STUDIES OF SOME

SCHIFF'S BASE - TRANSITION METAL COMPLEXES

Being a Thesis submitted to the University
of London for the Degree of Doctor of Philosophy
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by

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ABSTRACT

This thesis describes the preparation and investigation of a number of Schiff's base-transition metal complexes and their reaction with nitric oxide.

Throughout this work the aims kept in view have been (a) to obtain in a pure state air sensitive compounds, (b) to characterise the compounds using available physical techniques, and (c) to correlate their properties by means of current chemical theories and to emphasise similarities between these and related but established compounds.

The metals investigated are Mn(II), Fe(II), Co(II), Ni(II) and Cu(II). The Schiff's bases are bis(salicylaldehyde)-ethylenediamine (Fig.1(a)) and many of its derivatives.

The cobalt compounds are oxygen carriers but their reaction with nitric oxide has been found irreversible. Eleven new five co-ordinate covalent nitrosyls of Co(I) have been isolated presumably possessing a tetragonal pyramidal structure. All have fractional magnetic moments (~0.6 Bohr Magnetons) and from magnetic studies over a temperature range 90°-300°K have been shown to exhibit temperature independent paramagnetism. Variations in the nitric oxide infra-red stretching frequency in this series of nitrosyls have been related to changes in the amount of double bond character in the cobalt-nitric oxide bond consequent upon electron withdrawal from or release to, the metal by substituents in the benzene
rings. This is believed to be one of the first 'inorganic' series in which such substituent effects have been studied.

Bis(salicylaldehyde)-ethylenediimineMn(II) and Fe(II) have been prepared, the latter for the first time in a pure state. These compounds reacted with nitric oxide but those of Ni(II) and Cu(II) did not.

It has been reported that bis(salicylaldehyde)-ethylenediimineCo(II) contains a bridging water molecule. This has not been confirmed.
The work described in this thesis was carried out in the Inorganic Research Laboratories of the Chemistry Department, Battersea College of Technology, under the supervision of the Head of the Department, Dr. J. E. Salmon, and the direction of Dr. L. F. Larkworthy, to whom thanks are due for their continued advice and encouragement throughout the work.

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CONTENTS

ABSTRACT .................................................. 2
ACKNOWLEDGMENTS ........................................ 4

SECTION I .................................................. 7
HISTORICAL INTRODUCTION ............................. 8
OBJECT OF THE WORK ................................... 15

SECTION II ............................................... 16
CO-ORDINATION NUMBER FIVE ......................... 17
NITRIC OXIDE COMPLEXES OF TRANSITION METALS .... 25

SECTION III ............................................... 33
PREPARATIVE METHODS ..................................
(a) AIR-SENSITIVE COMPOUNDS ......................... 34
(b) NITRIC OXIDE DERIVATIVES ......................... 49
(c) PREPARATION OF LIGANDS .......................... 66

SECTION IV ............................................... 70
EXPERIMENTAL TECHNIQUES ..........................
(a) ANALYTICAL METHODS ............................... 71
(b) MOLAR CONDUCTANCE MEASUREMENTS ............ 74
(c) MOLECULAR WEIGHT DETERMINATIONS ............. 75
(d) MAGNETIC SUSCEPTIBILITY MEASUREMENTS ....... 77
(e) INFRA-RED SPECTRA ................................ 78
### Contents (Cont'd.)

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page number</th>
</tr>
</thead>
<tbody>
<tr>
<td>(f)</td>
<td>ULTRA-VIOLET AND VISIBLE SPECTRA</td>
<td>78</td>
</tr>
<tr>
<td>(g)</td>
<td>THERMOGRAVIMETRIC ANALYSIS</td>
<td>81</td>
</tr>
<tr>
<td>(h)</td>
<td>PURIFICATION OF REAGENTS</td>
<td>81</td>
</tr>
<tr>
<td>SECTION V</td>
<td></td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>RESULTS AND DISCUSSION</td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>NITRIC OXIDE ABSORPTIONS, MOLECULAR WEIGHT</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AND CONDUCTANCE MEASUREMENTS</td>
<td>87</td>
</tr>
<tr>
<td>(b)</td>
<td>MAGNETIC SUSCEPTIBILITY MEASUREMENTS</td>
<td>89</td>
</tr>
<tr>
<td>(c)</td>
<td>INFRA-RED SPECTRA</td>
<td>104</td>
</tr>
<tr>
<td>(d)</td>
<td>ULTRA-VIOLET AND VISIBLE SPECTRA</td>
<td>127</td>
</tr>
<tr>
<td>(e)</td>
<td>THERMOGRAVIMETRIC ANALYSIS</td>
<td>134</td>
</tr>
<tr>
<td>SECTION VI</td>
<td></td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>CONCLUSIONS</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>SUGGESTIONS FOR FURTHER WORK</td>
<td>152</td>
</tr>
<tr>
<td></td>
<td>REFERENCES</td>
<td>154</td>
</tr>
</tbody>
</table>
SECTION I

HISTORICAL INTRODUCTION

OBJECT OF THE WORK
HISTORICAL INTRODUCTION

Schiff's Base Complexes of Cobalt

Schiff's bases are the condensation products obtained by reaction between aldehydes or ketones and primary amines [1].

\[ R_1R_2C = O + RNH_2 \rightarrow R_1R_2C = NR + H_2O \]

Many of these compounds have been used as co-ordinating agents in recent times [2,3,4,5,6,7,8,9,10,11].

The work recorded in this thesis is concerned with the structure and reactions of metal complexes of the quadridentate Schiff's base, bis(salicylaldehyde)-ethylenediamine (salen, Fig.1(a)) and its derivatives. Pfeiffer [12] et al. obtained a complex between this Schiff's base and Co(II) which turned from red to black on exposure to air. Tsumaki [13] found that the original colour could be restored when the black powder was heated in a stream of carbon dioxide and attributed the colour change to reversible oxygenation. Calvin [2] investigated this and many similar compounds substituted in the 3,3' or 5,5' positions. It was found that bis(salicylaldehyde)-ethylenediaminecobalt(II) (henceforward called cobalt salen) and its ring substituted derivatives reversibly absorbed one molecule of oxygen per two atoms of cobalt. Another series of cobalt(II) compounds, similar to cobalt salen but with \( \gamma,\gamma' \)-diaminodi-propylamine in place of ethylenediamine, reversibly absorbed one molecule
of oxygen per atom of cobalt.

Calvin [14,15] also studied the reversible oxygenation process in solution and obtained the thermodynamic, rate constant, X-ray and magnetic data. It was found that the oxygenation cycle could be repeated a few times in solution, but hundreds of times using the solid, before irreversible oxidation occurred. The X-ray data showed cobalt salen to be planar with the exception of the ethylene hydrogens, the molecules being arranged in layers (Fig. 1(c)). The gap between the layers (3.34Å) was sufficient to accommodate an oxygen molecule [16(a)]. Upon oxygenation the layers were distorted, yielding the arrangement (Fig.1(d)). In the complexes obtained from 3-fluorosalicylaldehyde and o-hydroxyacetophenone, the spacing in the \( b \) direction was increased from 7.97Å in cobalt salen to 8.60Å and 8.71Å respectively, due to steric effects between the fluoro- and methyl groups on adjacent molecules. Substitution increased the rate of oxygenation but did not alter the capacity for oxygen absorption. The oxygen was said to be covalently bonded to each cobalt atom forming a 'peroxide' or 'peroxo' bridge between the two atoms. This form of bridging has been well established for many cobalt compounds [17,18].

The unoxygenated cobalt salen possessed one unpaired electron \( (\mu_{\text{eff.}} = 2.5 \text{B.M.}) \) and during oxygenation the moment decreased linearly to a fractional value \( (\mu_{\text{eff.}} = 0.69 \text{B.M.}) \). The oxygenated compound was considered diamagnetic, the small moment arising from incomplete oxygen
absorption. Calvin [14] stated cobalt salen was a spin-paired square planar complex \(3d^4s^4p^2\) hybridisation) and on oxygenation gave a five co-ordinate cobalt compound \(3d^4s^4p^2\) hybridisation). Kimball [37] considered such a hybridisation compatible with a tetragonal pyramidal arrangement.

Diehl [3, 19] also investigated cobalt salen and related compounds. He concluded that cobalt salen was binuclear, the two units being joined by an 'aquo' bridge. Upon oxygenation a 'peroxide' bridge was formed yielding six co-ordinate cobalt. He determined the water content by re-fluxing the compound with pyridine, distilling off the pyridine which he believed displaced the water, and titrating the distillate with the Karl - Fischer reagent. The results obtained were low, for a single water bridge, \(\%\) water found = 2.3, expected = 2.69. Using Diehl's method, Stewart, Estep and Sebastian [20] concluded that water was present in cobalt salen. Diehl further pointed out that the compound prepared under anhydrous conditions was not capable of oxygen absorption. Calvin, however, isolated two forms of cobalt salen in the presence of water which did not absorb oxygen. He attributed the failure to do so to a different crystal arrangement from that found in 'active' cobalt salen. Other workers [21] found that oxygenated and deoxygenated cobalt salen reacted directly with the Karl - Fischer reagent, but no water was present, the reaction being oxidation of cobalt(II) to cobalt(III) by the reagent. Ueno and Martell [22] make no mention of absorptions arising from water in the
infra-red spectrum of cobalt salen. According to Bailar [23(a)] and more recently by Vogt [24] et al. cobalt salen would be the only example of a compound possessing an 'aquo' bridge.

Diehl [3] noted that solid cobalt salen absorbed both nitric oxide and nitrogen dioxide. One molecule of nitric oxide reacted with one molecule of cobalt salen but the uptake of nitrogen dioxide was not stoichiometric, presumably due to reaction with the ligand. The nature of the products was not investigated.

Cobalt salen resembles haemoglobin in that both compounds absorb oxygen [25], but differs in that in the solid state it does not react with carbon monoxide.

Compounds of salen with metals other than cobalt

Pfeiffer [12] prepared a manganese(II) compound of the formula
\[ \text{C}_{16} \text{H}_{14} \text{N}_2 \text{O}_2 \text{Mn}^{II} \text{C}_{2} \text{H}_6 \text{N}_2 \] (manganese salen) containing one molecule of ethylenediamine of crystallisation. Aerial oxidation of this compound in chloroform or pyridine gave a product having the formula \( \text{C}_{16} \text{H}_{14} \text{N}_2 \text{O}_2 \text{Mn}^{III} \text{OH} \). Asmussen and Soling [26] obtained a similar manganous complex to that of Pfeiffer without ethylenediamine of crystallisation, by mixing manganous chloride and salen in ethanol under nitrogen. The red product had a magnetic moment of 5.29 B.M. at room temperature. The spin only value for five unpaired electrons is 5.92 B.M. and for a fully spin-paired square planar arrangement 1.73 B.M. The temperature variation of the
susceptibility showed a region of inflexion at 110°K together with a large value of $\Theta = 75°K$. Asmussen and Soling attributed the inflexion to a change in the crystal which increased the 'exchange' forces. A decrease in atomic distances would explain this effect but no X-ray work has been reported. The room temperature magnetic moment, though somewhat low, was taken as indicating a spin-free complex.

Pfeiffer [12] obtained a dimeric ferric complex with salen corresponding to the formula $(C_{16}H_{14}N_{2}O_{2}Fe)_{2}O$ in which the iron atoms were joined by an 'oxo' bridge. Although a ferrous complex was not isolated the author indicated that it may be formed by mixing ferrous acetate and salen in pyridine. Bailes and Calvin [14] determined the magnetic susceptibility of a compound formed between ferrous iron and salen which was said to contain half a molecule of ethylenediamine of crystallisation. The authors considered the moment obtained (5.06 B.M.) to be somewhat high for spin-free ferrous iron and suggested oxidation may have occurred.

Klemm and Raddatz [27] investigated the magnetic properties of compounds formed from ferric iron and bis(salicylaldehyde)-o-phenylenediimine as well as salen. An attempt to prevent oxidation of ferrous complexes during their preparation was made by Breuil [28] who studied complexes with ethylenediamine under an atmosphere of hydrogen.

Pfeiffer [12] prepared nickel(II) and copper(II) compounds corresponding to cobalt salen by reacting bis(salicylaldehyde)nickel(II) and
bis(salicylaldehyde)copper(II) with ethylenediamine. The nickel compound was diamagnetic and square planar according to Klemm and Raddatz [27]. Calvin [14] found that the copper complex had one unpaired electron ($\mu_{\text{eff.}} = 2.0$ B.M.) and molecular weight determinations by Pfeiffer [12] in boiling pyridine indicated it to be monomeric in solution. X-ray data by von Stackelberg [29], and more recently by Hall and Waters [30], showed that in the solid state the compound was dimeric (Fig.1(e)), with two long Cu-O bonds. The intermolecular bond was said to be formed by overlap of the unhybridised p orbital on the oxygen with a 3d$\alpha$:$\delta$p$^3$ hybrid orbital on the copper atom yielding a pyramidal arrangement. Ferguson [31], from crystal and solution spectra, concluded that in solution the complex was square planar.

Salen has been found to complex with a few other transition metals such as titanium(IV) [32] and vanadium(IV) [33] and other members of the periodic system including magnesium(II) [12], zinc(II) [33], cadmium(II) [12] and the uranyl ion [33,34].
Figure 1

Bis(salicylaldehyde)-ethylenediamine
Salen

Fig. 1(a)

Fig. 1(b)

Fig. 1(c)

Fig. 1(d)

Fig. 1(e)
The object of the work was as follows:

(a) To characterise the complexes formed by cobalt salen and its substituted derivatives with nitric oxide. To determine the effects of substituents, if any, on the infra-red stretching frequency of the co-ordinated nitric oxide and other properties of the compounds. These compounds also seemed likely to exhibit the uncommon co-ordination number of five.

(b) It was possible that changing the metal might lead to the formation of nitrosoyls of different stereochemistry, or to reaction of the co-ordinated ligand with nitric oxide. Thus, it was intended to extend the reaction with this gas to the salen complexes of neighbouring transition metals. The air sensitive Mn(II) and Fe(II) salen complexes had been reported but it was necessary to prepare and study these compounds more carefully with the rigorous exclusion of air.

(c) Owing to the conflicting evidence concerning the presence of water in cobalt salen, further work was necessary.
SECTION II

CO-ORDINATION NUMBER FIVE

NITRIC OXIDE COMPLEXES OF TRANSITION METALS
CO-ORDINATION NUMBER FIVE

Five co-ordinate compounds are comparatively rare [35a] oxygenated cobalt salen is apparently five co-ordinate, and, in the present work, many five co-ordinate nitrosyls have been prepared; thus a review of this co-ordination number is desirable.

The two most common arrangements of five groups about a central metal [36] are trigonal bipyramidal (Fig. 2(a)) and square pyramidal (Fig. 2(b)).

According to group theory calculations by Kimball [37], combining one s, three p and one d orbital should yield a trigonal bipyramidal structure, although no distinction was made between 'upper' and 'lower' d orbitals. The use of 'upper' d orbitals (sp³d) hybridisation could yield, according to Linnett and Mellish [38], both trigonal bipyramidal and square pyramidal arrangements, with the former being more probable. The same authors, considering the disposition of electrons in a d¹⁰s²p⁶ structure, in which five electron pairs are bonding, conclude that an octahedral shape with a lone pair at an apex (d²sp³ hybridisation) was likely. Daudel and Bucher [39] concluded that the use of 'lower' d orbitals, i.e. (n-1)dnsnp³ hybridisation, would favour a square pyramidal arrangement. Their work, however, has been criticised [40] because they did not apply the condition of mutual orthogonality to their evaluated hybrid orbitals.
However, the trigonal bipyramidal arrangement may be considered to arise from a combination of two hybridisations: $sp^2$ yielding the trigonal planar bonds, and $d_{2p_z}$ forming the linear and longer axial bonds. The square pyramidal structure arises from $d_{x^2-y^2}$ $sp^2$ hybridisation and a $p_z$ orbital.

The trigonal bipyramidal structure is more common than the tetragonal pyramidal. Jensen [41] assigned the former arrangement to compounds of the type $R_2^3MX_2$, $R =$ alkyl or aryl group; $M =$ P, As, Sb; $X =$ Halogen, on the basis of their zero dipole moments. The halogen atoms are trans to one another, the hybridisation being nsnp$^3(n)d$. The vanadium compounds $VX_3 \rightarrow Y_2$ [42,43] $X =$ Cl, Br; $Y =$ NMe$_3$,PF$_3$, SME$_2$ also have trigonal bipyramidal structures, the halogens occupying the planar positions. Harris [44] et al. considered the compounds $[Cu(1,10-phenanthroline)_2X]^+$ where $X =$ Cl$, Br$, and $[Cu(2,2'-bipyridyl)_2X]^+$ where $X =$ Cl$, Br$, I$, SCN$, to be trigonal bipyramidal or square pyramidal. X-ray crystallographic work by Barclay and Kennard [45] on the related compound $Bi(s,2,2'-bipyridyl)Cu(II)iodide$ showed it to be trigonal bipyramidal with the iodide atom in the trigonal plane. The spectroscopic evidence on the compounds $[Cu(chel)_2ClO_4]PF_6$ [46] where chel = 1,10-phenanthroline or bipyridyl, shows the perchlorate to be co-ordinated giving complexes similar to those above.

It appears that when the five bonded groups are identical the more
symmetrical trigonal bipyramidal structure is often formed. For instance, the pentahalides of phosphorus, antimony, niobium [47], tantalum and molybdenum [48] all possess this structure in the gas phase but, except for antimony pentachloride [49], become dimeric with slightly distorted octahedra in the solid state [50]. Iron pentacarbonyl [51] and the isoelectronic ions Mn(CO)$_5^-$, Co(N=CR)$_5^+$, are also trigonal bipyramidal. In the complex anion Ni(CN)$_5^{3-}$ [52,53,54] a trigonal bipyramidal arrangement might have been expected as a result of all the groups being identical. However, the cyanide groups are considered to be positioned at the corners of a tetragonal pyramid. This probably results from the anion being [Ni(CN)$_5$N$_2$O]$^{3-}$, although the presence of a water molecule has as yet not been proved, giving rise to an octahedral arrangement. Without the water molecule an octahedral configuration could still result having a lone-pair of electrons at one apex. Other workers [55] doubt the existence of Ni(CN)$_5^{3-}$.

X-ray work on compounds of the type $^{11}$ (terpy)Cl$_2$ [56] where M = Zn, Cd, Cu; terpy = terpyridyl, has shown that the 'rigidity' of the ligand may force the metal to adopt a trigonal bipyramidal arrangement. A similar 'straight jacket' effect by the ligand occurs in the compounds [PtX(QAS)]Y [57] where X = Cl$^-$, Br$^-$, I$^-$, SCN$^-$; QAS = Tris(o-diphenylarsino-phényl)arsine (Fig.2(c)); Y = Cl$^-$, Br$^-$, SCN$^-$, CIO$_4^-$, BPh$_4^-$ . In these compounds the adoption of a trigonal bipyramidal structure is governed by the
potential trigonal symmetry of the ligand which makes possible the attachment of three arsenic atoms in an identical manner when the central arsenic atom is placed at one apex. X-ray work on [PtI(QAS)]BPh$_4$ [58] has shown the heavy atoms to be at the corners of a trigonal bipyramid. (Fig. 2(a)). Lippert and Truter [59] by three dimensional X-ray data consider monoaquo-bis(acetylacetonato)zinc(II) to possess a distorted trigonal bipyramidal structure, and Beattie [60] et al. propose a similar arrangement for Me$_3$SnClPy, the three methyl groups lying in the trigonal plane.

The tertiary arsine group TAS (Me$_2$As(CH$_2$)$_3$AsMe(CH$_2$)$_3$AsMe$_2$) gives complexes of the type M$^{II}$Br$_2$TAS, where M = Ni, Pd, Pt[61]. That of nickel has been shown by means of X-ray diffraction [62] to be five co-ordinate with a slightly distorted tetragonal pyramidal structure (Fig. 3(a)), the Ni-Br$_2$ bond being longer than usual. The second Br atom in the related Pd and Pt complexes is present as Br$^-$, a change from five to fourfold coordination. A similar trend is apparent in the sequence Co, Rh, and Ir [63] for the isocyanide derivatives.

Nyholm et al. [64] consider the cations [M$^{II}$]$_2$(Diarsine)$_2$Halogen]$^{+}$ where M$^{II}$ = Ni, Pd, Pt to be tetragonal pyramidal assuming no solvation occurs. In the crystal, however, the metal is probably hexacovalent. The nickel(III) complex Ni(PF$_3$)$_2$Br$_3$ [65] (Fig. 3(b)) possesses a dipole moment of 2.5 Debye consistent with a tetragonal pyramidal arrangement. Hall and Moore [66] from a preliminary X-ray study consider
bis(salicylaldehyde)-ethylenediiminezinc(II)monohydrate to have the structure shown in Fig.3(c). The 'rigidity' of the planar ligand (salen) in part forces the tetragonal arrangement on the metal. An analogous arrangement has been suggested for bis(salicylaldehyde)-propane-1,2-diaminecopper(II)monohydrate [67], in which the out of plane Cu-H$_2$O bond is long (2.53 Å), due to the Jahn-Teller effect [68]. Crystal structure determinations on cupric formate [69] show a fifth bond at 31° to the normal from the plane containing the four oxygen atoms, to be present. Frasson [70] et al. have shown a very similar arrangement to exist, at low temperatures, in dimethylglyoximecopper(II).

Several five co-ordinate nitrosyls are known, i.e. Co$^{II}$X$_2$(NO)(Ph$_3$)$_2$ [71] where X = F, Cl, Br; Co$^I$(acetylacetone)$_2$NO [72]; Co$^{III}$($8$-amino-quinoline)$_2$NO [73] and nitrosodimethylthiocarbamatozinc(I) [74]. A detailed X-ray investigation has shown the last compound to be square pyramidal (Fig.3(a)). The angle between the metal and the nitric oxide is about 139° [75], and the cobalt atom lies slightly above the basal plane (Fig.3(c)). The exact position of the bond between the metal and the nitric oxide is not known but the nature of the bonding is similar to that in ethylene complexes (see Section II,(b),p. 31). Dithiocarbamato nitrosyls of other transition metals have been prepared [76,77], e.g. (Me$_2$NCS)$_2$FeNO and (Et$_2$NCS)$_2$FeNO, but little structural evidence is available.
Most cobalt(II) and cobalt(III) compounds are tetrahedral or octahedral but a few apparently five co-ordinate complexes have been reported [23(b)], for example, \([\text{Co(CN)}]_5^{3-}\) [78, 79] and \([\text{Co(CN)}]_5^{2-}\) together with oxygenated cobalt salen. The cobaltocyanide is in fact dimeric with cobalt – cobalt bonds [79, 80] and in solution may be \([\text{Co(CN)}]_{5\text{H}_2}\)\(^{3-}\). The compound first reported as \(\text{Ag}_2\text{Co(CN)}\) [81] was found to contain bridging cyanide groups [82]. \(\text{Cs}_3\text{CoCl}_5\) contains both \(\text{CoCl}_4^{2-}\) and separate \(\text{Cl}^-\) ions in its lattice.

Thus in some cases where stoichiometry might suggest five co-ordination the true co-ordination number is higher or lower.
Figure 2

Fig. 2(a)

Trigonal bipyramid

Fig. 2(b)

Square pyramid

Fig. 2(c)

Tris(o-diphenylarsinophenyl)arsine

Fig. 2(d)

[PtI(QAS)] BPh₄
Figure 3

Ni^{II}Br_{3}TAS

Fig. 3(a)

Ni^{III}(PET_{3})Br_{3}

Fig. 3(b)

Bis(salicylaldehyde)-ethylenediamine zinc(II)

Fig. 3(c)

Nitroso(dimethyldithiocarbamato)cobalt(I)

Fig. 3(d)
Nitric oxide is a colourless, paramagnetic gas [83,84]. As a free radical it is unusual in that at ambient temperatures it behaves as a stable molecule. Stability may be due to resonance [85] between the structures:

\[
\begin{align*}
\text{N} & \quad \text{O} \\
\text{N} & \quad \text{O}
\end{align*}
\]

The molecular orbital terminology for this molecule is:

\[
(c^1\pi^3)^2(c^2\pi^3)^2(c^2\pi^2)^2[n^2\pi_y = n^2\pi_z]^2[n^2\pi_y = n^2\pi_z]^1
\]

yielding a total bonding effect of one \(\sigma\) and two \(\pi\) bonds minus the effect of one electron in an antibonding \(\pi^*\) orbital, agreeing with the determined N - O bond length of 1.15\text{Å}.

Nitric oxide has a low ionisation potential (9.5 eV.) [86] and may lose an electron yielding the nitrosylium ion \(\text{NO}^+\), one of the main resonance structures of which is \([\text{N} \quad \text{O}^*\text{O}^+]_\text{+}^+\) [87a].

Alternatively nitric oxide may gain an electron forming the nitrosyl anion \(\text{NO}^-\). The electron affinity has not been established but ionic nitrosyls of the type \(\text{Na}^+\text{NO}^-\) have been obtained.

As well as forming many covalent and ionic compounds [88,89] nitric oxide yields co-ordination complexes with transition metals [90]. There are five formal ways in which nitric oxide may co-ordinate:
Considering each in turn:

(1) This consists of straightforward donation of an electron pair from the neutral nitric oxide molecule yielding paramagnetic complexes, the odd electron remaining in the antibonding orbital of the nitric oxide. It is possible to have two centres of paramagnetism, the metal and the NO. There is little evidence for the existence of this form of bonding. In paramagnetic ions such as \([\text{Mn(CN)}_5\text{NO}]^{2-}\) and \([\text{Cr(CN)}_5\text{NO}]^{3-}\) electron spin resonance studies indicate the odd electron to be associated mainly with the metal and hence the bonding is really of type (2). In the nitric oxide complex of haemoglobin, however, the odd electron is located on the nitric oxide molecule [91,92]. There are no infra-red data available on this form of bonding.
(2) This bonding is closely allied to that found in carbonyl complexes. The nitric oxide donates the odd electron to the metal reducing the oxidation state by one, and co-ordinates as the nitrosonium ion, three electrons being donated in all. According to the valence bond approach back bonding from the filled underlying d orbitals of the metal to a p orbital of the nitrogen occurs yielding the double bond resonance structure (II). An alternative explanation for this bonding is to regard it as similar to that in (I) where the odd electron of the nitric oxide molecule pairs with an odd electron of the metal forming the $\pi$ bond.

Bonding of type (2) is found in most nitric oxide complexes. The nitrosonium ion forms similar compounds to CO and CN$^-$ with which it is isoelectronic, as shown by the series:

$$K_2[Fe^{II}(CN)_5NO] \quad K_3[Fe^{II}(CN)_5CO] \quad K_4[Fe^{II}(CN)_6]$$

The carbonyls, nitrosyl carbonyls and simple metal nitrosyls obey the 'effective atomic number' rule [93]. According to this rule a metal will complex so as to attain the effective atomic number (E.A.N.) of the next inert gas. The E.A.N. is derived by subtracting from the atomic number of the metal the number of electrons lost in ion formation and then adding the number of electrons gained by co-ordination (two for each group in general, but three for NO$^+$).

In the series Ni$^0$(CO)$_4$ Co$^{II}$(NO)(CO)$_3$ Fe$^{II}$(NO)$_2$(CO)$_2$ [94] the
decrease in atomic number of the metal from nickel to iron is compensated by the increase in the number of nitric oxide groups. In each case the metal achieves the effective atomic number of krypton (36). These compounds are sometimes referred to as 'pseudo nickel' complexes.

The nitrosyl halides of the general formula \( M(\text{NO})_n X \) [95,96] contain co-ordinated \( \text{NO}^+ \), and their suggested structures are based on the E.A.N. rule; for instance, \( \text{Fe(NO)}_2 I \) and \( \text{Co(NO)}_2 X \), where \( X = \text{Cl,Br,I} \), are considered as being dimeric containing halogen bridging atoms. The diamagnetism of the iron compounds is accounted for by a metal-metal bond [97] between the iron atoms, which also increases the E.A.N. to that of krypton. A similar arrangement is postulated for the ester of Roussin's red salt [98].

Co-ordination complexes do not usually contain more than one nitric oxide molecule and are of the 'inner' rather than 'outer' orbital type. Two nitric oxide groups may be attached if the stable valency of the metal has more than one unpaired electron as in \( (\text{R}_2\text{NCS})_2 \text{Cr(NO)}_2 \) [79]. Electron pairing in the d orbitals increases the number of filled orbitals available for back donation to the nitric oxide. It is for this reason that ruthenium(III) forms so many nitrosyls [88].

It is interesting to note that no stable nitrosyls are formed by zinc, cadmium and mercury or metals of the main groups of the periodic table that use 'outer' orbitals in complex formation.
The infra-red stretching frequency of the nitric oxide group in nitrosyls using bonding of type (2) has been found to lie in the approximate range 1580-1950 cm\(^{-1}\) [99,100], whereas that of gaseous nitric oxide is at 1876 cm\(^{-1}\) [101] and the nitrosonium ion at about 2275 cm\(^{-1}\) [102,103]. The increase in frequency in going from the gas to the nitrosonium ion is due to the removal of the odd electron from the antibonding orbital. On co-ordination a lowering of frequency is to be expected. The range of frequencies for nitrosyl compounds is dependent upon the degree of back bonding from the metal. Consider the series:

\[
[\text{Fe}^{II}(\text{CN})_5\text{NO}]^{2-} \quad [\text{Mn}^{II}(\text{CN})_5\text{NO}]^{3-} \quad [\text{V}^{IV}(\text{CN})_5\text{NO}]^{5-}
\]

The oxidation state and electronegativity decrease in going from iron to vanadium, therefore the tendency to remove negative charge in accordance with the Pauling's electroneutrality [104] principle would be expected to increase thus lowering the nitric oxide stretching frequency. This is borne out in practice, the respective frequencies are 1944 cm\(^{-1}\), 1730 cm\(^{-1}\), and 1575 cm\(^{-1}\).

Several recently reported nitrosyls of chromium, molybdenum and cobalt [105,106] are considered to use bonding of type (2). The pentacyano-nitrosylferrate(II) anion \([\text{Fe}^{II}(\text{CN})_5\text{NO}]^{3-}\) was initially thought by Griffith to include bonding of neutral NO (Type (I)) [107], whilst other workers considered a formulation using co-ordination of NO\(^+\) more appropriate. However, electron spin resonance measurements show
the odd electron to be delocalised between the iron and the NO ligand.
Bernal [108] et al. suggest such metal-nitrosyl complexes should be con-
considered as molecular species with electrons delocalised to different
extents rather than containing charged ligands.

It has been found that in hydroxylic solvents conversion of NO$^+$ to
NO$_2^-$ occurs readily for free ions. Although hydrolysis can still take
place co-ordination of NO$^+$ tends to stabilise the group.

$$[\text{Fe(CN)}_5\text{NO}]^{2-} + 2\text{OH}^- \rightleftharpoons [\text{Fe(CN)}_5\text{NO}_2]^{4-} + \text{H}_2\text{O}$$

Little work has been done on such equilibria but the tendency to hydrolysis
varies markedly from complex to complex, some nitrosyls in fact may be
prepared in alkaline media.

(3) This involves an increase in the oxidation state of the metal
by donation of an electron from the metal to the nitric oxide molecule
followed by co-ordination of the NO$^-$ group by donation of an electron pair.
This form of bonding is not common but has been suggested in the compounds
$[\text{Co(NH}_3)_5\text{NO}]^{2+}$ and $[\text{Co(CN)}_5\text{NO}]^{3-}$ which from magnetic data are considered
analogous to $[\text{Co(NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Co(CN)}_5\text{Br}]^{3-}$ containing low spin Co(III)
and NO$^-$ [93,109].

Donation of an electron into the antibonding $2\pi^*$ orbital of the
nitric oxide would lower the stretching frequency several hundred wave
numbers, co-ordination would lower the frequency even further, and absorp-
tions at around 1100 cm$^{-1}$ are considered to be due to NO$^-$ [110].
Although co-ordination in nitrosyls is usually through the nitrogen atom,
the ultra-violet and visible spectra of \([\text{Co(NH}_3\text{)}_5\text{NO}]^{2+}\) indicate that bonding may be through the oxygen as in the nitrito complex \([\text{Co(NH}_3\text{)}_5\text{ONO}]^{2+}\).

Ardon and Herman [111] consider \([\text{Cr(H}_2\text{O)}_5\text{NO}]^{2+}\) to contain \(\text{NO}^-\).

The compound \(\text{Fe(NO)}_4\) has two nitric oxide stretching frequencies corresponding to \(\text{NO}^+\) and \(\text{NO}^-\) and has been designated \([\text{(NO)}^+\text{Fe}^{2-}\text{(NO)}^-]^0\).

(4) The metal-nitrogen-oxygen bond angle is not 180° as in bonding of type (2) but at an angle approaching 90°. The \(\pi\) electrons in the multiple bonds of the nitric oxide co-ordinate to the metal in a similar manner to that in ethylene-transition metal complexes [112]. In these compounds an empty hybrid orbital from the metal overlaps with the electron cloud between the carbon atoms. Back donation by the underlying filled d or dp hybrid orbitals of the metal into the antibonding orbitals on the ethylene molecule then occurs. (Diagram below).
This type of bonding is similar to that of type (2) and is considered to be present in bis(dithiocarbamato)cobalt(I)nitrosyl [76,77], although the NO+ is not bonded parallel to the plane of the four sulphur atoms (Fig.3(d)) due to differences in the electronegativities of oxygen and nitrogen. The nitric oxide stretching frequency in this compound is 1626 cm⁻¹ [99].

The metal-nitrogen-oxygen bond angle differs from 180°, though by a smaller amount than in the dithiocarbamato complex, in two ruthenium complexes [113,114] where the ruthenium-nitrogen-oxygen bond angles are approximately 153°. In these compounds bonding to the metal appears to be solely through the nitrogen.

(5) This bonding resembles that of CO in the polynuclear carbonyls. Until very recently only one compound was known to possess a bridging NO group, namely \((\text{C}_5\text{H}_5)\text{Mn}_2(\text{NO})_3\) [115]. Two structures have been proposed, one of which contains two bridging NO groups, the other, one bridging group. Two infra-red stretching frequencies occur, at 1732 cm⁻¹ and 1510 cm⁻¹. The first is considered to be due to NO+ and the other to bridging nitric oxide groups. A similar frequency change is observed between bridging and non-bridging carbon monoxide groups in iron enneacarbonyl [116]. King and Bisnette [117] recently concluded that in the compounds \([\text{C}_5\text{H}_5\text{Cr(NO)}_2]_2\) and \([\text{C}_5\text{H}_5\text{MnNO}]_2\), the former contained bridging NO groups, the latter possibly both bridging NO and CO groups.
SECTION III

PREPARATIVE METHODS

(a) AIR-SENSITIVE COMPOUNDS.
(b) NITRIC OXIDE DERIVATIVES.
(c) PREPARATION OF LIGANDS.
PREPARATIVE METHODS

(a) AIR-SENSITIVE COMPOUNDS.

Owing to the ease with which the Schiff's base-transition metal complexes studied in this work oxidised irreversibly in solution, they were prepared, filtered, washed and stored under anaerobic conditions.

The apparatus (Fig. 4) used for these operations resembled that described by Larkworthy [118]. Commercial "oxygen-free" nitrogen was passed over heated copper powder deposited on kieselguhr and then through a chromous sulphate bubbler [119] to remove last traces of oxygen. The gas, which entered the apparatus at E, was previously dried with concentrated sulphuric acid followed by magnesium perchlorate.

General procedure:

The metal salt, dissolved in a deoxygenated solvent, was placed in flask A (100 ml.) fitted with a double-coned (B14) tap (6 mm bore). Flask A was flushed several times with nitrogen before being filled with the gas. This operation was performed at the point F on the main apparatus using flexible and removable connections. The Schiff's base and solvent were placed in the larger flask B (250 ml.). Flask A was then inverted and joined to B as shown in the
diagram. With taps 1 and 2 open and tap 3 closed, flask B was flushed several times with nitrogen, then heated under nitrogen to dissolve the Schiff's base. Having obtained solution of the Schiff's base the metal salt was added slowly by opening tap 4, this addition was facilitated by having flask B under slightly reduced pressure. Between each addition the reactants were heated. After addition was complete taps 1 and 2 were closed and flask A detached. With tap 3 open the heating was continued, a fast flow of nitrogen being maintained throughout the apparatus so that sucking back would not occur during momentary cooling of the reaction mixture. When the reaction was complete flask B was inverted about the joint G, cleaned where it had been exposed to the atmosphere, and the filtration unit joined to it. (Fig. 5) All the apparatus was clamped securely in position.

The filtration unit was flushed out several times with nitrogen and left under reduced pressure. With taps 5 and 6 open the solid was transferred from the flask B, via tap 1, to the sinter S, the filtrate being collected in flask J. Suction could be applied when required by opening tap 7. The solid on the sinter was washed several times with deoxygenated solvents pushed over from flask C by nitrogen pressure. When filtration was complete the apparatus was filled with nitrogen, taps 5 and 6 closed and the filter removed from the main apparatus. The solid was transferred into the T-piece of the 'pig' (L) by
APPARATUS FOR PREPARATION OF AIR SENSITIVE COMPOUNDS

Figure 4

To Manometer

Purified Nitrogen Inlet

Outlet through traps.

Two Way Tap

Three Way Tap

A

B

C

E

F

Pump
**Figure 5**

FILTRATION APPARATUS

TO MAIN APPARATUS

FLEXIBLE CONNECTION TO POINT F.
means of a brass rod R contained in a rubber bladder K which was attached at HH' to a ball joint M. The rod could be moved backwards, forwards and sideways about the ball joint. If at any time the filtration apparatus was under reduced pressure or left to stand, the bladder was previously filled with nitrogen and wired to the rod at II'. This minimised oxidation of the product by air that may have diffused through the bladder. Before transferring the solid, the wire at II' was removed and by movements of the rod the solid was pushed into the 'pig'. At this stage the filtration unit was again joined to the main apparatus. The bladder and rod were removed and replaced by a sealed ball and socket joint M' against a fast stream of nitrogen. The whole apparatus was then immediately evacuated. The solid in the 'pig' was dried under reduced pressure, and, if necessary, at an elevated temperature by surrounding the T-piece of the 'pig' with an oil bath. When the solid was dry the filtration unit was again detached from the main apparatus, and the solid shaken into the long glass tubes T in which it was sealed under vacuum.

Because the cobalt compounds reversibly absorbed oxygen once dry it was not necessary to use the bladder or the 'pig'. These were replaced by a sealed ball and socket joint M' and cap N before filtration.

Details of preparations:

Unless otherwise stated the methods described above were always
used. In all cases where the compound was appreciably soluble in the solvent, the filtrate from the preparation readily oxidised when exposed to air. Heating the solution under reduced pressure would not restore the original colour, irreversible oxidation apparently occurring.

The quantities of solvents used in the preparations were not critical and are only stated when of particular significance.

Bis(salicylaldehyde)-ethylenediaminecobalt(II).

The method of Diehl [19] was used. To a solution of bis(salicylaldehyde)-ethylenediamine (5.36 g., 2.0 x 10⁻² Moles) together with caustic soda (1.51 g., 3.7 x 10⁻² Moles) and sodium acetate (0.1 g.,) in hot water (60 ml.), a solution of hexahydrated cobaltous chloride (4.76 g., 2.0 x 10⁻² Moles) in water (10 ml.) was added. The reddish-brown paste which formed was filtered off and then washed with oxygen-free water (50 ml.) and 96% ethyl alcohol (50 ml.). The product was dried in vacuo at 117°C for three hours yielding a rust coloured powder in excellent yield (80 - 90%). Recrystallisation was not carried out owing to the poor solubility of the product.

Found: Co 18.19 C₁₆H₂₄N₂O₂Co requires Co 18.14%.

The analysis agreed with that of Bailes and Calvin [2] (See Section V,p.121).

Bis(3-methoxysalicylaldehyde)-ethylenediaminecobalt(II).

The method of Diehl [3] was performed in the air. To a 99% aqueous solution of ethylenediamine (3 g., 5.0 x 10⁻² Moles) in 95% ethyl alcohol
(50 ml.) was added cobaltous acetate (12.45 g., 5.0 x 10^-2 Moles) contained in 50/50 ethanol-water mixture (200 ml.) and the mixture heated to 60°C. To this solution salicylaldehyde (15.2 g., 10.0 x 10^-2 Moles) dissolved in 70% ethyl alcohol (100 ml.) was added. A clear brown solution formed which gave a yellow precipitate on standing. The product was filtered off and washed with 50% ethanol (100 ml.) then recrystallised from 96% alcohol. A golden yellow hydrated product was obtained from the red alcoholic solution.

\[
\text{Found: Co 14.50 C}_{18}H_{16}N_2O_4CoH_2O \text{ requires Co 14.61%}
\]

\[
\text{C}_{18}H_{18}N_2O_4CoH_{1\frac{1}{2}}O \text{ requires Co 14.30%}
\]

The product was activated by heating at 170°C in vacuo for two hours yielding a maroon product. A weight loss of 5.1% occurred (theoretical for one molecule of water per two atoms of cobalt = 4.46%). The 'active' compound turned black and increased in volume on exposure to dry air, weight increase = 3.91%. Theoretical value for one molecule of oxygen per two atoms of cobalt = 4.16%.

Red solutions were obtained when the hydrated compound was dissolved in chloroform or pyridine.

**Bis(5-nitrosalicylaldehyde)-ethylenediaminecobalt(II).**

Neither of the two methods used by Bailes and Calvin [2] to prepare this compound gave satisfactory products. Their preparations, which were
performed in pyridine and also n-propyl alcohol, gave what appeared to
be solvated products.

A similar method to that of Marvel and Tärkoy [120] was used.*

To the Schiff's base (1.20 g., $3.35 \times 10^{-3}$ Moles) dissolved in hot purified
dimethylformamide [121, 122] a solution of cobaltous acetate ($0.83$ g.,
$3.35 \times 10^{-3}$ Moles) in the same solvent was added. A deep red solution
formed which was warmed gently, but not boiled, for one hour under nitrogen.

On cooling and leaving to stand very dark red crystals were deposited.
The product was filtered and washed with hot deoxygenated water, then
pumped dry at room temperature. Once the product was dry the apparatus
was opened to the air and the product removed and heated in vacuo for
two hours. The final compound was a deep red.

Found: Co $14.03$  

The compound turned black on exposure to air increasing in weight
by $2.42\%$. Although this did not equal the theoretical value for absorp-
tion of one molecule of oxygen per two atoms of cobalt ($3.88\%$), it was
an improvement on the capacity of the compound obtained by Bailes and
Calvin [2] ($1.5\%$), a figure closer to the theoretical would probably have
been obtained if the oxygen pressure had been increased.

**Bis(3-nitrosalicylaldehyde)-ethylenediaminecobalt(II)**

To bis(3-nitrosalicylaldehyde)-ethylenediamine ($1.63$ g., $4.55 \times 10^{-3}$
Moles) in hot dimethylformamide (20 ml.) was added under nitrogen, a slight
excess of cobaltous acetate (1.17 g., $4.7 \times 10^{-3}$ Moles) in the same solvent (10 ml.). A deep-red solution formed which on reducing the bulk of solvent, gave fine red-brown needles.

The product was filtered and washed with deoxygenated water. After drying at room temperature it was 'activated' by heating in vacuo at 170°C for one hour. The final product was red-brown in colour similar to that of Bailes and Calvin [2]. Evaporation of the filtrate in vacuo gave very large crystals of the compound.

Found: Co 14.25  \( \text{C}_6 \text{H}_{12} \text{N}_4 \text{O}_6 \text{Co} \) requires Co 14.19%

The dry compound turned black on exposure to air, the original colour could be restored by heating the solid under reduced pressure.

**Bis(5-chlorosalicylaldehyde)-ethylenediiminecobalt(II)**

This compound had not been prepared before.

To bis(5-chlorosalicylaldehyde)-ethylenediimine (1.0 g., $2.96 \times 10^{-3}$ Moles) in dimethylformamide (25 ml.) a solution containing an excess of cobaltous acetate (1.09 g., $4.38 \times 10^{-3}$ Moles) in the same solvent (10 ml.) was added. On addition of the metal salt the yellow solution turned red which deepened to red-brown as the addition continued. After standing under nitrogen for forty-eight hours red-brown needles were deposited.

The product was filtered, and washed with acetone, water and again with acetone. It was slightly soluble in acetone. The compound was
dried in vacuo at room temperature for two hours and found to be stable in air, no increase in weight was observed after prolonged exposure. Heating the product at 100°C in vacuo for one hour yielded a decrease in weight of 7.2%. On exposure to air a colour change from red-brown to almost black occurred, accompanied by a weight increase of 1.84% (theoretical value for one molecule of oxygen per two atoms of cobalt is 4.07%). The original colour could be restored by heating the black compound under reduced pressure.

Found: Co 14.74 C 49.35 H 3.46 N 6.60% C₁₆H₁₂N₂₂Co
requires Co 14.77 C 46.75 H 3.38 N 7.10%

Bis(o-hydroxyacetophenone)-ethylenediaminecobalt(II)


An aqueous solution containing a slight excess of cobaltous acetate (1.28 g., 5.14 x 10⁻³ Moles) was added slowly to a hot solution of bis(o-hydroxyacetophenone)-ethylenediamine (1.48 g., 5.0 x 10⁻³ Moles) in dimethylformamide. An orange-red precipitate was obtained immediately which was gently heated for thirty minutes. After filtration the product was washed with hot deoxygenated water, dried at room temperature for one and a half hours and activated by heating at 150°C in vacuo for two hours. On activation the loss in weight was 5.45%, one molecule of water
corresponds to 4.85%. The final product was orange-red and increased in weight slowly on exposure to air.

Found: Co 16.51 C_{18}H_{18}N_{2}O requires Co 16.65%

Bis(5-methylsalicylaldehyde)-ethylenediaminecobalt(II)

The method used was similar to that of Bailes and Calvin [2].

To a hot solution of bis(5-methylsalicylaldehyde)-ethylenediamine (1.50 g., 5.07 x 10^{-3} Moles) in dimethylformamide was added a solution of cobaltous acetate (1.28 g., 5.14 x 10^{-3} Moles) in the same solvent. A red solution was obtained which gave red-brown crystals on standing. The product was filtered and washed with water and ether, and dried at room temperature in vacuo. After 'activating' at 100°C for one and a half hours a loss in weight of 7.73% occurred. Bailes and Calvin recorded a loss of 8.00% under similar conditions. The final product was brick red and apparently did not absorb oxygen at atmospheric pressure.

Found: Co 16.72 C_{18}H_{18}N_{2}O requires Co 16.72%

Bis(5-methoxysalicylaldehyde)-ethylenediaminecobalt(II)

Diehl [3] obtained an 'inactive' product by reaction of the disodium salt of the Schiff's base in aqueous alcohol with cobaltous chloride.

Cobaltous acetate (2.13 g., 8.35 x 10^{-3} Moles) in dimethylformamide was added to a hot solution of bis(5-methoxysalicylaldehyde)-ethylenediamine (2.72 g., 8.25 x 10^{-3} Moles) also in dimethylformamide. A deep red
solution was formed from which dark red needles deposited on cooling.
The volume of solvent was reduced by evaporation, the product filtered under
nitrogen, and then washed with water. The crystalline, dark red, almost
black product was dried at room temperature, and then at 170°C in vacuo
for one hour. The resulting product did not absorb oxygen on exposure
to air.

Found: 15.18% C_{10}H_{18}N_{2}O requires Co 15.32%

An attempt to prepare bis(acetylacetonate)-ethylenediaminecobalt(II)
from freshly precipitated cobaltous hydroxide [4,123] gave very little
product even after refluxing the reaction mixture under nitrogen for
three days.

Bis(salicylaldehyde)-ethylenediaminemanganese(II).

A solution containing a slight excess of manganous acetate (4.0 g,
1.63 x 10^{-2} Moles) in deoxygenated water (30 ml.) was added to an alcoholic
solution (50 ml.) of bis(salicylaldehyde)-ethylenediamine (4.03 g,
1.50 x 10^{-2} Moles) containing almost two equivalents of caustic soda
(1.15 g., 2.9 x 10^{-2} Moles). An immediate yellow-orange precipitate
was obtained which on gentle refluxing under nitrogen for two hours gave
a uniform orange product. The product was filtered using the technique
described above followed by washings with water and acetone. After drying
at room temperature under reduced pressure the solid was transferred to
the 'pig' by means of the rod and bladder and dried again at 100°C in vacuo.
The resulting orange powder was sealed in the long glass tubes of the 'pig' (see Fig. 5) under vacuum.

\[
\text{Found: } \begin{array}{llllll}
\text{Mn} & 17.22 & \text{C} & 55.34 & \text{H} & 4.02 \\
& & \text{N} & 8.33 & \text{Mn requires} & \text{C}_6\text{H}_4\text{N}_2\text{O}_2
\end{array}
\]

Although the metal and nitrogen analyses agree with the expected values the carbon and hydrogen percentages are low in the same proportion. This indicates that an impurity was present in the sample for the carbon and hydrogen analysis. It was noticed that when sealed tubes were broken very small pieces of glass occasionally contaminated the sample. Such small pieces were unimportant in macroanalyses, e.g. metal analysis, but they could markedly affect the microanalytical results.

The orange compound did not appear to oxidise rapidly in air, but when moistened with various solvents, e.g. acetone, chloroform, nitrobenzene, or water, it darkened immediately. Incomplete reaction resulted if the Schiff's base was not in solution as the disodium salt, a yellow precipitate being obtained on cooling the reaction mixture. Mixing solutions of salicylaldehyde, ethylenediamine and manganous acetate in a manner similar to that of Pfeiffer [12], but under nitrogen, did not yield identifiable compounds.

**Bis(salicylaldehyde)-ethylenediamineiron(II)**

An aqueous solution (30 ml.) containing a slight excess of ferrous
sulphate (3.84 g., 1.43 \times 10^{-2} \text{ Moles}) was added slowly to a boiling aqueous solution (50 ml.) of bis(salicylaldehyde)-ethylenediamine (4.01 g., 1.44 \times 10^{-2} \text{ Moles}) containing almost two equivalents of caustic soda (1.11 g., 2.77 \times 10^{-2} \text{ Moles}) together with a small quantity of sodium acetate (0.21 g., 1.47 \times 10^{-3} \text{ Moles}), under nitrogen. A floculent brown precipitate formed immediately from the red-brown solution. The reaction mixture was boiled (30 mins.) and allowed to cool under nitrogen. Filtration was carried out by the technique described above, the product being washed three times with deoxygenated water and dried at room temperature. The maroon compound was sealed under vacuum in storage tubes which included a magnetic susceptibility tube.

Found: Fe 17.06 C 59.39 H 4.2 N 8.38% \( \text{C}_{16} \text{H}_{14} \text{N}_{2} \text{Fe} \) requires Fe 17.35 C 59.70 H 4.38 N 8.70%

The product was quite soluble in 96% ethyl alcohol and in carbon tetrachloride, the latter seemingly causing decomposition. Hydrolysis or oxidation of the compound did not occur during reaction as shown by the reddish coloured filtrate which had a pH = 7, did not smell of salicylaldehyde and gave positive tests for ferrous iron. Exposure of the filtrate to air gave a light brown solution which became almost colourless on bubbling sulphur dioxide through, and deep red-brown when oxygen replaced the sulphur dioxide. The light brown filtrate could not be rendered colourless by heating under reduced pressure. It seemed some
reversible oxygenation could occur but not by physical means. If the
Schiff's base was not used as the disodium salt it did not dissolve com-
pletely, and it was hydrolysed by the sulphuric acid produced during
reaction with the ferrous sulphate, hydrolysis still occurred if ferrous
oxalate was used instead of ferrous sulphate.

The maroon product changed to light brown on prolonged exposure to
air, but when moistened with dimethylformamide or 96% ethyl alcohol a
yellow brown product formed immediately. This is likely to be the oxo-
bridged ferric compound first prepared by Pfeiffer [12] (Section I (a), p.12).

**Bis(salicylaldehyde)-ethylenediaminonickel(II)**

This compound was prepared in air by the method of Pfeiffer [12]
using \( \frac{1}{100} \) th. of the stated quantities. The product was obtained in good
yield (70-80%). An alternative method of preparation was to add an aqueous
solution (40 ml.) of nickel sulphate (5.4 g., \( 1.92 \times 10^{-2} \) Moles) slowly,
with shaking, to a hot alcoholic solution (70 ml.) of bis(salicylaldehyde)-
ethylenediamine (5.0 g., \( 1.86 \times 10^{-2} \) Moles). The mixture was heated under
reflux for one hour and left to stand. After the product had separated it
was filtered, washed with hot water, alcohol and then ether. The orange
needles obtained by recrystallisation from chloroform (400 ml.) were
dried at 100°C in air.

**Bis(salicylaldehyde)-ethylenediaminocopper(II)**

The preparation was carried out in air using Pfeiffer's [12] method
and \( \frac{1}{100} \) th. of the stated quantities. The product was obtained in good yield
(80-90%) and recrystallised from chloroform, followed by air drying at
110°C-120°C.
(b) NITRIC OXIDE DERIVATIVES

The apparatus is shown in Fig. 6. Tap F corresponds to the same point on the main apparatus as shown in Fig. 4.

The nitric oxide was generated by mixing aqueous solutions of ferrous sulphate (278 g. in 1000 ml.) acidified with 36N sulphuric acid (55 ml.), and sodium nitrite (69 g. in 1000 ml.) \[124\]. To remove oxides of nitrogen the gas was passed through two traps before entering the apparatus at A, the first contained a freezing mixture of alcohol and solid carbon dioxide and the second, caustic soda pellets.

There were two general preparative methods.

**Method (1)**

The Schiff's base and solvent were placed in flask B which was attached to a smaller flask G containing the metal salt in a suitable solvent. The entire apparatus was evacuated, flushed several times with nitrogen, and then left under vacuum. With tap F closed to the outlet, tap 2 closed and taps 3, 4 and 5 appropriately placed, nitric oxide was passed into the gas burette (capacity = 200 cc.). The gas could be sucked into the gas burette by lowering the mercury reservoir (not shown). By turning tap 5 and opening taps 6 and 7 the reaction flasks were filled with nitric oxide to atmospheric pressure. Tap 5 was then turned through ninety degrees (shown in Fig. 6 as \[1\]) to isolate the burette and reactants under nitric oxide. Any pressure build up in the remainder of the apparatus was
relieved by opening tap 1 at intervals.

After levelling the mercury in the burette the magnetic stirrer (MM") was started and the solvent equilibrated with the gas. By proceeding in this manner a check could be made on the possible reaction of the Schiff's base and/or the metal salt with nitric oxide prior to mixing the reactants. After equilibration (one hour) the gas pressure was reduced by lowering the reservoir to a convenient level. The Schiff's base was then dissolved by very gentle heating after which the flask was allowed to cool to room temperature without agitation, and the mercury re-levelled.

The barometric pressure and temperature were noted. Usually the Schiff's base remained in solution, although on long standing it would crystallise. With tap 6 closed the metal salt solution was tipped into the solution of the Schiff's base by stages, tap 6 being opened at intervals and the uptake recorded. After addition of the metal salt was complete the reaction mixture was tipped from flask B to C and back again several times to ensure complete mixing. The reaction was allowed to continue until no further change in the mercury levels occurred. At this stage the temperature and barometric pressure were again recorded.

The apparatus was then evacuated and with tap 5 in position "flushed with nitrogen before finally filling to atmospheric pressure.

After detaching the reaction vessels the product was rapidly filtered in air and washed several times with suitable solvents before dying at room
temperature under reduced pressure.

**Method (2)**

The procedure and apparatus were essentially the same as in method (1) except flask C was replaced by D. This flask contained the activated complex under nitrogen (previously prepared by reaction of the metal salt with the Schiff's base, see Section III(a)). The solvent alone in flask B was equilibrated with nitric oxide before mixing with the solid in D. After equilibration, tap 7 was opened, the reactants mixed by shaking the flasks, and the preparation continued as in method (1).

In general method (1) was preferred because it gave analytically purer products and moreover, previous preparation of the 'activated' complex was unnecessary. Minor modifications in individual preparations are mentioned where appropriate.

When volatile solvents were used vapour pressure corrections were applied [125,126].

Except when otherwise stated one molecule of nitric oxide was absorbed per gram atom of cobalt complexed with the Schiff's base (see Section V, Table 4, p. 84).

**Details of Preparations**

**Nitrosylbis(salicylaldehyde)-ethylenediaminecobalt(I)**

Cobalt salen (0.75 g., $2.31 \times 10^{-3}$ Moles), previously heated under vacuum at 120°C for two hours to remove absorbed water and any oxygen, was
Figure 6

APPARATUS FOR NITROSYL PREPARATIONS
rapidly weighed into flask D (Fig. 6) and left under nitrogen. In flask B, purified chloroform [127] (25 ml.) was equilibrated with nitric oxide. During evacuation of the apparatus flask B was surrounded by an ethanol-solid carbon dioxide freezing mixture to reduce evaporation of the chloroform. Reaction with nitric oxide occurred immediately the cobalt salen and chloroform were mixed, the solution becoming almost black. The black crystalline product which separated during reaction was filtered off at the pump, washed quickly with chloroform and dried under reduced pressure at 50°-60°C until no smell of chloroform could be detected. Recrystallization was carried out by refluxing the product with chloroform (400 ml. per gram of solid). Evaporation of the solvent to a quarter of the original volume gave well formed black crystals, yield approximately 60%. When viewed under a microscope the crystals were seen to be hexagonal plates, with a tendency to cling together.

Found: Co 16.49 C 53.91 H 4.00 N 11.36% \( \text{C}_{16} \text{H}_{14} \text{N}_3 \text{O}_3 \text{Co} \)

requires

Co 16.59 C 54.08 H 3.97 N 11.83%

The product remained unchanged on exposure to air and was soluble in acetonitrile, dimethylformamide, nitrobenzene, methylene chloride and ethylene dichloride. The last two solvents apparently caused decomposition, a green product depositing on standing. Nast [74] also observed decomposition of nitrosyl bis(acetylacetonato)cobalt(I) in chlorinated solvents,
yielding green compounds.

A bulk preparation of the nitrosyl was carried out by adding the activated cobalt salen (10 g., $3.4 \times 10^{-2}$ Moles) against a stream of nitrogen, to a reaction flask containing chloroform (40 ml.). The apparatus was evacuated and nitric oxide bubbled through the mixture until reaction seemed complete. The product obtained by this method was identical to that from the small scale preparation.

Performing the reaction with nitric oxide at 50°-60°C gave two products after recrystallisation. One contained about 21 - 22% cobalt, the other 12 - 13% cobalt. These compounds were not investigated further.

Nitrosylbis(3-methoxysalicylaldehyde)-ethylenediaminecobalt(II)

Bis(3-methoxysalicylaldehyde)-ethylenediamine (1.32 g., $3.99 \times 10^{-3}$ Moles) in dimethylformamide (15 ml.) contained in flask B, and cobaltous acetate (0.996 g., $4.0 \times 10^{-3}$ Moles) dissolved in the same solvent (10 ml.) in flask C were equilibrated with nitric oxide. Flask B was warmed to dissolve the Schiff's base and allowed to cool undisturbed. On mixing the reactants a brown solution was obtained accompanied by rapid absorption of nitric oxide. A brown solid deposited as the reaction proceeded. The solid was filtered rapidly in air, washed with water, acetone, and ether, and dried at room temperature in vacuo. It was a dark brown-green powder, stable in air and obtained in 60% yield.
Found: Co 14.16  C 52.19  H 4.14  N 9.99%  \text{C}_{18}^{}\text{H}_{18}^{}\text{N}_{0.5}^{}\text{Co}
requires
Co 14.20  C 52.04  H 4.38  N 10.12%

The Schiff's base separated on mixing the reactants, but this did not affect the overall reaction. The product was quite soluble in dimethylformamide, chloroform, acetonitrile, pyridine and nitrobenzene, yielding brown solutions, but insoluble in water, carbon tetrachloride, benzene and cyclohexane.

Before the nitrosyl was successfully obtained by method (1), method (2) was tried many times with various solvents. As shown in Table 1 the uptake of nitric oxide was usually near the expected value except with cyclohexane. The compound was very poorly soluble in this non-coordinating solvent and a coating of product on the undissolved material led to incomplete reaction. Analysis for cobalt of the products from various solvents showed them to be indefinite and to have a tendency to retain the solvent. Recrystallisation always caused decomposition. In pyridine the reaction was rapid until one molecule of nitric oxide had been absorbed, but then it continued slowly and indefinitely. Presumably there was some additional reaction with the ligand or with the solvent. However, a reasonably pure product (see below) was obtained from pyridine by stopping the reaction when one molecule of nitric oxide had been absorbed, and by using a minimum of solvent so that the product separated rapidly.
### TABLE 1

**Reaction of Nitric Oxide with bis(3-methoxysalicylaldehyde)-ethylenediamine-cobalt(II)**

<table>
<thead>
<tr>
<th>General Method Used</th>
<th>Moles of Nitric Oxide Absorbed per Gram Atom of Cobalt complexed with the Schiff's base</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method (2)</td>
<td>1.03</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.11</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.93</td>
<td>Chloroform</td>
</tr>
<tr>
<td>&quot;</td>
<td>Continuous</td>
<td>Pyridine</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.02</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.00</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.10</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.92</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.42</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.82</td>
<td>Acetonitrile</td>
</tr>
</tbody>
</table>

Bis(3-methoxysalicylaldehyde)-ethylenediaminecobalt(II) (1.25 g, 3.25 x 10^-3 Moles), previously activated, was sealed under nitrogen in flask D. Pyridine (15 ml.) was equilibrated with nitric oxide in flask B. On mixing the reactants a rapid absorption of nitric oxide occurred which was terminated after one molecule of the gas had been absorbed. A
green-brown compound separated during the reaction and was filtered off immediately. The product was washed with acetone and dried at room temperature in vacuo and then at 170° - 180°C for six hours. A loss in weight of 2.4% occurred yielding a brown product.

**Found:** C 14.21 H 4.55 N 9.31% C<sub>18</sub>H<sub>18</sub>N<sub>3</sub>O Co requires C 14.20 H 4.38 N 10.12%

Although the reaction in pyridine eventually gave a reasonably pure product removal of the solvent was difficult and the microanalysis indicated some loss of nitric oxide.

**Nitrosylbis(6-nitrosalicylaldehyde)-ethylenediaminecobalt(I)**

Flask B contained bis(6-nitrosalicylaldehyde)-ethylenediamine (0.39 g., 1.09 x 10<sup>-3</sup> Moles) dissolved in warm dimethylformamide (5 ml.). Flask C contained solid cobaltous acetate (0.30 g., 1.2 x 10<sup>-3</sup> Moles) which was added slowly to the Schiff's base after equilibration of the reactants with nitric oxide. An immediate reaction occurred yielding a chocolate brown product. The product was filtered, washed with dimethylformamide, alcohol, water and alcohol again, then dried in vacuo at room temperature.

**Found:** C 43.19 H 2.87 N 15.36% C<sub>16</sub>H<sub>12</sub>N<sub>5</sub>O Co requires C 43.11 H 2.73 N 15.73%

**Nitrosylbis(5-nitrosalicylaldehyde)-ethylenediaminecobalt(I)**

After equilibrating bis(5-nitrosalicylaldehyde)-ethylenediamine
(0.86 g., 2.42 x 10^{-3} Moles) in dimethylformamide (20 ml.) and cobaltous acetate (0.61 g., 2.45 x 10^{-3} Moles) also in dimethylformamide (10 ml.), with nitric oxide, the reactants were mixed. An almost black solution resulted which gave blue-black crystals after rapid absorption of nitric oxide. The product was filtered in air, washed with water, ethyl alcohol and ether, then dried at room temperature under reduced pressure. Black crystals were obtained in low yield (55%) owing to the solubility of the product in dimethylformamide.

**Found:** Co 13.40 C 43.82 H 3.06 N 15.49% Co requires C_{16}H_{12}N_{1}O_{Co}

**Compliance:** Co 13.23 C 43.11 H 2.72 N 15.73%

Preliminary attempts to prepare this nitrosyl using the previously prepared cobalt - Schiff's base complex (method 1) gave indefinite compounds from chloroform, pyridine and acetonitrile.

**Nitrosylbis(3-nitrosalicylaldehyde)-ethylenediiminecobalt(1)**

Bis(3-nitrosalicylaldehyde)-ethylenediimine (0.95 g., 2.66 x 10^{-3} Moles) in dimethylformamide (15 ml.) and cobaltous acetate (0.75 g., 2.93 x 10^{-3} Moles) also in dimethylformamide (10 ml.) were equilibrated with nitric oxide and then mixed. Rapid absorption of nitric oxide occurred giving a black product. Filtration was performed in air and the compound washed with water, ethyl alcohol and ether followed by vacuum drying at room temperature.
**Nitrosylb(is(5-chlorosalicylaldehyde)-ethylenediimine)cobalt(I)**

Mixing bis(5-chlorosalicylaldehyde)-ethylenediimine (1.0 g., 2.96 x 10^{-3} Moles) contained in dimethylformamide (20 ml.) and cobaltous acetate (0.79 g., 3.17 x 10^{-3} Moles) dissolved in the same solvent (10 ml.) under nitric oxide gave a black crystalline solid. The product was filtered in air, washed with ethyl alcohol and ether, and then vacuum dried at room temperature. The product, obtained in 60% yield, was found to be quite soluble in ethyl alcohol and nitrobenzene.

**Nitrosylb(is(4-chlorosalicylaldehyde)-ethylenediimine)cobalt(I)**

The preparation and separation of the black product, after rapid absorption of nitric oxide, were carried out as for the 5-chloro compound. The quantities used were: Bis(4-chlorosalicylaldehyde)-ethylenediimine (0.69 g., 2.05 x 10^{-3} Moles) in dimethylformamide (10 ml.), cobaltous acetate (0.69 g., 2.77 x 10^{-3} Moles) in dimethylformamide (10 ml.).
Nitrosylbis(acetylacetone)-ethylenediaminecobalt(I)

On mixing a slight excess of bis(acetylacetone)-ethylenediamine (1.64 g., $7.32 \times 10^{-3}$ Moles) in absolute alcohol (10 ml.) with cobaltous acetate (1.69 g., $7.68 \times 10^{-3}$ Moles) in water (5 ml.) under nitric oxide the solution darkened depositing a black crystalline product. After concentrating the solution the product was filtered and recrystallised from ethyl alcohol under nitrogen followed by vacuum drying at room temperature.

Found: Co 18.61 C 46.77 H 5.79 N 13.19% \text{Co requires} \quad \text{requires} \\
\text{Calculated: Co 18.92 C 46.30 H 5.84 N 13.50%}

This nitrosyl was apparently more stable than the majority of related compounds prepared; analyses and infra-red spectra showed that no change occurred on recrystallisation provided this was done under nitrogen. The product when dry was stable in air, but in solution changed rapidly from purple to brown.

It was necessary to correct for the vapour pressure of the solvent in determining the amount of nitric oxide absorbed.

The metal salt was invariably used in a slight excess throughout the nitric oxide uptakes but owing to the higher solubility of the acetylacetone Schiff's base in aqueous alcohol, it was the reactant used in excess for this reaction.

Performing the uptake in dimethylformamide gave rise to a rapid which continued absorption of nitric oxide at a reduced rate past the point of one molecule
of nitric oxide absorption (see reaction of bis(3-methoxysalicylaldehyde)-ethylenediaminecobalt(II) in pyridine, this section, p. 55).

**Nitrosylbis(o-hydroxyacetophenone)-ethylenediaminecobalt(I)**

Bis(o-hydroxyacetophenone)-ethylenediamine (1.0 g., 3.38 x 10^{-3} Moles) in dimethylformamide (10 ml.) and cobaltous acetate (0.86 g., 3.45 x 10^{-3} Moles) in the same solvent (4 ml.) were equilibrated with nitric oxide. On mixing the reactants a rapid absorption of nitric oxide occurred giving a black crystalline product. This was filtered in air and the solid washed with water, ethanol and ether; then dried at room temperature in vacuo. The final product was black and obtained in 70% yield.

Found: Co 15.34 C 56.54 H 5.15 N 10.75% C_{18}H_{18}N_{3}O Co requires Co 15.38 C 56.40 H 5.27 N 10.98%

**Nitrosylbis(5-methylsalicylaldehyde)-ethylenediaminecobalt(I)**

Bis(5-methylsalicylaldehyde)-ethylenediamine (1.0 g., 3.38 x 10^{-3} Moles) in dimethylformamide (10 ml.) and cobaltous acetate (0.92 g., 3.69 x 10^{-3} Moles) also in dimethylformamide (5 ml.) were equilibrated with nitric oxide. On mixing a dark brown colouration formed together with a rapid absorption of the gas yielding a brown compound. The product was filtered in air, washed with ethanol and dried at room temperature in vacuo.

Found: Co 15.65 C 56.53 H 4.98 N 10.82% C_{18}H_{18}N_{3}O Co requires Co 15.38 C 56.40 H 5.27 N 10.98%
The product was very soluble in dimethylformamide and attempts to precipitate the compound using diethyl ether gave compounds of indefinite composition.

Nitrosylbis(5-methoxysalicylaldehyde)-ethylenediiminecobalt(I)

Bis(5-methoxysalicylaldehyde)-ethylenediime (1.51g., $4.9 \times 10^{-3}$ Moles) in dimethylformamide (20 ml.), and cobaltous acetate (1.40g., $5.62 \times 10^{-3}$ Moles) in the same solvent (10 ml.) were equilibrated with nitric oxide. A green-brown compound was precipitated during the rapid absorption of the gas. The product was filtered in air, washed with water, ethanol and ether, then dried under reduced pressure at room temperature. A 70% yield of the product was obtained.

Found: Co 14.26 C 52.09 H 4.52 N 9.86% C$_{18}H_{18}N_0$Co requires Co 14.20 C 52.04 H 4.38 N 10.12%

The quantitative results of the nitric oxide absorptions for all the cobalt compounds prepared are shown in Table 4, Section V, p. 84.

Some preliminary work, carried out with the manganese(II) and the iron(II) compounds, is described in detail below.

Reaction of Bis(salicylaldehyde)-ethylenediiminemanganese(II) with nitric oxide

Preparations based on methods (1) and (2) above were carried out.
Method (1)

Bis(salicylaldehyde)-ethylenediamine (1.03 g., 3.84 x 10^{-3} Moles) in dimethylformamide (30 ml.) and manganous acetate (1.02 g., 4.16 x 10^{-3} Moles) also in dimethylformamide (10 ml.) were separately equilibrated with nitric oxide. On mixing, a brown solution formed which gave a green-brown product. The product was filtered in air, washed with water, acetone and ether, then dried at room temperature under reduced pressure. The gas uptake was rapid corresponding to 0.74 Moles of nitric oxide per gram atom of manganese complexed with the Schiff's base.

\[
\text{Found: Mn 13.20} \quad \text{C}_{16}H_{14}N_2O_2MnN\text{O requires Mn 15.63}\%
\]

\[
\text{C}_{16}H_{14}N_2O_2Mn_2N\text{O requires Mn 15.98}\%\]

Bis(salicylaldehyde)-ethylenediamine (1.0 g., 3.73 x 10^{-3} Moles) in chloroform (20 ml.), and manganous acetate (0.95 g., 3.88 x 10^{-3} Moles) in aqueous ethanol (15 ml.) were equilibrated with nitric oxide. On mixing, the solution turned brown but no solid was deposited. A slow absorption of 0.75 - 0.9 Moles of nitric oxide per gram atom of manganese complexed with the Schiff's base occurred.

Method (2)

Bis(salicylaldehyde)-ethylenediaminemonomanganese(II) (0.39 g., 1.21 x 10^{-3} Moles), contained in a notched, sealed tube, was placed between a ball and socket joint. (This joint replaced flask C and tap 7 in Fig. 6).
The solvent (chloroform, 25 ml.) was equilibrated with the nitric oxide in flask B, after which the tube containing the manganese complex was broken using the ball and socket joint, and the solid washed into flask B. A slow absorption of nitric oxide occurred (1.8 moles per gram molecule of manganese - Schiff's base complex, in twenty-four hours) yielding a brown product. The reaction mixture did not react with oxygen, the compound was filtered in air and recrystallised from chloroform.

Both methods gave products of similar manganese content. The fractional uptake found by method (1) may be due to hydrolysis by the acetic acid generated in the reaction. Further work is necessary to determine the nature of the products.

**Reaction of Bis(salicylaldehyde)-ethylenediimineiron(II) with nitric oxide**

The preparation was performed as in method (2) above. Bis(salicylaldehyde)-ethylenediimineiron(II) (0.5 g., 1.55 x 10^-3 Moles), prepared prior to reaction (see Section III(a), p. 46) was kept in flask D under nitrogen. Dimethylformamide (30 ml.) was equilibrated with nitric oxide in flask B, after which the reactants were mixed under the gas. A rapid reaction occurred in which 0.98 moles of nitric oxide per gram molecule of complex was absorbed, to give a brown solution. No solid was deposited and in air the solution changed from brown to deep red.

The above reaction was repeated and after one molecule of nitric oxide had been absorbed the apparatus was evacuated and filled with oxygen. Approximately half a molecule of oxygen per gram atom of iron complex was rapidly
absorbed, the solution changing from brown to deep red. It was not possible to isolate any solid material from the above solutions.

However, mixing bis(salicylaldehyde)-ethylenediamineiron(II) (0.7 g., $2.2 \times 10^{-3}$ Moles) with 96% ethanol (20 ml.) under nitric oxide gave a rapid uptake of 0.80 moles of the gas per molecule of iron complex. A brown-green product separated which was filtered under nitrogen.

Found: Fe 16.14 C$_{16}H_{14}N_2O_2$Fe NO requires Fe 15.86%

A correction for the vapour pressure of the solvent was applied. Exposure of the filtrate from the preparation to air gave a rapid colour change from red to brown. The compound when dampened with the solvent also changed to red in air, although when dry seemed quite stable (see Section V, p.120 for further work on this compound).

Carrying out the reaction as method (2) eliminated absorption of nitric oxide by the ferrous sulphate solution [128]. But more important it prevented the hydrolysis that occurs when an aqueous solution of ferrous sulphate is mixed with the Schiff's base in dimethylformamide. The hydrolysis of the product and the Schiff's base results from the sulphuric acid produced during the reaction. A preliminary reaction using ferrous acetate, prepared prior to reaction, in place of ferrous sulphate gave a rapid reaction with nitric oxide and subsequently with oxygen. No solid, however, could be isolated from the reaction mixture.

The nickel(II), copper(II), and zinc(II) complexes did not react with nitric oxide either by method (1) or method (2).
(c) PREPARATION OF LIGANDS

The preparative method used by Diehl [19] proved to be generally successful for the Schiff's bases studied.

(1) **Bis(salicylaldehyde)-ethylenediimine**

An alcoholic solution of ethylenediamine (6.0 g., 0.1 Mole) was added to a boiling alcoholic solution of salicylaldehyde (24.5 g., 0.2 Mole). Yellow platelets were immediately precipitated which after filtration were recrystallised from ethanol or dimethylformamide. The latter was the better solvent. The product was dried at 110° - 120°C in air.

(2) **Bis(6-nitrosalicylaldehyde)-ethylenediimine**

The aldehyde was prepared from m-nitrophenol by the Reimer-Tiemann reaction [129], and condensed with ethylenediamine. Care was taken not to add an excess of the amine because the nitro-substituted Schiff's bases were soluble in an excess of ethylenediamine, due to the formation of the ethylenediamine salt of the moderately acidic nitrophenols.

(3) **Bis(5-nitrosalicylaldehyde)-ethylenediimine**

The aldehyde and the amine were condensed as in (1). A yellow powder precipitated which caused violent bumping on continued heating. The product was purified by recrystallisation from dimethylformamide, not by sublimation [120] and then dried in air at 120°C.

(4) **Bis(3-nitrosalicylaldehyde)-ethylenediimine**

This aldehyde was prepared by nitration of salicylaldehyde [3]
yielding tan crystals. Condensation with ethylenediamine as in (1) gave an orange-yellow powder. The product was recrystallised from dimethylformamide, washed with ethanol, and dried in air at 110° - 120°C.

(5) Bis(5-chlorosalicylaldehyde)-ethylenediimine

The substituted aldehyde was prepared from m-chlorophenol using Liggett and Diehls [130] modification of the Duff [131] reaction. Its condensation with ethylenediamine as in (1) gave yellow platelets. These were recrystallised twice from ethanol and dried at 110° - 120°C in air.

Found: C 57.20 H 4.11 N 8.12 Cl 22.0% C₁₆H₁₄N₂O₂Cl₂ requires C 57.10 H 4.19 N 8.30 Cl 21.04%

(6) Bis(4-chlorosalicylaldehyde)-ethylenediimine

The aldehyde was prepared from m-chlorophenol by means of the Reimer-Tiemann reaction [132]. Condensation with ethylenediamine was performed as in (1) yielding a yellow powder. The product was recrystallised from ethanol, and dried in air at 110° - 120°C.

(7) Bis(acetylacetone)-ethylenediimine

The method of Martell [133] et al. was used, and the product recrystallised from carbon tetrachloride to give colourless needles.

(8) Bis(o-hydroxyacetophenone)-ethylenediimine

The preparation was carried out as in (1) with salicylaldehyde replaced by o-hydroxyacetophenone. A lemon yellow product was obtained which was recrystallised from ethanol. The yellow needle-like product
was dried at 110° - 120°C.

(9) Bis(5-methylsalicylaldehyde)-ethylenediamine

The aldehyde was prepared from \( p \)-cresol by means of the modified Duff [130] reaction. Condensation with ethylenediamine was performed as in (1). The product was recrystallised from ethanol to form yellow platelets, and dried at 110° - 120°C.

(10) Bis(5-methoxysalicylaldehyde)-ethylenediamine

The aldehyde was prepared from \( p \)-methoxyphenol using the modified Duff [130] reaction. Condensation with ethylenediamine was performed as in (1) and the product was recrystallised from dimethylformamide. A yellow powder was obtained which was dried in air at 110° - 120°C.

(11) Bis(3-methoxysalicylaldehyde)-ethylenediamine

The preparation was performed as in (1), using commercial \( o \)-vanillin. The product was recrystallised from dimethylformamide as a yellow powder, which was dried in air at 110° - 120°C.

The preparations above gave Schiff's bases in excellent yields (80 - 90%). A list of melting-points is shown in Table 2.

An attempt to prepare the 4-nitro substituted aldehyde using the method of Segesser and Calvin [134] was not successful.
The amine in all cases was ethylenediamine and except where stated the aldehyde was salicylaldehyde, or a substituted derivative. In Table 2 the substituents only are entered.

<table>
<thead>
<tr>
<th>Schiff's base</th>
<th>Melting-point obtained °C</th>
<th>Literature value of melting-point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsubstituted</td>
<td>123</td>
<td>123 [19]</td>
</tr>
<tr>
<td>6,6'-dinitro</td>
<td>189 - 191</td>
<td>-</td>
</tr>
<tr>
<td>5,5'-dinitro</td>
<td>275 - 277 (decomposition ?)</td>
<td>275 - 277 [120]</td>
</tr>
<tr>
<td>3,3'-dinitro</td>
<td>246-247 (decomposition)</td>
<td>-</td>
</tr>
<tr>
<td>5,5'-dichloro</td>
<td>174 - 175</td>
<td>-</td>
</tr>
<tr>
<td>4,4'-dichloro</td>
<td>148 - 149</td>
<td>148.5 [135]</td>
</tr>
<tr>
<td>Bis(acetylacetonate)-ethylenediamine</td>
<td>109 - 110</td>
<td>113 [133]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>111 [4]</td>
</tr>
<tr>
<td>Bis(2-hydroxyacetophenone)-ethylenediamine</td>
<td>193.5 - 194.5</td>
<td>195 [3]</td>
</tr>
<tr>
<td>5,5'-dimethyl</td>
<td>164</td>
<td>164 [130]</td>
</tr>
<tr>
<td>5,5'-dimethoxy</td>
<td>164</td>
<td>161 [3]</td>
</tr>
<tr>
<td>3,3'-dimethoxy</td>
<td>162</td>
<td>161 [3]</td>
</tr>
</tbody>
</table>
SECTION IV

EXPERIMENTAL TECHNIQUES

(a) ANALYTICAL METHODS
(b) MOLAR CONDUCTANCE MEASUREMENTS
(c) MOLECULAR WEIGHT DETERMINATIONS
(d) MAGNETIC SUSCEPTIBILITY MEASUREMENTS
(e) INFRA-RED SPECTRA
(f) ULTRA-VIOLET AND VISIBLE SPECTRA
(g) THERMOGRAVIMETRIC ANALYSIS
(h) PURIFICATION OF REAGENTS
EXPERIMENTAL TECHNIQUES

(a) ANALYTICAL METHODS

Volumetric Estimation of Cobalt

A back titration method using the disodium salt of ethylenediamine tetraacetic acid (E.D.T.A.), similar to that of Harris and Sweet [136] was used.

Samples of the complex (0.1 g.) were weighed by difference into wide-necked conical flasks (250 ml.). To the solid, concentrated nitric acid (5 ml.), concentrated perchloric acid (5 ml.) and concentrated sulphuric acid (2 ml.) were added. The mixture was then heated just to dryness. After cooling, the cobalt sulphate formed was dissolved and transferred to larger conical flasks (1000 ml.) with deionised water (400 ml.). To the solution a known volume of E.D.T.A. (0.01 Molar) was added in a two or threefold excess. The E.D.T.A. solution was previously standardised against a zinci sulphate solution [137]. The resultant solution was then neutralised to methyl red using dilute ammonium hydroxide and boiled for a few minutes to ensure quantitative formation of the cobalt - E.D.T.A. complex. After cooling the solution its pH was adjusted to 10 with dilute ammonium hydroxide, and a few drops of Eriochrome Black T solution added as indicator. The excess of E.D.T.A. was back titrated against a standard zinci sulphate solution until the colour change blue to red occurred.

The clarity of the end-point in the back titration was dependent on
the amount of acid remaining after decomposition of the complex. During preliminary determinations the decomposition was taken just to fumes of sulphur trioxide. This solution after neutralisation to pH 10 and dilution with water (50 ml.) gave indistinct end-points. However, the same method applied to standard cobalt solutions omitting the addition of acids gave clear end-points. Evaporating to dryness samples of the complex to which acids were added and diluting with a large quantity of water greatly reduced the ionic strength of the solution and eliminated this effect.

The method was found to be reliable to within 1%. All determinations were carried out in triplicate, the mean value only is stated in the analysis results in Section III, Parts (a) and (b).

In all the preparations performed under nitrogen contamination of the product by tap-grease could lead to low analytical figures for cobalt. This was minimised by washing the product with organic solvents whenever possible. However, complete removal was not always achieved. Grease would show up as a scum during the decomposition stage.

A quick but less accurate preliminary determination of cobalt was occasionally performed gravimetrically as follows. A weighed sample of the complex (0.1 g.) was carefully ignited in air, the temperature not exceeding 900°C. After cooling the black residue in a desiccator, it was weighed as Co₇O₄ [16(b), 138]. The method was accurate to within 4 - 5%.
Volumetric Estimation of Manganese

A combination of two methods was used [139, 140].

Samples of the complex (0.1 g.) were weighed quickly into wide-necked conical flasks and decomposed in the same manner as for the cobalt estimation. Water (200 ml.) was added to the solid remaining after decomposition and sulphur dioxide bubbled through until solution was complete. Excess sulphur dioxide was removed by boiling, and the solution adjusted to pH 4 - 5 using methyl red. Sufficient Rochelle salt was added to prevent precipitation of manganese hydroxide, together with a spatula end of ascorbic acid. A two or threefold excess of standard E.D.T.A. solution was added and the whole heated to 70° - 80°C. After cooling, the pH was adjusted to 10 using dilute ammonium hydroxide and a few drops of Eriochrome Black T solution added. The excess E.D.T.A. was back titrated as in the cobalt estimation.

The residue remaining after decomposition with concentrated acids was not readily soluble in water, but reduction with sulphur dioxide afforded solution. This procedure did not affect the accuracy of the method (see Table 3). Addition of ascorbic acid prevented oxidation of the manganese to the dioxide. Better end-points were obtained using the back titration method rather than the direct method.
TABLE 3

<table>
<thead>
<tr>
<th>Solution</th>
<th>Manganese present (mg.)</th>
<th>Manganese found (mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Standardised KMnO₄ solution, reduced with sulphur dioxide</td>
<td>17.74</td>
<td>17.80</td>
</tr>
<tr>
<td>(2) Solution evaporated to dryness with concentrated acids. Residue dissolved in water using sulphur dioxides.</td>
<td>17.74</td>
<td>17.81</td>
</tr>
</tbody>
</table>

**Gravimetric Estimation of Iron**

Samples of the complex (0.1 g.) were ignited slowly in air to dull red heat. The pink product was weighed as Fe₂O₃· [16c].

**Analysis of Carbon, Hydrogen and Nitrogen**

Micro-analyses for these elements were carried out in the Micro-analytical Laboratories of the Max Planck Institute, Mülheim, Germany by Dr. Alfred Bernhardt.

**(b) Molar Conductance Measurements**

All measurements were carried out using a Mullard conductivity
bridge type GM 4140/1. All determinations but one were carried out in air using a cell with conventional dip-in electrodes. In the case of nitrosyl bis(acetylacetonato)-ethyleneiminediiminecobalt(I) the measurement was performed under nitrogen using the apparatus shown in Fig. 7. After determining the resistance of the solvent a sample of the complex was weighed into the blunt end of a ball and socket joint C. Into compartment A a suitable volume of solvent was placed to yield on mixing an approximately 0.001 Molar solution. The apparatus was connected to point F on the main apparatus (see Section III, Fig. 4), evacuated, flushed several times with nitrogen and then filled with the gas to atmospheric pressure. With tap 1 closed the solid and solvent were brought into contact by tipping the apparatus from side to side. After solution was complete it was transferred to compartment B via tap 1, and the resistance recorded. The apparatus was again evacuated and filled with air, the change in resistance of the solution was determined at time intervals.

All readings were taken at 25°C in a thermostat using nitrobenzene (A.R. reagent, dried over calcium chloride) and dimethylformamide [121, 122] as solvents.

(c) MOLecULAR WEIGHT DETERMINATIONS

Owing to the insolubility of the complexes in solvents possessing an appreciable vapour pressure an Isopiestic method could not be used [141, 142].
APPARATUS FOR CONDUCTANCE MEASUREMENTS IN ABSENCE OF AIR

Figure 7
Rast's method [143, 144] gave spurious results, crystallisation soon occurred even from 0.001 Molar solutions on cooling.

The Beckmann Cryoscopic method [145] had been used previously by other workers with some Schiff's base complexes [146] and found application with a few of the nitrosyls prepared (see Section V, Table 5). Nitrobenzene (A.R. reagent, dried over calcium chloride) was used as the solvent.

(a) MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Measurements were made on the complexes by the Gouy method [147(a)]. The compounds were in powder form and contained in perspex tubes using 10 cms. length samples.

The magnet was of a Humphreys-Sucksmith type capable of a field variation up to about 9000 Gauss. Fitted to the magnet was a cryostat temperature control unit [148], similar to that used by Figgis and Nyholm [149], yielding a temperature range 90° - 400°K. Weight changes were measured on a Stanton SM 12 balance.

Determinations were carried out in an atmosphere of nitrogen at three different field strengths between the temperature range 90° - 350°K. The molar susceptibility (\( \chi_M \)) of the compound was calculated from the simplified formula,

\[
\chi_M = \frac{2\omega_x\omega_y\omega_z}{Wx^2}
\]
w = Weight change, in and out of field.

$g =$ Acceleration due to gravity.

$I =$ Specimen length.

$M =$ Molecular weight of compound.

$W =$ Specimen weight.

$H =$ Field strength.

Owing to the weak paramagnetism of the compounds and the complex nature of the ligands their diamagnetism was determined experimentally where possible rather than from Pascal's constants [150] (Section V (d), Table 12).

The effective magnetic moment was calculated from

$$\mu_{\text{eff.}} = 2.84 \sqrt{\chi_A T}$$

$$\chi_A =$ Susceptibility of central metal atom.

$T =$ Temperature in degrees absolute.

(e) **INFRA-RED ABSORPTION SPECTRA**

The spectra were recorded on a Grubb-Parsons double-beam grating instrument, type GS 2A. The compounds were mullsed with 'nujol' and examined between rock-salt plates.

(f) **ULTRA-VIOLET AND VISIBLE SPECTRA**

The absorption spectra were recorded over the range 1,000 μμ -
270 μ using one centimetre matched silica cells on a Unicam SP 500
spectrophotometer. The samples were maintained at 25°C using a SP 570
constant temperature housing. All solutions were made up and kept under
nitrogen using the apparatus shown in Fig.8. This was attached to point F
on the main apparatus (see Section III, Fig.4). The compound was weighed
into the blunt end of a ball and socket joint A and the apparatus, minus
the cell attachment, weighed. A suitable volume of solvent was placed
into flask B and the apparatus evacuated, flushed several times with
nitrogen, then filled with the gas and weighed again. The cell attachment
was joined at C and the entire apparatus evacuated. Tap 1 was closed
and the complex mixed with the solvent and then transferred to the cell.
The apparatus was then filled with nitrogen by opening tap 1 and the cell
plus contents isolated by closing tap 2. The cell was detached at C
and placed in the cell housing of the spectrophotometer; both cell and
housing were then covered with a black cloth. The cell compartment lid
could not be used because of the protruding stem and tap attached to the
cell. The solution could be diluted as required by reattaching the cell
to C, evacuating the apparatus and tipping some of the solution into flask B.
The cell was then detached and the remaining apparatus cleaned out and
more solvent placed into flask B and weighed as above. The solvent and
solution were then mixed under vacuum as were the solid and solvent de­
scribed previously, after reattaching the cell at C.
Figure 8
APPARATUS FOR SPECTROPHOTOMETRIC STUDIES UNDER NITROGEN

Pump
Nitrogen inlet.

A
Compound

C

B
Solvent

Spectrophotometric cell
Purified dimethylformamide was used as the solvent in all determinations. Solutions of concentrations $10^{-4}$ to $10^{-5}$ Molar were used.

(g) THERMOGRAVIMETRIC ANALYSIS

The thermal decomposition in air of a few of the compounds prepared was studied using an automatic direct reading 'Stanton' thermobalance, model HT - D. Weight losses over the temperature range, room temperature - 650°C were recorded.

(h) PURIFICATION OF REAGENTS

Cobaltous acetate tetrahydrate

Commercial cobaltous acetate was recrystallised from dilute acetic acid, then washed with 96% ethyl alcohol and dried in air at 40° - 50°C.

Found Co 23.72, 23.71 C,H,O,Co, 4H,O requires Co 23.68%

Dimethylformamide

A method similar to that of Thomas and Rochow [122] was used. Dimethylformamide (3 litres) was dried over barium oxide, then filtered and distilled under reduced pressure, using a nitrogen 'bleed'. The middle fraction (b.pt. 54°C, pressure = 1.5 cms. Hg) was retained (1½ litres), the first and last fractions not being used. The purified dimethylformamide was stored under nitrogen in a flask (2 litres), resembling a large wash bottle. Samples were drawn from the flask by applying nitrogen pressure to the inlet. After obtaining the sample the nitrogen flow
was connected to the outlet and bubbled through the solvent to exclude all air. The flask was then sealed under nitrogen.

Advantages of dimethylformamide as a solvent

(1) It was not necessary to apply a vapour pressure correction for the solvent during the preparation of the nitrosoys (b.pt. 150°C at 760 mm.).

(2) Both cobaltous acetate and the Schiff's bases were very soluble in this solvent. This is the first time dimethylformamide has found general application on the compounds studied.

(3) It would seem possible from preliminary work that some of the cobalt-Schiff's base complexes could be recrystallised from this solvent under nitrogen.

Chloroform

The chloroform was shaken six times with half its own volume of water, then dried over calcium chloride for at least 24 hours. Distillation was performed in air at atmospheric pressure, and the distillate stored in the dark (b.pt. 61°C at 760 mm.).
SECTION V

RESULTS AND DISCUSSION

(a) NITRIC OXIDE ABSORPTIONS, MOLECULAR WEIGHT AND
    CONDUCTANCE MEASUREMENTS

(b) MAGNETIC SUSCEPTIBILITY MEASUREMENTS

(c) INFRA-RED SPECTRA

(d) ULTRA-VIOLET AND VISIBLE SPECTRA

(e) THERMOGRAVIMETRIC ANALYSIS
### TABLE 4

**THE QUANTITATIVE NITRIC OXIDE ABSORPTIONS BY COBALT COMPOUNDS**

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Moles NO/gram atom cobalt complexed</th>
<th>Method See Section III (h)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsubstituted</td>
<td>1.06; 1.01; 1.01</td>
<td>(2)</td>
<td>Chloroform</td>
</tr>
<tr>
<td>6,6'-dinitro</td>
<td>1.04</td>
<td>(1)</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>5,5'-dinitro</td>
<td>1.03; 1.01; 0.99</td>
<td>(1)</td>
<td>&quot;</td>
</tr>
<tr>
<td>3,3'-dinitro</td>
<td>1.02; 1.01</td>
<td>(1)</td>
<td>&quot;</td>
</tr>
<tr>
<td>5,5'-dichloro</td>
<td>1.00; 0.98</td>
<td>(1)</td>
<td>&quot;</td>
</tr>
<tr>
<td>4,4'-dichloro</td>
<td>0.96; 0.99</td>
<td>(1)</td>
<td>&quot;</td>
</tr>
<tr>
<td>Acetylacetone-</td>
<td>1.03; 0.97</td>
<td>(1)</td>
<td>Water/Ethanol</td>
</tr>
<tr>
<td>ethylenediamine compd.</td>
<td></td>
<td></td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>α-hydroxyacetophenone</td>
<td>1.02; 0.99</td>
<td>(1)</td>
<td>&quot;</td>
</tr>
<tr>
<td>ethylenediamine compd.</td>
<td></td>
<td></td>
<td>&quot;</td>
</tr>
<tr>
<td>5,5'-dimethyl</td>
<td>1.01; 1.02; 0.99</td>
<td>(1)</td>
<td>&quot;</td>
</tr>
<tr>
<td>5,5'-dimethoxy</td>
<td>1.00</td>
<td>(1)</td>
<td>&quot;</td>
</tr>
<tr>
<td>3,3'-dimethoxy</td>
<td>1.07</td>
<td>(1)</td>
<td>&quot;</td>
</tr>
<tr>
<td>Compound</td>
<td>Molecular weight (monomer value)</td>
<td>Solvent</td>
<td></td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>----------------------------------</td>
<td>--------------------------</td>
<td></td>
</tr>
<tr>
<td>Unsubstituted</td>
<td>355.2</td>
<td>Nitrobenzene</td>
<td></td>
</tr>
<tr>
<td>5,5'-dichloro</td>
<td>424.2</td>
<td>Nitrobenzene</td>
<td></td>
</tr>
<tr>
<td>o-hydroxyacetophenone-ethylenediamine compd.</td>
<td>383.2</td>
<td>Nitrobenzene</td>
<td></td>
</tr>
<tr>
<td>3,3'-dimethoxy</td>
<td>415.3</td>
<td>Deposition from nitrobenzene on standing</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 5

MOLECULAR WEIGHTS OF SOME COBALT-SCHIFF'S BASE NITROSYLS
## Table 6

**Molar Conductances of Cobalt Nitrosyls at 25°C**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar Conductance mhos mol. ( \cdot ) cm. (^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitrobenzene</td>
</tr>
<tr>
<td>Unsubstituted</td>
<td>0.58</td>
</tr>
<tr>
<td>6,6'-dinitro</td>
<td>-</td>
</tr>
<tr>
<td>5,5'-dinitro</td>
<td>Insoluble</td>
</tr>
<tr>
<td>3,3'-dinitro</td>
<td>Insoluble</td>
</tr>
<tr>
<td>5,5'-dichloro</td>
<td>0.01</td>
</tr>
<tr>
<td>4,4'-dichloro</td>
<td>-</td>
</tr>
<tr>
<td>Acetylacetone-ethylenediamine compd.</td>
<td>0.27(^*)</td>
</tr>
<tr>
<td>o-Hydroxyacetophenone-ethylenediamine compd.</td>
<td>0.04</td>
</tr>
<tr>
<td>5,5'-dimethyl</td>
<td>0.02</td>
</tr>
<tr>
<td>5,5'-dimethoxy</td>
<td>0.04</td>
</tr>
<tr>
<td>3,3'-dimethoxy</td>
<td>2.06</td>
</tr>
</tbody>
</table>

* These determinations were performed under nitrogen.

+ After exposure to air.

↑ Continuous increase in conductance after preparation of solution.

Specific resistance of nitrobenzene = \( 1.37 \times 10^7 \) ohms cm.\(^*\).

Specific resistance of dimethylformamide = \( 5.5 \times 10^5 \) ohms cm.\(^*\).
RESULTS AND DISCUSSION

(a) NITRIC OXIDE ABSORPTIONS: MOLECULAR WEIGHT AND CONDUCTANCE MEASUREMENTS

The results in Table 4 show that without exception one molecule of nitric oxide reacted with one molecule of the cobalt-Schiff's base complex, in the compounds isolated and investigated.

The Beckmann cryoscopic method for molecular weight determinations found a limited use. It appears that the compounds are monomeric (see Table 5) although no great significance can be attached to the actual value obtained.

The results in Table 6 show the compounds to be non-conducting in nitrobenzene and dimethylformamide. The usual range of molar conductances for different electrolytes in these solvents at approximately 25°C and concentrations of 0.001 Molar, are given in Table 7.

TABLE 7

<table>
<thead>
<tr>
<th>Electrolyte Type</th>
<th>Molar Conductance Range, mhos.mol. (^{-1})cm. (^{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitrobenzene</td>
</tr>
<tr>
<td>(M^+X^-)</td>
<td>20 - 35 [151]</td>
</tr>
<tr>
<td>(M^{2+}(X^-)_2)</td>
<td>30 - 40 [152]</td>
</tr>
</tbody>
</table>
The measurements carried out using dimethylformamide in air showed a steady increase in conductance up to a maximum of approximately 50 mhos mol⁻¹ cm⁻² (indicated by arrows in Table 6). However, performing the measurement under nitrogen (see acetylacetone-ethylenediamine compound) eliminated this effect. Two possible causes of this behaviour are:

1. Aerial oxidation in dimethylformamide giving a conducting species.
2. Absorption of water by the solvent and reaction of the NO⁺ group with this water to give a nitro group, (see Section II (b), p. 36).

\[
\text{NO}^+ + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + 2\text{H}^+
\]

This is similar to the conversion,

\[
\text{Ni(OH)NO(OMe)}_2 \rightarrow \text{NiNO}_2(\text{OMe})\text{MeOH}[156]
\]

which occurs in alcohol.

The resultant effect of both possibilities could be:

\[
\begin{array}{c}
\text{NO}^+ \\
\text{C} \\
\text{N} \\
\end{array}
+ 2\text{O}^{2-} 
\rightarrow 
\begin{array}{c}
\text{NO}_2^- \\
\text{C} \\
\text{N} \\
\end{array}
\]

A similar reaction has been postulated for the nitroprussides [16(d)] but the reaction in general has not been investigated.
RESULTS AND DISCUSSION

(b) MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Cobalt-Schiff's base nitrosyls

The results in Tables 8, 9, and 10 show that the room temperature magnetic moments of the Cobalt-Schiff's base nitrosyls lie in the range 0.5 - 0.6 B.M. If the nitric oxide was coordinated as NO\(^+\) to the metal, then the cobalt would effectively have an oxidation state of +1 and diamagnetism would be expected for spin-paired complexes. However, small moments of the above order can be accounted for in three main ways.

1) Temperature Independent or Van Vleck Paramagnetism (TIP)

\[ \mu_{\text{eff.}} = 2.84 \sqrt{\chi_A x T} \]

This form of paramagnetism apparently arises from perturbation of the diamagnetic ground state of the metal by the magnetic field, described by 'mixing in' with the ground state a level possessing a different orbital contribution. If the two levels are separated by an energy (hv) that is considerably greater than kT then thermal population between the two levels does not occur and the susceptibility remains constant as the temperature varies. The equation

\[ \mu_{\text{eff.}} = 2.84 \sqrt{\chi_A x T} \]

then reduces to the form

\[ \mu_{\text{eff.}} \propto \sqrt{T} \]
Thus, if the observed paramagnetism arises in this way, a plot of $\mu_{\text{eff.}}$ against $\sqrt{T}$ should be linear. Examples where TIP alone contributes to the moment are KMnO$_4$ ($d^0$), $70 \times 10^{-6}$ c.g.s.u. and a number of cobalt(III) amines ($d^6$) [159], $60 - 120 \times 10^{-6}$ c.g.s.u. TIP is usually compounded with the molar susceptibility of the metal ion, and has been allowed for in the Langevin-Debye expression for the susceptibility

$$\mu_{\text{eff.}} = 2.84 \sqrt{\frac{\chi_A - \chi_N}{\chi_N}}$$

$\chi_N$ is the TIP contribution to the susceptibility and is often quite marked in one unpaired electron systems, amounting to something like $50 \times 10^{-6}$ c.g.s.u. in the molar susceptibility at room temperature. For instance, in the cupric ion TIP adds $60 \times 10^{-6}$ c.g.s.u. to the molar susceptibility of some $1500 \times 10^{-6}$ at room temperature.

(2) Incomplete pairing of electron spins due to some form of interaction between the metal ions which would otherwise have an integral number of unpaired electrons. Datar and Datar [160] suggested that the small moments associated with TIP could arise from this effect. Nyholm [158], however, points out that such paramagnetism would be temperature dependent.

(3) A third way of accounting for such low moments was postulated by Nast [72] who assumed an equilibrium between two forms of the bis(acetylacetone)cobalt(I) nitrosyl. One form was considered diamagnetic; the other to contain two unpaired electrons with the equilibrium lying well towards the diamagnetic form. However, temperature dependence of the
susceptibility would be expected and perhaps some variation with substituents. Such an effect was not observed for the compounds studied in this work.

Figures 9 and 10 show that the linear relationship between $\mu_{\text{eff}}$ and $\sqrt{T}$ holds true for the 5,5'-dinitro, dichloro, dimethyl and dimethoxy substituted nitrosyl derivatives. Although the determinations were carried out at three field strengths, for simplicity only one set of results for each compound is shown graphically. The results in Tables 8 and 9 show the susceptibility to be essentially constant over the temperature range studied and field independent. From the results in Table 10 and the graphs in Figure 11, cobalt salen nitrosyl and the acetylacetone-ethylenediamine nitrosyl owe their fractional moments primarily to TIP, but the effect is not so obvious as with the previously mentioned nitrosyls. The susceptibilities of both compounds are somewhat temperature dependent, although the dependence did not become marked until below 160°C for the cobalt salen nitrosyl. It is suggested that a very small amount of paramagnetic impurity may cause the change in susceptibility with temperature, the effect becoming more noticeable at low temperatures. It was mentioned previously that, in general, these nitrosyls were not particularly stable on prolonged contact with solvents, although it was possible to re-crystallise these two compounds, which yield slightly discordance magnetic results, to give analytically pure products (Section III(b)). Even though the
Figure 9.

\[
\mu_{\text{eff}(\text{Co})} \text{ against } \sqrt{T^0 K}
\]

\[
\begin{align*}
\sqrt{T^0 K} & \\
4 & 8 & 12 & 16 & 20
\end{align*}
\]

\[
\log_{10} H_\Delta^3 = 7.8451
\]

Bis(5NO_2-SALICYLALDEHYDE)-ETHYLENEDIIMINE COBALT (I) NITROSYL.

\[
\mu_{\text{eff}(\text{Co})} \text{ against } \sqrt{T^0 K}
\]

\[
\begin{align*}
\sqrt{T^0 K} & \\
4 & 8 & 12 & 16 & 20
\end{align*}
\]

\[
\log_{10} H_\Delta^3 = 7.8451
\]

Bis(5Cl-SALICYLALDEHYDE)-ETHYLENEDIIMINE COBALT (I) NITROSYL.
Figure 10.

\[ \mu_{\text{eff}(\text{Co})} \text{ AGAINST } \sqrt{T^0K} \]

\[ \text{Bis (5CH}_3\text{-SALICYLALDEHYDE)-ETHYLENEDIIMINE COBALT} \Theta \text{ NITROSYL} \]

\[ \log_{10} H^2 = 7.8451 \]

\[ \mu_{\text{eff}(\text{Co})} \text{ AGAINST } \sqrt{T^0K} \]

\[ \text{Bis (5CH}_3\text{-SALICYLALDEHYDE)-ETHYLENEDIIMINE COBALT (1) NITROSYL} \]
Figure II.

Bis (SALICYLALDEHYDE)-ETHYLENEDIIMINE COBALT (I) NITROSYL

$\log_{10} H^2 = 7.6569$

Bis (ACETYLACETONE)-ETHYLENEDIIMINE COBALT (I) NITROSYL

$\log_{10} H^2 = 7.8451$
acetylacetone-ethylenediamine nitrosyl was recrystallised under nitrogen
a trace of paramagnetic impurity may have been formed. Cobalt salen
nitrosyl was very difficult to pack and appeared to be 'electrostatic'.
The field dependence of this compound may arise from packing difficulties
rather than from any ferro-magnetic impurity. Too much significance
should not be attached to slight deviations from linearity because large
errors can occur in the very small pulls (0.00050 gs.) being measured.

It is concluded that the cobalt-Schiff's base nitrosyls essentially
contain no unpaired electrons, being spin-paired complexes of cobalt(I) (d^8)
with nitric oxide co-ordinated as NO^+ (See Section VI).

The manganese salen compound (Fig.12) possessed a moment of about
5.1 B.M. (Table 11) at room temperature and was field independent. A
Curie-Weiss relationship was obeyed yielding θ = 63°. Asmussen and
Soling [26] obtained a similar moment (5.29 B.M.) which for a manganese(II)
spin-free complex is somewhat low (spin only moment = 5.92 B.M.). The
decrease in moment could arise from antiferromagnetic interactions between
neighbouring molecules rendering the system magnetically undilute. Signi-
ficance can only be attached to θ if confirmation of the antiferromagnetic
nature of the compound is carried out by measurements in solution or using
the method of 'isomorphous substitution' [147(c)]: unfortunately these
measurements were not carried out but bis(salicylaldehyde)-ethylenediamine-
zinc(II) [33] is suggested as a diluent. Using the equation
Figure 12

$\frac{1}{\chi_M} \times 10^4$ AGAINST $T^0K$

$\log_{10} H_2 = 7.3251$

$\theta = 63^\circ$
assuming the low moment is due to antiferromagnetism, a value of $\mu_{\text{eff.}} = 5.67$ at room temperature is obtained.

The moment for ferrous salen (5.05 B.M.) agrees with that expected for a spin-free ferrous complex (4.90 B.M.) (Fig. 13). Its slight field dependence could be due to packing errors or to a very small amount of ferromagnetic impurity. The compound was sealed under vacuum in a susceptibility tube, (see Section III(a), p. 46). Although Bailes et al. [14] obtained a similar moment they took no elaborate precautions to exclude air.

The electronic arrangements and probable hybridisations for the manganese(II) and iron(II) salen complexes are indicated below

![Diagram of Mn$^{2+}$ salen and Fe$^{2+}$ salen complexes with hybridisation](http://example.com/diagram.png)

Both complexes may be described as being of the 'outer' orbital type.
Bis(SALICYLALDEHYDE)-ETHYLENEDIIMINE IRON (II)

$\nu_{\gamma}(Fe) \times 10^{-4}$ AGAINST $T^0K$

$\log_{10} H_z^2 = 7.3251$

Figure 13
TABLE 8

Magnetic Susceptibility Measurements on Cobalt-Schiff's base Nitrosyls.

**Nitrosylbis(5-nitrosalicylaldehyde)-ethylenediaminecobalt(I).**

Temperature °K 298.5 291.5 267.5 236.5 200.5 178.0 148.0 107.0 89

<table>
<thead>
<tr>
<th></th>
<th>(\chi_A) x 10^6</th>
<th>(\mu_{\text{eff.}}) (B.M.)</th>
<th>(\chi_A) x 10^6</th>
<th>(\mu_{\text{eff.}}) (B.M.)</th>
<th>(\chi_A) x 10^6</th>
<th>(\mu_{\text{eff.}}) (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_1)</td>
<td>105.9</td>
<td>0.50</td>
<td>116.3</td>
<td>0.51</td>
<td>105.9</td>
<td>0.51</td>
</tr>
<tr>
<td>(H_2)</td>
<td>109.9</td>
<td>0.54</td>
<td>106.4</td>
<td>0.49</td>
<td>113.4</td>
<td>0.49</td>
</tr>
<tr>
<td>(H_3)</td>
<td>105.9</td>
<td>0.47</td>
<td>127.8</td>
<td>0.47</td>
<td>119.1</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Diamagnetic correction = 171.3 x 10^-6 c.g.s.u.

**Nitrosylbis(5-chlorosalicylaldehyde)-ethylenediaminecobalt(I).**

Temperature °K 297.5 267.5 236.0 204.0 168.5 135.3 94.0

<table>
<thead>
<tr>
<th></th>
<th>(\chi_A) x 10^6</th>
<th>(\mu_{\text{eff.}}) (B.M.)</th>
<th>(\chi_A) x 10^6</th>
<th>(\mu_{\text{eff.}}) (B.M.)</th>
<th>(\chi_A) x 10^6</th>
<th>(\mu_{\text{eff.}}) (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_1)</td>
<td>127.5</td>
<td>0.55</td>
<td>127.5</td>
<td>0.55</td>
<td>127.5</td>
<td>0.55</td>
</tr>
<tr>
<td>(H_2)</td>
<td>127.1</td>
<td>0.52</td>
<td>127.8</td>
<td>0.52</td>
<td>127.8</td>
<td>0.52</td>
</tr>
<tr>
<td>(H_3)</td>
<td>128.6</td>
<td>0.56</td>
<td>128.3</td>
<td>0.56</td>
<td>128.3</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Diamagnetic correction = 128.6 x 10^-6 c.g.s.u.

\[ \log_{10} H_1^2 = 7.9350 \quad H = \text{Field strength} \]
\[ \log_{10} H_2^2 = 7.8451 \]
\[ \log_{10} H_3^2 = 7.6569 \]
TABLE 9

Magnetic Susceptibility Measurements on Cobalt-Schiff's base Nitrosyls (Contd)

**Nitrosylbis(5-methylsalicylaldehyde)-ethylenediaminecobalt(I)**

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>297.5</th>
<th>284.5</th>
<th>234</th>
<th>229</th>
<th>202.5</th>
<th>168</th>
<th>136.5</th>
<th>110.5</th>
<th>94.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_A x 10^6$</td>
<td>75.5</td>
<td>69.8</td>
<td>-</td>
<td>72.71</td>
<td>74.12</td>
<td>69.8</td>
<td>62.8</td>
<td>68.4</td>
<td>78.4</td>
</tr>
<tr>
<td>$\mu_{\text{eff.}} (\text{B.M.})$</td>
<td>0.43</td>
<td>0.49</td>
<td>-</td>
<td>0.37</td>
<td>0.35</td>
<td>0.31</td>
<td>0.26</td>
<td>0.25</td>
<td>0.24</td>
</tr>
<tr>
<td>$\chi_A x 10^6$</td>
<td>71.1</td>
<td>71.1</td>
<td>-</td>
<td>67.6</td>
<td>67.6</td>
<td>71.12</td>
<td>65.9</td>
<td>71.1</td>
<td>62.4</td>
</tr>
<tr>
<td>$\mu_{\text{eff.}} (\text{B.M.})$</td>
<td>0.41</td>
<td>0.39</td>
<td>-</td>
<td>0.35</td>
<td>0.33</td>
<td>0.31</td>
<td>0.27</td>
<td>0.25</td>
<td>0.22</td>
</tr>
<tr>
<td>$\chi_A x 10^6$</td>
<td>71.0</td>
<td>76.4</td>
<td>76.38</td>
<td>-</td>
<td>76.38</td>
<td>68.3</td>
<td>71.10</td>
<td>65.6</td>
<td>69.4</td>
</tr>
<tr>
<td>$\mu_{\text{eff.}} (\text{B.M.})$</td>
<td>0.41</td>
<td>0.41</td>
<td>0.38</td>
<td>-</td>
<td>0.35</td>
<td>0.30</td>
<td>0.28</td>
<td>0.24</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Diamagnetic correction = 170.5 x $10^{-6}$ c.g.s.u.

**Nitrosylbis(5-methoxysalicylaldehyde)-ethylenediaminecobalt(I)**

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>298</th>
<th>264.5</th>
<th>236.0</th>
<th>204.0</th>
<th>169.0</th>
<th>136.5</th>
<th>106.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_A x 10^6$</td>
<td>92.15</td>
<td>99.3</td>
<td>99.3</td>
<td>106.5</td>
<td>111.3</td>
<td>106.5</td>
<td>104.1</td>
</tr>
<tr>
<td>$\mu_{\text{eff.}} (\text{B.M.})$</td>
<td>0.47</td>
<td>0.46</td>
<td>0.44</td>
<td>0.42</td>
<td>0.39</td>
<td>0.34</td>
<td>0.30</td>
</tr>
<tr>
<td>$\chi_A x 10^6$</td>
<td>101.6</td>
<td>104.5</td>
<td>104.9</td>
<td>116.7</td>
<td>119.9</td>
<td>116.7</td>
<td>119.9</td>
</tr>
<tr>
<td>$\mu_{\text{eff.}} (\text{B.M.})$</td>
<td>0.49</td>
<td>0.47</td>
<td>0.45</td>
<td>0.44</td>
<td>0.40</td>
<td>0.36</td>
<td>0.32</td>
</tr>
<tr>
<td>$\chi_A x 10^6$</td>
<td>95.6</td>
<td>104.9</td>
<td>104.9</td>
<td>109.6</td>
<td>114.3</td>
<td>118.7</td>
<td>123.7</td>
</tr>
<tr>
<td>$\mu_{\text{eff.}} (\text{B.M.})$</td>
<td>0.48</td>
<td>0.47</td>
<td>0.45</td>
<td>0.43</td>
<td>0.39</td>
<td>0.36</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Diamagnetic correction = 147.1 x $10^{-6}$ c.g.s.u.

$\log_{10} H_1^2 = 7.9350$  
$H =$ Field strength

$\log_{10} H_2^2 = 7.8451$  
$\log_{10} H_3^2 = 7.6569$

**Nitrosylbis(3-methoxysalicylaldehyde)-ethylenediaminecobalt(I)**

$\mu_{\text{eff.}} (\text{Co}) = 0.68, 0.67$ B.M. at 294°K

Diamagnetic correction = 188.50 x $10^{-6}$ c.g.s.u.
### TABLE 10

Magnetic Susceptibility Measurements on Cobalt-Schiff's base Nitrosyls (Contd.)

#### Nitrosylbis(salicylaldehyde)-ethylenediaminecobalt(I)

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>292.5</th>
<th>262.1</th>
<th>232.0</th>
<th>200.0</th>
<th>184.0</th>
<th>153.8</th>
<th>102.5</th>
<th>92.8</th>
<th>89.7</th>
<th>87.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>187.5</td>
<td>193.9</td>
<td>182.7</td>
<td>183.9</td>
<td>190.1</td>
<td>214.8</td>
<td>219.6</td>
<td>227.6</td>
<td>227.6</td>
<td></td>
</tr>
<tr>
<td>$(H_1)\mu_{eff.}(B.M.)$</td>
<td>0.66</td>
<td>0.64</td>
<td>0.59</td>
<td>0.54</td>
<td>0.52</td>
<td>0.49</td>
<td>0.42</td>
<td>0.41</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>205.1</td>
<td>217.5</td>
<td>202.7</td>
<td>201.1</td>
<td>205.1</td>
<td>229.9</td>
<td>237.3</td>
<td>240.0</td>
<td>247.2</td>
<td></td>
</tr>
<tr>
<td>$(H_2)\mu_{eff.}(B.M.)$</td>
<td>0.69</td>
<td>0.68</td>
<td>0.62</td>
<td>0.56</td>
<td>0.55</td>
<td>0.44</td>
<td>0.42</td>
<td>0.42</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>228.2</td>
<td>246.9</td>
<td>239.4</td>
<td>224.5</td>
<td>249.1</td>
<td>242.2</td>
<td>254.4</td>
<td>265.7</td>
<td>269.4</td>
<td></td>
</tr>
<tr>
<td>$(H_3)\mu_{eff.}(B.M.)$</td>
<td>0.73</td>
<td>0.72</td>
<td>0.67</td>
<td>0.60</td>
<td>0.61</td>
<td>0.55</td>
<td>0.46</td>
<td>0.45</td>
<td>0.44</td>
<td></td>
</tr>
</tbody>
</table>

Diamagnetic correction = $170.8 \times 10^6$ c.g.s.u.

$\log_{10} H_1^2 = 7.8451$  
$\log_{10} H_2^2 = 7.6569$  
$\log_{10} H_3^2 = 7.4756$

#### Nitrosylbis(acetylacetone)-ethylenediaminecobalt(I)

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>349.0</th>
<th>323.0</th>
<th>310.5</th>
<th>296.5</th>
<th>265.5</th>
<th>235.5</th>
<th>200.0</th>
<th>168.5</th>
<th>132.5</th>
<th>99.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>205.2</td>
<td>186.7</td>
<td>189.1</td>
<td>190.9</td>
<td>201.5</td>
<td>208.9</td>
<td>224.4</td>
<td>256.9</td>
<td>300.1</td>
<td>366.4</td>
</tr>
<tr>
<td>$(H_1)\mu_{eff.}(B.M.)$</td>
<td>0.76</td>
<td>0.70</td>
<td>0.69</td>
<td>0.69</td>
<td>0.66</td>
<td>0.63</td>
<td>0.60</td>
<td>0.58</td>
<td>0.57</td>
<td>0.54</td>
</tr>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>210.1</td>
<td>185.0</td>
<td>188.2</td>
<td>199.1</td>
<td>213.2</td>
<td>213.2</td>
<td>221.0</td>
<td>257.0</td>
<td>299.2</td>
<td>366.2</td>
</tr>
<tr>
<td>$(H_2)\mu_{eff.}(B.M.)$</td>
<td>0.77</td>
<td>0.69</td>
<td>0.69</td>
<td>0.69</td>
<td>0.68</td>
<td>0.64</td>
<td>0.60</td>
<td>0.58</td>
<td>0.57</td>
<td>0.54</td>
</tr>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>212.5</td>
<td>179.4</td>
<td>197.8</td>
<td>198.1</td>
<td>219.8</td>
<td>207.7</td>
<td>224.6</td>
<td>258.8</td>
<td>294.6</td>
<td>364.6</td>
</tr>
<tr>
<td>$(H_3)\mu_{eff.}(B.M.)$</td>
<td>0.77</td>
<td>0.68</td>
<td>0.70</td>
<td>0.69</td>
<td>0.69</td>
<td>0.63</td>
<td>0.60</td>
<td>0.58</td>
<td>0.56</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Diamagnetic correction = $152.2 \times 10^6$ c.g.s.u.

$\log_{10} H_1^2 = 7.9350$  
$\log_{10} H_2^2 = 7.8451$  
$\log_{10} H_3^2 = 7.6569$
TABLE 11

Magnetic Susceptibility Measurements on Manganese(II) and Iron(II) Compounds

**Bis(salicylaldehyde)-ethylenediaminomanganese(II)**

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>297.0</th>
<th>266.0</th>
<th>236.0</th>
<th>204.5</th>
<th>169.0</th>
<th>136.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>11,228</td>
<td>12,298</td>
<td>13,458</td>
<td>15,028</td>
<td>17,028</td>
<td>19,288</td>
</tr>
<tr>
<td>$\mu_{\text{eff.}} \times 10^6$</td>
<td>5.18</td>
<td>5.13</td>
<td>5.06</td>
<td>4.98</td>
<td>4.82</td>
<td>4.60</td>
</tr>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>11,038</td>
<td>12,408</td>
<td>13,398</td>
<td>14,878</td>
<td>17,348</td>
<td>18,998</td>
</tr>
<tr>
<td>$\mu_{\text{eff.}} \times 10^6$</td>
<td>5.14</td>
<td>5.16</td>
<td>5.05</td>
<td>4.96</td>
<td>4.86</td>
<td>4.57</td>
</tr>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>10,678</td>
<td>12,268</td>
<td>13,718</td>
<td>15,028</td>
<td>17,278</td>
<td>19,168</td>
</tr>
<tr>
<td>$\mu_{\text{eff.}} \times 10^6$</td>
<td>5.06</td>
<td>5.10</td>
<td>5.11</td>
<td>4.98</td>
<td>4.85</td>
<td>4.59</td>
</tr>
</tbody>
</table>

Diamagnetic correction = 175.1 x 10^{-6} c.g.s.u.

**Bis(salicylaldehyde)-ethylenediamineiron(II)**

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>298.0</th>
<th>266.0</th>
<th>236.0</th>
<th>206.0</th>
<th>169.0</th>
<th>136.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>9,942</td>
<td>10,977</td>
<td>12,357</td>
<td>14,577</td>
<td>16,607</td>
<td>20,617</td>
</tr>
<tr>
<td>$\mu_{\text{eff.}} \times 10^6$</td>
<td>4.89</td>
<td>4.86</td>
<td>4.85</td>
<td>4.92</td>
<td>4.76</td>
<td>4.78</td>
</tr>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>10,607</td>
<td>11,786</td>
<td>13,227</td>
<td>15,297</td>
<td>18,147</td>
<td>22,297</td>
</tr>
<tr>
<td>$\mu_{\text{eff.}} \times 10^6$</td>
<td>5.05</td>
<td>5.03</td>
<td>5.02</td>
<td>5.04</td>
<td>4.97</td>
<td>4.97</td>
</tr>
<tr>
<td>$\chi_A \times 10^6$</td>
<td>11,017</td>
<td>12,407</td>
<td>13,587</td>
<td>15,377</td>
<td>18,447</td>
<td>22,647</td>
</tr>
<tr>
<td>$\mu_{\text{eff.}} \times 10^6$</td>
<td>5.15</td>
<td>5.10</td>
<td>5.09</td>
<td>5.05</td>
<td>5.00</td>
<td>5.01</td>
</tr>
</tbody>
</table>

Diamagnetic correction = 166.9 x 10^{-6} c.g.s.u.

$\log_{10} H_1^2 = 7.6569 \quad H = \text{Field strength}$

$\log_{10} H_2^2 = 7.3251$

$\log_{10} H_3^2 = 6.5950$
**TABLE 12**

Diamagnetic Corrections for Complexes

(All values x $10^{-6}$/grm. mole.)

<table>
<thead>
<tr>
<th>Compound (nitrosyl)</th>
<th>Semi-empirical value using Schiff's base</th>
<th>Summation using Pascal's constants [150]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsubstituted</td>
<td>170.8</td>
<td>158.6</td>
</tr>
<tr>
<td>5,5'-dinitro</td>
<td>171.3</td>
<td>161.5</td>
</tr>
<tr>
<td>5,5'-dichloro</td>
<td>128.6</td>
<td>186.7</td>
</tr>
<tr>
<td>3,3'-dimethoxy</td>
<td>188.50</td>
<td>191.5</td>
</tr>
<tr>
<td>5,5'-dimethoxy</td>
<td>147.1</td>
<td>191.5</td>
</tr>
<tr>
<td>5,5'-dimethyl</td>
<td>170.5</td>
<td>182.3</td>
</tr>
<tr>
<td>Acetylacetonone-ethylendimine compd.</td>
<td>152.2</td>
<td>140.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Semi-empirical value</th>
<th>Summation using</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese(II)salen</td>
<td>175.1 [26]</td>
<td>163.0</td>
</tr>
<tr>
<td>Iron(II)salen</td>
<td>166.9</td>
<td>154.8</td>
</tr>
</tbody>
</table>

The semi-empirical values shown in column two were used in the calculations for $\mu_{\text{eff.}}$ (see Section IV (d), p.78).
RESULTS AND DISCUSSION

(c) INFRA-RED SPECTRA

Although the spectra were usually recorded over the range 4000\textsuperscript{-1} to 700 cm.\textsuperscript{-1} only those regions containing absorptions pertinent to the discussion are stated in detail.

The absorption due to the nitric oxide group was located by comparing the spectra of the nitrosyl derivative and the corresponding parent compound, or the Schiff's base where the parent compound was not available, as shown in Figures 14, 15 and 16. From Table 13 it is evident that the nitric oxide stretching frequency varies with the position and nature of the substituents in the benzene rings, the frequency changing from 1696 cm.\textsuperscript{-1} with the strongly electron-withdrawing nitro-group, to 1614 cm.\textsuperscript{-1} with the electron-repelling methyl group. It is reasonable to conclude from the magnetic data (this Section) and the region of the infra-red absorptions that the nitric oxide is bonded essentially as NO\textsuperscript{+} with considerable back bonding from the metal (see Section II(b)). Lowering of the characteristic nitric oxide stretching frequency is attributed to a decrease in the bond order of the group arising from back bonding from the metal.

The amount of back bonding from the metal increases with the negative change built upon the metal by coordination.

Considering the structural formula below, the oxygen atoms cannot double bond with the metal because neither the cobalt nor the oxygen atoms have orbitals that are empty or can readily be made so.
TABLE 13
INFRA-RED ABSORPTIONS ATTRIBUTED TO THE NITRIC OXIDE STRETCHING FREQUENCY

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,5'-dinitro</td>
<td>1696</td>
</tr>
<tr>
<td>4,4'-dichloro</td>
<td>1686</td>
</tr>
<tr>
<td>3,3'-dinitro</td>
<td>1667</td>
</tr>
<tr>
<td>6,6'-dinitro</td>
<td>1663</td>
</tr>
<tr>
<td>Acetylacetone derivative</td>
<td>1660</td>
</tr>
<tr>
<td>5,5'-dichloro</td>
<td>1638</td>
</tr>
<tr>
<td>3,3'-dimethoxy</td>
<td>1635</td>
</tr>
<tr>
<td>5,5'-dimethoxy</td>
<td>1631</td>
</tr>
<tr>
<td>Unsubstituted</td>
<td>1624</td>
</tr>
<tr>
<td>o-hydroxyacetophenone</td>
<td>1618</td>
</tr>
<tr>
<td>derivative</td>
<td></td>
</tr>
<tr>
<td>5,5'-dimethyl</td>
<td>1614</td>
</tr>
</tbody>
</table>
Figure 14

CoSalen Nitrosyl

5CH₃ Substituted Nitrosyl

CoSalen

5CH₃ Substituted Parent Compound

Bis (Salicyl Aldehyde) - Ethylenediamine

Bis (SCH₃-Salicyl-Aldehyde) - Ethylenediamine
Figure 15

Bis (SNO₂ - SALICYLALDEHYDE) - ETHYLENEDIIMINE COBALT - (I) NITROSYL

Bis (SNO₂ - SALICYLALDEHYDE) - ETHYLENEDIIMINE COBALT (II)

Bis (SNO₂ - SALICYLALDEHYDE) - ETHYLENEDIIMINE
Figure 16

Bis (5Cl - SALICYLALDEHYDE) - ETHYLENEDIIMINE COBALT (I) NITROSYL

Bis (4CI - SALICYLALDEHYDE) - ETHYLENEDIIMINE COBALT (I) NITROSYL

Bis (5Cl - SALICYLALDEHYDE) - ETHYLENEDIIMINE COBALT (II)

Bis (4CI - SALICYLALDEHYDE) - ETHYLENEDIIMINE
However the nitrogen atom (\(-\text{HC}-\text{N}\)) can accept an electron pair from the cobalt atom if the process occurs to give an empty p orbital on the nitrogen. The reverse process cannot take place because the cobalt does not have orbitals available for accepting electrons. The lower frequency of the nitric oxide group in the \(\sigma\)-hydroxyacetophenone-ethylenediamine compound (1618 cm\(^{-1}\)) compared with the acetylacetonate-ethylenediamine nitrosyl (1660 cm\(^{-1}\)) indicates that in the \(\sigma\)-hydroxyacetophenone derivative the phenyl group is acting as an electron source (+I) so that the electron density around the metal is greater. The slightly higher frequency (1624 cm\(^{-1}\)) for the unsubstituted compound is to be expected because the +I effect of the methyl group is absent although that of the phenyl group remains.

\(\nu(\text{NO})\) acetylacetonate-ethylenediamine compound > \(\nu(\text{NO})\) unsubstituted compound > \(\nu(\text{NO})\) \(\sigma\)-hydroxyacetophenone-ethylenediamine compound

It is interesting to note that the stretching frequency of the nitric oxide group in nitrosoylbis(acetylacetone)cobalt(I) (1675 cm\(^{-1}\)) [72] is higher than that in nitrosoylbis(acetylacetone)-ethylenediaminecobalt(I) (1660 cm\(^{-1}\)). In the former compound the cobalt atom is bonded to four oxygen atoms, but in the latter to two oxygen and two nitrogen atoms. As nitrogen is less electro-negative than oxygen [87(b)], it is probable that more charge will be transferred to the metal in the bis(acetylacetone)-ethylenediamine case. Thus more back bonding occurs, lowering the nitric oxide stretching frequency.
Substituent effects in the Benzene Rings

Substituents in the 5,5' positions

Electron-attracting and electron-repelling groups produce the charge distributions (a) and (b) respectively compared with benzene [162].

\[
\begin{align*}
\delta^+ & \rightarrow \delta^+ \\
\delta^+ & \rightarrow \delta^+ \\
\delta^- & \rightarrow \delta^- \\
\delta^- & \rightarrow \delta^- \\
\end{align*}
\]

The inductive effect of the substituent is transmitted mesomerically as shown. The smaller charges reach the meta positions inductively from the adjacent ortho and para positions. A substituent that acts mesomERICALLY gives rise to the same charge displacements as shown in (a) and (b) but the effect is more marked. Thus 5,5' substituents cause greater electron density changes at the 2,2' positions adjacent to the coordinated O atoms, than at the 1,1' positions adjacent to the \[\text{CH} \quad \text{N}\] groups.
As a result the oxygen atoms would be expected to transmit the greater part of the substituent effects inductively to the metal, and then to the nitric oxide. The electron density on the oxygen atoms would be expected to decrease markedly along the series Me, H, Cl, NO₂, and this is borne out by the increase in the frequencies of the corresponding nitrosyl derivatives. The nitro-group will give rise to the charge distribution shown in (a) because of the inductive effect of the positively charged nitrogen atom

\[ +N\equiv^00^- \]

... and also acting mesomerically (-M)

Thus the charge displacements will be very marked with the nitro-substituents as shown by the high nitric oxide stretching frequency obtained \((1696 \text{ cm}^{-1})\).

The 5,5' dichloro substituents can act mesomerically (+M) to give the charge displacements (b) which would lower the frequency, or inductively (-I) yielding (a) which would increase the frequency. However, as usual the inductive effect (a) predominates (cf. p-chlorophenol is a stronger acid than phenol) [163], thus increasing the frequency although not so much as with the nitro-group. Methoxy-groups, like chlorine substituents, can exert two effects. The inductive effect (-I), as in (a) would be expected
to cause an increase in frequency, and the mesomeric effect as in (b) should decrease the frequency. It is usually found that the mesomeric effect predominates if the CH₂O group is in the para position (cf. anisic acid is a weaker acid than benzoic [164]) and thus a decrease in frequency would be expected. However, an increase was obtained, and it is suggested that in this series of compounds the behaviour deviates from that generally found in substituted benzene compounds, the -I effect alone being important.

**Substituents in the 4,4' positions**

Substituents in the 4,4' positions act as in (c) and (d); and now the greater electron density changes occur at positions 1,1' attached to which are the — CH — N groups; these will then constitute the more important pathway for the transmission of electronic effects to the metal and the nitric oxide.
In fact the inductive effects (-I) may be transmitted mesomerically all the way to the nitric oxide group, see diagram below.

The nitric oxide stretching frequency is higher for the 4,4' dichloro compound (1686 cm.\(^{-1}\)) than for the 5,5' dichloro compound (1638 cm.\(^{-1}\)) because in the latter the effect of the substituents is transmitted mesomerically as far as the oxygen and then inductively to the metal, but in the 4,4' dichloro compound a conjugated system operates through to the nitric oxide. It is pertinent to mention that nitro groups in the 4,4' positions would act through the \(-\text{HC}==\text{N}\) groups in a similar manner to the 4,4' dichloro substituents, but their -I effects would be greater and, instead of a weak +M effect, they would have a strong -M effect. Therefore 4,4' nitro substituents should greatly increase the nitric oxide stretching
frequency. It was for this reason that attempts were made to prepare the 4,4' dinitro compound. Electron release from the 4,4' positions should not have such a marked effect on the nitric oxide group as electron attraction because the effect would be transmitted inductively from the nitrogen to the cobalt, the metal having no orbitals that can be made available for \(-\text{CH}_2\equiv\text{N}\) to occur.

**Substituents in the 3,3' and 6,6' positions**

Substituents in these positions, particularly the large methoxy and nitro groups, may well be sterically hindered owing to the proximity of groups at the 1,1' and 2,2' positions. If the substituents are twisted out of the plane of the benzene rings then their mesomeric effects will not function fully. However, their inductive effects will still operate. Thus the 3,3' and 6,6' substituents increased the nitric oxide stretching frequency as expected, although the 6,6' dinitro compound might have been expected to yield a higher frequency than 3,3' dinitro owing to conjugation through the \(-\text{CH}\equiv\text{N}\) group. If the (+M) effect of the methoxy substituents is not operating in the system existing in the compounds, perhaps due to steric hindrance, then the -I effect of the group would yield the increase in frequency found experimentally.
Quantitative Correlation of Substituent Effects

With Nitric Oxide Stretching Frequencies

Hammett [165(a), 166] found that a given reaction series involving meta and/or para substituted benzene derivatives could be represented by an equation of the form

\[ \log_{10} k - \log_{10} k^0 = \psi C \]

where \( k \) = a property such as the rate or dissociation constant of a given substituted benzene derivative,

\( k^0 \) = the same property for the unsubstituted benzene derivative

\( \psi \) = a reaction constant and depends only on the reaction,

\( C = \log_{10} \frac{k_i}{k_{i0}} \) where \( k_i \) and \( k_{i0} \) are the ionisation constants for the substituted and unsubstituted benzoic acids. The value of \( C \) depends on whether the substituent is meta or para to the points in the aromatic system to which its electronic effects are being transmitted, and on whether it releases electrons to, or withdraws them from, this point. Electron withdrawing substituents have positive \( C \) constants; electron releasing ones have negative \( C \) constants. Plotting \( \log_{10} k - \log_{10} k^0 \) or simply \( \log_{10} k \) against \( C \) for a reaction involving a series of benzene derivatives gave linear plots. The effect of substitution in an aromatic system on the infra-red stretching frequency of a particular group has been studied in several purely organic series [167, 168]. In place of \( \log_{10} k \)
or \( \log_{10} k \) \(-\log_{10} k^0 \) for \( V - V_0 \) ore used,

where \( V \) = infra-red stretching frequency of a group in the substituted com-

Table 14 contains the nitric oxide stretching frequencies and \( \sigma \) 

\( 4,4' \) and \( 5,5' \) derivatives studied. Consider 

first the \( 5,5' \) substituents which are para to the oxygen atom and meta to 

The \( 5,5' \)-dimethoxy nitrosyl is exceptional, presumably because it 

\( 4,4' \) substituents are meta to oxygen and para to the \( -\text{CH} = \text{N} \) 

Thus it appears that \( 4,4' \)-substituents exert a marked effect through the 

\( -\text{CH} = \text{N} \) group as well as through oxygen.
Substituents in the 3,3' and 6,6' positions were not considered because these are ortho to the groups at 2,2' and 1,1' and the Hammett relation no longer applies.

It has been assumed that the adjacent groups at 1,1' and 2,2' do not interact with each other and the $\sigma$ constants derived from the ionisation constants of benzoic acids are applicable. The linear plot apparently vindicates their use, but it is emphasised that their application is approximate.

### TABLE 14

Hammett Substituent Constants

<table>
<thead>
<tr>
<th>Substituent m or p w.r.t. 2,2'-oxygen</th>
<th>$\sigma$</th>
<th>Substituent m or p w.r.t. 1,1'-CH=N</th>
<th>$\sigma$</th>
<th>$\sigma_{\text{NO}}$</th>
<th>Stretching frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,5' p-nitro</td>
<td>+1.27</td>
<td>5,5' m-nitro</td>
<td>+0.710</td>
<td>1696</td>
<td></td>
</tr>
<tr>
<td>5,5' p-chloro</td>
<td>+0.227</td>
<td>5,5' m-chloro</td>
<td>+0.373</td>
<td>1638</td>
<td></td>
</tr>
<tr>
<td>4,4' m-chloro</td>
<td>+0.373</td>
<td>4,4' p-chloro</td>
<td>+0.227</td>
<td>1686</td>
<td></td>
</tr>
<tr>
<td>5,5' p-dimethoxy</td>
<td>-0.268</td>
<td>5,5' m-dimethoxy</td>
<td>+0.115</td>
<td>1635</td>
<td></td>
</tr>
<tr>
<td>Unsubstituted</td>
<td>0</td>
<td>Unsubstituted</td>
<td>0</td>
<td>1624</td>
<td></td>
</tr>
<tr>
<td>5,5' p-dimethyl</td>
<td>-0.170</td>
<td>5,5' m-dimethyl</td>
<td>-0.069</td>
<td>1614</td>
<td></td>
</tr>
</tbody>
</table>

Intermolecular interactions between the substituents of one molecule and the nitric oxide group of a neighbouring molecule could cause infra-red frequency shifts, i.e.
Repulsion between the electrons on the oxygen atom of the nitric oxide group and the negative end of the dipole associated with the nitro group would tend to displace electrons towards the nitrogen atom as shown. This would oppose back bonding from the metal and increase the nitric oxide bond order and stretching frequency compared with that in the unsubstituted compound. An electron-repelling group (+I) would tend to have the reverse effect.

However, the observed shifts were considerably larger than those commonly arising from intermolecular effects [169]. Disubstitution indicates that the substituent effects are approximately additive, i.e. the 3,3', 5,5' tetranitro-substituted nitrosyl has a nitric oxide stretching
Figure 17

NITRIC OXIDE STRETCHING FREQUENCY AGAINST SUBSTITUENT CONSTANT.
frequency of 1724 cm\(^{-1}\) [170]. This would not be expected if the frequency changes resulted from intermolecular interaction. The correlation between nitric oxide stretching frequencies and Hammett's substituent constants shows the effects to be intramolecular.

Spectra of manganese and iron compounds

The spectrum of bis(salicylaldehyde)-ethylenediaminecobalt(II) is reported in detail (see Table 17) for the first time. Owing to the similarity between the spectra of manganese salen and cobalt salen, absorption assignments were taken as for the cobalt compound [22]. Although a definite nitrosyl derivative was not obtained, preliminary studies on the compounds resulting from reaction of the manganese complex and nitric oxide showed a strong absorption around 1623 cm\(^{-1}\), possibly due to the nitrosyl group.

Table 17 also contains the detailed infra-red spectrum of the iron(II)-Schiff's base complex, again for the first time. Comparison of the spectra of the nitrosyl derivative obtained from the reaction in 96% ethanol (see Section III(b), p.65) and that of the parent compound showed a strong absorption at 1712 cm\(^{-1}\) characteristic of NO\(^+\) coordination.

Presence of water in bis(salicylaldehyde)-ethylenediaminecobalt(II)

Lattice and coordinated water both absorb at 3550 - 3200 cm\(^{-1}\) (antisymmetric and symmetric O - H stretching modes) [171] and at
1630 - 1600 cm$^{-1}$ (H - O - H) bending mode. Co-ordinated water, however, also absorbs around 795 cm$^{-1}$ in (Ni (glycine)$_2$)$_2$ $2H_2O$ and at 875 cm$^{-1}$ in CuSO$_4$.$5H_2O$ due to wagging, twisting and rocking modes that are activated by co-ordination to the metal.

Bis(3-methoxysalicylaldehyde)-ethylenediaminecobalt(II) is known to form a hydrate (see Section III, (a)). As Figure 18 shows, the characteristic water absorptions are observed at 3550 - 3170 cm$^{-1}$ and at 1650 cm$^{-1}$. These disappear on strong heating under vacuum. Thus water can be detected from the infra-red spectrum of this type of compound. However, bis(salicylaldehyde)-ethylenediaminecobalt(II) did not exhibit the characteristic absorptions of water. A sample of the heated complex was boiled with water for two hours under nitrogen so as to assist possible hydrate formation, then heated in vacuum according to Diehl [19]. The spectrum of the product still did not indicate the presence of water. Ueno and Martell [22] do not mention absorption due to water in their spectrum of cobalt salen. The cobalt analyses of the carefully dried parent compound (see Section III (a), p.39) agreed with those of Bailes and Calvin [2], who did not mention the presence of water in the complex. A bridging water molecule, if present, would presumably possess a tetrahedral configuration, and as all recent structural work with metal complexes of bis(salicylaldehyde)-ethylenediamine and similar ligands shows the arrangement to be planar about the metal, the planar portions would 'clash' as well as being
inclined to one another (see diagram below.) If the oxygenated compound was binuclear, as stated by Diehl [19], then the oxygen molecule would have to link points A and B. Such an arrangement would prove difficult for a 'peroxide' group [172].

Alternatively, if the oxygen molecule linked point B with a corresponding point B' on another molecule, then, although the bridging oxygen would be satisfied, the possibility of the planar rings clashing is still present.

Diehl [3] considered that the 3CH₂O substituted compound absorbed water during oxygenation in a damp atmosphere, although the presence of water was not necessary for oxygenation. This was confirmed by exposing an oxygenated sample of the complex to damp air. Bands at 3550 - 3170 and 1650 cm⁻¹ reappeared.
Figure 18

Bis(3CH$_3$O-SALICYLALDEHYDE)-ETHYLENEDIIMINE COBALT (II) (HYDRATED)

Bis(3CH$_3$O-SALICYLALDEHYDE)-ETHYLENEDIIMINE COBALT (II) (AFTER 'ACTIVATION'-ANHYDROUS)
TABLE 15
INFRA-RED ABSORPTIONS OF COBALT COMPOUNDS STUDIED

<table>
<thead>
<tr>
<th>Compound</th>
<th>Frequencies cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsubstituted nitrosyl</td>
<td>1624(^{&lt;}) vs. 1598m. 1582w,(sh) 1531m.</td>
</tr>
<tr>
<td>Unsubstituted parent compound</td>
<td>1616m. 1597m.(sh) 1538m.</td>
</tr>
<tr>
<td>Unsubstituted Schiff's base</td>
<td>1631m. 1610m. 1577s. 1495m.</td>
</tr>
<tr>
<td>3,3'-dimethoxy nitrosyl</td>
<td>1662w.(sh) 1639(^{&lt;}) vs. 1604m. 1537w.</td>
</tr>
<tr>
<td>3,3'-dimethoxy parent compound</td>
<td>1634w. 1605m. 1536w.</td>
</tr>
<tr>
<td>3,3'-dimethoxy Schiff's base</td>
<td>1634m. 1580w.</td>
</tr>
<tr>
<td>3,3'-dimethoxy, hydrated</td>
<td>1650m. 1624m. 1597m. 1540w.</td>
</tr>
<tr>
<td>parent compound</td>
<td>3550 - 3170 (Broad band)</td>
</tr>
<tr>
<td>5,5'-dimethoxy nitrosyl</td>
<td>1642 (sh) 1631vs. 1538m.</td>
</tr>
<tr>
<td>5,5'-dimethoxy parent compound</td>
<td>1597m. 1534m.</td>
</tr>
<tr>
<td>5,5'-dimethoxy Schiff's base</td>
<td>1645w. 1613w. 1592m. 1497s.</td>
</tr>
<tr>
<td>6,6'-dinitro nitrosyl</td>
<td>1663(^{&lt;}) m. 1638s. 1620m. 1602m. 1515s.</td>
</tr>
<tr>
<td>6,6'-dinitro Schiff's base</td>
<td>1628s. 1578m. 1522s.</td>
</tr>
<tr>
<td>5,5'-dinitro nitrosyl</td>
<td>1696(^{&lt;}) m. 1629m. 1597m. 1550m.</td>
</tr>
<tr>
<td>5,5'-dinitro parent compound</td>
<td>1658w. 1603m. 1550m.</td>
</tr>
<tr>
<td>5,5'-dinitro Schiff's base</td>
<td>1642s. 1610s. 1633s.</td>
</tr>
<tr>
<td>3,3'-dinitro nitrosyl</td>
<td>1667(^{&lt;}) s. 1637s. 1595m. 1538m. 1504m.</td>
</tr>
<tr>
<td>3,3'-dinitro parent compound</td>
<td>1618s. 1605m. 1543m. 1506m.</td>
</tr>
<tr>
<td>3,3'-dinitro Schiff's base</td>
<td>1653s. 1616m. 1531s. 1511(sh)</td>
</tr>
</tbody>
</table>

\(^{<}\)Peak attributed to the nitric oxide stretching frequency.
### TABLE 16

**INFRARED ABSORPTIONS OF COBALT COMPOUNDS STUDIED** (Contd.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Frequencies cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,5'-dichloro nitrosyl</td>
<td>1638(\text{s}), 1622(\text{s}), 1525(\text{m}).</td>
</tr>
<tr>
<td>5,5'-dichloro parent compound</td>
<td>1602(\text{m}), 1516(\text{m}).</td>
</tr>
<tr>
<td>5,5'-dichloro Schiff's base</td>
<td>1635(\text{m}), 1544(\text{m}).</td>
</tr>
<tr>
<td>4,4'-dichloro nitrosyl</td>
<td>1686(\text{s}), 1639(\text{sh}), 1618(\text{m}), 1590(\text{m}), 1517(\text{m}).</td>
</tr>
<tr>
<td>4,4'-dichloro Schiff's base</td>
<td>1626(\text{m}), 1597(\text{w}), 1570(\text{m}), 1515(\text{w}).</td>
</tr>
<tr>
<td>Bis(acetylacetone)-ethylene diamine nitrosyl</td>
<td>1660(\text{vs}), 1586(\text{m}), 1575(\text{m}), 1509(\text{m}).</td>
</tr>
<tr>
<td>Bis(acetylacetone)-ethylene diamine Schiff's base</td>
<td>1618(\text{s}), 1586(\text{m}), 1516(\text{m}).</td>
</tr>
<tr>
<td>Bis(g-hydroxyacetophenone)-ethylene diamine nitrosyl</td>
<td>1618(\text{s}), 1599(\text{s}), 1581(\text{s}), 1528(\text{m}).</td>
</tr>
<tr>
<td>Parent compound of above</td>
<td>1600(\text{s}), 1565(\text{s}), 1515(\text{m}).</td>
</tr>
<tr>
<td>Schiff's base</td>
<td>1610(\text{s}), 1570(\text{m}), 1503(\text{m}).</td>
</tr>
<tr>
<td>5,5'-dimethyl nitrosyl</td>
<td>1614(\text{s}), 1530(\text{m}).</td>
</tr>
<tr>
<td>5,5'-dimethyl parent compound</td>
<td>1653(\text{m}), 1600(\text{m}), 1506(\text{m}).</td>
</tr>
<tr>
<td>5,5'-dimethyl Schiff's base</td>
<td>1619(\text{m}), 1595(\text{m}), 1528(\text{m}).</td>
</tr>
</tbody>
</table>
### TABLE 17

**Infrared Absorptions of Manganese and Iron Compounds Studied**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Frequencies cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis(salicylaldehyde)-</td>
<td>1642m. 1618m. 1595w. 1550m. 1531m.</td>
</tr>
<tr>
<td>ethylenediiminemanganese(II)</td>
<td>1511w.(sh) 1342m. 1277m. 1235w. 1181m.</td>
</tr>
<tr>
<td></td>
<td>1140s. 1120m. 1088w. 1045w. 1025w.</td>
</tr>
<tr>
<td></td>
<td>990w. 970w. 943m. 900-885(broad band)</td>
</tr>
<tr>
<td></td>
<td>857m. 848w.</td>
</tr>
<tr>
<td>Bis(salicylaldehyde)-</td>
<td>1712*3. 1642w. (sh) 1626S 1600m. 1536m.</td>
</tr>
<tr>
<td>ethylenediimineiron(II); nitrosyl derivative.</td>
<td></td>
</tr>
<tr>
<td>Bis(salicylaldehyde)-</td>
<td>1629m. 1600s. 1543m. 1531m.</td>
</tr>
<tr>
<td>ethylenediimineiron(II)</td>
<td>1348m. 1340w. 1330w. 1323w. 1285m.</td>
</tr>
<tr>
<td></td>
<td>1242w. 1192m. 1145m. 1127m. 1092w.</td>
</tr>
<tr>
<td></td>
<td>1053m. 1030w. 980w. 971w. 952m.</td>
</tr>
<tr>
<td></td>
<td>943w.(sh) 907m. 891w.(sh) 861m. 850m.</td>
</tr>
<tr>
<td></td>
<td>787w. 762m.(sh) 752s. 743w. 735s.</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

(a) ULTRA-VIOLET AND VISIBLE SPECTRA

Gray et al [173] have applied a general molecular orbital approach to compounds containing one particularly strong metal — NO or metal — CO bond and derived a molecular orbital energy level scheme resulting from coordination of 5 or 6 ligands. The treatment is applicable to octahedral and effectively tetragonal pyramidal complexes. By means of this molecular orbital scheme the authors explained the spectrum of Fe(NO)[S₂CN(CH₃)₂]₂ below 30,000 cm⁻¹. The compound was considered as containing Fe(I) and NO⁺ with a metal ground state [ndₓz, ndᵧz]₄[ndₓᵧ]²[ndₓ²₋₂]¹ or in their notation [εσ⁺²][b₂][b₁σ⁻¹]. The three bands observed were assigned to the transitions

\[ b₁σ⁻¹ \rightarrow εσ⁺² \]
\[ b₂ \rightarrow εσ⁺² \]
\[ εσ⁺² \rightarrow εσ⁺² \]

in order of increasing energy, where εσ⁺² is the antibonding orbital arising from the ndₓz, ndᵧz metal orbitals and the antibonding orbitals of the nitric oxide. All the above transitions are from orbitals mainly located on the metal to εσ⁺², which is essentially localised on the NO, i.e. they are charge transfer transitions.

The intense εσ⁺² \rightarrow εσ⁺² transition (ε~5 - 6,000) has been observed
in other nitric oxide complexes, such as [Fe(H₂O)₅NO]²⁺ [174] at 310.5 μm and particularly Co(NO)[S₂CN(CH₃)₂]₂ [175] at 320 μm. The three nitrosyls studied in this work all possess intense absorptions in the region 320 - 330 μm (ε = 8,000 - 10,000) which possibly correspond to the επ⁺ → επ⁻ transition. For example, Figures 20 and 21 show that cobalt salen nitrosyl and the 5,5'-dimethyl nitrosyl absorb near 400 μm (ε = 6,000) and 320 μm (ε = 8,000 - 10,000) whereas nitrosyl bis(acetylactone)-ethylenediiminecobalt(I), Figure 19 (which has no phenyl groups) absorbs only at 330 μm (ε = 10,900). Thus the 400 μm absorption seems to arise from the phenyl groups [176]. This is partly verified by the 5,5'-dimethyl substituted parent compound which also absorbs at 410 μm as does the nitrosyl.

The acetylacetone nitrosyl shows some complex absorption in the 400 - 600 μm region which is partly obscured by the phenyl absorptions in the aromatic compounds. Further work is necessary before these absorptions can be assigned. However, Gray predicted and observed a band around 970 μm for nitrosyl bis(dimethylthiocarbamato)iron(I) arising from the 'd - d' transition b₂ → b₁. Such a band would not be expected for Co(I) (d⁸) spin paired complexes because both levels would be filled. As expected even in concentrated (5 x 10⁻⁴ Molar) solutions no absorptions were observed in the 1,000 - 900 μm region.

Preliminary qualitative studies on the bis(o-hydroxyacetophenone) and bis(5-methoxysalicylaldehyde)-ethylenediiminecobalt(I) nitrosyls showed that these compounds also absorb strongly in the regions 400 μm and 320 - 330 μm.
Figure 19
BIS(ACETYLACETONE)-ETHYLENEDIIMINE COBALT(I) NITROSYL

Molar Extinction Coefficient

Wavelength (λ) mµ

E × 10⁻²
Figure 20

Bis( salicylaldehyde) ethylenediamine cobalt(I) nitrosyl

Molar Extinction Coefficient

$\varepsilon \times 10^{-2}$
Figure 21

BIS (5CH$_3$-SALICYLALDEHYDE)-ETHYLENEDIIMINE COBALT (I) NITROSYL AND PARENT COMPOUND

- • NITROSYL
- ○ PARENT COMPOUND

Molar Extinction Coefficient

$\varepsilon \times 10^{-2}$

Wavelength (\(\lambda\)) m\(\mu\)

1000 900 800 700 600 500 400 300 250
TABLE 18
ULTRAVIOLET AND VISIBLE DATA FOR SOME OF THE COBALT COMPLEXES

Nitrosy1bis(acetylacetonel-ethylenediaminocobalt(I) :

Concentration 5.45 x 10^-5 Molar

<table>
<thead>
<tr>
<th>Wavelength μm</th>
<th>Molar extinction coefficient (ε)</th>
<th>Wavelength μm</th>
<th>Molar extinction coefficient (ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0</td>
<td>410</td>
<td>752.3</td>
</tr>
<tr>
<td>950</td>
<td>0</td>
<td>400</td>
<td>1,247</td>
</tr>
<tr>
<td>900</td>
<td>0</td>
<td>390</td>
<td>1,963</td>
</tr>
<tr>
<td>850</td>
<td>0</td>
<td>375</td>
<td>3,707</td>
</tr>
<tr>
<td>800</td>
<td>0</td>
<td>360</td>
<td>5,578</td>
</tr>
<tr>
<td>750</td>
<td>0</td>
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<td>6,606</td>
</tr>
<tr>
<td>700</td>
<td>55.04</td>
<td>340</td>
<td>7,523</td>
</tr>
<tr>
<td>650</td>
<td>183.5</td>
<td>335</td>
<td>8,110</td>
</tr>
<tr>
<td>600</td>
<td>367.0</td>
<td>330</td>
<td>8,221</td>
</tr>
<tr>
<td>575</td>
<td>458.6</td>
<td>325</td>
<td>8,110</td>
</tr>
<tr>
<td>550</td>
<td>458.6</td>
<td>315</td>
<td>7,670</td>
</tr>
<tr>
<td>525</td>
<td>513.9</td>
<td>310</td>
<td>7,375</td>
</tr>
<tr>
<td>500</td>
<td>560.9</td>
<td>300</td>
<td>7,193</td>
</tr>
<tr>
<td>475</td>
<td>587.0</td>
<td>290</td>
<td>7,670</td>
</tr>
<tr>
<td>450</td>
<td>605.4</td>
<td>280</td>
<td>10,390</td>
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Nitrosylbis(salicylaldehyde)-ethylenediaminocobalt(I) :

Concentration 9.17 x 10^-5 Molar

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<th>Wavelength μm</th>
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Figure 21

Bis(5CH₃-salicylaldehyde)-ethylenediimine cobalt (I) nitrosyl and parent compound.

- Nitrosyl
- Parent compound
RESULTS AND DISCUSSION

(e) THERMOGRAVIMETRIC ANALYSIS

Nitrosylbis(salicylaldehyde)-ethylenediiminecobalt(I)

From Figure 22 it is apparent that a weight loss of 9 - 10% occurred in the region 210$^\circ$ - 300$^\circ$C. After this initial loss in weight an intermediate II was formed which decomposed at 330$^\circ$ - 340$^\circ$C to the metal oxide. Loss of the nitric oxide molecule corresponds to a weight loss of 8.5%, which is somewhat lower than that found. However, Figure 23 shows that cobalt salen itself starts decomposing at 250$^\circ$C. Thus two reactions are occurring concurrently: loss of nitric oxide and ligand decomposition. The decomposition was stopped after the initial weight loss (Fig. 22, graph 2) and the infra-red spectrum of the product compared with that of cobalt salen oxygenated, cobalt salen and the original nitrosyl. As expected the peak attributed to the nitric oxide stretching frequency was absent. Considerable changes had also occurred in the region below 1300 cm$^{-1}$ and the peaks were not well defined. This suggested that some additional decomposition had taken place. The nitric oxide could not be removed without this additional decomposition even in a vacuum at an elevated temperature. Thus the reaction with nitric oxide is not reversible.

The Schiff's base (salen) was stabilised by co-ordination to cobalt since this increased the temperature at which decomposition commenced from 130$^\circ$ to 250$^\circ$C. Oxygenated cobalt salen (Figure 24) began to lose oxygen
above 80°C and started to decompose at about 200°C compared with 250°C for the unoxygenated compound. Oxygenation causes expansion of the crystal lattice (cf. increase in $b_0$ direction, Section I (a) p. 9). Presumably the removal of oxygen leaves a temporarily more open framework which is more susceptible to thermal decomposition.

**Presence or absence of water in cobalt salen**

The sample studied thermogravimetrically was prepared by Diehl's method [19] and vacuum dried at 120°C. From Figure 23 there was initially a slight increase in weight due to buoyancy effects. Then between 45°C and 85°C a decrease in weight occurred, which, since the solid had already been dried at 120°C in vacuo, was probably due to the loss of a small amount of oxygen absorbed between weighing and heating the sample. This was verified by recording the sample weight increase on standing in air and repeating several times the oxygenation/deoxygenation procedure. The region BB' in Figure 23 represents a stable phase corresponding to unoxygenated cobalt salen. The percentage weight losses recorded in Table 22 are larger than the absolute values because calculations were based on the compound being initially unoxygenated. A factor of 0.98 converts the percentage weight losses to those with respect to the partially oxygenated sample. There was no obvious stable phase between 120°C and 500°C that could be attributed to loss of water. Most hydrated compounds lose co-ordinated water below 300°C, for instance Wendlandt et al [177] found that in [Co(NH$_3$)$_5$H$_2$O]$_3$,
GRAPH OF PERCENTAGE WEIGHT LOSS AGAINST TEMPERATURE

BIS(SALICYLALDEHYDE) - ETHYLENEDIIMINE COBALT (I) NITROSYL

- • refers to Table 20
- ▲ refers to Table 21

Temperature °C

% weight loss

75.30%
Graph of percentage weight loss against temperature for bis(salicylaldehyde)-ethylenediamine cobalt(II)$_2$H$_2$O.

Figure 23
GRAPH OF PERCENTAGE WEIGHT LOSS AGAINST TEMPERATURE
BIS(SALICYLALDEHYDE) - ETHYLENEDIIMINE COBALT (II) OXYGENATED

Figure 24
X = Cl\textsuperscript{−}, Br\textsuperscript{−}, I\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−} water removal always occurred below 125°C.

Experiment demonstrating the unimportance of water in the oxygenation of cobalt salen

Diehl [3] considered that without the water bridge in cobalt salen the compound would not carry oxygen. In order to determine the water he refluxed the compound with anhydrous pyridine, which he considered displaced the water, distilled off the pyridine and titrated the water carried over in the pyridine with the Karl-Fischer reagent (see Section I (a)). The following experiment was carried out in order to check Diehl's assumptions.

A small sample of cobalt salen (0.53 g.) was found to have an oxygen carrying capacity of 4.92% (theoretical value = 4.93%). The sample was deoxygenated in vacuo at 120°C, then refluxed with pyridine (100 ml.) under nitrogen, and three quarters of the pyridine distilled off. According to Diehl this should have removed any water contained in the compound. The orange pyridinate, which crystallised from the residue, was filtered off under nitrogen (see Section III (a) p.35), and dried in vacuo at room temperature for eight hours. Once dry it was stable in air. On heating the pyridinate in vacuo at 170°C for two hours it lost 19.21% by weight (one mole of pyridine = 19.54%) to give a maroon product with an oxygen carrying capacity of 5.0%. The reactions discussed above may be represented schematically as:
It was concluded that treatment of cobalt salen with pyridine, as above, did not impair its oxygen carrying capacity although any water present should have been removed [3, 20]. Thus water is not important for oxygenation to take place, contrary to the conclusion of Diehl. Other evidence [15, 21, 22] (this Section) indicates that no water is present, but Sebastian et al [20] have repeated Diehl's experiment and obtained similar results. However, only the experiment recorded here was performed under nitrogen. On exposure to air a solution of cobalt salen in pyridine immediately turns black, and a pyridinate peroxide can be isolated [2]. It may be that in air at the temperature of boiling pyridine catalytic oxidation of pyridine, or of the complex itself, formed water or some other distillable product which reacted with the Karl-Fischer reagent.
In all cases an eight hour heating programme was used. A negative sign indicates a weight increase.

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<th>% weight loss</th>
<th>Temp°C</th>
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Repetition (in part) of Thermogravimetric Analysis of nitrosylbis(salicylaldehyde)-ethylenediaminecobalt(I).

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### TABLE 22

**THERMOGRAVIMETRIC DATA FOR BIS(SALICYLALDEHYDE)-ETHYLENEDIIMINECOBALT(II)**

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# TABLE 23

**THERMOGRAVIMETRIC DATA FOR BIS(SALICYLALDEHYDE)-ETHYLENEDIIMINECOBALT(II) - OXYGENATED**

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SECTION VI

CONCLUSIONS

SUGGESTIONS FOR FURTHER WORK
CONCLUSIONS

The results in Section V show the cobalt-Schiff's base nitrosyls to be monomeric, non-conducting, five co-ordinate compounds of cobalt(I) resulting from co-ordination of the nitrosonium group (NO⁺) to the square planar Co. (II) Schiff's base complexes.

It is significant that the infra-red, ultra-violet and magnetic data of the nitrosyls prepared in this work closely resemble those for nitrosyl-bis(dimethyldithiocarbamato)-cobalt(I) [77]. This is the only compound to date on which a comprehensive X-ray analysis has been carried out [75], and the close similarity of the compounds suggests that the nitrosyls studied in this thesis also possess a square pyramidal arrangement. An X-ray study is being carried out on nitrosylbis(acetylacetonato)-ethylendiamine-cobalt(I) at this College [178]. The compounds are essentially diamagnetic, the odd electron from the nitric oxide being paired with the cdd electron on the already spin-paired cobalt(II) square planar parent compounds. The possible metal hybridisations are:

\[
\begin{array}{c}
\text{Co(I) } d^8 \\
\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\downarrow
\end{array}
\end{array}
\begin{array}{c}
\text{3d} \\
\text{4s} \\
\text{4p}
\end{array}
\text{ds}^p\text{sp}^3
\]

\[
\text{d}^1 \text{sp}^3
\]

\[
\text{d}^2 \text{sp}^3
\]

and $d^2sp^3$ hybridisation would give an octahedral arrangement having a lone-pair at one apex.

The exact orientation of the nitric oxide with respect to the metal is as yet unknown. It may be bonded end-on through the nitrogen yielding a linear $M-N-O$ arrangement or parallel to the Schiff's base plane using the $\pi$ electrons of the $N-O$ bond to attach itself to the metal, i.e.

$$
\begin{align*}
  &M \quad || \quad N \\
  &\quad \quad \quad \quad O
\end{align*}
$$

or intermediate between the two. Alderman and Owston [74, 75] consider the $\pi$ bonding arrangement to be present in the dimethylthiocarbamato complex, with deviations from the parallel due to the electronegativity differences of nitrogen and oxygen.

The mechanism of electron shifts that affect the bond order of the nitric oxide with various substituents in the benzene rings can be explained whether the nitric oxide is bonded 'end-on' or parallel to the ligand plane. The two positions will be considered in turn.

**Linear Bonding of the Nitric Oxide Group**

The nitrosonium group is bonded to the metal by an electron pair donated from an $sp$ hybrid (or $2s$) orbital on the nitrogen into a $d_{sp^3}$ or $d^2sp^3$ hybrid orbital of the metal, Figure 25 (a). Back bonding from the metal to the $p$ orbital of the nitric oxide occurs by means of the filled $3d_{xz}$ or $3d_{yz}$ metal orbitals, the $3d_{xy}$ remaining non-bonding. The $p$ orbital
of the nitrogen is vacated by the process. Thus, increasing the electron density on the imino nitrogen or phenolic oxygen atoms (see Section V, (e)) causes the degree of overlap between the \( d_{xz} \) and \( d_{yz} \) orbitals and the nitrogen (NO) p orbital to increase in order to reduce the charge on the metal; this, in turn, decreases the bond order between the nitrogen and the oxygen of the nitric oxide. Electron withdrawal from the vicinity of the metal by the process Figure 25(a) would increase the nitric oxide bond order. The \( d_{xz} \) and \( d_{yz} \) orbitals can partake in bonding with the nitric oxide and the imino nitrogen atoms. The extent to which these d orbitals overlap in one direction or the other will affect the bond order of the nitric oxide. Rotation of the nitric oxide about its linear axis permits overlap of either of the d orbitals with the nitric oxide p orbital. The situation may be represented as resonance between the structures:

\[ \text{Diagram with two resonance structures} \]
An alternative explanation is to consider the effect of placing electrons in the antibonding orbitals of nitric oxide. As mentioned in Section II (b) the NO⁺ group contains two empty antibonding orbitals, \( \pi^2p_y \) and \( \pi^2p_z \). Any electrons added to the nitrosonium group will fill these orbitals first. The situation is analogous to that in the linearly bonded carbonyl complexes [35 (b)]. The 2s orbital of the nitrogen (NO) and the \( d_z^2 \) orbital of the metal form a \( \sigma^- \) bond. Back bonding from the metal occurs by means of the \( 3d_{xz} \) and \( 3d_{yz} \) metal orbitals overlapping with the two antibonding orbitals of the nitric oxide, Figure 25 (b). An increase in electron density around the cobalt atom causes a greater concentration of charge in the antibonding orbitals of the nitric oxide group resulting in a lowering of the bond order. If the process occurs there is a reduction in orbital overlap between the cobalt and the nitric oxide which lowers the electron density in the antibonding orbitals, the bond order increasing in consequence.

**Parallel Bonding of the Nitric Oxide Group**

This arrangement may be explained by considering the bonding as analogous to that suggested as being present by Chatt [112] et al in the platinum ethylene complex \( K[\text{C}_2\text{H}_4\text{PtCl}_3] \text{H}_2\text{O} \) and by Griffith [92] in oxyhaemoglobin. In both compounds hybrid metal orbitals are used in the \( \sigma^- \) bond formation, thus in the nitrosyls prepared here the cobalt atom may use \( \text{dsp}^3 \) or \( \text{d}^2\text{sp}^3 \) hybrid orbitals. Back bonding may occur by means
of the $3d_{xz}$ and $3d_{yz}$ orbitals into the antibonding orbitals of the nitric oxide. Both antibonding orbitals may be used because there is free rotation about the $N - O$ axis, Figure 25 (c). The nitric oxide has an equal chance to overlap with both of the metal $d_{xz}, d_{yz}$ orbitals at the same time. This situation may possibly be visualised as the nitric oxide revolving around an upturned cone of negative charge as shown in the diagram.

The two forms of metal-nitric oxide attachment are extreme cases and from the structural evidence available on the dimethyldithiocarbamato compound the absolute mode of bonding is probably somewhere between the two.
Figure 25

Diagrams are not to scale.

- Only one \( \pi \)-bonding metal orbital and nitric oxide antibonding orbital are shown.

\( \sigma \)-type bond

\( \pi \)-type bond
SUGGESTIONS FOR FURTHER WORK

(1) An increase in the N - O bond order with substituents should be accompanied by a decrease in the M - NO bond order (Section V (e), also this Section) and vice versa. Investigation in the KBr region should confirm this. However, the M - O bonds, the ligands, and the other M - N bonds absorb in this region; and $^{15}$NO would probably be needed for accurate assignments.

(2) Solution measurements would show whether solid state effects on the NO stretching frequency are at all comparable with substituent effects. Such measurements would be limited by the poor solubility of the nitrosyls as well as the sensitivity of their solutions to air.

(3) A comprehensive study of the ultra-violet and visible absorption spectra of the nitrosyls in solution under nitrogen might detect substituent effects and also yield accurate assignments for the absorption bands. Reflectance spectra would also show whether the solvent causes absorption changes.

(4) Extension of the cobalt-nitrosyl series, with particular emphasis on substituents in the 4,4' positions.

(5) Investigation of the magnetic moment of manganese(II) salen in solution under nitrogen as well as in the presence of a solid diluent to investigate possible antiferromagnetic interactions.
Further work into the reaction between iron(II) and manganese(II) salen with nitric oxide is required, together with the secondary reaction of the ferrous compound with oxygen.

If it is assumed that the hydrogen atoms of the ligand will not exchange with D$_2$O then the mass spectrographic analysis of cobalt salen prepared in D$_2$O instead of water should indicate if a water bridge is present in the compound. Alternatively cobalt salen prepared under aqueous conditions could be refluxed with D$_2$O or enriched water and any exchange between the D$_2$O and the hydrogens of an aquo bridge could be detected as above.
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[175] Carlin, contained in ref. (174)
Five-Co-ordinate Compounds of Cobalt

Most complex compounds of cobalt are of oxidation state +3 and six-co-ordinate, or of oxidation state +2 and four- or six-co-ordinate. Until recently, only a few apparently five-co-ordinate complexes had been reported.

These were the anions $[\text{Co(CN)}_5]^-$ and $[\text{Co(CN)}_6]^{3-}$, and the oxygen-carrying Schiff's base compounds (A) and (B).

Formula (A) shows the planar four-co-ordinate configuration suggested by Calvin et al., but Diehl believed that the true structure was five-co-ordinate with a water molecule bridging two cobalt atoms. However, tetrahedrally disposed bonds around the bridging oxygen atom would prevent the parallel arrangement of molecules of (A) deduced from X-ray evidence. In addition, Ueno and Martell do not report any infra-red absorptions due to water in the compound and this is supported by other investigations. There is no direct proof that the secondary amino group in (B) is co-ordinated to the cobalt atom. The cobaltocyanide ion, in the solid state, has been found to be dimeric, with cobalt–cobalt bonds, and in aqueous solution is probably $[\text{Co(CN)}_6\text{H}_2\text{O}]^{3+}$. The compound first reported to be $\text{Ag}_2\text{Co(CN)}_6$ (ref. 5) is now believed to contain bridging cyanide groups. So perhaps none of these compounds contains five-co-ordinate cobalt.

Many other five-co-ordinate compounds of cobalt have now been reported, but a detailed X-ray examination has been carried out only on nitrosyl(dimethylthiocarbamato) cobalt (I) (ref. 7), which has the square pyramidal structure (C) with the N–O bond inclined at 139° to the pyramidal axis and forming an unsymmetrical π-complex with the cobalt atom.
Other apparently five-co-ordinate compounds are:

\[
\text{Co}^{	ext{II}}\text{(PET)}_3\text{Cl}_2 \text{ (ref. 8)}, \quad \text{Co}^{	ext{II}}\text{MeAs[(CH}_2\text{)}_3\text{AsMe}_2\text{]}_2\text{Br}_3 \text{ (ref. 9a)}, \quad \text{Co}^{	ext{II}}\text{MeAs[(CH}_2\text{)}_3\text{AsMe}_2\text{]}_2\text{I}_2 \text{ (ref. 9b)}, \quad \text{Co}^{	ext{II}}\text{(CNR)}_6 \text{ (refs. 10, 17)}, \quad \text{Co}^{	ext{II}}\text{(PET)}_3\text{Br}_2 \text{ (ref. 11)}, \quad \text{Co}^{	ext{II}}\text{Br}_{3\text{[(PH(C}_6\text{H}_5\text{)]_3\text{]}_2}} \text{ (ref. 12), Co}^{	ext{II}}\text{X}_2\text{(PET)}_3\text{,} \quad \text{Co}^{	ext{II}}\text{X}_2\text{(NO)}\text{(PET)}_3\text{,} \quad \text{X} = \text{F, Cl, Br}^+\text{, Co}^{	ext{II}}\text{(acetylacetone)}_2\text{ (NO)} \text{ (ref. 14)}, \quad \text{and } \text{[Co}^{	ext{II}}\text{(8-aminocinoline)}_2\text{(NO)}\text{]}_2 \text{ (ref. 15)}\).
\]

Their likely configurations are square (or tetragonal) pyramidal, and trigonal bipyramidal\textsuperscript{16}. Compounds marked with an asterisk have been assigned pyramidal structures. No detailed account of the first compound in the list has appeared, and the last is unusual in containing cobalt (III) and co-ordinated NO\textsuperscript{-}.

Compounds such as cobalt carbonyl hydride HCo(CO)\textsubscript{4} and its methyl-substituted derivative CH\textsubscript{3}Co(CO)\textsubscript{4} (ref. 18a) are formally five-co-ordinate. In the former the carbonyl groups are tetrahedrally disposed with the H atom buried\textsuperscript{18\textsuperscript{6}} in the electron density of the metal and making little contribution to the stereochemistry of the molecule. Even the methyl compound appears to have essentially a tetrahedral configuration\textsuperscript{18\textsuperscript{6}}.

We have found that compound (A) and several substituted forms (Table 1) will form mononitrosyls. These give non-conducting solutions in nitrobenzene, and molecular weight determinations show the parent, the 5,5'-dichloro, and the 7,7-dimethyl compounds to be monomeric in nitrobenzene. They have magnetic moments of about 0.5 Bohr magnetons at room temperature, and that of the 5,5'-dinitro compound increases linearly with 1/\textit{T}. It therefore arises from temperature independent paramagnetism, no unpaired electrons are present, and electron pairing has occurred between the cobalt (II) atom (3d\textsuperscript{7}) and the NO molecule. From the magnetic results the compounds may be regarded as containing cobalt (III) and co-ordinated NO\textsuperscript{-}, or cobalt (I) and co-ordinated NO\textsuperscript{+}. However, their infra-red spectra show absorptions at the lower end of the range\textsuperscript{19} ascribed to co-ordinated NO\textsuperscript{+} (Table 1). These compounds are isoelectronic with (C), which has a similar nitrosyl absorption\textsuperscript{19} at 1,626 cm\textsuperscript{-1}, and we believe them to be of the same structure. The planar nature of the parent compound would favour the formation of a square or, more accurately, tetragonal structure on five co-ordination.

Temperature-independent paramagnetism of the above magnitude could contribute largely to the fractional magnetic moment of 0.87 Bohr magnetons at room temperature reported for Co(acetylacetone)\textsubscript{2} NO. It is not necessary, then, to postulate\textsuperscript{14} an equilibrium between a diamagnetic compound containing cobalt (I) and NO\textsuperscript{-}, and a paramagnetic compound containing cobalt (II) and neutral NO. The infra-red band at 1,675 cm\textsuperscript{-1}, typical of co-ordinated NO\textsuperscript{+}, indicates the former structure.
Table 1

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<tr>
<td>7,7'-dimethyl</td>
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<tr>
<td>5,5'-dinitro</td>
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The increase in the infra-red absorption frequencies with the substitution of electron-attracting groups (Table 1) shows that electron removal from the cobalt atom increases the N-O bond order, presumably by decreasing the extent of \( \delta_m - \pi_n \) double bonding from the metal to the co-ordinated nitric oxide.

If no bridging water molecule is present in the parent compound \((A)\) then the pyridine adduct of \((A)\), and its oxygenated form in which an oxygen molecule bridges two cobalt atoms, contain five-co-ordinate cobalt. The oxygenated form has been considered to contain a peroxide bridge\(^5\), but if the axis of the oxygen molecule were at right angles to the line joining the cobalt atom to give a \( \pi \)-bonded complex, as has now been found for other cobalt compounds containing peroxide bridges\(^6\), the bonding of NO and O\(_2\) would be analogous. There is some evidence that this type of bonding occurs in the nitric oxide compound of hemoglobin\(^2\) and in oxyhemoglobin\(^2\).

The readiness of cobalt to form five-co-ordinate compounds can be related to the tendency of the metal to achieve (cobalt (I), 3d\(^8\)) or approach (cobalt (II), 3d\(^7\)) the effective atomic number of the next inert gas\(^4\).

We have found that other Schiff's base complexes of cobalt (II), including the oxygen-carrying compound \((B)\), will react with NO. This is also true for similar complexes of other transition metals, and we are investigating the nature of the products.

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