the Oxidation of Olefins by the Bimetallic System of Metal Nitro Complex and Olefin Activator

Figure 5.6(b) Catalytic Oxidation of Olefins by the Bimetallic System
of the cobalt nitrosyl $\text{Co(L}_4\text{)}\text{NO}$ occurs in the presence of a Lewis acid, not a base such as pyridine which strongly inhibits the reaction.\textsuperscript{368} In the previous studies\textsuperscript{322} the cobalt nitrosyls were found to be oxidised only in the presence of a Lewis base, and the formation of the 6-coordinate nitrosyl complex $(B)\text{Co(L}_4\text{)}\text{NO}$ was shown to be the rate-determining step in this process.

As a consequence of the use of a Lewis acid, the rate of catalytic oxidation decreases when the nitro complex $(B)\text{Co(L}_4\text{)}\text{NO}_2$ is the catalyst rather than the corresponding nitrosyl. The pyridine present in the nitro complex is not strongly bound to the 5-coordinate cobalt nitrosyl and so interacts with the Lewis acid to decrease its effective concentration, leading to a lower rate of oxidation. Water produced as a byproduct in the oxidation hydrolyses the Lewis acids and decreases their ability to bind to the nitro ligand. Consequently, the rate of alcohol oxidation declines with time until eventually it ceases. Also, when $\text{BF}_3\cdot\text{Et}_2\text{O}$ is used as an activator, disproportionation of cobalt nitro complexes to a mixture of reoxidisable cobalt nitrosyl and an inactive cobalt nitrato species: $2\text{Co(L}_4\text{)}\text{NO}_2 \rightarrow \text{Co(L}_4\text{)}\text{NO} + \text{Co(L}_4\text{)}\text{NO}_3$ may also serve to decrease the reaction rate. The weaker Lewis acid $\text{Li}^+$ does not lead to this disproportionation.\textsuperscript{368}

Attempts to oxidise olefins by these nitro complexes activated with Lewis acids failed.\textsuperscript{364-5,369} However, since the coordinated nitro group is formally a nitrogen bound monoanionic ligand $\text{Co}^+\cdot\text{NO}_2^-$, it could function as a weak oxygen centred nucleophile. Thus, the alternative approach of activating the olefin towards nucleophiles\textsuperscript{369} by $\pi$-coord-
ination to the group VIII metals Pd(II) and Rh(III) was investigated. This led to successful stoichiometric and catalytic oxidations of olefins by bimetallic systems.\(^{369}\) The bimetallic systems contain a metal nitro complex, either (py)Co(salphen)NO\(_2\) or (py)Co(TPP)NO\(_2\) as the oxygen transfer agent, and a metal olefin complex (formed \textit{in situ} from PdCl\(_2\)(PhCN)\(_2\)) which acts as olefin activator. The stoichiometric oxidation of ethylene to acetaldehyde and terminal olefins to 2-alkanones in anhydrous oxygen-free solvents, with concomitant reduction of the metal nitro complex to the corresponding nitrosyl,\(^{369}\) takes place as shown in Figure 5.6(a).

When exposed to molecular oxygen the same mixture of the cobalt nitro complex and PdCl\(_2\)(PhCN)\(_2\) catalyses the oxidation of ethylene to acetaldehyde, and higher olefins to ketones.\(^{369}\) The reaction rate for the catalytic oxidation of ethylene was found to be constant with time, but was dependent on partial pressures of ethylene and oxygen present. The reoxidation of the nitrosyl ligand appears to be the rate-determining step in the catalytic cycle. The reaction rate increased when Co(TPP)NO was used in place of the nitro complex (py)Co(TPP)NO\(_2\). The pyridine which is released from the nitro complex on reduction to nitrosyl complex, can bond to the palladium complex and block the activation of the olefins. However, when the nitrosyl is used as the catalyst the reaction proceeds only in coordinating solvents such as DMF, DMSO, or THF which function as the sixth ligand required to reoxidise the nitrosyl group.\(^{364-5}\) Figure 5.6(b) gives the mechanism for the catalytic olefin oxidation. The catalytic oxidation of the higher olefins is
slower, and only a limited number of turnovers can be achieved due to side reactions.\textsuperscript{369}

This type of oxygen transfer reaction to olefins can also be carried out in a monometallic system where the metal complex serves as the olefin-activating centre and the oxidant.\textsuperscript{370-1} The first complex of this type was PdCl(NO\textsubscript{2})-(MeCN)\textsubscript{2} prepared either from PdCl\textsubscript{2}(MeCN)\textsubscript{2} and one equivalent of AgNO\textsubscript{2}, or by the oxidation of [Pd(NO)Cl]\textsubscript{n} with molecular oxygen.\textsuperscript{370-1} The nitro complex and its nitrosyl precursor react cleanly with ethylene and higher olefins to produce acetaldehyde and ketones respectively. Andrews and coworkers\textsuperscript{372} and Diamond \textit{et al.}\textsuperscript{373} have also investigated the use of these metal nitro complexes for epoxidation of alkenes, and Andrews \textit{et al.}\textsuperscript{374} have also studied the mechanisms of O atom transfer from metal nitro ligands to oxidisable substrates.

The reduction by CO of a series of nickel complexes NiX(NO\textsubscript{2})L\textsubscript{2} (X = Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, NO\textsubscript{2}\textsuperscript{-}; L = tertiary phosphine) to NiX(NO)L\textsubscript{2} has been reported.\textsuperscript{375-8} Labelling studies \textsuperscript{\textsuperscript{18}O} have revealed that the oxygen in the product CO\textsubscript{2} originates in the nitro ligand,\textsuperscript{379} and kinetic studies\textsuperscript{380} on the dinitro complex (X = NO\textsubscript{2}\textsuperscript{-}, L = PMe\textsubscript{3})\textsuperscript{381} suggest that the rate-determining step is activation of CO by its bonding to the metal to give a 5-coordinate transition state, NiX(NO\textsubscript{2})(CO)L\textsubscript{2}, which on O atom transfer from NO\textsubscript{2} to CO rapidly decays to give the 4-coordinate nitrosyl NiX(NO)L\textsubscript{2} and CO\textsubscript{2}.\textsuperscript{380}

Similarly the Ru and Os complexes M(NO\textsubscript{2})\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} undergo a facile oxygen transfer resulting in the formation of nitrosyl complexes M(NO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}, CO\textsubscript{2} and some OPPh\textsubscript{3}.\textsuperscript{382}

The reaction of coordinated nitrosyl with nitric oxide
is known to yield a variety of products, including N₂, N₂O and either nitro (NO₂⁻) or hyponitrito (N₂O₂²⁻) complexes. The hyponitrito complexes may react further with H⁺ to liberate N₂O. Reactions of this type are considered as metal-catalysed homogeneous disproportionations of NO.¹⁵⁷

Coordinated NO is not a stable ligand and kinetics of gaseous NO exchange with transition metal nitrosoyls has been measured, and found to be first order with respect to complex concentration in CoX(NO)₂(PPh₃) complexes.³⁸⁵ Nitrosyl transfer reactions have been studied, and intermolecular nitrosyl transfer processes to other complexes, and to metalloproteins³⁸⁷ are known. Intermolecular transfer of linearly bound nitrosyl ligand in the 4-coordinate complexes M(NO)(PR₃)₃ (M = Rh, Co) to coordinatively unsaturated transition metal complexes occurs very readily and is thought to proceed through formation of an intermediate bridging nitrosyl complex, M(μ-NO)M'.³⁸⁶,³⁸⁸ Doyle et al.³⁸⁷,³⁸⁹-³⁹⁰ have reported that Co nitrosyl complexes undergo nitrosyl transfer to iron haemoproteins, and [CoCl(en)$_2$(NO)]ClO₄, [Co(dmg)$_2$(NO)(ROH)] (dmg = dimethylglyoximate(1−)), and [Co(tmg)$_2$(NO)(ROH)] (tmg = tetramethylenglyoximate(1−)) selectively transfer the nitrosyl ligand to iron(II) haemoproteins. Kinetic investigations³⁸⁹ of these latter reactions with deoxyHb as nitrosyl acceptor, described the formation of HbNO as first order in haemoprotein and first order in cobalt nitrosyl complex.

Structural conversion of a transition metal nitrosyl from a linear to a bent form is an attractive way to generate a coordinatively unsaturated metal, since bending changes the
nitrosyl from a 3-electron to a 1-electron donor ligand:
\[
\begin{align*}
\text{LnM—N=O} & \quad \longrightarrow \quad \text{LnM—N} \\
\text{me}^- \text{metal} & \quad \longrightarrow \quad (m-2)e^- \text{metal}
\end{align*}
\]

Reduction of a metal nitrosyl complex may facilitate the linear to bent structural change in addition to leading to a more nucleophilic group.\(^{147,155}\) Redox studies on MNO coordination compounds have shown that reduction may irreversibly labilise one of the ligands,\(^{392-3}\) or more often involve reversible transfer to a molecular orbital based predominantly on the nitrosyl group,\(^{394}\) on another ligand\(^{395}\) or on the metal.\(^{396}\)

The concept of stereochemical control of valence is based on the principle that overall stereochemistry of the complex can determine the M-L charge distribution, the geometry of the MNO moiety, and its chemical reactivity.\(^{151,397-402}\) Such a situation is classically seen from the structures\(^{397,400}\) of \([\text{Co(diars)}_2\text{NO}](\text{ClO}_4)_2\) and \([\text{Co(diars)}_2(\text{NO})(\text{NCS})](\text{NCS})\) in which CoNO in the former is 179° and in the latter 132°. In \([\text{Co(diars)}_2\text{NO}]^2+\) the NO group may be regarded as a 3-electron donor (NO\(^+\)) so that the 18-electron configuration is attained. In \([\text{Co(diars)}_2(\text{NO})(\text{NCS})]^-\) the bent NO\(^-\) donates 1-electron and the 18-electron rule is also satisfied.

The intramolecular redox equilibria of cobalt nitrosyl complexes were further studied by Collman et al.\(^{284,403}\) who had also earlier suggested the possibility of conformational equilibria between two forms (bent-linear) of metal nitrosyl
bonding, whereby the coordination geometry would change as the metal and nitrosyl undergo a formal internal redox reaction. Compounds of the type \( \text{CoX}_2(\text{NO})(\text{PR}_3)_2 \) were first described by Chatt who observed the presence of two bands in the NO stretching region. Collman et al. prepared a series of such compounds and presented experimental evidence consistent with such hybridisation isomerisation. Assignments of \( v_{\text{NO}} \) were confirmed by \(^{15}\text{N} \) substitution and the valence bond isomers (I) and (II) were proposed to be in equilibrium (Figure 5.7).

Figure 5.7 Conformational Equilibria for \( \text{CoX}_2(\text{NO})(\text{PR}_3)_2 \) Complexes

(I) \quad (II)

Irídium and rhodium \( \text{MX}_2(\text{NO})(\text{PR}_3)_2 \) analogues are known but these exist in the bent \( \text{NO}^- \) form, and thus serve as models for isomer (II). The fact that such temperature dependent isomers exist is probably due to low intervening energy barriers which are explained by the orbital correlation arguments of Enemark and Feltham. Collman et al. further substantiated their hypothesis of conformational isomers with detailed IR and X-ray photoelectron spectral studies, and the single crystal structure determination of the room temperature form of \( \text{CoCl}_2(\text{NO})(\text{PPh}_2\text{Me})_2 \), which
exhibits a somewhat distorted trigonal bipyramidal form with CoNO \(164.5(6)^\circ\) (classified as linear NO\(^+\)), with no evidence for the coexistence of the square pyramidal bent NO\(^-\) isomer in the crystal used. The low temperature form could not be suitably crystallised for structure determination.\(^{403}\)

The next Section contains results of \(^{15}\)N and \(^{59}\)Co NMR investigations of further \(^{15}\)N labelled square pyramidal cobalt(III) nitrosyls, and results of \(^{15}\)N and \(^{59}\)Co NMR investigations of several \(^{15}\)N labelled nitro complexes follow in Section 5.1.2.2. The nitro complexes were studied in an attempt to establish the products of decomposition and oxidation of the bent nitrosyl group. Transformations of this kind are relevant to the cured meat system. A variable-temperature multinuclear NMR spectroscopic study of CoCl\(_2\)(\(^{15}\)NO)(PPh\(_2\)Me)\(_2\) is presented in Section 5.1.2.3, in an investigation of the solution fluxionality of this complex.

5.1.2 Results and Discussion

5.1.2.1 Cobalt(III) Nitrosyl Complexes

Table 5.1 gives NMR and IR spectroscopic data and relevant structural data for the square pyramidal cobalt(III) complexes with bent apical nitrosyl and chelating basal coligands measured to date, giving \(S_4\), \(S_2N_2\), \(N_4\), ONON, or ONON coordination in the equatorial plane with a range of substituents in the chelate and phenylene rings. Representative structures of these complexes are shown in Figure 5.8. The compounds prepared in this work are marked (*) in Table 5.1 and preparative details are given in Chapter 3. Other compounds marked (+) were satisfactorily prepared in conjunc-
Table 5.1 Spectroscopic and Structural Data for Square Pyramidal Cobalt(III) Complexes With Bent Apical Nitrosyl Ligand

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta^{(15}\text{N})$ (ppm)</th>
<th>$\hat{\alpha}$ (°)</th>
<th>N-O (Å)</th>
<th>M-N (Å)</th>
<th>$\nu^{(14}\text{NO})$ (cm$^{-1}$)</th>
<th>$\delta^{(59}\text{Co})$ (ppm)</th>
<th>$\nu^{(15}\text{NO})$ (cm$^{-1}$)</th>
<th>$W_{1/2}$ (Hz)</th>
</tr>
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<tbody>
<tr>
<td><strong>S$_4$ Coligands</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Co(S$_2$CNR$_2$)$_2^{15}\text{NO}^g$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R = Me$^c$</td>
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<td><strong>S$_2$N$_2$ Coligands</strong></td>
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<td><strong>N$_4$ Coligands</strong></td>
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<td>Κ (cm L mol⁻¹)</td>
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**OONN (Acacen Type) Coligands**

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<td>Co(benacen)¹⁵NO²,g</td>
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### OONN (Salen Type) Coligands

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<td>1.793</td>
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<td>Co(salen)(^{15})NO(^g)</td>
<td>725.4(^b)</td>
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<td>1.071</td>
<td>1.809</td>
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<td>7658(^c)</td>
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<td>(+) Co(salphen)(^{15})NO(^d)</td>
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<td>(1595)</td>
<td>8100(^d)</td>
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<td>9300</td>
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<td>(+) Co(3,5-(NO(_2))(_2)-salen)(^{15})NO(^d)</td>
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<td>1725</td>
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### ONON (Oximato Type) Coligands

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<th>ν (cm⁻¹)</th>
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<th>ν (cm⁻¹)</th>
<th>ν (cm⁻¹)</th>
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<td>Co(keto)(_2)(^{15})NO(^c),(^g)</td>
<td>740.3</td>
<td>126.3</td>
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<td>1.806</td>
<td>1675</td>
<td>8478</td>
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<td>(+) Co(3MeOsalox)(_2)(^{15})NO</td>
<td>817.0(^d)</td>
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<td></td>
<td>1667(^f)</td>
<td>8446(^d)</td>
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<tr>
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<td>756.6br(^b)</td>
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<td>(1650)(^f)</td>
<td>9623(^b)</td>
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<td></td>
<td>549.9w</td>
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<tr>
<td>Compound</td>
<td>15NO&lt;sup&gt;a&lt;/sup&gt;</td>
<td>ν&lt;sub&gt;1&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>ν&lt;sub&gt;2&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>ν&lt;sub&gt;3&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>ν&lt;sub&gt;4&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>ν&lt;sub&gt;5&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
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</tr>
<tr>
<td>Co(salox)&lt;sub&gt;2&lt;/sub&gt;15NO&lt;sup&gt;g&lt;/sup&gt;</td>
<td>824.1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>115.7</td>
<td>1.48</td>
<td>1.838</td>
<td>1672</td>
<td>8966&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>(+) Co(5Cl-salox)&lt;sub&gt;2&lt;/sub&gt;15NO&lt;sup&gt;d&lt;/sup&gt;</td>
<td>828.7</td>
<td>123.4</td>
<td>1.070</td>
<td>1.841</td>
<td>1690</td>
<td>9890</td>
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<tr>
<td>Co(5NO&lt;sub&gt;2&lt;/sub&gt;-salox)&lt;sub&gt;2&lt;/sub&gt;15NO&lt;sup&gt;d&lt;/sup&gt;</td>
<td>833.1</td>
<td></td>
<td></td>
<td></td>
<td>1705</td>
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ONON (Iminato Type) Complexes

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<th>Compound</th>
<th>15NO&lt;sup&gt;b&lt;/sup&gt;</th>
<th>ν&lt;sub&gt;1&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>ν&lt;sub&gt;2&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>ν&lt;sub&gt;3&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>ν&lt;sub&gt;4&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>ν&lt;sub&gt;5&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>ν&lt;sub&gt;6&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
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<tr>
<td>(+) Co(NMesalim)&lt;sub&gt;2&lt;/sub&gt;15NO&lt;sup&gt;b&lt;/sup&gt;</td>
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<td></td>
<td></td>
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<tr>
<td></td>
<td>536.5 weaker</td>
<td></td>
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<tr>
<td>(*) Co(NPhsalim)&lt;sub&gt;2&lt;/sub&gt;15NO&lt;sup&gt;b&lt;/sup&gt;</td>
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a) <sup>15</sup>N shifts relative to neat liquid nitromethane and <sup>59</sup>Co shifts relative to aqueous K₃[Co(CN)₆] solution, high frequency positive; br signifies a broad resonance, w a weak (vw, very weak) additional resonance. W<sub>1/2</sub> is the <sup>59</sup>Co line width at half-height. Spectra were measured at 25°C in deuterated solvents b to e. References for the structural data are given in the text. IR stretching frequencies were measured in nujol mull, unless otherwise indicated. b) CD₂Cl₂. c) CCl₃. d) (CD₃)₂SO. e) (CD₃)₂CO. f) KBr disc. g) Reference 279. The symbols (*) and (+) are described in the text.
Figure 5.8 Structures of the Cobalt Nitrosyl Complexes

[Co(salphen)NO]

[Co(sacacen)NO]

[Co(amben)NO]

[Co(acacen)NO]; \( R = \text{Me}, R' = \text{H} \)

[Co(acacpn)NO]; \( R = R' = \text{Me} \)

[Co(benacen)NO]; \( R = \text{Ph}, R' = \text{H} \)

[Co(NPhsalim)\(_2\)NO]; \( R = \text{Me}, R' = \text{H} \)

[Co(NMesalim)\(_2\)NO]; \( R = \text{Me}, R' = \text{H} \)

[Co(salen)NO]; \( R = R' = \text{H} \)

[Co(5-t-Busalen)NO]; \( R = 5\text{-t-Bu}, R' = \text{H} \)

[Co(3,5-(NO\(_2\))\(_2\)salen)NO]; \( R = 3,5\text{-}(NO\(_2\))\(_2\), R' = \text{H} \)

[Co(7-Mesalen)NO]; \( R = \text{H}, R' = \text{Me} \)

[Co(3-MeOsalox)\(_2\)NO]; \( R = 3\text{-MeO}, R' = \text{H} \)

[Co(5-Clsalox)\(_2\)NO]; \( R = 5\text{-Cl}, R' = \text{H} \)

[Co(5-NO\(_2\)salox)\(_2\)NO]; \( R = 5\text{-NO}_2, R' = \text{H} \)

[Co(ketox)\(_2\)NO]; \( R = \text{H}, R' = \text{Me} \)
tion with undergraduate project students (A. N. Stephens, P. A. Duffin, and S. Lytton) under the general supervision of Dr L. F. Larkworthy. No preparative details for these compounds are given in this work. Structural data for the known cobalt nitrosyls of bis(dithiocarbamate), bis(ethylenediamine), TPP, acacen and benacen, salen, 7-Me-salen, and bis(ketox), bis(salox), and bis(5-Cl-salox) coligands are included for comparison.

None of these 5-coordinate complexes with chelating basal coligands exhibits any fluxionality as previously observed for 5-coordinate [RuCl(NO)(PPh$_3$)$_2$] (see Figure 2.17, Chapter 2). The NMR and IR spectroscopic data confirm that the square pyramidal structure observed in the solid state persists in solution. The tetradentate porphyrin ligands constrain the 5-coordinate nitrosyls to square pyramidal structure both in solid state and solution. The tetradentate Schiff base ligands are not flexible when coordinated, and the oximate nitrosyl complexes (ketox, salox) are kept rigidly square pyramidal by strong hydrogen bonding between the bidentate basal ligands. There are no constraints on the nitrosyls of the other bidentate coligands, dithiocarbamate and ethylenediamine, but they are thought to retain their solid state square pyramidal conformation in solution from the position of the $^{15}$N NMR resonances.

Each complex was made with $^{14}$NO and $^{15}$NO and although the IR spectra are complicated there was no difficulty in identifying the NO stretching vibration by comparison with the ligand spectrum and the shift on isotopic substitution. The large range of over 850 ppm in $^{15}$N shifts in cobalt nitrosyls depending on the MNO angle may be seen from Figure
2.14 in Chapter 2 and Tables 5.1 and 5.2 (linear MNO systems). In Table 5.1 there is also a large range of $^{59}$Co shifts of over 3000 ppm. The $^{15}$N shifts of these bent nitrosyls extend the known range for diamagnetic nitrogen compounds by 200 ppm. From the structural data in Tables 5.1 and 5.2 it may be seen that the nitrogen shielding decreases (the shift increases) from linear to bent MNO. $^{15}$N NMR spectroscopy is thus a sensitive indicator of whether the nitrosyl ligand is bent or linear because of the deshielding caused by the low energy $n_N \rightarrow \pi^*_{\text{NO}}$ paramagnetic circulations in the bent Co(III)NO$^-$ form as discussed in Section 2.3.8.2.1, Chapter 2. As shown in Table 5.2 for some representative linear nitrosyls of Fe, Co, Ru, and Rh the $^{15}$N resonances are at medium field near the free ligand NO$^+$. Slightly bent dinitrosyls with MNO down to ca. 160° are slightly deshielded relative to linear mononitrosyls.

The connection between $^{59}$Co shift and geometry of the MNO moiety with the various groups of basal coligands (N$_4$, OONN, ONON, etc.) in Table 5.1 is not so easy to rationalise. The shielding of the transition metal nucleus depends largely on d-d paramagnetic circulations (see Section 2.3.8.2.2.1, Chapter 2). These in turn are sensitive to the ligand field splittings of these relatively weak ligands and are modified by interaction with the nitrosyl frontier orbitals, which determine the nitrogen shift. The ability of the NO ligand to bend is explained by the close correspondence in energies of the HOMO ($n_N$) and LUMO ($\pi^*_{\text{NO}}$) orbitals, to those of the ligand field orbitals.

The compounds [Co(en)$_2^{15}$NO]($\text{ClO}_4$)$_2$, Co(acacpn)$^{15}$NO, and Co(amben)$^{15}$NO give rise to more than one $^{15}$N resonance (Table
Table 5.2 Spectroscopic and Structural Data for Some Linear Nitrosyl Complexes$^a,b$

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>$\delta^{(15}N)^c$ (ppm)</th>
<th>$\hat{\text{MNO}}$ (°)</th>
<th>N-O (Å)</th>
<th>M-N (Å)</th>
<th>$\nu^{(14}N)$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(NO)(NH$_3$)$_5$]Cl$_3$</td>
<td>H$_2$O</td>
<td>-29.0</td>
<td>172.8</td>
<td>1.17</td>
<td>1.77</td>
<td>1913</td>
</tr>
<tr>
<td>Na$_2$[Fe(CN)$_5$]$^{(15}NO$]</td>
<td>H$_2$O</td>
<td>-13.5</td>
<td></td>
<td></td>
<td></td>
<td>1944</td>
</tr>
<tr>
<td>[Co(CO)$_3$(NO)]</td>
<td>C$_6$H$_6$</td>
<td>14</td>
<td>180</td>
<td>1.10</td>
<td>1.76</td>
<td>1805</td>
</tr>
<tr>
<td>trans-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[RhCl($^{15}NO$)(P-i-Pr)$_3$]ClO$_4$</td>
<td>CDCl$_3$</td>
<td>24.0</td>
<td></td>
<td></td>
<td></td>
<td>1842</td>
</tr>
<tr>
<td>$^{15}NO$_2(PPh$_3$)$_2$</td>
<td>C$_6$D$_6$</td>
<td>50.7</td>
<td>170.6</td>
<td>1.19</td>
<td>1.78</td>
<td>1615</td>
</tr>
<tr>
<td>[Rh(NO)($^{15}NO$)(PPh$_3$)$_2$]ClO$_4$</td>
<td>CD$_2$Cl$_2$</td>
<td>81.4</td>
<td>158.9</td>
<td>1.16</td>
<td>1.82</td>
<td>1714</td>
</tr>
</tbody>
</table>

a) Data taken from reference 279. b) If $^{15}N$ is not indicated, $^{14}N$ was measured by wide-line methods, and the uncertainty may be 10ppm or so because of broad lines and referencing uncertainties. c) Relative to neat liquid nitromethane, high-frequency positive; normally measured at 25°C, with 99% $^{15}N$ enrichment on a 400-MHz spectrometer.
5.1). This is indicative of distinct isomeric species in the particular solvent. In the spectrum of Co(amben)$_{15}$NO in CD$_2$Cl$_2$ there is an intense peak at 734.3 ppm with a weaker peak at 698.5 ppm. In Co(amben)NO, the ligand amben differs from salen derivatives (Figure 5.8) in having -NH$^-$ as the donor group instead of phenolic oxygen, -O$^-$. Consequently, there are three possible orientations of the ligand in this nitrosyl complex depending on the orientation of the -NH groups and of the nitrosyl, i.e. (1) where both the -NH groups point away from the NO group, (2) where they both point toward the NO group, or (3) one -NH up and the other down. If the two sides of the ligand plane are not equivalent and both -NH groups project from the same side then attack of NO would presumably be favoured on the 'unhindered' side. These isomeric possibilities could conceivably lead to slightly different nitrogen shifts in the compound. However, in the $^{59}$Co data the additional less intense peak is also much sharper. Another possibility is intramolecular hydrogen bonding between the oxygen of the CoNO moiety and a -NH group, and this could be intermolecular. Clearly, measurement of $^1$H and $^{13}$C NMR of the unlabelled nitrosyls would be invaluable in determining which of these possibilities is correct.

In the $^{15}$N NMR spectrum of Co(acacpn)$_{15}$NO there are two resonances; one at 711.5 ppm and a less intense peak at 726.7 ppm. However, in the isolation of the $^{14}$N complex, addition of water to a methanol solution gave the compound which analysed as a monohydrate. Similar addition of water to the $^{15}$N complex failed to yield any product and it was necessary to take the mixture to dryness to isolate the labelled product, which could then also have been the monohydrate. In the $^{15}$N
NMR spectrum (d$_6$-DMSO) of Co(acacpn)$_{15}$NO the appearance of
the two peaks suggests two species, one with H$_2$O trans- to NO
instead of DMSO. This is not the only possibility for Co(acac-
qn)NO because the carbon atom bearing the methyl group in the
propylene backbone of the acacpn ligand is asymmetric (Figure
5.8) as a consequence of containing four different substit­
uents (-H, -CH$_2$-, -CH$_3$, -N=). Therefore two absolute configur­
ations (i.e. R and S forms) can exist. Attack of NO at either
side of the planar Co(II)(acacpn) complex will lead to cis-
and trans-isomers of the NO and methyl groups with respect to
the CoN$_2$O$_2$ plane, with the trans- form possibly being
favoured. There are four isomers: (R)-trans-, (R)-cis-, (S)-trans-, and (S)-cis- thus possible. Clearly, this problem
would be resolved by $^1$H and $^{13}$C NMR of the nitrosyl complex
which should give clear indication of isomers present from
number and position of the methyl group resonance(s).

The two peaks present in the $^{15}$N and $^{59}$Co spectra of
[Co(en)$_2$$^{15}$NO]$_2$$^{2+}$ are possibly due to an equilibrium between
coordinated trans-OCIO$_3^-$ and d$_6$-acetone, since in the crystal
structure a OCIO$_3^-$ anion is weakly coordinated to cobalt
trans- to NO$^-$. However, trans-OCIO$_3^-$ is not expected to be
the major species in solution.

It is seen from the salox series of cobalt nitrosyls in
Table 5.1 that Co(3-methoxysalox)$_2$$^{15}$NO gives two resonances
in CD$_2$Cl$_2$, one at 756.7 ppm (with a cobalt shift of 8446 ppm)
and a much weaker nitrogen resonance at 549.9 ppm. However,
in d$_6$-DMSO the single nitrogen resonance is at 817 ppm with a
very broad $^{59}$Co resonance at 9623 ppm. This solvent shift of
60 ppm is the largest observed in this work on changing from
a chlorinated solvent to the coordinating DMSO. It is assumed
that the usual trans-ONON arrangement of donor atoms of these salox species, as shown in Figure 5.8, is responsible for the peaks at 817 ppm and 756.7 ppm in $d_6$-DMSO and $CD_2Cl_2$ respectively, with the effect of the coordinated DMSO base trans- to NO causing increased deshielding of nitrogen. However, the 3-methoxy group may through steric hindrance, or through interaction with the oxime OH group, influence the strong hydrogen bonding that is responsible for holding these complexes in rigid square pyramidal conformation, leading to small amounts of alternative structures in equilibrium with the predominant hydrogen bonded structure. A cis-Co$O_2N_2$ arrangement of the two 3-MeOsalox ligands is a possibility. In the N-substituted salicylaldimine complexes, Co(N-Mesalim)$_2$NO and Co(N-Phsalim)$_2$NO the trans-ONON conformation is more likely due to steric hindrance of the R groups, but there is no hydrogen bonding to stabilise a square pyramidal structure with bent apical NO and a trigonal bipyramidal structure is also possible. There were weak and uncertain $^{15}$N signals at 549.8 and 536.5 ppm for Co(N-Mesalim)$_2^{15}$NO and at 966.2 ppm for Co(N-Phsalim)$_2^{15}$NO. It is plain that more work is needed on the bidentate and 3-substituted ligands. It was also observed that generally in the salox series the nitrogen lines were broadened by unresolved coupling to $^{59}$Co. The quadrupolar line widths depend on the square of the electric field gradient at the $^{59}$Co nucleus ($I = 7/2$) and on the correlation time (inverse tumbling rate), and it appears that small electric field gradients could arise at the central nucleus in the irregular ligand environments.

The NMR and other results for the porphyrin complexes are discussed in Chapter 4.
It is known that the conformation of complex and the MNO angle are sensitive to crystal lattice effects\textsuperscript{158} and therefore the structure of these nitrosyls may be slightly different in solution and in the solid state.\textsuperscript{179} This reasoning can be extended so that the structure may vary slightly with solvent. This could be detected by studying the solvent dependence of nitrogen shift. In solution, association of a coordinating solvent molecule (DMSO, acetone) \textit{trans} to NO is possible, but hardly any change in the electronic spectrum of solutions of bent nitrosyls was observed on addition of nitrogen and phosphorus bases.\textsuperscript{322} However, electronic spectroscopy would not be as sensitive to small changes in MNO bending as nitrogen NMR. Coordination of base would force electron density onto nitrogen and therefore increase nitrogen shift. From Table 5.1 it is seen that for the relatively 'flexible' bidentate dithiocarbamate complex, Co(S\textsubscript{2}CNMe\textsubscript{2})\textsubscript{2}\textsuperscript{15}NO there is virtually no change in nitrogen resonance in going from noncoordinating CDCl\textsubscript{3} to coordinating d\textsubscript{6}-DMSO. The square pyramidal benacen and salen compounds show a small change in nitrogen resonance of \textit{ca.} 4 ppm and \textit{ca.} 12 ppm respectively on going from CDCl\textsubscript{3} or CD\textsubscript{2}Cl\textsubscript{2} to d\textsubscript{6}-DMSO. The nitrogen shifts in [Co(en)\textsubscript{2}\textsuperscript{15}NO]\textsuperscript{2+} and Co(3MeO-salox)\textsubscript{2}\textsuperscript{15}NO on changing solvents have been discussed above. Table 5.1 shows a small trend to lower \textsuperscript{59}Co shielding if d\textsubscript{6}-DMSO is used instead of CDCl\textsubscript{3} or CD\textsubscript{2}Cl\textsubscript{2} for the 5-coordinate benacen, salen, and dithiocarbamato nitrosyls; this could also indicate weak coordination by DMSO. As well as the above trends of \textsuperscript{15}N (and \textsuperscript{59}Co) shielding there are indications of lower \(v_{NO}\) values for benacen (\textit{ca.} 20 cm\textsuperscript{-1}) and ketox (\textit{ca.} 40 cm\textsuperscript{-1}) nitrosyls with the more basic solvent DMSO compared to
CH$_2$Cl$_2$ or nujol mull; whereas in salen the frequency is about 40 cm$^{-1}$ lower in DMSO or nujol mull than in CH$_2$Cl$_2$.

Figure 5.9 illustrates the correlation between nitrogen shielding and M-NO bond length and shows that the tendency is for the nitrogen shielding to decrease with M-NO bond length. A longer M-NO bond indicates less back-bonding and less shielding in the MNO moiety. Figure 5.10 illustrates the related trend for the nitrogen shielding to decrease with increase in $v_{NO}$, i.e. with less back-bonding. This correlation is poorer than that in Figure 5.9 probably because the values of $v_{NO}$ are from solid state spectra and the NMR results for solutions.

Figure 5.11 shows the general tendency for the nitrosyl and cobalt shielding to increase together, both increasing with increase in back-bonding and formal removal of electron density both from nitrogen and cobalt into the $\pi^*$ orbitals. The general trend is predicted by consideration of the two equations in Chapter 2 for nitrogen and cobalt shielding. However, the actual connection between the properties for the two nuclei is far from simple and the correlation is not as good as expected since there will be individual influences on the two nuclei. It was mentioned in Chapter 2 that the energy term in the shielding equation for a transition metal ion gives the shifts a 'spectrochemical' dependence with nuclear magnetic shielding tending to decrease with decrease in ligand field splittings. This very spectrochemical trend was observed in earlier work$^{279}$ for similar bent cobalt nitrosyls, and nitrogen and cobalt shielding decreased with decrease in the energy of the visible absorption band maxima, which is made up of contributions from d-d and M-L charge
Figure 5.9 Correlation of the Nitrogen Shift with the Co-N Bond Distance in the Bent Nitrosyl Ligand
Figure 5.10 Correlation of the Nitrogen Shift with the NO Stretching Frequency in the Bent Nitrosyl Ligand
Figure 5.11 Correlation of the Nitrogen and Cobalt Shifts in the Bent Nitrosyl Ligand (*, + = values from different solvents, see Table 5.1)

δ(¹⁵NO)/ppm

Key To Basal Ligand

Donor Set

- = $\text{S}_2\text{N}_2$
- = $\text{N}_4$
- = OONN
- = ONON

7-Mesalen

acacen O

benacen O

(ketox)$_2$

(3-MeOsalox)$_2$

O

salphen

OEP

TPP

(3-MeOsalox)$_2$

(salox)$_2$

(5-Clsalox)$_2$

sacacen

amben

(en)$_2$

(en)$_2$

salen$^+$

salen$^+$

6 (salox)

5 (Clsalox)

10 9 8 7

δ(⁵⁹Co)/ppt
transfer excitations. Since the spectrochemical series arranges ligands in order of ligand field strength\textsuperscript{300} then nuclear magnetic shielding would be expected to decrease in the donor atom sequence N > O > S.\textsuperscript{338} However, a nephelauxetic influence is imposed by the radial factor <r\textsuperscript{-3}>\textsubscript{d} which tends to decrease the nuclear magnetic shielding from the softer to the harder ligands (S > N > O) with decrease in electron delocalisation to these donor atoms (large <r\textsuperscript{-3}>\textsubscript{d}).\textsuperscript{338} The nephelauxetic (or cloud-expanding) effect arises from the combination of orbitals on the metal and ligands to form larger molecular orbitals through which the electrons can move. Ligands which can delocalise the metal d-electron cloud over a larger space (those containing larger donor atoms with d-orbitals for \pi-bonding) are most effective in this manner.\textsuperscript{300}

The above two influences of spectrochemical effect involving the excitation energy term \Delta E and nephelauxetic effect on the radial term <r\textsuperscript{-3}>\textsubscript{d} (as related to delocalisation and covalency) in combination serve to decrease the nuclear magnetic shielding in the order N > O i.e. for ligands with donor atoms from the same row of the periodic table.\textsuperscript{338} However, these two factors are in opposition for ligands containing donor atoms from different rows i.e. nuclear magnetic shielding should decrease as N > O > S (spectrochemical) and S > N > O (nephelauxetic). For partially filled d shells the nephelauxetic influence is dominating for ligating atoms down the periodic group,\textsuperscript{338} giving S > N > O. These trends may be observed from Table 5.1 where the cobalt shielding tends to decrease in the sequence of basal donor atom sets: S\textsubscript{4} > S\textsubscript{2}N\textsubscript{2} > N\textsubscript{4} > OONN > ONON. Correlations
of increased shielding of a transition metal nucleus with increase in ligand field strength and nephelauxetic ability of the ligands are documented in Section 2.3.8.2.2.1.

Other evidence is that nitrogen deshielding on bending the nitrosyl increases with a decrease in the ligand field splitting is shown by the greater deshielding for Co complexes than for Ru, Rh, Os, Ir etc. as ligand field splittings increase from the first to the second and third transition series. The higher shielding in the dithiocarbamate series relative to the Schiff base series correlates with higher $^{59}$Co shielding (greater splitting of ligand field). The highest shielding is in fact observed for the sulphur coligands, and this may be explained by their increased nephelauxetic effect (increased back-bonding with sulphur), whereas the lowest shielding is seen for the most electronegative (O, N) coligands such as in the ketox and salox derivatives. Shorter M-NO bond lengths and larger MNO angles are commonly found in complexes of the softer (As, S) compared with the harder (N, O) coligands. The bending of the MNO unit increases with $\sigma$- and $\pi$-donor ability of these basal ligands. Superimposed on the relative shielding effects of the donor atom sets are substituent effects. Table 5.1 illustrates that the shielding is reduced further (and $v_{\text{NO}}$ increased) by introduction of electron-withdrawing substituents such as Cl and NO$_2$ groups in the phenylene rings of the salens and salox's or with electronegative oxygen directly attached to the nitrogen donor atoms as in the salox's versus the salens. Electron-releasing substituents (alkyl groups) on imine nitrogen have the opposite effect of causing higher shielding e.g. ketox versus salox and 7Mesalen
versus salen. Electron-attracting ring substituents in Co(salen)NO derivatives were found to increase $v_{NO}$ consistent with decrease in back-bonding from metal to NO. Deshielding appears to be associated also with electron-withdrawal by phenyl, phenylene or other aromatic rings in the ligands as exemplified by the sequence in $^{15}N$ shielding of the $N_4$ ligands: en (717.5) > amben (734.3) > OEP (760.1) > TPP (770.7). The electron-releasing ethyl groups of OEP give greater $^{15}N$ shielding than TPP.

The cobalt nucleus is deshielded in these nitrosyls by $>8000$ ppm relative to complexes with stronger ligands such as linear NO$^+$ and CO. The cobalt shielding for the dithiocarbamate nitrosyls with donor set [CoNS$_4$] is very similar to that for [CoS$_6$] (see Chapter 2) in the corresponding tris(dithiocarbamate) compounds. Also, the cobalt shielding in the 5-coordinate Schiff base nitrosyls [CoN$_3$O$_2$] resembles that of [CoN$_6$], [CoN$_5$O], and [CoN$_4$O$_2$] octahedral Co(III) complexes.

The recognition of the use of nephelauxetic (covalency) parameters derived from optical spectroscopy in cobalt nuclear magnetic shielding has been discussed in Chapter 2. Orthoaxial complexes (in which the ligands lie linearly on the cartesian axes) were found to give a good linear relationship between $^{59}Co$ magnetogyric ratio and the corrected energy term $h/\beta$ (where $h$ is the energy of the first d-d band and $\beta$ the nephelauxetic ratio). The results with non-orthoaxial complexes such as [Co(en)$_3$]$^{3+}$ and [Co(ox)$_3$]$^{3-}$ were much less regular. Significant shifts are also observed for distorted geometries due to chelating or bulky ligands. These factors must be considered to be operational within the correlation illustrated in Figure 5.11 where
individual distortions of the basal ligands e.g. small bite angle of dithiocarbamate versus en complexes serve to obscure any trends and are mainly responsible for the large scatter observed.

That the spectrochemical and nephelauxetic effects of the donor sets of the basal ligands are clearly, though intricately, interconnected for the $^{15}$N and $^{59}$Co nuclei is due to the close matching of the energies of the $\pi^*_{\text{NO}}$ and d orbitals, and the resultant extensive mixing that occurs.\[^{279}\]

5.1.2.2 Cobalt(III) Nitro Complexes

Early in this work unsuccessful attempts to characterise CoNO groups by natural abundance $^{15}$N NMR measurements were made. During the long acquisition times, oxidation to CoNO$_2$ species by traces of oxygen was thought to occur, even though the nitrosyl solutions were made up under nitrogen. Oxidation of nitrosyls is known to give nitro compounds.\[^{322}\] Weak resonances similarly attributed also appeared in the spectra of the enriched nitrosyls with amben, benacen, salen, ketox, salox, 5-NO$_2$-salox, and 3,5-dinitrosalox coligands. In order to obtain well characterised solids several enriched nitrosyls have been deliberately oxidised to CoNO$_2$ compounds in the presence of base which is axially coordinated in the product. No base was added to nitrosyl solutions prepared under nitrogen for NMR investigation; oxidation products of these presumably contain axially coordinated solvent.

From Table 5.3 it may be observed that the $^{15}$N resonances fall into three main groups: (1) those about -3 ppm, (2) those more negative, i.e. -6 to -34 ppm and, (3) those between 35 to 90 ppm. The signals between 35 to 90 ppm are
Table 5.3 NMR and Infrared Spectroscopic Measurements of Cobalt(III) Nitro Complexes in Solution and in the Solid State. The Base or Associated Solvent Molecule is Trans to the Nitro Ligand\(^a\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\delta(^{15}\text{N}))/ppm</th>
<th>IR Band Assignments (cm(^{-1}))</th>
<th>(\delta(^{59}\text{Co}))</th>
<th>(W_{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitrate Nitro Nitrite</td>
<td>(v_{as})  (v_s)  (\delta\text{ONO})  (\varphi_w)  (v_{M-N}) (ppm) (Hz)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>S(_4) Coligands</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>((^*)) [(py)Co(S(_2)CNMe(_2))(_2^{15}\text{NO}_2)](_e)</td>
<td>-34.4</td>
<td>804</td>
<td>6905</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>-21.0</td>
<td></td>
<td>7162</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>-5.9</td>
<td></td>
<td>7389</td>
<td>800</td>
</tr>
<tr>
<td>((^*)) [(py)Co(S(_2)CNPr(_i))(_2^{15}\text{NO}_2)](_e)</td>
<td>-3.2w</td>
<td></td>
<td>6417</td>
<td>1950</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6458</td>
<td>1050</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6460</td>
<td>1700</td>
</tr>
<tr>
<td><strong>S(_2N(_2) Coligands</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(py)Co(sacacen)(_{15}\text{NO}_2)](_d)</td>
<td>-3.5  66vw</td>
<td>1300(^f)  804(^f)</td>
<td>n.o.</td>
<td></td>
</tr>
<tr>
<td><strong>N(_4) Coligands</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Co(amben)(_{15}\text{NO}_2)](_b,g)</td>
<td>-4.1  87.1  209.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Evidence</td>
<td>Bond Lengths (Å)</td>
<td>Bond Angles (°)</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>-----------------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
<td>(*) [(py)Co(OEP)\textsuperscript{15}NO\textsubscript{2}]\textsuperscript{b}</td>
<td>-2.4</td>
<td>1435 sh, 1345 n.o., 648 385 8204s 950</td>
<td>(1405) (1310) (810) (648) (385) 8305 9050</td>
<td></td>
</tr>
<tr>
<td>(*) [(1MeIm)Co(OEP)\textsuperscript{15}NO\textsubscript{2}]\textsuperscript{b}</td>
<td>-2.4</td>
<td>1460 1345 845 620 400 8307 160</td>
<td>(1445) (1315sh) (830) (620) (390) 8613 315</td>
<td></td>
</tr>
<tr>
<td>(*) [(py)Co(TPP)\textsuperscript{15}NO\textsubscript{2}]\textsuperscript{b}</td>
<td>-2.5 38.3</td>
<td>1430 1310 820 640 370 7902 2500</td>
<td>(1405) (1295) (813) (640) (370)</td>
<td></td>
</tr>
<tr>
<td>(*) [(1MeIm)Co(TPP)\textsuperscript{15}NO\textsubscript{2}]\textsuperscript{b}</td>
<td>-2.9</td>
<td>1410 1315 820 620 375 8077 170</td>
<td>(1405) (1295) (811) (620) (375) 8233 1220</td>
<td></td>
</tr>
</tbody>
</table>

**OONN (Acacen Type) Coligands**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Evidence</th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(py)Co(acacen)\textsuperscript{15}NO\textsubscript{2}]\textsuperscript{c}</td>
<td>-1.8vw</td>
<td>1312\textsuperscript{f}, 812\textsuperscript{f} n.o.</td>
<td></td>
</tr>
<tr>
<td>[Co(benacen)\textsuperscript{15}NO\textsubscript{2}]\textsuperscript{d,g}</td>
<td>-3.0</td>
<td>7612 2300</td>
<td></td>
</tr>
</tbody>
</table>

**OONN (Salen Type) Coligands**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Evidence</th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(*) [(py)Co(7Mesalen)\textsuperscript{15}NO\textsubscript{2}]\textsuperscript{d}</td>
<td>-3.9 52.6</td>
<td>- - - - - n.o.</td>
<td>(1375) (1295) (810) (565) (385)</td>
</tr>
<tr>
<td>Compound</td>
<td>50.0</td>
<td>1415</td>
<td>1315</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>-------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>[(py)Co(salen)]_{15}^{\text{NO}_2}]^d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>62.7</td>
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**ONON (Oximato Type) Coligands**

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\[ \text{[Co(3,5-(NO\textsubscript{2})\textsubscript{2}salox)\textsubscript{2}\textsuperscript{15}NO\textsubscript{2}]^d} \quad 202.5w \quad \text{n.o.} \]

\[ \text{[Co(dmg)\textsubscript{2}\textsuperscript{15}NO\textsubscript{2}]^d} \quad 38.5 \]

a) \textsuperscript{15}N shifts relative to neat liquid nitromethane and \textsuperscript{59}Co shifts relative to \textsubscript{K\textsubscript{3}}[\text{Co(CN)}\textsubscript{6}], high frequency positive; w signifies a weak (vw, very weak) resonance. n. o. means not observed. \textsuperscript{1/2} is the \textsuperscript{59}Co line width at half-height. Spectra were measured at 25°C in deuterated solvents b to e. IR spectra were measured in KBr disc, unless otherwise indicated. b) CD\textsubscript{2}Cl\textsubscript{2}. c) CDCl\textsubscript{3}. d) (CD\textsubscript{3})\textsubscript{2}SO. e) (CD\textsubscript{3})\textsubscript{2}CO. f) Nujol mull. g) Signal developed on standing of a solution of nitrosyl compound under inert atmosphere, with loss of nitrosyl signal. h) signal developed on standing of a solution of nitrosyl compound under air, with loss of nitrosyl signal. (*) signifies solid nitro complex prepared in this work.
believed to be due to the coordinated nitro group, and when there are two signals for one compound, one may be due to DMSO or acetone replacing the nitrogenous base in solution. In the dithiocarbamates, acetone may replace pyridine, and in sacacen, 7-Mesalen, salen, and salphen, DMSO may replace pyridine. The signals near -3 ppm are assigned to free nitrate, \( \text{NO}_3^- \), and since these are found in the majority of experiments, therefore all contain some nitrate. The other more negative signals, thought to be due to coordinated nitrate, are not found in all samples. However, for the dithiocarbamates these signals could be due to nitro ligand in view of the relatively high field nitrosyl resonances observed (Table 5.1).

Perhaps the best evidence for the above assignments comes from a \( ^{14}\text{N} \) NMR spectrum of aqueous \([\text{Co(NO}_2]_6\)^{3-} aged for four hours. Three lines were apparent, a sharp line at -4 ppm (relative to MeN\( \text{O}_2 \)) due to free \( \text{NO}_3^- \), a reasonably broad line (linewidth 170 Hz) at 231 ppm assigned to free nitrite, \( \text{NO}_2^- \), and a very broad line at 91 ppm (linewidth 2200 Hz) due to complexed nitrite. The N-bonded nitro ligand (M-\( \text{NO}_2 \)) is expected to resonate at medium field in the region of MeNO\( _2 \) and \( \text{NO}_3^- \), rather than at low field as nitrite ion does which has a lone pair on nitrogen. Supporting evidence comes from \( ^{15}\text{N} \) NMR measurements of bent nitrosyl and nitro ligands in some square pyramidal \([\text{RhNO}]^8 \) complexes, where \( \text{trans-}[\text{RhCl}^{15}\text{NO})(^{15}\text{NO}_2)(\text{PR}_3)_2] \) was found to give room temperature \( \delta^{15}\text{NO}_2 (\text{CD}_2\text{Cl}_2) \) of 45.8 ppm (\( R = \text{Cy} \)), 43.6 ppm (\( R = \text{Pr}^3 \)), and 43.6 ppm (\( R = \text{Ph} \)) (doublets with \( ^1J(\text{Rh}^{15}\text{N}) \) between 27 to 29 Hz) at medium field relative to neat liquid MeNO\( _2 \). On the same reference scale, aqueous Na\( ^{15}\text{NO}_2 \).
resonates at 230 ppm. The recently reported $^{15}\text{N}$ NMR resonances (D$_2$O) of cis- and trans-[Co($^{15}$NO$_2$)$_2$(en)$_2$]$^+$ (85.0 and 95 ppm respectively) and cis- and trans-[CoCl($^{15}$NO$_2$)(en)$_2$]$^+$ (71.0 and 68.5 ppm respectively) relative to Me$^{15}$NO$_2$ are also in good agreement with our assignments for coordinated nitro group.

The small shifts of 25 ppm upfield of NO$_3^-$ ion for various nitrato complexes in nonaqueous solvents agree with our assignment of coordinated NO$_3^-$ (Table 5.3) The high field resonances of oxidation products containing S-coligands only may, however, arise from coordinated CoNO$_2$ because of the higher spectrochemical and nephelauxetic effects of sulphur donor atoms.

The nitrogen resonance at 209.3 ppm for Co(amben)$^{15}$NO$_2$, which developed on standing of the enriched nitrosyl solution under an inert atmosphere, may be evidence of the O-bonded nitrito ligand -ONO, because MeONO is reported to resonate 44 ppm upfield of saturated aqueous nitrite ion (NO$_2^-$ resonates some 230 ppm downfield of MeNO$_2$). Co(amben)$^{15}$NO$_2$ also shows a resonance at 87.1 ppm assigned to coordinated -NC>2, and this is the only example in Table 5.3 of a possible nitro to nitrito ("N O$_2$ -ONO) isomerism. NMR studies of specifically labelled [Co(NH$_3$)$_5$ONO]$^{2+}$ (20 % enriched $^{17}$O) shows that spontaneous intramolecular O-to-O exchange (scrambling) in the nitrito ligand competes with the spontaneous O-to-N isomerism, although the nitro isomer is present to >99 % at equilibrium. The $^{15}$N shift of the -O$^{15}$NO ligand would not be expected to vary much from compound to compound as the influence of the coligand donor atoms would be buffered somewhat by the ligating oxygen.
The $^{15}\text{N}$ NMR spectrum of the square planar hyponitrite complex $[\text{Pt(II)}(0,0'-{^{15}\text{N}}_2\text{O}_2)(\text{PPh}_3)_2]$ formed from $\text{Pt(PPPh}_3)_3$ and $^{15}\text{NO}$ is a singlet at 34.9 ppm. The complex has a 5-membered chelate ring. Bridging hyponitrito species are also a possibility in these cobalt systems. However, it is unlikely that hyponitrite is formed in the present systems. The only complex showing similar resonances is $\text{Co(ketox}_2{^{15}\text{NO}_2}$ with peaks at 36.6 (DMSO) and 36.6 ppm (CDCl$_3$), with little solvent dependence; but these are thought to be due to coordinated nitro groups. Free hyponitrite, $\text{"ONNO"}$, $2\text{Na}^+$ (aq) has a nitrogen resonance of 83 ppm and it is not likely to have much of a coordination shift because of the buffering effects of the ligating oxygens.

The trends apparent for the $^{15}\text{N}$ and $^{59}\text{Co}$ spectra of the nitrosyls in Table 5.1 are also present for the nitro compounds in Table 5.3. The nitrosyl complexes with sulphur coligands have both nitrogen and cobalt shifts that are considerably shielded (i.e. lower shift) compared to the complexes with the ONON oximato coligands. The same basic trend is observed in this nitro series where the cobalt shielding tends to decrease $S_4 > N_4 > O\text{ONN} > O\text{NON}$ (c.f. $S_4 > N_4 > O\text{ONN} > O\text{NON}$ for nitrosyls in Table 5.1). Correlations of increased shielding of a transition metal nucleus with increase in ligand field strength and nephelauxetic ability of ligands were documented in Chapter 2, and while the axial ligands must have some effect the trends for the basal ligands are roughly the same.

Table 5.3 also presents infrared data for the nitro complexes which were isolated as solid compounds. It was not possible to measure solution infrared spectra in the
situations where the extra $^{15}$N signals (nitro/nitrato) developed on decomposition of the enriched nitrosyl solutions. The assignments to the various vibrational modes given were made on the basis of their $^{15}$N shifts, and the values obtained agree with the typical ranges given in Table 2.1, Chapter 2 for the N-bonded nitro group. The $v_{as}$, $v_s$, values for the nitro complexes are raised in frequency compared to the free ion values of 1250 ($v_{as}$) and 1335 ($v_s$) cm$^{-1}$ in NaNO$_2$, as is typical for the N-bonded nitro group. The complexes all exhibit the wagging mode ($\rho_w$) at ca. 620 cm$^{-1}$ which is also characteristic of nitro complexes. There is no evidence for the presence of nitrito complexes (M-O-N=O) due to the lack of characteristic bands (in nitrito complexes the symmetric stretch, $v_s$ of the free nitro group shifts to $v_{N-O}$ ca. 1050-1150 cm$^{-1}$ on coordination). As a general rule nitrito isomers are unstable and usually revert eventually to nitro isomers. There is also no evidence for the presence of chelating or bridging nitro groups (see Section 2.3.6.1).

The $^{15}$N shifts given in Table 5.3 strongly indicate free (and possibly coordinated) nitrato species in nearly all of the solutions of these 'nitro' complexes. If this is so we should be able to identify these species in solution and in the solid state from infrared measurements. Both unidentate and the more common bidentate coordination modes of the planar nitrate ion split the $v_3$ band of the free ion into two components, and it has been observed that $v_3$ (1390 cm$^{-1}$) of the free NO$_3^-$ ion splits into two bands (1481-1531 and 1253-1290 cm$^{-1}$), and that $v_1$ (1050 cm$^{-1}$, Raman active) of the free ion appears in the IR when the nitrate group coordinates
as a unidentate ligand ($C_{2v}$ symmetry). Splitting of the $v_3$ band is generally larger in the bidentate mode than in the unidentate mode.\textsuperscript{417} The infrared spectra of some similar complexes of cobaloxime, [Co(dmg)$_2$(NO$_2$)(B)] and [Co(dmg)$_2$-(H$_2$O)(B)](NO$_3$) (B = substituted imidazoles) have been reported.\textsuperscript{418} In the nitro cobaloximes the three main NO$_2^-$ group bands appear at ca. 1420, 1325, and 826 cm$^{-1}$ suggesting N-bonded nitro group, and these are in very good agreement with our results in Table 5.3. The cobaloxime complexes containing the nitrate group as a counterion exhibit a strong unsplit band at ca. 1380 cm$^{-1}$ ($v_3$) and two IR active bands at ca. 835 cm$^{-1}$ ($v_2$) and 750 cm$^{-1}$ ($v_4$). The absence of an IR inactive $v_1$ band as well as the presence of a very strong but unsplit $v_3$ band at 1380 cm$^{-1}$, establish that NO$_3^-$ is not involved in covalent bonding. The IR spectra of the solid complexes prepared in this work indicate only the N-bonded nitro species, and there is no evidence that these solid compounds contain either free or coordinated NO$_3^-$ ion.

Bidentate NO$_3^-$ ion has however been shown to coordinate to iron and cobalt porphyrin complexes, and the crystal structure\textsuperscript{419} of [Co(III)(OEP)(O,O'-NO$_3$)(bis-N-substituted porphyrin)] ($v_{\text{max}}$ 1511 cm$^{-1}$ (NO$_3$)) shows the NO$_3^-$ ion to be coordinated in a symmetric bidentate fashion with cobalt-oxygen distance of 2.03 Å. This nitrate group is very labile and is displaced by acetone on recrystallisation. However the crystal structure\textsuperscript{420} of 6-coordinate [Fe(III)(TPP)(O,O'-NO$_3$)] ($v_{\text{max}}$ 1275br, 1544sh (NO$_3$)) reveals the nitrate coordination in an unsymmetrical bidentate fashion. Iron-oxygen distances are 2.019 and 2.323 Å, and the planar nitrate ion is oriented between pyrrole nitrogen atoms in order to minimise steric
interactions, although $^1$H NMR data of this paramagnetic iron(III) complex indicates rapid rotation of coordinated NO$_3^-$ in solution.

The IR assignments for the cobalt nitro compounds given in Table 5.3 do not agree with the previous work. Clarkson and Basolo give unassigned infrared data for their cobalt nitro Schiff base complexes: (py)Co(salen)NO$_2$ ($v_{\text{max}}$ 1412, 1213, and 840 cm$^{-1}$), (py)Co(acacen)NO$_2$ (1312, 1208, and 812 cm$^{-1}$), (py)Co(benacen)NO$_2$ (1325, 826 cm$^{-1}$), (py)Co(sacacen)-NO$_2$ (1300, 804 cm$^{-1}$), and (py)Co(S$_2$CNMe$_2$)$_2$NO$_2$ (1308, 1214, and 816 cm$^{-1}$), and frequently mention that the spectrum was masked by ligand absorptions. In light of the work here based on $^{15}$N substitutions the resonances at ca. 1400 cm$^{-1}$ may be assigned to $v_{\text{as}}$, those at ca. 1300 cm$^{-1}$ to $v_s$ and those at 820 cm$^{-1}$ to $\delta_{\text{ONO}}$; and these are included in Table 5.3 for comparison. The peaks at ca. 1210 cm$^{-1}$ are probably due to coordinated pyridine. Yamamoto has published infrared assignments for (py)Co(TPP)NO$_2$ ($v_{\text{as}}, 1306, v_s, 1210, \text{ and } \delta_{\text{ONO}} 812$), (1MeIm)Co(TPP)NO$_2$ (1310, 1200, 810) and other TPP complexes (where axial base = 4Mepy, pip, Im) that are clearly at odds with data in Table 5.3. The data of Yamamoto may be reassigned as for that above. Further support for the assignments here comes from Andrews et al. who give $^{14}$N($^{15}$N)-based assignments for (py)Co(TPP)NO$_2$ of $v_{\text{as}}$NO$_2$ 1424 (1399), $v_s$NO$_2$ 1308 (1290), and $\delta_{\text{ONO}}$ 815 (807) cm$^{-1}$. These are in excellent agreement with our results.

The evidence above from IR and NMR data is that the solid intact cobalt nitro complexes are decomposing in solution during the NMR measurements to mixtures of nitro and nitrato complexes. The infrared data and the crystal
structure determination of one of the nitro complexes, (py)Co(TPP)NO₂ (Section 4.3.1) suggests that we originally started with intact nitro complexes. However, the nitro group in this complex is severely disordered in the solid state. The NMR data and the crystal structure determination of one of the decomposed 'nitro' complexes, [Co(TPP)(1MeIm)₂]NO₂ (Section 4.3.1) shows that decomposition of nitro complex occurs on extended oxidation and other treatment (recrystallisation). The time factor between dissolution of complex and measurement of spectrum is very important. If the nitro solutions were left to stand for a long time during measurement of ⁵⁹Co and ¹⁵N spectra then many adverse processes could occur. In the case of the dtc complexes the ⁵⁹Co NMR spectra were measured five days before the ¹⁵N spectra (due to time available on the spectrometer), therefore considerable decomposition could have occurred and the ⁵⁹Co peaks may not correspond to the ¹⁵N peaks measured. For the porphyrin nitro complexes the ⁵⁹Co and ¹⁵N spectra of both TPP complexes were measured on the same day. For (py)Co-(OEP)¹⁵NO₂ the ⁵⁹Co spectrum was measured one day before the ¹⁵N spectrum, and for the 1MeIm OEP complex two days before. Therefore these spectra ought to hold reasonably true. However, all the porphyrin spectra show free nitrate signals, except for (py)Co(TPP)¹⁵NO₂ which shows nitro as well.

It is evident from this work that the NO₂⁻ group is a very reactive (labile) ligand which can be both reduced and oxidised quite easily to lead to a whole series of complexes. The CoNO₂ is a weak oxygen-centred nucleophile, and metal nitro complexes are very efficient oxygen transfer agents as detailed in the introduction. It may be possible that the
(B)Co(L₄)NO₂ complexes are transferring oxygen to solvent (e.g., dimethylsulphoxide, Me₂S=O to give dimethylsulphone, Me₂S(=O)₂), to axial base (pyridine to give pyridine N-oxide), to active portions of basal ligand (-NH- in amben, =NOH in oximes, C=N in Schiff base) or to another CoNO₂ group in a disproportionation reaction. However, nitrosyl would be generated in each of these processes, and there is no evidence for Co¹⁵NO in the ¹⁵N spectra. In general ⁵⁹Co data in conjunction with ¹⁵N results should give information on fragmentation in solution, and extra ¹⁵N lines will be accompanied by extra ⁵⁹Co signals. However, this is not generally the case in Table 5.3.

It has been reported that free NO can disproportionate by reacting with coordinated NO⁻ to give a coordinated nitro group, with liberation of N₂O.¹⁵⁷ Miki has reported that reaction of Co(quin)₂NO with excess NO in CH₂Cl₂ gives [NO][Co(III)(quin)₂(NO₃)(NO₂)] with liberation of N₂O at room temperature,⁴²² and that [Co(4Mequin)₂(NO)(py)] reacts similarly to produce [NO][Co(II)(4Mequin)₂(NO₃)(py)] plus N₂O.⁴²³ The IR spectrum of [NO][Co(4Mequin)₂(NO₃)(py)] gave bands characteristic of NO⁺ and NO₃⁻; and the strong band at 2170 cm⁻¹ (2106, ¹⁵N) was assigned to the stretching vibration of NO⁺. The strong bands at 1411 (1390), 1323 (1301), and 813 (813) cm⁻¹ were assigned to the NO₂ antisymmetric stretch, the symmetric stretch, and the out-of-plane bending vibrations of the NO₃⁻ respectively, with similar assignments for the nitro-nitrato complex. The splitting of the nitrate v₃ band by about 100 cm⁻¹ in these compounds suggested NO₃⁻ coordination to the cobalt as a unidentate ligand. However, free ¹⁵N₂O or ¹⁵N₂ were not detected in the solutions of the
'nitro' complexes in Table 5.3, and there is no evidence for similar disproportionations occurring in these systems. Dissolved $^{15}\text{N}_2$ resonates at ca. -80 ppm, and the $\pi$-bonded N atom in $^{15}\text{N}_2\text{O}$ becomes more shielded to resonate at ca. -145 ppm relative to Me$^{15}\text{NO}_2$ at zero ppm.\textsuperscript{263}

The chemistry of the square pyramidal cobalt nitrosyls on oxidation may lead to quite uncommon and unpredictable chemistry. In the presence of O$_2$ and H$_2$O an ether solution of Co(dmg)$_2$NO was reported\textsuperscript{424} to be rapidly oxidised firstly to [Co(dmg)$_2$(NO)$_2$(H$_2$O)] and eventually to a diamagnetic complex formulated as [Co(II)(dmg)$_2$(NO)(H$_2$O)][Co(III)(dmg)$_2$(NO$_2$)]-2H$_2$O. It was considered that in the complex, Co(II) is bound to Co(III) through a bridging nitrosyl group.\textsuperscript{424} However, $v_{\text{NO}}$ of 1628 cm$^{-1}$ did not clearly indicate the existence of a $\mu_2$-NO group. The complex Co(salen)NO has been reported to react with NO in organic solvents in the air to give Co(salen)NO.nHNO$_3$.nH$_2$O ($n = 1$ and 2) ($v_{\text{NO}}$ 1640 cm$^{-1}$), where the phenolic oxygens of salen were considered to be protonated to give coordinated salenH$^+\text{NO}_3^-$ or salen(H$^+\text{NO}_3^-$)$_2$ ligand respectively.\textsuperscript{425} But from the reported $v_3$ (NO$_3^-$) of 1300 cm$^{-1}$ this was more likely coordinated NO$_3^-$. Again, there is absolutely no evidence for the possibility of similar transformations occurring in solutions of our cobalt nitro complexes, but the above work does indicate how complex these nitrosyl-nitro systems can be. Possibly in our systems, water (from wet DMSO/acetone) could displace nitro ligand to form HNO$_2$/HNO$_3$, plus Co(II) because we observe extra signals in DMSO/acetone than in chlorinated solvents.

Chemical and electrochemical oxidations of nitro complexes of Ru(II) generate a reactive nitro complex of Ru(III)
which rapidly undergoes an intermolecular disproportionation at the nitro ligand to give both nitrosyl and nitrato complexes. The mechanism was thought to proceed by transfer of oxygen from one nitro group to another via a nitro-nitrito isomerism. Further work indicated that on electrochemical oxidation at 25°C, the Ru\(^{II-NO_2^-}\) moiety in trans-[RuCl(NO\(_2\))(py)\(_4\)] rapidly changes to the three species, (Ru\(^{IV=O^{2-}}\)), (Ru\(^{III-OH^-}\)), and (Ru\(^{II-NO^+}\)), whilst oxidation at ca. 40°C gave (Ru\(^{III-ONO_2^-}\)) and (Ru\(^{II-NO^+}\)) in the manner described above. Again, whilst it is attractive to imagine that such complex transformations are operating in our CoNO\(_2\) systems, the fact is that these disproportionation reactions generate nitrosyl species, and since Co\(^{15}NO\) has not been detected in the \(^{15}N\) NMR data in Table 5.3 this cannot be so. Therefore a mechanism whereby these CoNO\(_2\) species could give CoNO\(_3\) and free NO\(_3^-\) in a process that does not involve disproportionation to CoNO and CoNO\(_3\) must be suggested. Further evidence comes from the literature.

Trogler and Marzilli have reported that (B)Co(dmg)\(_2\)NO (B = tBupy, CNpy, 1MeIm, PPh\(_3\)) reacts with oxygen in CH\(_2\)Cl\(_2\) to form a mixture of predominantly nitrato (>50% of (B)Co-(dmg)\(_2\)NO\(_3\)) and a lesser amount of nitro (<50% of (B)Co-(dmg)\(_2\)NO\(_2\)) complexes. The reaction was not clean in that small amounts of unidentified side products (<10%) were also formed. The complexes [Ru(NO)\(_2\)(PPh\(_3\))\(_2\)], \(^{382}\) [Ir(NO)(PPh\(_3\))\(_2\)]-Cl, \(^{429}\) [IrCl\(_2\)(NO)(CO)(PPh\(_3\))\(_2\)], \(^{429}\) and [Pt(NO)(NO\(_3\))(PPh\(_3\))\(_2\)]\(^{377}\) exhibit similar behavior and produce exclusively nitrato complexes. A reasonable explanation of these results may be proposed from the recent demonstration that Co(dmg)\(_2\)NO dissociates and exchanges NO with various metalloproteins.
The dissociated NO can also react with molecular oxygen or \( \text{MbO}_2 \) to form peroxynitrate ion, \( \text{ONOO}^- \) which then reacts with the parent complex \( \text{Co(dmg)}_2 \) to form the observed nitrato complex \( \text{Co(dmg)}_2\text{NO}_3 \). The \( \text{MbO}_2 \) is serving as a superoxide donor for nitric oxide to give peroxynitrate ion which undergoes subsequent isomerisation to nitrate. However, the parent complex \( \text{Co}^{\text{II}}(\text{dmg})_2 \) is also known to rapidly react with dioxygen to form mononuclear \( \text{Co(dmg)}_2(\text{O}_2) \) with subsequent (rapid) formation of the dinuclear \( \mu\text{-peroxo-dicobaloxime(III)}, [(\text{dmg})_2\text{CoO}_2\text{Co(dmg)}_2] \), followed by slower disproportionation to \( \mu\text{-superoxo-dicobaloxime(III)}, [(\text{dmg})_2\text{CoO}_2\text{Co(dmg)}_2]^+ \), and either of these dinuclear cobalt dioxygen species is able to oxidise \( \text{Mb} \). It is also possible that these superoxo \( \text{O}_2^- \) or peroxo \( \text{O}_2^{2-} \) species can react with dissociated NO (or possibly coordinated NO) and yield the nitrato complex. The reaction of NO with different peroxo complexes is well documented and this reaction type is strongly suggested by the collapse of the Ru-bound peroxo and nitrosyl ligands in \( \text{[Ru(O}_2\text{(NO)(NO}_3\text{)-} \text{(PPh}_3\text{)}_2] \) into a nitrato ligand. The reaction pathway to cobalt nitrato complexes via superoxo or peroxo intermediates is supported by the observation that \( \text{Co(Pc)NO} \) (Pc = phthalocyanine(2-)) dissociates NO and yet it is oxidised only to a nitro complex \( \text{Co(Pc)NO}_2 \) in presence of \( \text{O}_2 \). This is probably because the parent \( \text{Co(Pc)} \) does not readily form a superoxo complex.

The NMR measurements of the previously isolated nitro complexes in Table 5.3 were run in air because it was assumed that the solutions were not air-sensitive. The above proposed mechanism of oxidation of \( \text{CoNO} \) to \( \text{CoNO}_3 \) by cobalt-dioxygen
complexes is applicable to our CoNO$_2$ systems. Cobalt-dioxygen complexes with Schiff bases are well known, however, there is no direct evidence for their presence in these solutions. The best evidence could come from the $^{59}$Co NMR measurements. Eaton et al. measured the $^{59}$Co NMR spectra of some Co(III)-$\mu$-peroxo compounds of type ([Co(salen)]$_2$O$_2$(L)$_2$) where L = DMSO ($\delta^{59}$Co 8369 ppm, $w_{1/2}$ 12800 Hz), L = DMF (8375, 13600), L = H$_2$O (8375, 13200) and for various chelating amines at 7400 to 7700 ppm. Further $^{59}$Co NMR work reported rates of reduction of similar cobalt-dioxygen complexes with Fe(II) ion to Co(II) species and H$_2$O. While it is not proposed that the cobalt shifts in Table 5.3 are due to [Co$^{\text{III}}$(O$_2^{2-}$)]$^{\text{III}}$ species, the results for the Schiff base and porphyrin 'nitro' complexes are in the same general range, but are substantially less broad than the above values. In the instances where cobalt spectra were not observed in this work, it is possible that the molecule was doubling in size, therefore leading to excessively broad (and non-detectable) lines, since linewidth is proportional to molecular volume.

Cobalt-dioxygen complexes are reasonable oxidants for hydroxylation and oxidative dehydrogenation of organic compounds, including that of coordinated coligand. The detection of H$_2$O$_2$ from solutions of decomposed $\mu$-peroxo Co(III) species indicate that the $\mu$-peroxo bridge dissociates from the dioxygen complex as H$_2$O$_2$. Hydrogen peroxide could conceivably oxidise CoNO$_2$ to CoNO$_3$ species. The possible reason that the CoNO$_2$ systems seem to convert eventually to free NO$_3^-$ plus unknown cobalt species is due to the fact that the 'intermediate' CoNO$_3$ species do not participate in oxygen transfer reactions, and so the CoNO$_2$ is trapped as free
NO₃⁻ after dissociation from CoNO₃.

It is evident that much more work is needed for these very labile CoNO₂ systems. Multinuclear time course NMR experiments similar to the ⁵⁹Co, ¹⁴N, and ¹⁷O NMR study²⁷⁰ of [Co(NO₂)₆]³⁻ are required for these CoNO₂ complexes both in air and under inert atmosphere.

### 5.1.2.3 A ¹⁵N and ³¹P NMR Study of the Fluxionality in CoCl₂(¹⁵NO)(PPh₂Me)₂

Figure 5.12 gives the ¹⁵N NMR spectrum of the title compound in CD₂Cl₂ at 293 K. The broad medium field singlet at 254.11 ppm is of moderate intensity. The nitrogen shift is intermediate for linear and bent cobalt nitrosyl (see Figure 2.14, Chapter 2).²⁷⁹ An attempt to measure the ⁵⁹Co NMR spectrum of this solution was unsuccessful as was an attempt to obtain a low temperature ¹⁵N NMR spectrum of a second sample.

The ³¹P[¹H] NMR spectra of CoCl₂(¹⁵NO)(PPh₂Me)₂ at -98°C and -88°C are shown in Figure 5.13. There are two broad singlets at 42.5 and 31.6 ppm (relative intensity 1:4) in the -98°C spectrum, and similar singlets at 42.05 and 31.7 ppm (relative intensity 1:4.5) in the -88°C spectrum, with the 31.6 ppm signal slightly increasing in intensity at the higher temperature. Both ³¹P spectra contain several low intensity side bands. The room temperature ³¹P NMR spectra of this complex was not measured due to decomposition of the solutions. The room temperature ¹H NMR spectrum of the unlabelled complex gave a single methyl triplet (1:2:1) centred at 2.5 ppm consistent with trans-phosphine groups. This is due to the phenomenon of 'virtual-coupling' of the trans-phosphines from overlap of the same metal orbitals
Figure 5.12 $^{15}\text{N}$ NMR Spectrum of CoCl$_2$($^{15}\text{NO}$)(PPh$_2$Me)$_2$ in CD$_2$Cl$_2$ at 293 K (20°C)

$\delta^{15}\text{N} 254.11$ ppm
Figure 5.13 $^{31}$P$[^1]$H NMR Spectra of CoCl$_2$(NO)$_2$(PPh$_2$Me)$_2$ in CD$_2$Cl$_2$ at (a) -98°C and (b) -88°C
by these ligands. The phosphorus nuclei couple with the α-hydrogens with equal strength, and the methyls are split into a triplet by the two $^{31}\text{P}$ atoms rather than the expected doublet from one $^{31}\text{P}$ ($I=1/2$). The $^1\text{H}$ NMR spectrum thus precludes cis- and trans-isomers and indicates rapid equilibrium on the $^1\text{H}$ NMR timescale. Cooling to $-80^\circ\text{C}$ does not freeze out two methyl group signals.

Collman proposed rapid conformational change from square pyramidal (SP) to trigonal bipyramidal (TBP) structure (see Figure 5.7) to explain the infrared results. However, an X-ray crystal structure determination found only the TBP structure contradicting the evidence from X-ray photoelectron and IR spectroscopy which clearly show the presence of two distinct species at room temperature. For $\text{CoCl}_2(\text{NO})-(\text{PPh}_2\text{Me})_2$ both solution and solid state IR spectra exhibit two peaks assigned to the nitrosyl stretches of the two conformations. The higher $v_{\text{NO}}$ of 1750 cm$^{-1}$ arises from the linear nitrosyl, TBP structure, and the lower $v_{\text{NO}}$ of 1640 cm$^{-1}$ from the bent nitrosyl in a SP structure with $>85\%$ in the TBP form. Variable-temperature solution IR shows the TBP form to become more predominant as the temperature drops.

Enemark and Feltham refute Collman's claim that the crystal structure is a distorted TBP and propose that an irregular coordination exists with $\text{CoNO}$ of 164.3° which is significantly different from 180°. They suggest that the two NO stretching frequencies can also be attributed to two distinct conformers differing primarily in the rotational orientation of a nonlinear NO group, rather than to SP→TBP dynamics. These conformations have the NO group bent in the Cl-Co-Cl plane and alternately in the P-Co-P plane. The
bending of the NO group could also be accompanied by changes in the Cl-Co-Cl angle, but it is unlikely that the P-Co-P angle will change much because of the bulky phosphines.

The presence of a broad medium field singlet in the $^{15}\text{N}$ spectrum at room temperature shows that the actual fluxionality is fast on the $^{15}\text{N}$ NMR timescale, and the observed signal is a time-averaged peak at room temperature. It is unfortunate that the low temperature $^{15}\text{N}$ spectrum was unsuccessful, because it might have been possible to 'freeze-out' the low temperature NO$^+$ conformation, or have been possible to resolve the spectrum into two $^{15}\text{N}$ peaks indicative of the two different conformers. The low temperature $^{31}\text{P}$ NMR spectra shows two major peaks, consistent with the proposed mechanism of a conformational change. Within each conformation the two chemically equivalent PPh$_2$Me groups give rise to a single resonance. The observation of two such signals clearly suggests the presence of two conformers, with fast fluxionality on the $^{31}\text{P}$ NMR timescale. Since the linear NO$^+$ form increases as the temperature drops, then the largest $^{31}\text{P}$ NMR peak must correspond to this species, even though this peak is seen to fractionally increase in intensity in the slightly warmer (-88°C) solution spectrum. It is unfortunate that the room temperature $^{31}\text{P}$ NMR failed, because presumably at high temperature the exchange rate would become fast, and the two signals would gradually collapse into a broad singlet as the temperature increased.

From the nitrogen spectrum it is not possible to suggest that either Collman's SP$\rightarrow$TBP theory or Enemark and Feltham's vibrational conformer theory is correct, i.e. whether the medium field signal is due to fast fluxionality
about the MNO bond or to fluxionality of the whole complex from SP to TBP and vice versa. The low temperature $^{31}$P spectra are consistent with the room temperature $^{15}$N spectra, i.e. two species at low temperature coalescing into one species at room temperature as the reaction rate of fluxionality goes up. On the evidence of the $^{15}$N and $^{31}$P spectra the non-observation of the $^{59}$Co NMR spectrum could be due to exchange broadening at room temperature, therefore cooling the solution would be useful. It is clear that more variable temperature multinuclear ($^{59}$Co, $^{15}$N, $^{31}$P) NMR experiments are required to elucidate the fluxional process occurring in CoCl$_2$(NO)(PPh$_2$Me)$_2$. 
5.2 An $^{170}$ NMR Study of Some $^{170}$-Labelled μ-Peroxocobalt(III) Complexes

5.2.1 Introduction

Transition metal dioxygen ($O_2$) complexes have been intensively studied, this work being stimulated by the important role of oxygen-binding metalloproteins. Molecular $O_2$ which has two unpaired electrons (a groundstate triplet) can be reduced by two one-electron processes without O-O bond cleavage to give superoxide ($O_2^-$) and peroxide ($O_2^{2-}$) species respectively:

\[
\begin{align*}
+e^- & \quad O_2^- & \quad +e^- \\
O_2 & \quad -e^- & \quad O_2^{2-} - e^- \\
- & \quad - & \\
\end{align*}
\]

(5.14)

and each of these species is able to act as a ligand towards transition metals. Coordination of dioxygen to a transition metal ion is a redox process, and electrons are transferred from the metal to the dioxygen, in contrast to a simple Lewis base electron donor ligand such as CO. Dioxygen only forms complexes with metals which can undergo facile one- or two-electron oxidations. Molecular dioxygen compounds can be obtained as follows: (1) from $O_2$ by reversible oxidative addition reactions with coordinatively unsaturated complexes, (2) from $O_2$ by irreversible reactions involving oxidation of metal ions to form bridged complexes, and (3) from deprotonation of $H_2O_2$ by metal aqua ions.

$\eta^1$ and $\eta^2$ bonding modes for dioxygen complexes are known. The superoxide ion $O_2^-$ can be bound in the follow-
ing modes as a $1^-$, 2 electron donor:

\[
\begin{align*}
\text{Monodentate} & \quad \begin{array}{c}
\text{Dinuclear bidentate} \\
\text{unidentate}
\end{array} \\
\end{align*}
\]

The $\eta^2$ O$_2$-bridged superoxo complexes have O-O distances in the range 1.10-1.30 Å, with $v_{O-O}$ in the range 1075-1195 cm$^{-1}$ [O$_2^-$, 1.33 Å, 1145 cm$^{-1}$ respectively]. For cobalt bridging superoxide complexes the unpaired electron is delocalised over the two metal atoms and the dioxygen moiety, and according to EPR studies lies in a molecular orbital of $\pi$-symmetry relative to the planar MO$_2$M (or MO$_2$ group in mononuclear complexes).\textsuperscript{441-3} The $v_{O-O}$ in $\eta^1$ O$_2$ complexes is rather insensitive to the nature of the metal and the coligand-s and cobalt $\eta^1$ dioxygen complexes exhibit $v_{O-O}$ in the range 1105-1160 cm$^{-1}$, with Co-O-O ca. 120°, and O-O ca. 1.28 ± 0.02 Å. The O-O distance and O$_2$ vibrational frequencies for O$_2$ are 1.21 Å and 1556 cm$^{-1}$ (Raman). End-on unidentate superoxo groups are found in Co(acacen)(O$_2$)(DMF) and [Co(CN)$_5$(O$_2$)]$^{3-}$.\textsuperscript{441-3}

The peroxide ion O$_2$$^2-$ may be bound as a $2^-$, 4 electron donor in the following bidentate modes:

\[
\begin{align*}
\text{mononuclear} & \quad \text{bridging} \\
\text{triangular} & \quad \text{staggered} \\
\end{align*}
\]

\text{symmetrical}
In all cases complex formation is accompanied by a significant increase in the O-O interatomic distance, and a considerable decrease in \( \nu_{0-0} \). Both effects are more marked for peroxo compounds than for the superoxo compounds and can be interpreted in terms of a transfer of electron density from the metal into antibonding orbitals of \( \text{O}_2 \) therefore weakening the O-O bond. For these bidentate peroxo compounds the O-O bond distances are relatively independent of the nature of the metal and coligands and are fairly constant in the range 1.40-1.50 Å (\( \text{O}_2^{2-}, 1.49 \) Å). The stretching frequencies, \( \nu_{0-0} \) for the bridging species lie in the region 790-930 cm\(^{-1}\), with the triangular species having \( \nu_{0-0} \) around 850 cm\(^{-1}\) (\( \text{O}_2^{2-}, 802-842 \) cm\(^{-1}\)).\(^{441-3}\)

The initial oxygenation product of cobalt(II) salts in cold aqueous ammonia is brown \([\text{(NH}_3\text{)}_5\text{CoO}_2\text{Co(NH}_3\text{)}_5]X_4\).\(^{323}\) This diamagnetic \( \mu \)-peroxo (\( \text{O}_2^{2-} \)) complex reacts further by one-electron oxidation to give paramagnetic green \([\text{(NH}_3\text{)}_5\text{CoO}_2\text{Co(NH}_3\text{)}_5]X_5 \ (\mu_{300 \text{ ca. } 1.7 \text{ BM})} \) formally containing the superoxide ion \( \text{O}_2^- \) with the odd electron equally distributed between the two Co nuclei.\(^{444}\) Formation of the singly bridged \( \mu \)-peroxo dicobalt ammine complexes may be represented by:

\[
2[\text{Co}^{\text{II}}(\text{NH}_3)_X]^{2+n} + \text{O}_2 \rightarrow [(\text{NH}_3)_5\text{CoO}_2\text{Co(NH}_3)_5]^{4+} + 2X^n \ (5.15)
\]

\(^{18}\)O-Labelling experiments have demonstrated that the bridging dioxygen ligand in dinuclear \( \mu \)-peroxo complexes originates entirely from gaseous dioxygen,\(^{323}\) and indicate that the reaction involves direct attack of cobalt(II) ion by dioxygen in two steps:
([Co\textsuperscript{II}(NH\textsubscript{3})\textsubscript{5}X\textsuperscript{2+n}] + O\textsubscript{2} \rightarrow [Co(NH\textsubscript{3})\textsubscript{5}O\textsubscript{2}\textsuperscript{2+} + X\textsubscript{n} (5.16)

[Co(NH\textsubscript{3})\textsubscript{5}O\textsubscript{2}\textsuperscript{2+} + [Co\textsuperscript{II}(NH\textsubscript{3})\textsubscript{5}X\textsuperscript{2+n}] \rightarrow [\text{[NH\textsubscript{3})\textsubscript{5}Co\textsuperscript{III}O\textsubscript{2}Co\textsuperscript{III}(NH\textsubscript{3})\textsubscript{5}]^{4+} + X\textsubscript{n} (5.17)

The first sequence of steps may involve an oxidative addition of O\textsubscript{2} to give a transient Co\textsuperscript{IV} species which then reacts with another Co\textsuperscript{II} species to give the product. These singly bridged species (for ligands like NH\textsubscript{3} and CN\textsuperscript{-}) are isolable as moderately stable solid salts\textsuperscript{323} but decompose fairly easily in H\textsubscript{2}O or acids to give Co(II) species, O\textsubscript{2}, and NH\textsubscript{4}\textsuperscript{+}.

The open-chain monobridged \(\mu\)-peroxo complex above may be cyclised to the brown dibridged \(\mu\)-peroxo-\(\mu\)-amido species by warming to 35\textdegree C in ammoniacal solution:\textsuperscript{323}

\[
\text{[\text{[NH\textsubscript{3})\textsubscript{5}CoO\textsubscript{2}Co(NH\textsubscript{3})\textsubscript{5}]^{4+} \rightarrow [\text{[NH\textsubscript{3})\textsubscript{4}Co} \]
\]

\[
\text{O}_{2} \text{Co(NH\textsubscript{3})\textsubscript{4}]^{3+} + NH\textsubscript{4}\textsuperscript{+}} (5.18)

The amount of the diamagnetic dibridged complex reaches a maximum of about 40\% after about 90 minutes of digestion of the monobridged starting material in aqueous ammonia at about 35\textdegree C in the presence of about 1 equivalent of KOH.\textsuperscript{323}

Both the open-chain and cyclic diamagnetic species contain low spin Co(III) and bridging peroxide O\textsubscript{2}\textsuperscript{2-} ions, and in \([\text{[NH\textsubscript{3})\textsubscript{5}CoO\textsubscript{2}Co(NH\textsubscript{3})\textsubscript{5}]^{4+}\) the O-O distance of 1.47 \(\text{Å}\) is the same as in H\textsubscript{2}O\textsubscript{2}.\textsuperscript{445} Just as the monobridged \(\mu\)-peroxo species can be oxidised in a one-electron step to a superoxide containing species the brown dibridged \(\mu\)-peroxo-\(\mu\)-amido species can also be oxidised to a paramagnetic green
and ESR results for the $^{17}$O-labelled dibridged species show that the unpaired electron is shared by the cobalt atoms via the oxygen bridge, rather than by direct overlap of cobalt orbitals, or via the $\mu$-amido bridge.

In view of the complex equilibria and rapid interchange between these various cobalt ammine complexes, an attempt was made to measure the $^{17}$O and $^{59}$Co NMR spectrum for $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$ and investigate any changes with respect to time in these solutions. No $^{59}$Co NMR spectrum was observed for this species, but the following results were observed in $^{17}$O NMR.

### 5.2.2 Results and Discussion

Figures 5.14 and 5.15 show the infrared and $^{17}$O NMR spectra for $[(NH_3)_5Co^{17}O_2Co(NH_3)_5](NO_3)_4 \cdot 2H_2O$. The IR spectrum ($v_{as}$ Co-O) of this compound has been previously assigned from $^{18}$O-isotopic shifts, and strong infrared inactive bands assignable to $v_{0-0}$ are found around 800 cm$^{-1}$ in the Raman spectrum of the unlabelled compound. The NMR spectra were run in several ways to achieve optimum conditions. Figure 5.15(a) was run normally using severe baseline corrections. This has the effect of disguising peaks of more than about 1000 Hz wide and hence the initial spectrum shows little detail. The remaining spectra were recorded using a probe modification which reduces probe ringing to about 1/60th and consequently there is no baseline correction, and broad peaks
Figure 5.14 Infrared Spectra of the $^{17}$O-Labelled and Unlabelled Cobalt $\mu$-Peroxo Compound: (a) [(NH$_3$)$_5$Co$^{17}$O$\text{O}_2$Co-$\text{O}_2$Co(NH$_3$)$_5$](NO$_3$)$_4$.2H$_2$O (b) [(NH$_3$)$_5$Co$^8$O$_2$Co(NH$_3$)$_5$](NO$_3$)$_4$.2H$_2$O
Figure 5.75  O NMR Spectra for [(NH$_3$)$_5$Co$_2$Co(NH$_3$)$_5$]-(NO$_3$)$_4$.2H$_2$O Recorded at Various Intervals After Dissolution
(a) 0.5 hr after dissolution (b) 1.5 hr after dissolution
(c) 24 hr after dissolution (d) 8 days after dissolution
(for operating conditions see text)
that are present may be genuine. In all NMR spectra [Figure 5.15(a) to (d)] there is a reproducible but narrow peak at 418 ppm which is thought to be \(\text{NO}_3^-\) anion, because the chemical shift of \(\text{NO}_3^-\) has previously been reported at 410 ppm and 420 ppm. If we now discuss the individual spectra in Figure 5.15 in turn: (a) this spectrum was run normally about 1/2 hour after dissolution. Little detail is seen except for the solvent (\(\text{D}_2\text{O}\)) peak at 0-5 ppm, and the nitrate peak at 418 ppm. However, there is a peak with negative intensity at 275 ppm which is masked by the severe baseline correction. (b) This spectrum was recorded using the probe modification after 1.5 hours. As well as the solvent and the \(\text{NO}_3^-\) peaks present there is a very broad peak at 222 ppm and another less broad peak at 133 ppm in an approximate integral ratio of 4:1 (the integration curves are not shown on the spectra for clarity). The peak at 222 ppm is also at approximately the same integral intensity as the reference peak at 0-5 ppm. (c) This spectrum was recorded after 24 hours and the peak at 222 ppm has broadened considerably and its integral intensity relative to the solvent reference peak decreased by about 1/4. The peak at 133 ppm, present in spectrum (b) has disappeared and apart from the \(\text{NO}_3^-\) peak at 418 ppm, little other detail is observed. (d) This spectrum was measured some 8 days later; there is still the \(\text{NO}_3^-\) peak at 418 ppm but in the ca. 200 ppm region there is now a very broad peak of fairly large integral intensity.

Not much detail is seen in spectrum (a) because the ideal spectrometer conditions were being set up. After 1.5 hours we should apparently get ca. 40% concentration (maximum yield) of the \(\mu\)-peroxo-\(\mu\)-amido dibridged diamagnetic
species, which is reported to form in about 1.5 hours in the presence of nearly one equivalent of KOH. The KOH catalyst was not added in this experiment, so the formation of the dibridged species should be much slower, and the final yield may be less than the reported 40%. In spectrum (b) the intensity of the peak at 133 ppm is about 1/4 of the peak at 222 ppm, and these lines may be due to the presence of the dibridged and monobridged species respectively. ¹⁷O chemical shifts for some MO₂ complexes are in the range 325-385 ppm, and Bu⁻OO-Buᵗ resonates at between 269-281 ppm, therefore our signal at 222 ppm assigned to monobridged peroxide may be real. In spectrum (c) the peak at 133 ppm assigned to the dibridged species has gone, and the peak at 222 ppm assigned to the monobridged species has decreased in intensity. The diamagnetic µ-peroxo-µ-amido species would appear to have reacted further. After 8 days there is a very broad peak at 195 ppm in spectrum (d). It is possible that an appreciable concentration of the paramagnetic (5+) µ-superperoxo-µ-amido species could be responsible for this spectrum. There appeared to be no indication of H₂O₂ (at 174 to 187 ppm) in the ¹⁷O NMR of these solutions of decomposing µ-peroxo cobalt(III) species which could indicate that the dioxygen bridges were dissociating from these compounds.

The results presented here for the solution equilibria of [(NH₃)₅CoO₂Co(NH₃)₅]⁴⁺ are hardly conclusive and more ¹⁷O NMR work needs to be attempted. In these particular ¹⁷O NMR measurements it appears to have taken quite some time to get the ideal instrument conditions correct for observation of the ¹⁷O signals, whilst the unstable compound(s) were decomposing in solution. For future measurements it may be
necessary to supply two identical samples, one to enable the correct instrumental conditions to be found, and the other to follow the $^{17\text{O}}$ NMR events immediately after dissolution. Although not shown in the diagrams an attempt was made to measure the $^{17\text{O}}$ NMR spectrum of $[(\text{NCS})(\text{en})_2\text{Co}^{17\text{O}}\text{Co-(en)}_2\text{(SCN)}](\text{SCN})_2$ under identical conditions to the spectra above, however, no peaks were observable at ca. 200 ppm. All these spectra illustrate the extreme difficulty in this work. Lack of signals in an $^{17\text{O}}$ NMR spectrum may be due to many reasons including slow molecular tumbling of the high molecular weight complexes, rapid exchange between free paramagnetic and bound diamagnetic dioxygen, too few $^{17\text{O}}$ nuclei, or dilution of $^{17\text{O}}$ by $^{16\text{O}}$. However, $^{17\text{O}}$ enrichment has precluded the last two reasons but the first two could apply. Significantly, previous attempts to measure $^{17\text{O}}$ NMR spectra in $\eta^2$-peroxo complexes has failed.\textsuperscript{453-4} Despite the use of highly enriched $^{17\text{O}}_2$ (95 %) samples, no signal could be observed for HbO\textsubscript{2} or in IrX(O\textsubscript{2})(CO)(PR\textsubscript{3})\textsubscript{2} (50 % $^{17\text{O}}$).\textsuperscript{453-4} However, for 10 % $^{17\text{O}}$ enriched $[(\text{CN})_4\text{OMo(\eta^2-O_2)}][(\text{N(PPh}_3)_2)]$ the peroxidic oxygen has recently been detected as a broad signal at 487 ppm ($\omega_{1/2}$ 1800 Hz)\textsuperscript{455} and the terminal oxo group as a sharp line at 705 ppm ($\omega_{1/2}$ 80 Hz). $^{17\text{O}}$ NMR should be useful in the study of peroxidic transition metal derivatives, provided there is no exchange with molecular dioxygen.\textsuperscript{455}
5.3 Rapid Electronic Relaxation Between $S = 3/2$ and $S = 1/2$

Spin States in Fe(salphen)NO

5.3.1 Introduction

The nature of spin state transitions in various transition metal complexes has been intensively investigated. Spin state transitions have been largely observed for 6-coordinate transition metal complexes possessing 3d electronic configurations. Such high spin (HS) to low spin (LS) crossover behavior implies that the crystal field strength is comparable in magnitude to the exchange energy corresponding to the crossover of the HS and LS ground states.

When the ligand field splitting has an intermediate value such that the two states of the complex have similar energies (i.e. the difference is of the order of $kT$), then the two states can coexist in measurable amounts at equilibrium.

Spin state transitions have been essentially investigated in octahedral complexes of Fe(II) [$t_{2g}^6(1A_1) \rightarrow t_{2g}^4e_g^2(5T_2)$] and Fe(III) [$t_{2g}^5(6A_1) \rightarrow t_{2g}^3e_g^2(2T_2)$] which involves transfer of two electrons between orbitals ($\Delta S = 2$), and in Co(II) [$t_{2g}^6e_g^1 \rightarrow t_{2g}^5e_g^2$] which involves transfer of a single electron ($\Delta S = 1$), and also to a lesser extent for Ni(II) and Co(III) complexes. However, spin state transitions have also been observed for complexes possessing lower than octahedral symmetry. The direct manifestation of the spin state equilibrium (i.e. the orbital reoccupation) is known to be accompanied by significant M-L bond length variations, also the molecular volume diminishes on passing from the HS to LS state. Changes to these parameters and others including cooperativity, vibronic
modes, spin interconversion rates, entropy changes etc., may be measured by numerous methods such as single crystal X-ray crystallography, high resolution X-ray powder diffraction, variable temperature magnetochemistry, Mossbauer (for iron complexes), EPR, EXAFS, DSC etc., usually as a function of temperature or pressure.

The major driving force of a spin state transition from the LS to the HS state is the gain in entropy which is provided in part by the change in total spin, and in part by the associated changes in molecular configuration and vibrational frequencies, with no breaking or reformation of bonds occurring. Even so, there is also kinetic control on spin crossover phase transitions of the formation and growth to a critical size of nuclei of the two spin phases. In solid systems where thermally driven transitions between HS and LS states are observed, two different types of transition mechanism may be identified: (1) discontinuous (or abrupt) transitions which are described in terms of abrupt changes with temperature of the important physical properties and these occur at a well-defined transition temperature, $T_c$, and (2) continuous (or gradual) transitions which take place over an extended range of temperature and here $T_c$ is defined as the temperature at which the HS fraction is exactly half (i.e. $n_{HS} = 0.5$).

Despite the available structural information on spin state transitions, the assignment of a particular spin transition to one of the two categories of either discontinuous or continuous transition is often not obvious on the basis of magnetic, spectroscopic, and Mossbauer effect measurements alone. But where a detailed analysis of crystallo-
graphic data as a function of temperature is available then a reliable assignment of the spin transition is possible in most cases. 457

In discontinuous transitions experimental evidence for a crystallographic phase change is provided by the observation of individual X-ray diffraction patterns for the two spin states, the relative intensity of the two patterns being strongly temperature dependent in the region of $T_c$. Thus, one pattern replaces the other as the transition progresses in either direction. 456 Hysteresis is an important property of discontinuous transitions and arises as a difference in the transition temperature depending upon whether the transition point is approached from low or high temperatures. The transformation does not take place at the true critical temperature $T_c$ but at a higher and lower temperature usually denoted $T_c^\uparrow$ and $T_c^\downarrow$ respectively with a metastable region between the two. The presence of hysteresis and the existence of a crystallographic phase change are the consequence of pronounced domain formation of majority and minority phases in the transition region. A domain is formed by a number of molecules of like spin, either HS or LS. The conversion from one state to the other is effected by change of temperature (or pressure). The overall shape of the hysteresis for an observed physical quantity arises from the superposition of the individual curves for a large number of domains. The size of domains is limited in various ways e.g. by grain boundaries, cracks, and dislocations in the crystal. Particle size effects, grinding and magnetic dilution experiments (by doping the sample into a diamagnetic host) all serve to alter the sharpness of a discontinuous transition, consistent with
the domain formation theory.\textsuperscript{456} Discontinuous type transitions arise for compounds with strong cooperative interaction between the individual complex molecules.\textsuperscript{460}

Continuous type spin transitions are described in terms of a gradual change with temperature of the relevant physical properties.\textsuperscript{456} The X-ray diffraction patterns reveal a continuous shift with temperature and diffraction peaks of a single phase are obtained. The position of the lines gradually shifts with temperature from the original position of the parent phase to that of the product phase, in either direction. A crystallographic phase change is not therefore involved, and the transition extends in general over a wide range of temperature. This being so, the characteristic transition temperature $T_c$ is not as well defined as for the discontinuous type transition. Latent heat of transition and hysteresis effects are equally not observed. The continuous transition may be regarded as a solid solution of two spin isomers within the same lattice and domain formation plays a minor role. There are many more continuous than discontinuous systems.\textsuperscript{456-7} Continuous type spin transitions are found for compounds with weak cooperative interaction between the individual complex molecules, and a wide distribution of the nuclei of the minority spin constituent.\textsuperscript{463}

The basic difference between the two types of transition is believed to be due to the distribution of the two spin phases in the lattice caused by different development of spin nuclei first formed, even though the conversion of spin state is thought to be initiated in the same manner, i.e. homogeneous nucleation at defect sites and grain boundaries caused by temperature fluctuations.\textsuperscript{456-7}
From infrared spectra and magnetic susceptibility measurements between 80 and 300 K for the [FeNO]$_7$ iron mononitrosyl, Fe(salen)NO, and a number of salen phenylene ring-substituted derivatives, the relatively rare $S = 3/2$ to $S = 1/2$ spin state transition was identified. The nature of the spin crossover was found to be modulated by substitution in the salen ligand. Later workers performed single crystal X-ray structural determinations on Fe(salen)NO at 296 K and 98 K. The complex has essentially square pyramidal coordination geometry at both temperatures with a strongly bent apical nitrosyl ligand. Only moderate changes in bond lengths and angles are observed on transition. Thus the FeNO angle changes from 147° above the transition to 127° below the transition. The distance of the iron atom from the mean plane of the equatorial salen ligand decreases by ca. 0.1 Å and an increased coplanarity of the salicylideneiminato moieties of the salen ligand is observed in the low temperature structure. The unit cell volume changes from $V = 1576 \text{ Å}^3$ at 296 K to $1513 \text{ Å}^3$ at 98 K.

The $S = 3/2$ to $S = 1/2$ transition in Fe(salen)NO was further studied in considerable detail by magnetic susceptibility methods and Mossbauer and EPR spectroscopy in the temperature range 4-300 K. The transition was found to be of the discontinuous type with the transition temperature $T_c = 175 \pm 3$ K. Hysteresis was observed in the Mossbauer spectra indicating that the transition is thermodynamically first order. Relaxation rates between the two spin states were found to be slow on the Mossbauer timescale (i.e. slower than $1 \times 10^{-7}$ s) and a superposition of the spectra of the two spin states is seen near $T_c$, with the spectra replacing each
other in the region near $T_c$ as the transition progresses in either direction of the temperature variation.

The complex $[\text{Fe(TMC)NO}(\text{BF}_4)_2]$, an $[\text{FeNO}]^7$ species with FeNO angle of $177^\circ$ and $v_{\text{NO}}$ $1840$ cm$^{-1}$, has been found to have a coordination geometry intermediate between a square pyramid and a trigonal bipyramid. The IR, EPR and Mossbauer data indicate an $S = 3/2$ to $S = 1/2$ spin equilibrium. The electronic relaxation between the two spin states of $[\text{Fe(TMC)NO}(\text{BF}_4)_2]$ was found to be rapid on the Mossbauer timescale.

The complex $\text{Fe(salphen)NO}$ was found to exhibit a similar spin state transition between $S = 3/2$ and $S = 1/2$ states, with $\mu_{\text{eff}}$ of 3.65 BM at 295 K decreasing to 1.80 BM at 88 K. The transition appeared to be of the continuous type and Mossbauer measurements performed at 300 and 77 K gave similar parameters to the values observed for $\text{Fe(salen)NO}$. The present investigation was undertaken in order to study more thoroughly the spin state transition in $\text{Fe(salphen)NO}$.

### 5.3.2 Results and Discussion

The grey-brown air-stable iron salphen nitrosyl was prepared as previously by reaction of nitric oxide with the iron(II)salphen complex. Ascorbic acid was used in the preparative procedure for the first time as a mild reducing agent, to prevent sample contamination with the oxo-bridged iron(III)salphen dimer. The effective magnetic moment, $\mu_{\text{eff}}$ of this $\text{Fe(salphen)NO}$ sample decreased from 4.13 BM at 295.1 K to 2.23 BM at 104.5 K, consistent with a change in spin state from $S = 3/2$ to $S = 1/2$ (Table 5.4). The overall shape of the $\mu_{\text{eff}}$ versus $T$ (K) variation in Figure 5.16 is
Table 5.4 Magnetic Data for Fe(salphen)NO

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\chi_A$ ($10^6$ cgsu)</th>
<th>$1/\chi_A$ (cgsu$^{-1}$)</th>
<th>$\mu_{\text{eff}}$ (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>295.1</td>
<td>7241</td>
<td>138.1</td>
<td>4.13</td>
</tr>
<tr>
<td>262.0</td>
<td>7882</td>
<td>126.9</td>
<td>4.06</td>
</tr>
<tr>
<td>245.0</td>
<td>8243</td>
<td>121.3</td>
<td>4.02</td>
</tr>
<tr>
<td>230.5</td>
<td>8660</td>
<td>115.5</td>
<td>4.00</td>
</tr>
<tr>
<td>204.5</td>
<td>9221</td>
<td>108.4</td>
<td>3.88</td>
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<tr>
<td>194.5</td>
<td>9389</td>
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<td>184.5</td>
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<td>3.63</td>
</tr>
<tr>
<td>177.5</td>
<td>7385</td>
<td>135.4</td>
<td>3.24</td>
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<tr>
<td>174.3</td>
<td>6816</td>
<td>146.7</td>
<td>3.08</td>
</tr>
<tr>
<td>166.0</td>
<td>6079</td>
<td>164.5</td>
<td>2.84</td>
</tr>
<tr>
<td>155.3</td>
<td>5494</td>
<td>182.0</td>
<td>2.61</td>
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<td>145.7</td>
<td>5366</td>
<td>186.4</td>
<td>2.50</td>
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<td>187.8</td>
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</tr>
<tr>
<td>120.5</td>
<td>5582</td>
<td>179.1</td>
<td>2.32</td>
</tr>
<tr>
<td>104.5</td>
<td>5935</td>
<td>168.5</td>
<td>2.23</td>
</tr>
</tbody>
</table>

Diamagnetic correction = $180 \times 10^{-6}$ cgsu.
Figure 5.16 Temperature Dependence of the Effective Magnetic Moment ($\mu_{\text{eff}}$) and the Reciprocal Magnetic Susceptibility ($\chi_A^{-1}$) of Fe(salphen)NO (ascorbic acid preparation)
comparable to that previously determined, however, the individual $\mu_{\text{eff}}$ values are slightly higher than the previous values. This may be due to poor tube packing, or perhaps to genuine impurities (see Mossbauer spectra and later discussion). From Figure 5.16 the change of spin state can be seen to be taking place between approximately 140 K and 190 K.

The Mossbauer spectra have been measured between 82.3 and 300.1 K. The results are shown in Table 5.5 and spectra at 82.3, 180.0, 190.3 and 300.1 K are illustrated in Figure 5.17. The temperature dependence of the quadrupole splitting, $\Delta E_Q$ and the isomer shift, $\delta_{\text{IS}}$ are shown in Figure 5.18. The measurements were performed for increasing and decreasing temperatures and no hysteresis effects were encountered, as is characteristic of continuous spin state transitions. From Figure 5.17 it is seen that all the $^{57}\text{Fe}$ Mossbauer spectra for $\text{Fe(salphen)}\text{NO}$ show a unique doublet that collapses into a broad singlet at the highest temperatures (300.1 K). The quadrupole doublet at 82.3 K is assigned to an $S = 1/2$ state of iron with characteristic isomer shift $\delta_{\text{IS}}$ of +0.265 mms$^{-1}$ and quadrupole splitting $\Delta E_Q$ of 1.756 mms$^{-1}$. The magnetic moment of 2.23 BM at 104.5 K (previously 1.80 BM at 87.8 K$^{468}$) supports this assignment. The unresolved Mossbauer doublet at 300.1 K with $\delta_{\text{IS}}$ of +0.416 mms$^{-1}$ and $\Delta E_Q$ of 0.182 mms$^{-1}$ is consistent with an intermediate ($S = 3/2$) spin state of iron. This is also suggested by the magnetic moment $\mu_{\text{eff}}$ of 4.13 BM at 295.1 K (previously 3.65 BM at 294.8 K$^{468}$). Thus the spin state transition is confirmed.

Mossbauer measurements commonly show a superposition of the separate quadrupole doublets of the two spin states in the intermediate temperature region; however, as seen
<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta E_Q$ (mm s$^{-1}$)</th>
<th>$\delta_{IS}$ (mm s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300.1</td>
<td>0.182</td>
<td>+0.416</td>
</tr>
<tr>
<td>274.7</td>
<td>0.194</td>
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<td>250.0</td>
<td>0.217</td>
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<tr>
<td>224.9</td>
<td>0.260</td>
<td>+0.413</td>
</tr>
<tr>
<td>199.7</td>
<td>0.376</td>
<td>+0.477</td>
</tr>
<tr>
<td>190.3</td>
<td>0.480</td>
<td>+0.434</td>
</tr>
<tr>
<td>184.8</td>
<td>0.716</td>
<td>+0.386</td>
</tr>
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<td>180.0</td>
<td>1.040</td>
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<td>175.2</td>
<td>1.227</td>
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<tr>
<td>170.0</td>
<td>1.355</td>
<td>+0.291</td>
</tr>
<tr>
<td>161.4</td>
<td>1.495</td>
<td>+0.279</td>
</tr>
<tr>
<td>155.1</td>
<td>1.565</td>
<td>+0.266</td>
</tr>
<tr>
<td>145.2</td>
<td>1.629</td>
<td>+0.263</td>
</tr>
<tr>
<td>135.0</td>
<td>1.676</td>
<td>+0.259</td>
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<td>124.8</td>
<td>1.705</td>
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</tr>
<tr>
<td>110.2</td>
<td>1.733</td>
<td>+0.260</td>
</tr>
<tr>
<td>95.0</td>
<td>1.751</td>
<td>+0.264</td>
</tr>
<tr>
<td>82.3</td>
<td>1.756</td>
<td>+0.265</td>
</tr>
<tr>
<td>165.8*</td>
<td>1.441</td>
<td>+0.278</td>
</tr>
<tr>
<td>175.0*</td>
<td>1.244</td>
<td>+0.306</td>
</tr>
<tr>
<td>185.3*</td>
<td>0.735</td>
<td>+0.401</td>
</tr>
<tr>
<td>194.9*</td>
<td>0.412</td>
<td>+0.436</td>
</tr>
<tr>
<td>215.1*</td>
<td>0.313</td>
<td>+0.444</td>
</tr>
</tbody>
</table>

a) Data are listed in the order of measurement. Those for increasing temperatures are marked with an asterisk in the T column. b) Experimental uncertainty ± 0.005 mm s$^{-1}$. c) Relative to metallic iron at 298 K. Experimental uncertainty ± 0.005 mm s$^{-1}$. 
Figure 5.17
57Fe Mossbauer Effect of Fe(salphen)NO at 300.1, 190.3, 180.0, 82.3 K. Solid Lines Represent Numerical Fittings to Lorentzian Line Shapes.
Figure 5.18 The Temperature Dependence of the Quadrupole Splitting $\Delta E_Q$ and the Isomer Shift $\delta_{IS}$
from Figure 5.17, only one quadrupole doublet is observed here. Thus, relaxation from the \( S = 1/2 \) to the \( S = 3/2 \) state and vice versa must be rapid on the time scale of Mossbauer spectroscopy, i.e. the rate that a given molecule interconverts (or spin flips) between the low spin and intermediate spin states is greater than ca. \( 10^7 \) s\(^{-1}\). This being so, the quadrupole doublet seen at each temperature has \( \delta_{IS} \) and \( \Delta E_Q \) values that are Boltzman weighted averages of the \( \delta_{IS} \) and \( \Delta E_Q \) values characteristic of the \( S = 1/2 \) and \( S = 3/2 \) spin states of the relative amounts of molecules in the sample that are in either state, similar to that seen for \([Fe(TMC)NO](BF_4)_2\).  

From the graph of \( \Delta E_Q \) versus \( T \) (K) in Figure 5.18 an estimate for the transition temperature of \( \sim 181 \) K may be made. Also, seen from Figure 5.18, the temperature dependence of \( \delta_{IS} \) exhibits no unusual behavior except in the region of the spin state transition, where in the intermediate region the \( \delta_{IS} \) values for the \( S = 1/2 \) and \( S = 3/2 \) states experience a continuous transition into each other due to the spin state transition. From the mean value of the isomer shift in this interval, the transition temperature may be estimated as \( T_c \sim 181 \) K in agreement with the value above, and from the trend of the magnetic data.

The apparent asymmetry of the 190.3 K spectrum in Figure 5.17 is not due to relaxation effects, but is caused by a small amount of impurity. The position of this impurity line at ca. 190 K coincides with the low velocity line of Fe(salphen)NO, thus producing an observed asymmetric total spectrum. The nature of this impurity remains unknown and it is possible that it may also be responsible for the observed
high values in the magnetic data measured here. Different line widths for the pure $S = 1/2$ and $S = 3/2$ states were also observed in the Mossbauer spectrum of Fe(salen)NO, a compound which slowly relaxes between the two spin states.\textsuperscript{466} An attempt to study the expected structural modification in Fe(salphen)NO by X-ray powder diffraction over the transition region was unsuccessful owing to the poor quality of the diffraction patterns, possibly due to poor crystallinity.

Another study of the $S = 3/2$ to $S = 1/2$ spin state transition of Fe(salphen)NO has recently appeared.\textsuperscript{469} The transition temperature was estimated to be 180 K in good agreement with the results here. In addition a magnetic phase transition due to antiferromagnetic coupling of the low spin iron centres was observed at $T = 6$ K.\textsuperscript{469} In the Mossbauer spectrum (versus sodium nitroprusside) at 300 K $\delta IS = 0.29$ mms\textsuperscript{-1} and $\Delta E_Q = 0.198$ mms\textsuperscript{-1}, while for a sample temperature of 100 K $\delta IS = 0.15$ mms\textsuperscript{-1} and $\Delta E_Q = 1.738$ mms\textsuperscript{-1}. In the EPR spectrum at 295 K a broad polycrystalline EPR signal was observed that changed markedly at about 180 K, and at 100 K two sharp lines were observed. The X-ray diffraction data were found to change continuously with temperature. From this study the authors were able to estimate the value of the electronic entropy, $\Delta S^0$, for the spin state transition of 286 J mol\textsuperscript{-1} K\textsuperscript{-1}, and concluded that significant changes in bond distances and/or angles must occur during the crossover. No discussion of the relaxation rate of Fe(salphen)NO was made, and this work should be considered complementary to the study here.

Based on previous molecular orbital schemes,\textsuperscript{188} Larkworthy and coworkers proposed\textsuperscript{468} that in the $S = 3/2$
state of Fe(salphen)NO (and therefore Fe(salen)NO also) that
the electronic configuration is \((d_{yz}, \pi^*_NO)^2, (d_{xz}, \pi^*_NO)^2,\)
\((d_{xy})^1, (\pi^*_NO, d_z^2)^1, (\pi^*_NO, d_yz)^1\) whereas in the \(S = 1/2\)
state the electronic configuration is \((d_{yz}, \pi^*_NO)^2,\)
\((d_{xz}, \pi^*_NO)^2, (d_{xy})^2, (\pi^*_NO, d_z^2)^1\). However, it was later
pointed out\(^{466}\) that the proposed configuration for the \(S =
1/2\) state where the unpaired electron resides in the \(d_z^2\)
orbital, while the \(\pi^*_NO\) antibonding orbitals are empty would
for an \([FeNO]^7\) complex lead to a linear FeNO geometry,\(^{151}\)
rather than the strongly bent geometry observed for
Fe(salen)NO. This criticism received support from the EPR
spectra of \(Fe(S_2CNMe_2)_2NO\) (which has linear FeNO geometry)
which indicates that the unpaired electron is in the \(d_z^2\)
orbital.\(^{470}\) Consequently, Feltham and coworkers\(^{467}\) proposed
the molecular orbitals for \([FeNO]^7\) shown in Figure 5.19. The
fact that both HS and LS forms of Fe(salen)NO have strongly
bent FeNO groups indicate that one component of \(\pi^*_NO\) is
occupied, while the fact that the square planar array of the
salen ligand is not distorted towards trigonal bipyramidal
group indicates that \(d_{xy}^2\) is not occupied in either spin
state.\(^{466}\) Feltham's orbital ordering\(^{466}\) corresponds to the
electron configuration for the quartet state of Fe(salphen)NO
proposed by Larkworthy\(^{468}\) if the separation between \(d_z^2\)
and \(\pi^*_NO\) is not too large. Such an electron configuration
places one of the three unpaired electrons in the \(\pi^*_NO\)
orbitals and this corresponds to the observed bent geometry
in the quartet state of Fe(salen)NO. Since the \(S = 1/2\) state
of Fe(salen)NO is known to have a bent geometry, Figure 5.19
was proposed to take account of this phenomena. The molecular
orbital diagrams are compatible for the HS and LS forms of
Figure 5.19 Schematic Molecular Orbital Levels for $S = 3/2$
and $S = 1/2$ [FeNO]$^7$ Iron Nitrosyl Complexes
Fe(salen)NO, Fe(salphen)NO, and [Fe(TMC)NO](BF$_4$)$_2$.

The observed effects on the Mossbauer spectra of Fe(salen)NO$^{466}$ were rationalised with the above orbital scheme, and can also be applied to the results here. The result of the transfer of electron density from a σ$^*$ orbital $d^2_{z^2}$ in the quartet state to an orbital with much greater d character $d_{xy}$ will increase the valence contribution to the electric field gradient in the low temperature form and consequently the quadrupole splitting $\Delta E_Q$ is larger for the $S = 1/2$ state. The orbital model presented by both Larkworthy et al.$^{468}$ and Feltham et al.$^{466}$ is consistent with the experimental data, but the real situation is very complex. The low symmetry of the iron Schiff base nitrosyls and the close spacing of the orbitals will mean that the levels are highly mixed, therefore the exact orbital composition is very dependent on the actual structures of the high and low temperature forms. Also, the extension of the conjugation (ethylene to phenylene bridge) in the equatorial Schiff base ligand should have an effect on the orbital levels, as will lack of suitable orbitals on the phenolic oxygens for electron delocalisation.

The spin crossover process of Fe(salphen)NO will be accompanied by structural changes to bond lengths and angles. The structural changes observed$^{465}$ between the low and high temperature forms for Fe(salen)NO have been mentioned above. An investigation of the crystal structure of Fe(salphen)NO at the two temperature extremes would be extremely useful since changes in bond lengths and angles should also be taken into account in the interpretation of the Mossbauer parameters of Fe(salphen)NO.
The rapid rate of spin transition observed for Fe(salphen)NO has only been reported in one other iron nitrosyl, [Fe(TMC)NO](BF$_4$)$_2$. However, this compound exhibits considerably different Mossbauer data to that of Fe(salphen)NO with $\Delta E_Q = 0.53$ mms$^{-1}$ and $\delta_{IS} = 0.46$ mms$^{-1}$ at 300 K ($S = 3/2$) and $\Delta E_Q = 0.645$ mms$^{-1}$ and $\delta_{IS} = 0.588$ mms$^{-1}$ at 10 K ($S = 1/2$); also [Fe(TMC)NO](BF$_4$)$_2$ has a high $v_{NO}$ of 1840 cm$^{-1}$ and a very distorted square pyramidal geometry with a linear FeNO group (FeNO $177^\circ$). The rapid rate of spin flipping in [Fe(TMC)NO](BF$_4$)$_2$ was attributed to extensive mixing of the quartet and doublet states by a vibronic mechanism, as a consequence of appreciable metal-ligand covalency and spin-orbital effects. In Fe(salen)NO the relaxation between spin states is slow on the Mossbauer timescale, the FeNO group is strongly bent (FeNO $147^\circ$ at room temperature) and $v_{NO}$ is low at 1712 cm$^{-1}$, and there is no distortion from square pyramidal geometry. Also, the Mossbauer parameters for Fe(salen)NO with $\Delta E_Q = 0.352$ mms$^{-1}$ and $\delta_{IS} = 0.440$ mms$^{-1}$ ($S = 3/2$) and $\Delta E_Q = 1.950$ mms$^{-1}$ and $\delta_{IS} = 0.281$ mms$^{-1}$ ($S = 1/2$) are reasonably similar to those found for Fe(salphen)NO. Because the structural characteristics of the two Schiff base nitrosyl complexes are expected to be basically similar it is thought that the rapid relaxation observed in [Fe(TMC)NO](BF$_4$)$_2$ is not a direct consequence of its different coordination geometry. The factors governing the rate of spin state relaxation in these iron nitrosyl complexes whether electronic, steric, or other in nature remain obscure at present.
REFERENCES


14. E. Antonini and M. Brunori, 'Haemoglobin and Myoglobin


32. S. W. Souci, Fleischwirtschaft, 10, 452-61, (1958), [CA 52 16641d]; M. Izumimoto, Obihiro Chikusan Daigaku Gakujutsu Kenkyu Hokoku, Dai-1-Bu, 11(2), 241-52, (1979), [CA 91 156207n].


82. K. Kon, N. Maeda, T. Suda, and T. Shiga, Taiki Osen


94. Reference 33, page 565.


289. Reference 105, page 775.


294. C. R. Kanekar and N. S. Biradar, *Current Sci.*, 35, 37,


337. C. W. Haigh and R. B. Mallion, Prog. NMR Spectrosc., 13, 303, (1980).


380. J. Kriege-Simonsen, T. D. Bailey, and R. D. Feltham,


Rapid Electronic Relaxation between $S = \frac{3}{2}$ and $S = \frac{1}{2}$ States in
$(N,N'-o$-Phenylenebis(salicylideneaminato))nitrosyliron, [Fe(salphen)NO]


Received October 2, 1986

Detailed studies of the $^{57}$Fe Mössbauer effect between 82.3 and 300.1 K have been employed to confirm the spin transition between the low-spin ($S = \frac{3}{2}$) and intermediate-spin ($S = \frac{1}{2}$) states in [Fe(salphen)NO] (salphenH$_2$ = $N,N'$-ethylenebis(salicylideneamine)). The spectra show that the transition is centered at $T_c \approx 181$ K, the electronic relaxation between the two spin states being rapid with $\tau \leq 1 \times 10^{-8}$ s. A linear dependence between the quadrupole splitting $\Delta E_Q$ and $\mu_B^2$ demonstrates that the $V_{zz}$ components of the EFG tensors of the two spin states are parallel and are of equal sign. The behavior of the Mössbauer absorption area in the region of $T_c$ indicates that marked changes of unit cell dimensions or molecular parameters or both are associated with the transition.

Spin-state transitions between $S = \frac{3}{2}$ and $S = \frac{1}{2}$ states in iron mononitrosyl complexes were observed for the first time by Earnshaw et al.$^1$ on the basis of magnetic susceptibility measurements and infrared spectra. Subsequently, the transition in [Fe(salen)NO] where salenH$_2$ = $N,N'$-ethylenebis(salicylideneamine) was studied in considerable detail.$^2$ The transition is of the discontinuous type, the transition temperature having been reported as $T_c = 175$ K. Hysteresis effects, which were observed both in magnetism$^3$ as well as in the absorption area of the Mössbauer effect,$^2$ indicate that the transition is thermodynamically first order. In the Mössbauer effect, individual spectra corresponding to the $S = \frac{3}{2}$ and $S = \frac{1}{2}$ states are observed. These spectra replace each other in the region of $T_c$ as the transition progresses in either direction of the temperature variation. Accordingly, the transition is slow on the Mössbauer effect time scale; i.e., the relaxation time for the change between the two spin states is slower than $1 \times 10^{-7}$ s. The structure of [Fe(salen)NO] was determined$^3$ at both 296 and 98 K, i.e., in the practically pure $S = \frac{3}{2}$ and $S = \frac{1}{2}$ states. The space group is orthorhombic $P$n$_2$$_1$n$_2$, with $Z = 4$ at both temperatures. The crystal structures are essentially similar with square-pyramidal coordination of the Fe atom, the NO group being in the axial position. At the molecular level, moderate changes of bond distances and angles are observed due to the transition. Moreover, a closer approach to coplanarity of the bond angle decreases from 147° above the transition to 127° below the transition. Thus the average distance between the Fe atom and the N atoms of the salen ligand remains constant at 2.02 Å at both temperatures. The quadrupole splitting $\Delta E_Q$ and isomer shift $\delta$ are the same in the $S = \frac{3}{2}$ state of iron, evidence for this being the discontinuous type. Mössbauer effect measurements performed at 300 and 77 K showed values of quadrupole splitting $\Delta E_Q$ and isomer shift $\delta$ rather similar to the values observed for the salen complex.

The present investigation has been initiated in order to characterize the spin-state transition in [Fe(salphen)NO] more thoroughly. The study is a contribution within our program to define the physical nature and the mechanism of spin-state transitions in more detail.$^5,6$

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**Experimental Section**

**Compound Preparation.** Samples of [Fe(salphen)NO] were prepared as described previously.$^4$ Ascorbic acid has been used in the preparative procedure to prevent contamination with the oxo-bridged iron(III) complex. The purity of the samples was checked by chemical analysis as well as by magnetic and Mössbauer effect measurements. Anal. Caled for [Fe(salphen)NO]: Fe, 60.03; H, 3.53; N, 10.50; S, 13.95. Found: C, 60.04; H, 3.75; N, 10.01.

**Physical Measurements.** The $^{57}$Fe Mössbauer spectra were measured with a spectrometer consisting of a constant-acceleration electromechanical drive and a Nuclear Data ND 2400 multichannel analyzer operating in the multiscale mode. The source used consisted of 50-mCi $^{57}$Co phodium at room temperature, the calibration being effected with a 25-μm iron foil absorber. All velocity scales and isomer shifts are referred to the iron standard at 298 K. For conversion to the sodium nitroprusside scale, add +0.257 mm s$^{-1}$. Variable-temperature measurements between 80 and 300 K were performed by using a custom-made cryostat, the temperature being monitored by means of a calibrated iron vs. constantan thermocouple and a cryogenic temperature controller (Thor Cryogenics Model E 3010-11). The Mössbauer spectra were least-squares fitted to Lorentzian line shapes, and the areas were corrected for the nonresonant background of the γ-rays. Measurements of X-ray powder diffraction at variable temperatures were obtained with a Siemens counter diffractometer equipped with an Oxford Instruments CP 108A flow cryostat and liquid nitrogen as coolant.

**Results**

The $^{57}$Fe Mössbauer effect for the complex [Fe(salphen)NO] has been measured between 82.3 and 300.1 K, the results being collected in Table I. In addition, Mössbauer spectra at 82.3, 180.0, 190.3, and 300.1 K are illustrated in Figure 1. The detailed temperature dependence of the quadrupole splitting $\Delta E_Q$ and the isomer shift $\delta$ is plotted in Figure 2. The measurements have been performed for increasing as well as for decreasing temperatures, the results displayed in the figure showing that no hysteresis effects are encountered. Figure 3 presents the temperature dependence of the line width $\Gamma$ and the total area $A$ from the Mössbauer spectra of the compound.

**Discussion**

From Figure 1 it is seen that all the measured $^{57}$Fe Mössbauer spectra for the [Fe(salphen)NO] complex show a unique doublet that collapses into a broad single line at the highest temperatures, e.g., 300.1 K. The quadrupole doublet that appears at 82.3 K is assigned to an $S = \frac{1}{2}$ state of iron, evidence for this being the

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Figure 1. $^{57}$Fe Mössbauer spectra of [Fe(salphen)NO] at 82.3, 180.0, 190.3 and 300.1 K. The full lines correspond to a least-squares fit to Lorentzian line shape.

Figure 2. Quadrupole splitting $\Delta E_Q$ (O and $\bullet$, left-hand scale) and isomer shift $\delta IS$ (□ and ■, right-hand scale) of [Fe(salphen)NO] as a function of temperature. Open signs correspond to decreasing temperature; solid signs correspond to increasing temperature.

Figure 3. Line width $\Gamma$ (mm s$^{-1}$; O and $\bullet$, right-hand innermost scale) and total area of the Mössbauer spectrum $A$ (□ and ■, left-hand scale) as functions of temperature. Open signs correspond to decreasing temperature; solid signs to increasing temperature. The dashed curve represents the intermediate-spin $S = \frac{3}{2}$ fraction $n_{\text{ss}}$ cf. eq. 1 (right-hand outermost scale). The values of $A$ have been corrected for the contribution of an unidentified impurity. The experimental uncertainty of $\Gamma$ is indicated for the individual points, that of $A$ is ±0.02.

Table I. $^{57}$Fe Mössbauer Effect Data for [Fe(salphen)NO]$^a$  

<table>
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<tr>
<th>$T$, K</th>
<th>$\Delta E_Q$, mm s$^{-1}$</th>
<th>$\delta IS$, mm s$^{-1}$</th>
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$^a$ Data are listed in the order of measurement. Those for increasing temperatures are marked with an asterisk in the $T$ column. For temperatures of 199.7 K and higher, line positions and line widths are strongly correlated.  
$^b$ Experimental uncertainty ±0.005 mm s$^{-1}$.  
$^c$ Relative to metallic iron at 298 K. Experimental uncertainty ±0.005 mm s$^{-1}$.  
$^d$ The total area is defined as $A = 2(\mu_{\text{meas}} - \mu_{\text{purp}})/(\pi f_G \Gamma_0)$ where $f_G$ is the Debye-Waller factor of the source and $\Gamma_0$ is the natural line width. Experimental uncertainty ±0.02.

encountered if the relaxation from the $S = \frac{1}{2}$ to the $S = \frac{3}{2}$ state and vice versa is rapid as compared to the time scale of Mössbauer spectroscopy ($\tau \leq 1 \times 10^{-8}$ s). The nucleus thus "sees" only the average of the $\Delta E_Q$ and $\delta IS$ values characteristic of the two spin states. It should be noted that the fractions $n_1$ and $n_H$ of the intermediate-spin ($S = \frac{3}{2}$) and low-spin ($S = \frac{1}{2}$) states, respectively, which will be used below, should in fact represent the probability of the system to be found in the corresponding state.

Detailed calculations of Mössbauer spectra for various relaxation times have been recently performed by Maeda and Takashima$^8$ on the basis of a stochastic model. In order to compare the present results with this type of calculations, the dependence of the quadrupole splitting $\Delta E_Q$ on the intermediate-spin fraction


Rapid Electronic Relaxation in [Fe(salphen)NO]

Figure 4. Quadrupole splitting $\Delta E_Q$ (mm s$^{-1}$) as a function of the effective magnetic moment $\mu_{\text{eff}}$ $(\mu_B)$. For the scale of the intermediate-spin ($S = 3/2$) fraction $n_l$ on the abscissa, refer to the text.

$n_l$ is required. The fraction $n_l$ can be calculated from the measured values of the effective magnetic moment $\mu_{\text{eff}}$ according to

$$n_l = \frac{\mu_{\text{eff}}^2 - \mu_l^2}{\mu_l^2}$$

In eq 1, we have assumed, for the effective magnetic moments of the spin states involved, the values $\mu_l = \mu(S = 3/2) = 3.1/2 = 1.73 \mu_B$ (spin-only value) and $\mu_l = \mu(S = 3/2) = 3.65 \mu_B$. These assumptions seem to be reasonable, since the measured values are $\mu_{\text{eff}} = 1.80 \mu_B$ at 87.8 K and 3.65 $\mu_B$ at 294.8 K. Here the effective magnetic moment values of the pure compound have been utilized. Moreover, the magnetic moment where the fraction of the $S = 3/2$ state assumes the value $n_l = 0.50$ obtained as $\mu_{\text{eff}} = 8.21/2 \mu_B$, and this value corresponds to the virtual transition temperature $T_c \approx 180$ K in good agreement with the results of Mössbauer effect measurements (see below).

The quadrupole splitting $\Delta E_Q$ appears to parallel the increase of the measured values of $\mu_{\text{eff}}^2$ in the transition region. This is demonstrated in Figure 4 where $\Delta E_Q$ is plotted as a function of $\mu_{\text{eff}}^2$. Evidently, the observed quadrupole splitting $\Delta E_Q$ is a linear function of $\mu_{\text{eff}}^2$ over the complete transition region where $\Delta E_Q$ is well represented by

$$\Delta E_Q = n_l \Delta E_Q^l + (1 - n_l) \Delta E_Q^l = \Delta E_Q^l - n_l(\Delta E_Q^l - \Delta E_Q^0)$$

Employing eq 1 for $n_l$, one immediately obtains

$$\Delta E_Q = \frac{\Delta E_Q^l + \Delta E_Q^l - \Delta E_Q^l}{\mu_l^2 - \mu_l^2 - \mu_l^2} - \frac{\Delta E_Q^l - \Delta E_Q^l}{\mu_l^2 - \mu_l^2} \mu_{\text{eff}}^2$$

(4)

In the range $\mu_l^2 \leq \mu_{\text{eff}}^2 \leq \mu_l^2$. If $\Delta E_Q^l$ and $\Delta E_Q^0$ are independent of temperature over the complete transition region, eq 4 represents exactly the observed behavior. This result demonstrates that the $V_{ss}$ components are indeed parallel and of equal sign. Moreover, from eq 2 and 4 one obtains the temperature-independent values $\Delta E_Q^l = 1.765$ mm s$^{-1}$ and $\Delta E_Q^0 = 0.175$ mm s$^{-1}$. These values may be compared with the measured values of the quadrupole splitting at the two limiting temperatures, viz. $\Delta E_Q = 0.182$ mm s$^{-1}$ at 300.1 K and $\Delta E_Q = 1.756$ mm s$^{-1}$ at 82.3 K. The center of the exchange of $\Delta E_Q$ provides an estimate for the transition temperature $T_c \approx 181$ K, viz. Figure 2, which value is consistent with the value of $T_c$ obtained on the basis of magnetic data.

The temperature dependence of the isomer shift exhibits no unusual behavior apart from the region of the spin-state transition. It is reasonable to expect, for spin-invariant complexes, that the isomer shift should increase with decreasing temperature, thus reflecting the temperature dependence of the second-order Doppler shift. This is indeed observed in the temperature range below $\sim 130$ K for the $S = 1/2$ state and above $\sim 200$ K for the $S = 3/2$ state; cf. Figure 2. In the intermediate region, the $\delta^0$ values for the $S = 1/2$ and $S = 3/2$ states experience a continuous transformation into each other due to the spin-state transition. From the mean value of the isomer shift in this interval, the transition temperature is again estimated as $T_c \approx 181$ K.

The line widths ($\Gamma$) for the two Mössbauer lines of the practically pure $S = 1/2$ state at low temperatures are close to 0.280 mm s$^{-1}$ and almost identical; similarly, for the pure $S = 3/2$ state at high temperatures, values of $\Gamma$ close to 0.46 mm s$^{-1}$ are obtained. The temperature dependence of $\Gamma$ in the transition region is displayed in Figure 3 and corresponds closely to the behavior of the intermediate ($S = 3/2$) spin fraction, $n_l$. The apparent asymmetry of the 190.3 K spectrum in Figure 1 is not due to relaxation effects as one could assume but is rather caused by a small amount of impurity. This impurity contributes at low temperature $\sim 4\%$ to the total area, its relative amount increasing at higher temperatures due to the rapid decrease of the total area, which is likewise displayed in Figure 3. In addition, the position of the impurity line at about 190 K coincides with the low-velocity line of the compound, thus producing the observed asymmetric total spectrum. The values of $\Gamma$ shown in Figure 3 have been obtained by a numerical fit of the Mössbauer spectra taking account of the mentioned impurity. Different line widths for the pure $S = 1/2$ and $S = 3/2$ states have been also encountered in the slowly relaxing compound [Fe(salen)NO].

The temperature dependence of the total area $A$ of the Mössbauer lines displayed in Figure 3 shows that the recoil-free fraction $f$ decreases considerably on transition from the $S = 1/2$ to the $S = 3/2$ state. This is in close correspondence to the findings for [Fe(salen)NO]. The behavior of $A$ in the region of $T_c$ indicates that some kind of modification of the lattice accompanies the change of spin state. On the basis of the analysis of multitemperature structure data for spin transition compounds it may be assumed that this behavior is caused by the modification of unit cell dimensions or the changes of metal-ligand bond lengths and bond angles at the transition or both. Similar changes of the recoil-free fraction at a spin-state transition have been encountered before.

An attempt has been made to follow the expected structural modification by measurements of the powder X-ray diffraction of [Fe(salphen)NO] over the transition region. Unfortunately, the diffraction patterns did not show sufficient details, possibly due to the poor size of the crystals of the substance.

Although in most spin-state transitions the relaxation between the two states is slow as compared to the time scale of Mössbauer spectroscopy, examples for rapid relaxation are known. These examples comprise, in particular, systems involving the spin states $^4A_2(t_2^2e^2)$ and $^2T_2(t_2^2)$ of iron(III) such as a number of dithiocarbamato, monothiocarbamato, and diselenocarbamato complexes. More recently, rapid interconversion of spin states has been reported for various Fe$^2+$/O$_2$ complexes with Schiff base ligands.

to be rather sensitive to slight changes in the constituents of the complex that are rather distant from the metal atom primarily concerned with the change of spin state. Thus changes in the counterion\(^{17}\) and in ligand substituents\(^{16}\) may drastically alter the character of the observed Mössbauer spectra. The exact origin of these effects, whether electronic, steric, or other in nature, is not known with certainty.

As far as iron nitrosyl complexes are concerned, the only reported example of a rapid \(S = \frac{3}{2} - \frac{1}{2}\) spin-state transition is \([\text{Fe}(\text{TMC})\text{NO}]\)(BF\(_4\))\(_2\) where TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tetramethylcyclam).\(^{18}\) However, this compound exhibits Mössbauer parameters considerably different from those of \([\text{Fe}(\text{salphen})\text{NO}]\). Thus at 300 K, the quadrupole splitting and the isomer shift of \([\text{Fe}(\text{TMC})\text{NO}]\)(BF\(_4\))\(_2\) have been reported as \(\Delta E_Q = 0.53 \text{ mm s}^{-1}\) and \(\delta^{IS} = +0.46 \text{ mm s}^{-1}\), respectively, whereas at 10 K, the values \(\Delta E_Q = 0.645 \text{ mm s}^{-1}\) and \(\delta^{IS} = +0.588 \text{ mm s}^{-1}\) have been obtained. The high-temperature values may be compared with the magnetic moment \(\mu_{eff} = 3.62 \mu_B\) at 286 K where the intermediate-spin (i.e. \(S = \frac{1}{2}\)) fraction may be estimated as \(n_1 \approx 0.84\); the low temperature values may be set against the moment value \(\mu_{eff} = 2.66 \mu_B\) at 4.2 K where \(n_1 \approx 0.34\). It should be noted that the \([\text{Fe}(\text{TMC})\text{NO}]\)(BF\(_4\))\(_2\) complex has a nearly linear FeNO group, a high NO stretching frequency of 1840 cm\(^{-1}\), and a geometry intermediate between a square pyramid and a trigonal bipyramid.\(^{18}\) On the other hand, the \([\text{Fe}(\text{salen})\text{NO}]\) complex, which shows a \(S = \frac{3}{2} - \frac{1}{2}\) transition of the discontinuous type, is characterized by Mössbauer parameters much more similar to those found for \([\text{Fe}(\text{salphen})\text{NO}]\), although the relaxation between the spin states is slow. Thus for the \(S = \frac{1}{2}\) state, \(\Delta E_Q = 0.352\) and \(\delta^{IS} = +0.440 \text{ mm s}^{-1}\), whereas for the \(S = \frac{3}{2}\) state, \(\Delta E_Q = 1.950\) and \(\delta^{IS} = +0.281 \text{ mm s}^{-1}\) have been reported.\(^2\) In \([\text{Fe}(\text{salen})\text{NO}]\), the FeNO group is strongly bent,\(^1\) the NO stretching frequency is low\(^1\) at 1712 cm\(^{-1}\), and the coordination unit is not noticeably distorted toward trigonal-bipyramidal geometry. It may be therefore assumed that the most significant structural characteristics in \([\text{Fe}(\text{salphen})\text{NO}]\) are similar to those of \([\text{Fe}(\text{salen})\text{NO}]\) rather than to those observed for \([\text{Fe}(\text{TMC})\text{NO}]\)(BF\(_4\))\(_2\). The rapid relaxation between the spin states \(S = \frac{1}{2}\) and \(S = \frac{3}{2}\) in the \([\text{Fe}(\text{TMC})\text{NO}]\)(BF\(_4\))\(_2\) complex is therefore not a consequence of different coordination geometry of this complex and must be rather determined by other factors.

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Ligand Field Effects in the Nuclear Magnetic Shielding of Nitrogen-15 and Cobalt-59 in Bent Nitrosyl Complexes of Cobalt(III)

Paul A. Duffin,1 Leslie F. Larkworthy,*1 Joan Mason,*2 Alan N. Stephens,1 and Russell M. Thompson1

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A range of square-pyramidal complexes of cobalt(III) with a bent apical nitrosyl ligand has been prepared and examined by $^{15}$N and $^{59}$Co NMR spectroscopy, in a study of nephelauxetic and spectrochemical effects at the metal and nitrogen nuclei in the bent Co–NO chromophore. The basal ligands in this comparison include dithiocarbamate, quadridentate Schiff base or porphine, and bis-chelating diamine or oximate, so as to give S$_4$, S$_2$N$_2$, N$_4$, OON or ON, ON coordination in the plane and a range of substituents in the chelate and phenylene rings. The shielding of both cobalt and nitrogen tends to decrease with decrease in the $M$(d)–$\pi^*(\text{NO})$ back-bonding, as indicated by the MN and NO bond distances, the MNO angle and the NO stretching frequency. The shieldings decrease from sulfur to nitrogen to oxygen coligands and also with electron withdrawal by ring substituents (and vice versa), i.e., with decrease in the ligand field splitting and in the nephelauxeticism of the coligands. These parallelisms of the cobalt and nitrogen shielding accord with the orbital theory that was developed to explain the bending of the MNO ligand and influences of the metal and coligands. Significant interdependence of spectrochemical and nephelauxetic effects at cobalt and nitrogen arises from the degree of overlap and similarity in energies of the frontier orbitals for the paramagnetic circulation at nitrogen [$n$(N)–$\pi^*(\text{NO})$] and at cobalt (d–d).

Introduction

$^{15}$N NMR spectroscopy is a sensitive indicator of the nature of the nitrosyl ligand, whether linear,3,4 strongly bent with MNO angle 120–130°,5–8 partially bent (as e.g., in dinitrosyls),9 or bridging.10 In terminal nitrosyls the nitrogen shielding decreases

(1) University of Surrey.
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(3) Botto, R. E.; Klothammer, B. W. S.; Legzdins, P.; Roberts, J. D. Inorg. Chem. 1979, 18, 2049.

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Bent Nitrosyl Complexes of Co(III)

Chart I

1. [Co(NO)(salox)]
2a. [Co(NO)(salox)], R=Me, R'=H
b. [Co(NO)(salox)], R=R'
c. [Co(NO)(salox)], R=Ph, R'=H
3. [Co(NO)(benzal)]
4a. [Co(NO)(salen)], R=R'+H
b. [Co(NO)(salen)], R=6-6-Bu, R'+H
c. [Co(NO)(salox)], R=3,5-(NO2)2, R'+H
d. [Co(NO)(salen)], R=3-Me, R'+H
5. [Co(NO)(salphen)]
6a. [Co(NO)(salox)], R=R'+H
b. [Co(NO)(salox)], R=3-OCH3, R'+H
c. [Co(NO)(salox)], R=3-OCH3, R'+H
d. [Co(NO)(salox)], R=3-NO2, R'+H
e. [Co(NO)(salox)], R=3,5-(NO2)2, R'+H

The shift increases as the MNO angle decreases. The strong deshielding in the strongly bent (MNO)7 nitrosyls of the present study resembles that in main-group nitroso (R-NO) or nitrosyl (NOX) compounds, which arise from low-energy (Na) -> (NO) paramagnetic circulations (magnetic dipole allowed excitations).11 These are made possible in metal nitrosyls by the development of a lone pair on the nitrogen as the nitrosyl bends, and the strongly bent ligand is usefully viewed as NO attached (to low-spin) cobalt(III).

The ability of the NO ligand to bend, in contrast to related ligands such as CO or N2, was explained in terms of the similarity of the energies of the HOMO and LUMO at nitrogen, the n(N) and (x*NO) orbitals, to those of the ligand field orbitals.12-14 Thus the shielding theory that suggested the strong dependence of the nitrogen shift on the degree of MNO bending also suggests a link between the nitrogen shift and that of the transition-metal nucleus. An objective of our investigation has been to explore this connection. The shielding of the metal nucleus depends on d-d paramagnetic circulations,15 which are sensitive (particularly with relatively weak ligands, as in the present study) to the ligand field splittings, which are modified by the interaction with the frontier orbitals of the nitroso which mediate the nitrogen shifts. Such a connection has more than theoretical interest since the reactivity, indeed lability, of the bent nitrosyl ligand is bound up with the ease of internal M(dx) -> NO(n) redox processes as involved in the bending.14,16,17 The "lone pair" on nitrogen is in fact a loose term for electron density in the MNO plane, which is high lying (avoids the x bonds) and also delocalized in d orbitals in the MNO plane, as discussed below, while the x*(NO) orbitals are good x-acceptors. Overall, shift of d-electron density onto nitrogen with bending of MNO predisposes the metal to reaction with nucleophiles, and the nitrosyl to reaction with electrophiles.

Thus the combination of 15N and 59Co NMR is particularly suitable as a probe of these orbital interactions. The remarkable range of over 850 ppm in 15N shift in cobalt nitrosyl complexes, depending on the MNO angle, may be linked to the equally remarkable range of 59Co shifts, over 19,000 ppm in toto, the largest range for spin-paired compounds of any nucleus. The square-pyramidal complexes of cobalt with bent apical nitrosyls are appropriate to this study, for two reasons. First, although five-coordinate, none show any signs of fluxionality, as observed in five-coordinate nitrosyl complexes with monodentate coligands and associated with an alternative trigonal-bipyramidal structure.8 The spectroscopic evidence confirms that the square-pyramidal structure is maintained in solution in each case. The quadridentate Schiff base ligands have little flexibility when coordinated, the keto and salox nitrosyls also are kept as square pyramids by strong hydrogen bonds among the basal ligands,2 and the complexes with bidentate ligands, such as dithiocarbamate, follow suit. Second, there is considerable scope for variation of the basal quadridentate or bis-chelate ligands (cf. 1-6; see Chart I) whether Schiff base,14,20,21 porphine, oxime,19 diamine, dithiocarbamate, etc. A

A further incentive has been that the distinctive position of the resonances makes the NMR spectroscopy a useful method of investigation of the redox reactions of the bent nitrosyls, some of which are evident in the NMR spectra, particularly with long acquisition times. The $^{13}$Co shifts and line widths provide a useful check on the nature of the species in solution, the dispersion of the shifts making up for the breadth of the lines. The bent nitrosyls of cobalt can function as oxygen-transfer agents, via a nitrosyl-nitro couple, and oxidation of the related myoglobin nitrosyl (in cured meats) is of importance to the food industry. The nitro ligand resembles the bent nitrosyl in its liability: linkage isomerism, ligand exchange, and reduction of Co(III) to Co(II) with loss of the NMR spectrum have been observed.

Experimental Section

To maximize sensitivity, the $^{15}$N spectra were measured with 99% $^{15}$-enrichment of the nitrosyl, on a 400-MHz spectrometer. Infrared spectra of Nujol mulls, KBr disks, or solutions of the $^{13}$NO and $^{15}$NO complexes were recorded over the range 4000–400 cm$^{-1}$.

The salenH$_2$ ligand, $N,N'$-ethylenbis(monothioacetylamidine) was prepared as before from salenH$_3$ and ethylenediamine(acetylamidine). The salenH$_3$ salphenH$_3$, 7-MesalenH$_3$, 5-NO$_3$salenH$_3$, and 5,5-(NO)$_3$salenH$_2$ ligands were obtained by condensation of the appropriate aldimeine by standard methods. 5,5-Dinitrosalicylaldehyde was prepared by nitration of salicylaldehyde, and the other aldehydes and 2-hydroxyacetophenone were obtained commercially. The oxidimes were prepared by reaction of hydroxylamine hydrochloride with salicylaldehyde or 5-chlorosalicylaldehyde.

The amibenH$_2$ ligand, $N,N'$-ethylenbis(2-aminobenzylideneamine), was made by the reduction of 2-nitrobenzaldehyde to 2-aminobenzaldehyde with sodium nitrite and supported by extensive hydrogen-bonding to the NH$_2$ groups. The cobalt spectrum shows an additional weaker line at higher frequencies, as expected for an O-bonded nitrosyl. In [Co(NO)(amben)$_2$] (3) three isomers are possible in principle, depending on the orientations of the nitrosyl and the two N–H groups. Both N–H groups project from the same side of the [Co(amben)] plane the attack of NO from the other side is presumably favored. In the cobalt spectrum, however, the additional weaker line is much sharper. In [Co(NO)(acacpn)] (2b) the nitrosyl and the methyl group may project from the same side or opposite sides of the Co(acacpn) plane, and the latter may be favored. The ligand is disymmetric, so that $R$ and $S$ forms are possible.

An interesting example of solid-state effects related to flexibility in the basal ligand is afforded by [Co(NO)(salen)] and its derivatives. The solid-state structure of [Co(NO)(salen)] contains two adjacent molecules that differ in their salen conformations and NO distances (1.071 and 1.163 Å), although the M–N distances are the same within the experimental uncertainty (mean values are given in Table 1). The conformation in [Co(NO)(7-Mesalen)] resembles the umbrella conformer in the [Co(NO)(salen)] structure, in which the two planes containing the phenylene groups are angled away from the nitrosyl, with a few degrees to the COONN plane; in the other (stepped) conformer of [Co(NO)(salen)] one of the phenylene planes is angled toward the nitrosyl and one is angled away from the nitrosyl. The two

Results and Discussion

Spectroscopic Measurements. Table I gives NMR and IR spectroscopic measurements for the square-pyramidal complexes with bent apical nitrosyl and chelating basal ligands. Structural parameters are included for comparison, so far as these are known, i.e., for the bis(dithiocarbamate), bis(ethylenediamine), TPP, acacen and benacen, sal, 7-Mesalen, bis(keox), - (salox), and -5-(C104) nitrosyls.

The NMR and IR spectroscopic evidence confirms that the square-pyramidal structure observed in the solid state persists in solution. Work in progress with solid-state $^{15}$N NMR has shown relatively small differences in nitrogen shift from the solution values: the isotropic shift for [Co(NO)(7-Mesalen)] is 719 ppm as compared with 710 ppm in CH$_2$Cl$_2$ solution. As mentioned above, none of the spectra show signs of fluxionality. The IR spectra are very rich, and there is a high degree of correspondence of the [Co(NO)(L)] spectrum (except for the band representing the NO stretching vibration) with that of the parent near-planar complex, whether in the solution or in the solid phase. Each of the complexes studied was made with $^{14}$NO and with $^{15}$NO, but the only significant spectral differences were those of the NO stretching frequencies, because of the abundance of the basal ligand vibrations.

Two nitrosyl resonances differing in intensity were observed for certain of the compounds, showing the presence of distinct species. In the solution of [Co(NO)(en)$_2$](ClO$_4$)$_2$ these might be complexes with either acetone or perchlorate at the ammonia site. In the solid state a perchlorate ligand was found, trans to the nitrosyl, and supported by extensive hydrogen-bonding to the NH$_2$ groups. The cobalt spectrum shows an additional weaker line at higher frequencies, as expected for an O-bonded nitrosyl. In [Co(NO)(amben)$_2$] (3) three isomers are possible in principle, depending on the orientations of the nitrosyl and the two N–H groups. Both N–H groups project from the same side of the [Co(amben)] plane the attack of NO from the other side is presumably favored. In the cobalt spectrum, however, the additional weaker line is much sharper. In [Co(NO)(acacpn)] (2b) the nitrosyl and the methyl group may project from the same side or opposite sides of the Co(acacpn) plane, and the latter may be favored. The ligand is disymmetric, so that $R$ and $S$ forms are possible.

An interesting example of solid-state effects related to flexibility in the basal ligand is afforded by [Co(NO)(salen)] and its derivatives. The solid-state structure of [Co(NO)(salen)] contains two adjacent molecules that differ in their salen conformations and NO distances (1.071 and 1.163 Å), although the M–N distances are the same within the experimental uncertainty (mean values are given in Table 1). The conformation in [Co(NO)(7-Mesalen)] resembles the umbrella conformer in the [Co(NO)(salen)] structure, in which the two planes containing the phenylene groups are angled away from the nitrosyl, with a few degrees to the COONN plane; in the other (stepped) conformer of [Co(NO)(salen)] one of the phenylene planes is angled toward the nitrosyl and one is angled away from the nitrosyl. The two
Various solvent effects are possible, such as loose association of a solvent molecule trans to the nitrosyl when a coordinating solvent such as Me₂SO or acetone is used, as may be necessary to get the complex into solution. Only small changes in the electronic spectrum, however, were reported on addition of nitrogen or phosphorus bases to solutions of the bent nitrosyls.²⁰ It has also been suggested that increased polarity of the solvent may influence the MNO angle by favoring a more polar form of the nitrosyl.²³ The magnitude of such effects can be seen by examination of Table I. As to the complexes with bidentate ligands, which might show greater flexibility, effectively the same nitrogen shift is observed for [Co(l5NO)(S₂CNMe₂)] in chloroform or Me₂SO solvent, and the difference in nitrogen shift is only 10 ppm for the two peaks given by [Co(l3NO)(en)₂]²⁺ which may represent.

References for the structural data are given in the text. IR stretching frequencies were measured on the Nujol mull, unless otherwise indicated. The frequencies are about 30 cm⁻¹ lower in the ²¹N compounds.* CH₃Cl. * CHCl₃. * Me₂SO. * Acetone. * CCl₄. * KBr disk.


Table I. Spectroscopic and Structural Data for Square-Pyramidal Cobalt(III) Complexes with a Bent Apical Nitrosyl

<table>
<thead>
<tr>
<th>compd</th>
<th>δ(¹⁵N)</th>
<th>MNO/deg</th>
<th>NO/Å</th>
<th>MN/Å</th>
<th>ν(¹⁴NO)/cm⁻¹</th>
<th>δ(⁵⁹Co)</th>
<th>W₁₂/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(NO)(en)(S₂CNMe₂)²⁺</td>
<td>717.5</td>
<td>1.806</td>
<td>0.38</td>
<td>1.806</td>
<td>8478</td>
<td>2100</td>
<td>2100</td>
</tr>
<tr>
<td>Co(NO)(en)(ClO₄)²⁻</td>
<td>727.6</td>
<td>1.806</td>
<td>0.38</td>
<td>1.806</td>
<td>7612</td>
<td>2100</td>
<td>2100</td>
</tr>
</tbody>
</table>

δ(¹⁵N) relative to neat liquid nitromethane and δ(⁵⁹Co) relative to aqueous K₃[Co(CN)₆]₃ high frequency positive; br signifies a broad resonance (ca. 20 Hz), w a weak (vw, very weak) additional resonance. W₁₂ is the ¹⁵N line width at half-height, not optimized. Measured at 25 °C in deuterated solvents d-x. IRA stretching frequencies were measured on the Nujol mull, unless otherwise indicated. The frequencies are about 30 cm⁻¹ lower in the ²¹N compounds. * CH₃Cl. * CHCl₃. * Me₂SO. * Acetone. * CCl₄. * KBr disk.


Table II. Analytical Data for the New Nitrosyl Complexes

<table>
<thead>
<tr>
<th>compd</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(NO)(ammon)</td>
<td>54.4 (54.4)</td>
<td>4.4 (4.6)</td>
<td>20.0 (19.8)</td>
<td>15.6 (16.1)</td>
</tr>
<tr>
<td>Co(NO)(acetacn):H₂O</td>
<td>45.9 (45.5)</td>
<td>5.9 (6.5)</td>
<td>12.1 (12.2)</td>
<td>12.1 (12.2)</td>
</tr>
<tr>
<td>Co(NO)(7-Mesalen)</td>
<td>56.2 (56.4)</td>
<td>4.6 (5.3)</td>
<td>10.6 (11.0)</td>
<td>10.6 (11.0)</td>
</tr>
<tr>
<td>Co(NO)(5,5-Busalen)</td>
<td>61.5 (61.7)</td>
<td>6.6 (6.4)</td>
<td>9.0 (9.9)</td>
<td>9.0 (9.9)</td>
</tr>
<tr>
<td>Co(NO)(3,5-(NO₂)₂salen)</td>
<td>36.8 (35.9)</td>
<td>1.7 (1.9)</td>
<td>18.1 (18.3)</td>
<td>18.1 (18.3)</td>
</tr>
<tr>
<td>Co(NO)(5-Cisalox)²⁻</td>
<td>38.9 (39.1)</td>
<td>2.4 (2.3)</td>
<td>9.1 (9.8)</td>
<td>9.1 (9.8)</td>
</tr>
<tr>
<td>Co(NO)(5,5-NOSalox)²⁻</td>
<td>36.8 (37.4)</td>
<td>2.9 (2.8)</td>
<td>14.3 (15.6)</td>
<td>14.3 (15.6)</td>
</tr>
</tbody>
</table>

NO stretching frequencies given for the salphen compound in Table I, similarly, suggest two NO environments in the solid, and doubling of the ¹⁵N peaks is observed in the solid-state NMR spectrum.²⁶

Various solvent effects are possible, such as loose association of a solvent molecule trans to the nitrosyl when a coordinating solvent such as Me₂SO or acetone is used, as may be necessary to get the complex into solution. Only small changes in the electronic spectrum, however, were reported on addition of nitrogen or phosphorus bases to solutions of the bent nitrosyls.²⁰ It has also been suggested that increased polarity of the solvent may influence the MNO angle by favoring a more polar form of the nitrosyl.²³ The magnitude of such effects can be seen by examination of Table I. As to the complexes with bidentate ligands, which might show greater flexibility, effectively the same nitrogen shift is observed for [Co(¹⁵NO)(S₂CNMe₂)²⁺] in chloroform or Me₂SO solvent, and the difference in nitrogen shift is only 10 ppm for the two peaks given by [Co(¹⁴NO)(en)²⁺]²⁺ which may represent.

Figure 1. Correlation of the nitrogen shift with the Co-N bond distance in the bent nitrosyl ligand.

association with acetone or perchlorate. Change from a chlorinated solvent to Me$_2$SO makes little difference in the nitrogen shifts of the benacen and salen nitrosyls (2c and 4a), although a larger change, of 50 ppm, is observed for [Co($^{15}$NO)(3-MeO-salox)$_2$] (6b).

Changes of a few wavenumbers in the NO stretching frequency, or 20 cm$^{-1}$ at most, are observed from the solid state to solution in CHCl$_3$, CH$_2$Cl$_2$, or Me$_2$SO for theacen complexes. Certain compounds show larger solvent effects: in the salen complex (4a) this frequency is 40 cm$^{-1}$ less in Me$_2$SO or a Nujol mull than in CH$_2$Cl$_2$, and in the keto complex (6e) the frequency is 40 cm$^{-1}$ less in Me$_2$SO than in a Nujol mull (so these differences are not systematic). In the keto compound, however, the $^{15}$N shielding is reduced by 40 ppm in the solid state compared to that in the solution. There may be a tendency for medium effects to increase with deshielding of the nitrogen, perhaps because small changes have a greater proportionate effect when excitation energies are small.

Correlation of the Nitrogen Shielding with MNO Structure. Figure 1 shows that there is a tendency for the nitrogen shielding to increase with decrease in the M—NO bond distance. This bond length reflects back-bonding in the M—N=O ligand, which is very strong for linear nitrosyls and less strong but still important in the bent ligand, as will be discussed. The M—NO distances, 1.7–1.85 Å in Table I, are reduced compared with MN bond lengths of 1.9–2.0 Å in the chelating ligands, and values near 2.0 Å in ammine or amine complexes in general.

Figure 2 shows the related trend for the nitrogen shielding to increase with decrease in the NO stretching frequency, and concomitant trends of increase in NO bond length and MNO angle are evident in Table I. These correlations are expected to be poorer than that with the M—N bond length because of the sensitivity of the geometry of the projecting nitrosyl to crystal forces and solvent interactions. As mentioned, these solvent effects are mostly small, but for certain compounds may be as large as 40 cm$^{-1}$.

Correlation of the Nitrogen and Cobalt Shifts. Figure 3 tests the prediction of a tendency for the nitrogen and cobalt shielding to increase together, both increasing with increase in the backbonding. The connection between these three is an intricate one, and a good correlation is not to be expected, as independent influences on the cobalt and nitrogen shielding are present also. The trend is discernible, with considerable scatter, some of which is systematic, as will be discussed.

In an "atom in a molecule" formulation of the shielding for a second-row element such as nitrogen the paramagnetic term $\sigma_p$, which largely determines the chemical shift $\delta$ (the two being defined with opposite sign), is given by

$$\delta = (2\mu_0/3\pi)\mu^2(\Delta E)^{-1}\langle r^3 \rangle P,$$

where $\mu_0$ is the magnetic moment, $\mu$ is the magnetic moment, $\Delta E$ is the energy difference between the ground and excited state, $r$ is the distance, and $P$ is the probability of spin. The term $\langle r^3 \rangle$ is a property of the atom in the molecule, and $P$ is the probability of spin.
excitation energy may be used. The magnetic field mixes into the ground state those (p-p) excited states that involve charge circulation (are magnetic dipole allowed), the more so the lower the excitation energy $\Delta E$. The paramagnetic circulations are the more effective (deshielding) the closer they are to the resonant nucleus $(r^3_p)$ large, and the larger is $P$, the angular imbalance of charge in the valence shell (an angular momentum term).

Several factors combine to increase the range, or sensitivity, of the nitrogen shifts in nitrosato nitrosyl compounds. $P$ is large for a bent planar group (and decreases with decrease in the MNO angle). The $n(N) = s(N)$ (NO) state is particularly low-lying since the HOMO is largely nonbonding, and the LUMO is low because of the electronegativity of nitrogen and oxygen. The $p(N)$ electron radius $(r_p)$ is reduced by the electronegative substituent oxygen but is increased by delocalization into d orbitals in the complex; the influence of the radial term $(r^3_p)$ is a quasi-nephelauxetic, or electron-cloud-expanding, effect.

For a transition metal the corresponding formulation is

$$-P = \frac{(2\mu_p/3\pi)\mu_B^2(\Delta E)^1}{3}\left(r^3_p\right)D_1$$

where $D_1$ is now the imbalance of charge in the d shell, $\Delta E$ represents an effective (or weighted mean) ligand field splitting, and $r$ is the d-electron radius. The deshielding of the metal nucleus is mediated by paramagnetic circulations of d electrons, and is greater the closer the d electrons to the metal nucleus and the smaller the energy or energies of d-d excitation. The $D_1$ term takes a maximum value of 12 when three d orbitals are filled and two are empty $(d^6)$ or vice versa (and varies rather little for a given coordination geometry and similar ligands), whereas $P$ takes a maximum value of 2. The very large shift range observed for cobalt can thus be related to its position in the periodic table:15 ligand field excitation energies tend to be lower in the first transition series than in the second or third, the radial function $(r^3_p)$ increases across the series with increase in effective nuclear charge, and the angular imbalance is large in the open d shells.

The energy term gives the shifts a "spectrochemical" dependence: the deshielding tends to decrease with decrease in the ligand field splitting. Indeed, the nitrogen and cobalt shielding was observed to decrease with decrease in energy of the visible absorption band (to which d-d and M $\rightarrow$ L charge-transfer excitation contribute) in the bent nitrosyls so far documented (thiocarbamate, acacen, salen, etc.). Following the spectrochemical series,40 the shielding would be expected to decrease in the sequence of basal ligating atoms $N > O > S$. The radial factor, however, imposes a nephelauxetic influence, tending to decrease the shielding as $S > N > O$, with decrease in delocalization (from the softer to the harder ligand).40 The two influences therefore combine to show the orbital interactions as the nitrosyl ligand bends. These can be associated also with electron withdrawal by phenyl, naphthyl, or other aromatic rings in the ligand, as in the sequence (in NO shielding) of the $N_4$ ligands (en)$_2$ $>$ ambcn $>$ TPP, and from acacen to benacen or salen, or from salen to salphen.

Overall, deshielding tends to correlate with reduction in strength of covalent bonding to the metal. Here, as in other series of compounds, low shielding of the metal nucleus correlates with instability of the complex.42 Conversely, covalency (and nephelauxetic) shielding are higher for the complexes with ligating sulfur.

The introduction of a nephelauxetic parameter $\beta$, derived from optical spectroscopy, into the shielding equation, has been achieved for a group of cobalt(III) complexes with ligating F, O, N, C, Cl, and Br.43 The energy term was expressed as $h/\beta$, where $h$ is the energy of the first (lowest energy) d-d band, and the radial function as $(r^3_p)\beta$. $\beta$ is defined as the ratio of the values of the Racah (interelectron repulsion) parameter $B$ in the complex and in the gaseous metal ion, and is obtained from the interval between the first and second d-d bands. A good fit to the shielding equation, extrapolating to the value of the magnetogyric ratio for $^{59}$Co, was obtained for orthoaxial complexes, in which the ligands lie on the Cartesian axes, but greater scatter arises with the distorted geometries of chelating ligands.43 This is a further factor that contributes to the blurring of the trends observed for the nitrosyls under discussion. The shielding of the nitrosyl ligand has a smaller bite than the others in Table I, and the points for the dithiocarbamate complexes lie above the lines determined by the other compounds in Figures 2 and 3.

Mixing of Nitrosyl and Ligand Field Orbitals. Interdependence of the $^{15}$N and $^{59}$Co shielding is a consequence of the matching of the $\sigma*(NO)$ and d orbital energies, and extensive mixing of the orbitals, which explains the range of MNO geometries.12,13 The low-lying $\sigma*(NO)$ orbitals are excellent d-electron acceptors, and $\sigma*(M-N)$ electron density in [MNO] complexes can be stabilized as a lone pair on nitrogen in the bent ligand.

Energy level diagrams have been calculated by the Wolfsberg–Heilmann method for [Co(NO)(NH$_3$)$_2$] and related ions with different coordination numbers.41 For piperazine and some other compounds, low-lying $\sigma*(NO)$ orbitals for nitrosyl bonded to five-coordinate iridium,13 to show the orbital interactions as the nitrosyl ligand bends. These results have been adapted in Figure 4 so as to show, schematically, the interrelation of the magnetically active excitation energies for $^{15}$N and $^{59}$Co in the bent nitrosyls. The d energy levels on the left of the diagram are appropriate to the umbrella shape of the basal ligand in the square pyramids: the cobalt is 0.1–0.5 Å above the plane of the coligating atoms, in the complexes in Table 1. The $z^2$ orbital is stabilized by s,p mixing so as to point more in the direction of the vacant site trans to the nitrosyl and is assumed to lie below the $\pi^*(NO)$ levels. The sequence and separation of the energy levels depend on the coligands and the details are not known, but the general conclusions are independent of these.

The two d orbitals in the MNO plane, the $z^2$ and $xz$, are the ones most strongly involved. Figure 5 shows their interaction with the n' orbital (with $\pi$(NO) symmetry) and $\pi^*(NO)$ orbital of 

the ligand. As can be seen in Figure 5a, the destabilizing interaction of the filled \( z^2 \) and \( n' \) orbitals is alleviated by MNO bending to ca. 125° for the nitrosyls in question, and a bonding interaction of the \( z^2 \) and \( \pi^*_{\text{NO}} \) orbitals then develops. Bending to this angle reduces the back-bonding from \( xz \) to \( \pi^*_{\text{NO}} \) (Figure 5b), while the back-bonding in the \( yz \) plane is only slightly reduced (Figure 5c).

Thus the "lone pair" on nitrogen consists of nonbonding electron density in the MNO plane, which in the HOMO in Figure 4 is delocalized in \( \pi^*_{\text{NO}} \), \( xz \), and \( z^2 \) orbitals. Figure 5d is a perspective view of the most important paramagnetic circulation determining the nitrogen shift, effectively \( n(N) \rightarrow \pi^*_{\text{NO}} \), using the \( \alpha'' \) LUMO (in Figure 4) formed from the \( \pi^*_{\text{NO}} \) and \( yz \) orbitals (Figure 5c). The atomic circulation at nitrogen shown in Figure 5d is of \( p_y - p_y \) type, with the \( p_y \) orbital at an angle of 35° to the \( z \) axis for a 125° MNO angle. In-plane and out-of-plane paramagnetic circulations of \( n'(\sigma-\text{NO}) \rightarrow \pi^*_{\text{NO}} \) type contribute also. The HOMO in Figure 3 is destabilized by the interaction with the \( z^2 \) orbital, the more so with better \( \sigma + \pi \) donation from the basal ligands. Thus weaker coligands reduce the nitrogen as well as the cobalt shielding, and coordination of a sixth ligand may have a similar effect. (If the \( z^2 \) orbital is sufficiently high lying, then the mainly \( \pi^*_{\text{NO}} \) orbitals are occupied in preference to ligand field orbitals.) Clearly, multiple factors are at work, but the extensive mixing of the \( \pi^*_{\text{NO}} \) LUMOs with the \( z^2 \), \( xz \), and \( yz \) orbitals acts to increase the nitrogen and the cobalt shielding as back-bonding increases.

Thus nephelauxetic and spectrochemical effects are interconnected for the two nuclei. Strictly, nephelauxeticism is defined for \( d \) electrons,\(^6\) but it clearly has an analogue for nonbonding \( p \) electrons such as the "lone-pair" electrons on nitrogen. The parallelism of eq 1 and 2 makes this point in the context of nuclear magnetic shielding. There is evidence for similar mutualities in other metal-ligand combinations,\(^12\) but the matching of the orbital energies enhances such effects for these cobalt nitrosyls.

Selective, or independent, influences on the nitrogen and the cobalt shielding have been mentioned as contributing to the scatter in Figures 1-3: these are, notably, medium effects, and distortions from axial symmetry in the coordination sphere. Further, the angular imbalance of charge in the nitrogen valence shell (\( P_2 \)) is clearly but not simply connected with that for cobalt (\( D_3 \)). Particularly important is the \( xy \rightarrow x^2 - y^2 \) circulation in the basal plane. This deshields cobalt but not nitrogen (cf. the increased shielding of protons attached to transition metals) and is highly sensitive to the nature of the basal ligands. Thus in Figure 3 the complexes with basal \( N_4 \) ligation would be better fitted by a line below the one drawn, displaced toward higher cobalt shielding, as expected from the higher nephelauxeticism of \( N_4 \) compared to that of \( O_2 N_2 \) ligators.

Overall, however, it is clear that the ligand field effects that mediate the \(^{59}\)Co shielding are linked with the factors controlling the \(^{15}\)N shielding, and the NMR results offer further support for the theoretical description of the bent nitrosyl complexes.

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