"THE REACTIVITY OF SMALL N-DONOR LIGANDS
AND THEIR RELEVANCE TO DINITROGEN FIXATION"

A THESIS
presented for the degree of
DOCTOR OF PHILOSOPHY
at the
AUSTRALIAN NATIONAL UNIVERSITY

JOHN RAYMOND BUDGE

MARCH, 1977
Except for the crystallographic studies on [MoNCO(S₂CNEt₂)₂(dmso)NO], [Et₄N][Mo(NCO)₂(S₂CNEt₂)₂NO] and [Mo(S₂CNEt₂)₂(CO)₂-μ-N₂H₄], the work described in this thesis is the candidate's own.
Abstract

The work which is presented in this thesis deals mainly with the reactivity of the nitric oxide molecule when bound to transition metal complexes.

In Chapter 1 a review of nitrosyl reactivity is presented which relates the type of reaction observed with the mode of nitrosyl coordination (i.e. NO⁺, NO° or NO⁻). Chapters 2-4 deal with the [M(S₂CNR₂)₂(NO)₂] complexes (M=Mo or W) and their reactivity towards anions such as azide, cyanate, cyanide, thiocyanate and diethylthiocarbamate. Dinitrogen oxide was evolved during these reactions and complexes of the type [ML₂(S₂CNR₂)₂NO]⁻ have been isolated for L = azide, cyanate, and thiocyanate. Labelling studies employing [Mo(S₂CNEt₂)₂(¹⁵NO)₂] have shown that the dinitrogen oxide comes from a reaction involving one nitrosyl group per molecule of complex. Kinetic studies have also been carried out on the reactions of [Mo(S₂CNR₂)₂(NO)₂] with azide and cyanate and the results support the conclusions drawn from the labelling work.

The relevance of nitrosyl reactivity to dinitrogen fixation arises from the similarity in the dinitrogen and nitric oxide molecules. When nitric oxide binds to a transition metal the odd electron in its π*(NO) level is usually donated to the metal and consequently the nitrosyl group may formally be regarded as NO⁺, isoelectronic with dinitrogen. Therefore, a study of nitrosyl reactivity might be expected to throw some light on the reactions of dinitrogen bound to transition metal complexes.
Chapter 5 discusses some aspects of dinitrogen fixation and principles similar to those developed for nitrosyl reactivity are applied to dinitrogen complex reactions.

Finally, Chapter 6 describes some reactions of the 16-electron complex \([\text{Mo}(S_2\text{CNEt}_2)_2(\text{CO})_2]\) with a variety of nitrogen and phosphorus donor ligands.
Acknowledgements

I would like to thank Professors I.G. Ross and R.L. Martin for allowing me the use of facilities in the Chemistry Department and Research School of Chemistry, respectively, of the Australian National University.

The work for this thesis was carried out under the main supervision of Dr. J.A. Broomhead and his general guidance, suggestions and encouragement are gratefully acknowledged. It has been a pleasure to work with him on this project. During Dr. Broomhead's sabbatical leave in 1975, Professor Martin undertook the interim supervision of the work and his comments and suggestions were much appreciated.

I would like to thank the following people for their advice and assistance: Professor A. Hambly, Dr. N. Gill, Dr. R. Johnson, Dr. P. Boyd, Dr. A. Jones and Dr. M. Sterns.

I am indebted to Mrs Janet Hope for her expert assistance in obtaining the cyclic and ac voltamograms for the \([\text{M(S}_2\text{CNR}_2\text{)}_2\text{(NO)}_2]\) complexes and to the nmr service of the Research School of Chemistry for computer simulating the spectrum of \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2\text{(NO)}_2]\).

The following members of the technical staff of the Department of Chemistry are thanked for their skilled assistance: Messrs. R. Nicholls, B. Machan, R. Briggs, E. Bellantoni, R. Dowhy, D. Harding, L. Wells and H. Benzin.

Finally I am grateful to Marie-Anna Lebovits for drawing the diagrams used in this thesis and to Mrs Margaret Keys for her excellent typing.
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<td>UV</td>
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ac voltametry

\[ E_p = \text{peak potential} \]
\[ \Delta E/2 = \text{peak width at half height} \]
\[ i_p/C = \text{peak current divided by complex concentration} \]

cyclic voltametry

\[ i_{p}^{f}/i_{p}^{b} = \text{The ratio of the peak currents on the forward and backward scans} \]
\[ \Delta E_{p} = \text{difference in the peak potentials} \]
\[ i_{p}^{f}/Cv^{1/2} = \text{forward peak current divided by complex concentration and scan rate to the power half.} \]
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The Reactivity of [Mo(S₂CNEt₂)₂(CO)₂]₂-µ-N₂H₄

References
1.0 Introduction

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The chemistry of NO bound to transition metal complexes is diverse and the reactions involving NO are often mechanistically complex. Research has shown that metal nitrosyl complexes are highly reluctant species and consequently MO schemes have been of considerable use in the rationalization of observed nitrosyl geometries.

However, the application of MO methods to the reactivity of nitrosyl groups has received relatively little attention.

In the following section (1.1) a brief outline of some of the chemistry of free NO will be given as a background to the bonding of coordinated nitrosyls.

CHAPTER 1

The Bonding and Reactivity of Transition Metal Nitrosyl Complexes

1.1 The Electronic Structure and Reactivity of Nitric Oxide

The MO treatment of the bonding in nitric oxide has been found to satisfactorily account for many of the observed physical properties of the molecule. A MO scheme for nitric oxide is shown in Figure 1.1 and the energies of four of the electronic levels indicated have been determined experimentally. The unpaired electron in the \( \text{I}^* \) (or \( \pi^*(\text{NO}) \)) level makes the molecule paramagnetic and as the
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In the following section (1.1) a brief outline of some of the chemistry of free NO will be given as a background to the later discussions on the reactivity of coordinated nitrosyls.

1.1 The Electronic Structure and Reactivity of Nitric Oxide

The MO treatment of the bonding in nitric oxide has been found to satisfactorily account for many of the observed physical properties of the molecule. A MO scheme for nitric oxide is shown in Figure 1.1 and the energies of four of the electronic levels indicated have been determined experimentally\(^3\). The unpaired electron in the \(2\pi^+\) (or \(\pi^*(\text{NO})\)) level makes the molecule paramagnetic and as the
Figure 1.1. A MO scheme for nitric oxide. The energies of the $4\sigma$, $5\sigma$, $1\pi^\pm$, and $2\pi^+$ levels were obtained from the adiabatic ionisation potentials of NO.
orbital is antibonding, it cancels some of the effect of the three filled bonding MO's. Consistent with this is the NO bond length of 1.15 Å, intermediate between that observed for NO⁺ species (1.06 Å = triple bond) and that expected for an NO double bond (~1.20 Å). The increase in bond order on going from NO to NO⁺ is also reflected by the nitrosyl stretching frequencies which are 1840 cm⁻¹ and 2150-2400 cm⁻¹, respectively.

The nitric oxide molecule contains one unpaired electron and surprisingly, shows little tendency to dimerise. X-Ray crystallography has established that the solid contains loosely bound (NO)₂ species which may have either a trapezoidal or rectangular shape, but it was not possible to determine how the molecules were oriented⁴. Infrared evidence for both cis and trans ONNO species has also been obtained in frozen matrices of N₂, CO₂ and argon⁵,⁶.

Nitric oxide is relatively easy to ionise (IP = 9.23 eV) and can function as a reducing agent:

\[ \text{e.g.} \quad 2\text{NO} + \text{X}_2 \rightarrow 2\text{NO}^+\text{X}^- \quad (1) \]
\[ \text{NO} + \text{MoF}_6 \rightarrow \text{NO}^+\text{MoF}_6^- \quad (2) \]
\[ \text{M}^{\alpha} + \text{NO} + \text{B} + \text{ROH} \rightarrow \text{M}^{\alpha-1} + \text{BH}^+ + \text{RONO} \quad (3) \]

Nitric oxide is also a good oxidising agent and equations (4) - (7) provide some examples of this.

\[ 2\text{NO} + \text{SO}_2 \rightarrow \text{SO}_3 + \text{N}_2\text{O} \quad (4) \]
\[ 2\text{NO} + \text{PR}_3 \rightarrow \text{N}_2\text{O} + \text{OPR}_3 \quad (5) \]
\[ 2\text{NO} + \text{CN}^- \rightarrow \text{N}_2\text{O} + \text{NCO}^- \quad (6) \]
\[ 2\text{Na} + 2\text{NO} \rightarrow \text{cis-}\text{Na}_2\text{N}_2\text{O}_2 \quad (7) \]
The product formed by reaction (7) was originally thought to be Na\(^{+}\)NO\(^{-}\), but this formulation was shown to be inconsistent with the infrared spectrum of the compound and it was suggested to contain the cis-hyponitrite anion. \(^{8,9}\)

"cis-Na\(_2\)N\(_2\)O\(_2\)" differs from the more commonly encountered trans-hyponitrite in several respects. \(^{10}\) For example, the former reacts with water to give N\(_2\)O and Na\(_2\)O while the latter dissolves without appreciable decomposition. The formation reaction (7) could be regarded as a coupling of two NO\(^{-}\) molecules.

Nitric oxide appears to behave as a Lewis acid in a number of reactions and molecules containing hyponitrite type structures are obtained. \(^{11}\) At 0°C, NO reacts with SO\(_3\)\(^{2-}\) in alkaline solution to give Na\(_2\)SO\(_3\)N\(_2\)O\(_2\) and the following mechanism was proposed \(^{11}\):

\[
\text{ON} + \text{SO}_3^{2-} \rightarrow [\text{ON} + \text{SO}_3]^{2-} \rightarrow \left[\begin{array}{c}
\text{O} \\
\text{N}
\end{array}\right]^{2-}
\]

Similarly, primary and secondary amines react with NO to give \([\text{NH}_2\text{R}_2]^+[\text{N}_2\text{O}_2\text{NR}_2]^-\). \(^{11}\)

The familiar reaction of NO with O\(_2\) to form brown NO\(_2\) has been studied intensively. The rate expression for the reaction was found to be \(\text{d}(\text{NO})/\text{dt} = k[\text{NO}]^2[\text{O}_2]\). \(^{12}\) Because of the negative temperature dependence of the rate it was thought that an equilibrium reaction preceded the rate determining step and the suggested mechanism was \(^{13}\):

\[
\begin{align*}
2\text{NO} & \overset{K}{\underset{k'}{\rightleftharpoons}} \text{N}_2\text{O}_2 \\
\text{N}_2\text{O}_2 + \text{O}_2 & \rightarrow 2\text{NO}_2 \quad (k = k'K)
\end{align*}
\]
Subsequent work on the reaction of NO with O₂ in the presence of a large excess of NO₂ showed that there were two parallel reactions. These were the dominant third order process mentioned above, in addition to a much slower process whose postulated mechanism was:

\[
\begin{align*}
&\text{NO} + \text{O}_2 + \text{NO}_2 \xrightarrow{K'} \text{NO}_3 + \text{NO}_2 \\
&\text{NO}_3 + \text{NO} \xrightarrow{k''} 2\text{NO}_2
\end{align*}
\]

It was later argued that the NO₃ in this mechanism could have a "nitrate" shape. Also, an alternative mechanism was suggested for the more rapid third order process. This involved an NO₃ species with a "peroxy" structure:

\[
\begin{align*}
&\text{NO} + \text{O}_2 \xrightarrow{K} \text{NO}_3 \text{ (peroxy)} \\
&\text{NO}_3 + \text{O}_2 \xrightarrow{k'} 2\text{NO}_2
\end{align*}
\]

The 'peroxy' and 'nitrate' structures of NO₃ are illustrated in Figure 1.2.

![Figure 1.2](image-url)

At 25°C NO is thermodynamically unstable with respect to disproportionation, N₂O and NO₂ being formed; but the molecule is kinetically inert.

\[
\begin{align*}
&3\text{NO}(g) \rightarrow \text{N}_2\text{O}(g) + \text{NO}_2(g) \\
&\Delta G°^\circ = -102.9 \text{ kJ/mole (24.6 kcal)}
\end{align*}
\]
However, over the temperature range 35-50°C and with NO pressures up to 400 atmospheres, this reaction readily occurs and follows third order kinetics\(^{16}\): 
\[
-d(NO)/dt = k[NO]^3.
\]
The suggested mechanism was:
\[
\begin{align*}
2NO & \xrightarrow{K} N_2O_2 \\
N_2O_2 + NO & \rightarrow N_2O + NO_2 \quad (k = k'K)
\end{align*}
\]

A number of other thermodynamically favourable reactions, some of which are catalysed by transition metal complexes, have been listed below:

\[
\begin{align*}
2NO(g) + CO(g) & \rightarrow N_2O(g) + CO_2(g) \\
\Delta G^\circ & = -372.2 \text{ kJ/mole (78.2 kcal)}
\end{align*}
\]

\[
\begin{align*}
2NO(g) & \rightarrow N_2(g) + O_2(g) \\
\Delta G^\circ & = -172.8 \text{ kJ/mole (41.3 kcal)}
\end{align*}
\]

\[
\begin{align*}
4NO(g) & \rightarrow N_2(g) + 2NO_2(g) \\
\Delta G^\circ & = -241.8 \text{ kJ/mole (57.8 kcal)}
\end{align*}
\]

\[
\begin{align*}
4NO(g) & \rightarrow O_2(g) + 2N_2O(g) \\
\Delta G^\circ & = -136.8 \text{ kJ/mole (32.7 kcal)}
\end{align*}
\]

The important features of NO reactivity will now be summarised:

(a) Molecules of NO show little tendency to dimerise.
(b) NO may be readily ionised to yield NO\(^+\).
(c) NO\(^-\) is an unstable species and apparently dimerises to the \(\alpha\)-hyponitrite anion.
(d) NO can act as a Lewis acid.
(e) The reaction of NO with O\(_2\) has been shown to proceed via two parallel reaction pathways. These are: (1) A dominant
third order process (2) A much slower NO\textsubscript{2} catalysed reaction. The former has been *postulated* to involve an NO\textsubscript{3} species with a "peroxy" structure while the latter was thought to have an NO\textsubscript{3} intermediate with a nitrate structure.

1.2 Bonding in Transition Metal Complexes

The nitric oxide molecule has been found to bind to transition metals in a variety of ways. Figure 1.3 shows some examples of the different types of coordination.

![Figure 1.3 NO Bonding in Transition Metal Complexes](image)

(a) (b) (c) (d)

NO is usually found coordinated to one transition metal (Figure 1.3(a) or (b)) but it can also function as a doubly or triply bridged ligand\textsuperscript{19} (Figure 1.3(c) and (d), respectively).

1.2.1 The NO\textsuperscript{+}, NO\textsuperscript{0} and NO\textsuperscript{-} Formalism

The following discussion applies to the NO molecule bound to one transition metal only. Traditionally, the NO molecule has been considered to bind to the metal in one of three states: NO\textsuperscript{+}, NO\textsuperscript{0} or NO\textsuperscript{-}. These three types of coordination will now be defined.
(a) **NO⁺ Coordination**

Here, the odd electron in the π*(NO) of NO is given up to the metal and the NO⁺ species formed donates a lone pair of electrons to the metal forming a ON⁺M sigma bond. In addition to this, overlap of metal d_π and π*(NO) orbitals allows some d_π→π*(NO) bonding. i.e. electron density from the metal can be delocalised into the π*(NO) orbitals through this bonding overlap. The sigma bonding in NO⁺ occurs through an sp hybridised lone pair and so provided that the two π*(NO) levels interact equally with the metal d orbitals, the M-N-O linkage should be linear. The valence bond representation for NO⁺ coordination is:

\[
q\begin{array}{cc}
\text{(+)} & \\
\text{(+)} & M - N = 0
\end{array}
\leftrightarrow
\begin{array}{cc}
\text{(+)} & \\
\text{(+)} & M = N = \bar{0}
\end{array}
\]

(b) **NO⁰ Coordination**

The NO molecule retains its unpaired electron in the π*(NO) level and binds to the metal in a manner similar to that described in (a).

(c) **NO⁻ Coordination**

NO accepts an electron from the metal to form NO⁻. Then an electron pair in an sp² hybridised orbital on the N is donated to the metal to form a sigma bond. A sp² hybridised lone pair is also localised on the N. For an sp² hybridised N, the M-N-O bond angle should be 120⁰. The valence bond representation of NO⁻ coordination is:

\[
q\begin{array}{cc}
\text{M} - \text{N} \rightarrow \text{O} & \leftrightarrow
\end{array}
\begin{array}{cc}
\text{M} - \text{N} \rightarrow \text{O} & \text{(-)}
\end{array}
\]

\[
q+1
\]

The above definitions are clearly formal ways of viewing the bonding in nitrosyl complexes and the specified charge on the NO should not be taken too literally. For example, in the NO$^+$ mode of coordination, the charge on the NO molecule will depend on the extent of $\pi$-back bonding from the metal. Molecules with high nitrosyl stretching frequencies (>1900 cm$^{-1}$) approximate the formal NO$^+$ coordination.

There has unfortunately been a considerable amount of controversy over the assignment of formal metal oxidation states in nitrosyl complexes$^{19,20}$. The highly covalent nature of the metal nitrosyl moiety makes such rigid formalisms on charge distribution pointless. However, it will be seen later in this chapter, that the assignment of formal metal oxidation states can be a useful aid for "electron bookkeeping" when discussing reactions of nitrosyl complexes.

1.2.2 The Prediction of Nitrosyl Geometry

In 1958 it was suggested$^{21,22}$ that the nitrosyl stretching frequency could be used as a criterion for determining the mode of coordination of NO. Most nitrosyl frequencies occurred in the range 1980-1580 cm$^{-1}$ and it was thought that these frequencies were characteristic of NO$^+$ coordination. However, with the increase in structural information on nitrosyl complexes, several reclassifications of the "regions" of nitrosyl frequencies were made$^{23}$. One recent reclassification assigned 2000-1750 cm$^{-1}$ to complexes.
of NO\(^+\) while NO\(^-\) coordination was between 1750-1500 cm\(^{-1}\).\(^{24}\) These regions may be taken as a rough guide, although they are by no means conclusive. The compounds listed in Table 1.1 illustrate this point. But it does appear that nitrosyl complexes with NO frequencies greater than 1850 cm\(^{-1}\) and/or N(1s) binding energies greater than 402 eV, can be assigned a linear (NO\(^+)\) geometry\(^1\). The nitrosyl stretching frequency and the N(1s) binding energy are related to the effective charge on the NO group and not to its geometry\(^1\). Thus a linear NO group with a very low NO frequency implies extensive electron delocalisation from the metal into the \(\pi^*(\text{NO})\) orbitals.

Recently, a set of empirical rules for predicting NO geometry based on the observed NO frequency was published\(^{30}\). A number of correction factors were added to or subtracted

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v) (NO) cm(^{-1})</th>
<th>M-N-O angle(^\circ)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe(CN)}_5\text{NO}]^2^-)</td>
<td>1939</td>
<td>178(1)</td>
<td>25</td>
</tr>
<tr>
<td>([\text{V(CN)}_5\text{NO}]^3^-)</td>
<td>1530</td>
<td>176</td>
<td>26</td>
</tr>
<tr>
<td>([\text{Mo(CN)}_5\text{NO}]^4^-)</td>
<td>1455</td>
<td>175.1(2.9)</td>
<td>27</td>
</tr>
<tr>
<td>([\text{IrI(P(\Omega)}_3\text{CO})\text{NO}]^+)</td>
<td>1720</td>
<td>125(3)</td>
<td>28</td>
</tr>
<tr>
<td>([\text{IrH(P(\Omega)}_3\text{NO}]^+)</td>
<td>1715</td>
<td>175(3)</td>
<td>29</td>
</tr>
</tbody>
</table>
from the observed NO frequencies and the corrected frequency was suggested to be diagnostic for nitrosyl geometry. Table 1.2 presents the corrections which were proposed.

Table 1.2

Corrections to Observed Nitrosyl Frequencies (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Metal</th>
<th>Group</th>
<th>Charge</th>
<th>Ligands</th>
<th>Coordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>First row -50</td>
<td>6B</td>
<td>+100</td>
<td>2+</td>
<td>-140 Third PR(_3)</td>
</tr>
<tr>
<td>Second row -30</td>
<td>7B</td>
<td>+50</td>
<td>1+</td>
<td>-80 Fourth PR(_3)</td>
</tr>
<tr>
<td>(Mo, -10)</td>
<td>8</td>
<td>0</td>
<td>Neutral</td>
<td>0</td>
</tr>
<tr>
<td>Third row 0</td>
<td>0</td>
<td></td>
<td>1-</td>
<td>+80 C(_5)H(_4)P(_3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-</td>
<td>+140 H(^+)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3-</td>
<td>+200</td>
</tr>
</tbody>
</table>

Corrected frequencies above 1610-1620 cm\(^{-1}\) were ascribed to a linear nitrosyl geometry whereas those below have a bent NO group. At the time of publication, only one exception had been noted and this was [IrI(P\(_3\))\(_2\)(CO)NO\(^+\)] (1720, 1640 cm\(^{-1}\)) which has a bent nitrosyl. The correction terms have been applied to a few compounds of interest in Table 1.3.

ESCA has also been applied to the problem of nitrosyl geometry predictions\(^{31}\). It was suggested that the difference between O(1s) and N(1s) binding energies tended to be 132 ± 2 eV for linear nitrosyls while for bent nitrosyls, the value was 128 ± 2 eV.
Table 1.3
The Prediction of Nitrosyl Geometry using the Ibers-Haymore Correction Factors

<table>
<thead>
<tr>
<th>Correction</th>
<th>[Mo(S₂CNEt₂)(NO)₂]</th>
<th>[IrBr(P₃O)₂(NO)₂]</th>
<th>[OsCl(P₃O)₂(CO)(NO)]</th>
<th>[Os(P₃O)₂(CO)₂NO]⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed frequencies (cm⁻¹)</td>
<td>1755, 1655</td>
<td>1540, 1500</td>
<td>1560</td>
<td>1750</td>
</tr>
<tr>
<td>Row</td>
<td>-10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Group</td>
<td>+100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ligand</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Coordination number</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Charge</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-80</td>
</tr>
<tr>
<td>Corrected frequency</td>
<td>1845, 1745</td>
<td>1540, 1500</td>
<td>1560</td>
<td>1670</td>
</tr>
<tr>
<td>Nitrosyl geometry (predicted)</td>
<td>linear, linear</td>
<td>bent, bent</td>
<td>bent</td>
<td>linear</td>
</tr>
<tr>
<td>Observed Geometry</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>linear¹</td>
</tr>
</tbody>
</table>

¹ No structural information available.
In the present literature there are several examples of both quantitative and qualitative applications of MO theory to various mononitrosyl systems. A general analysis of the bonding in nitrosyl complexes by Enemark and Feltham has achieved considerable success in the rationalisation of observed nitrosyl geometries. Also, Hoffman and coworkers, employing both extended Hückel calculations and qualitative MO arguments have made a significant contribution to the understanding of structure in pentacoordinate mononitrosyl complexes.

The most striking feature of the approach adopted by Enemark and Feltham is its simplicity. In the construction of MO schemes they have treated the \( \text{M(NO)}_x \) moiety as an inorganic functional group perturbed by the coordination of additional ligands. Since most nitrosyl complexes are low spin they may be described by one-electron MO schemes in which the energy separation between orbitals is greater than spin-pairing energies. For the prediction of mononitrosyl geometry, the results of some early MO studies by A.D. Walsh on the \([\text{O-N-O}]^n\) system were extended to the M-N-O situation. Walsh claimed that if electrons occupied an orbital which was antibonding with respect to all three atoms (ONO), then the system would bend and the electrons in the antibonding orbital were then localised in an sp\(^2\) type orbital on N. The corresponding statement for the M-N-O moiety is that, "if electrons occupy an orbital which is principally \( \pi^* (\text{NO}) \) in character then the nitrosyl will bend".
To illustrate the above principle, a number of octahedral mononitrosyl complexes will now be examined. In octahedral complexes, both the metal $d_{x^2-y^2}$ and $d_{z^2}$ orbitals are strongly antibonding and the $\pi^*(\text{NO})$ levels are considered to be intermediate between these and the remaining three $d$ orbitals. Figure 1.4 shows part of the MO scheme for an octahedral mononitrosyl in $C_{4v}$ symmetry, which has a linear NO group.

![MO Scheme for Six Coordinate Mononitrosyl Complexes](image)

It has been found convenient to classify nitrosyl complexes according to the number of $d$-type electrons. This corresponds to the number of $d$ electrons on the metal if the NO is treated as NO$^+$. For example, the complexes $[\text{Fe(CN)}_5\text{NO}]^{2-}$ and $[\text{Mn(CN)}_5(\text{NO})]^3-$ are $\{\text{M(NO)}\}^6$ systems, where the superscript denotes the number of $d$-type electrons. Both of these compounds will have the orbitals through to $1b_2$ filled.
(Figure 1.4) and the 3e levels ($\pi^*(\text{NO})$) remain empty. As expected, linear nitrosyls are observed for the two compounds.

In contrast, complexes such as $[\text{Co(NH}_3\text{)}_5\text{NO}]^{2+}$, $[\text{CoCl(en)}_2\text{NO}]^{2+}$ and $[\text{CoNCS(das)}_2\text{NO}]^+$ are $\{\text{M(NO)}\}^7$ and consequently a pair of electrons now occupy the 3e level. All of these compounds have strongly bent nitrosyl groups (Co-N-O angles of $-125^\circ$) consistent with the principle that occupation of $\pi^*(\text{NO})$ levels in mononitrosyl complexes leads to strong bending of the M-N-O moiety. The $\{\text{M(NO)}\}^7$ configuration occurs in the compounds $[\text{Fe(CN)}_5\text{NO}]^{3-}$ and $[\text{FeBr(das)}_2\text{NO}]^+$ and presumably one electron occupies the 3e level. The structure of the latter compound has been determined and the nitrosyl group was found to have an intermediate geometry (Fe-N-O angle of $148^\circ$).

On going to five coordination, the problem of predicting nitrosyl geometries is made difficult by the uncertainty in the relative energy ordering of the $d_{z^2}$ and $\pi^*(\text{NO})$ levels. Figure 1.5 shows the three extreme types of nitrosyl geometry observed for five coordinate $\{\text{M(NO)}\}^8$ systems.

![Figure 1.5](image)

Figure 1.5

Structures (a) and (b) are by far the most common but (c) is sometimes obtained if bulky substituents are present.
Enemark and Feltham claim that structure (a) results if \( \pi^*(\text{NO}) \) is lower in energy than \( d_{z^2} \) while the reverse order gives structure (b). In cases where the coordination geometry is intermediate between (a) and (b), the \( d_{z^2} \) and \( \pi^*(\text{NO}) \) are thought to be nearly degenerate and vibronic coupling is invoked to account for the observed structure (e.g. [CoCl\(_2\)(PO\(_2\)CH\(_3\))\(_2\)NO]; Co-N-O bond angle = 165°).

Hoffman and coworkers\(^2\) have adopted quite a different approach to the explanation of nitrosyl geometry in pentacoordinate nitrosyls. Their extended Hückel calculations suggest that the \( d_{z^2} \) orbital is always lower in energy than the \( \pi^*(\text{NO}) \) levels and the extent of bending depends upon the rates at which the \( d_{z^2} \) and \( d_{xz} \) orbitals are stabilised and destabilised respectively, as the nitrosyl bends. Figure 1.6 illustrates the 'significant' interactions proposed by Hoffman et al on bending the nitrosyl moiety.

\[\begin{align*}
\text{(a)} & \quad \text{destabilising interaction reduced} \\
\text{(b)} & \quad \text{interaction stabilising}
\end{align*}\]

\[\begin{align*}
\text{5}\sigma & \quad \text{On bending the } \pi \\
\text{bonding interaction with NO is reduced and an antibonding interaction is also introduced.}
\end{align*}\]
It is predicted that the higher $d_{z^2}$ is in energy, the more likely the nitrosyl group is to be bent.

In addition, several of the structural characteristics (e.g. the preference for NO to bend in the axial position only in five coordinate complexes) of pentacoordinate nitrosyl have been rationalised in terms of qualitative MO arguments.

A critical examination of the approach used by Hoffman and coworkers would require a detailed knowledge of the calculations involved and is outside the scope of this thesis. However, the following comments can be made about the work:

(a) The energies calculated using extended Hückel methods are only approximate and the relative energy orderings obtained must generally be taken "cum granulo salis". 19

(b) A further point concerns the use of the non-bonding $5\sigma$ orbital of NO as a basis orbital for the extended Hückel calculations.

(c) The interaction between $d_{z^2}$ and the nitrosyl lone pair ($5\sigma$) is only destabilising if the $d_{z^2}$ orbital is occupied.

Point (b) will be discussed in more detail. A bent nitrosyl has been considered to have an sp$^2$ hybridised N - one sp$^2$ hybrid contains a non-bonding pair of electrons (lone pair) and a second sp$^2$ lobe is directed toward the $d_{z^2}$ orbital as shown in Figure 1.7.
Figure 1.7

(n = orbital involved in the σ-bonding interaction with the metal)

The orbital directed towards $d_{z^2}$ has considerably more $p$ character than in the linear mode of coordination ($sp$ hybridisation) and therefore should be of higher energy. As a result, the interaction between $\eta$ and $d_{z^2}$ should increase on bending thereby raising the energy of $d_{z^2}$. This expectation is in direct opposition to what Hoffman and coworkers have suggested.

For the above reasons, the approach adopted by Enemark and Feltham seems to be the most consistent and will be used exclusively.

Most of the four coordinate mononitrosyl complexes ($\{iNO\}$) whose structures have been determined have tetrahedral geometries with a linear nitrosyl group, implying that $d_{z^2}$ is lower in energy than $\pi^*(NO)$. However, for $[\text{NiN}_3(\text{P} \text{O}_3)_2\text{NO}]^4$, an intermediate nitrosyl geometry was observed suggesting that the $d_{z^2}$ and $\pi^*(NO)$ orbitals may be nearly degenerate.

**Dinitrosyl Complexes**

As yet, there are no well established examples of trans dinitrosyl complexes. However, a recent report on the reaction of CoTPP(NO) with NO suggests that an unstable trans dinitrosyl species may be formed. All of the known
Dinitrosyl complexes have *cis* geometries\(^1\) and Figure 1.8 shows the molecular orbitals for the *cis-*(NO)\(_2\) moiety.

The metal orbitals used in the MO schemes are \(d_{z^2-y^2}\), \(d_{xz}\), \(d_{xy}\), \(d_{yz}\) and \(d_{x^2}\) which are obtained from the conventional \(d\) orbitals by the transformation \(y\to y\), \(x\to z\) and \(z\to x\). The lowest energy \(\pi^*\text{(NO)}\) orbital is considered to be \(\pi^*\text{b}_1\text{(NO)}\) because of its minimal interaction with the \(d_{xz}\) orbital.

There appear to be two possible consequences resulting from the occupation of the \(\pi^*\text{b}_1\text{(NO)}\) orbital:

(i) If the two nitrosyl groups are equivalent, they tend to bend away from each other, thereby reducing the antibonding interaction between them. Examples of this behaviour are found for the pseudotetrahedral \{M(NO)\(_2\)\}\(^1\text{0}\) complexes [Ru(P\(\Phi_3\))\(_2\)(NO)\(_2\)]\(^{+50}\) and [Ir(P\(\Phi_3\))\(_2\)(NO)\(_2\)]\(^{+51}\). Martin and Taylor\(^{44}\) have pointed out that a linear correlation

---

**Figure 1.8.** MO's for the *cis-*(NO)\(_2\) (Labels are for \(C_{2v}\) symmetry).
exists between the O-M-O and N-M-N bond angles for \( \{M(NO)_{2}\}_{10} \) complexes. The M(NO)\(_2\) moiety with O-M-O > N-M-N was termed the "repulso" conformer while the arrangement O-M-O < N-M-N was called the "attracto" conformer. Figure 1.9 depicts the two conformations.

!["attracto" conformer "repulso" conformer](image)

The "repulso" conformer, as mentioned above, arises from the occupation of the \( \pi^{*}_{b_1}(NO) \) level. The "attracto" conformer occurs when the \( d_{xz} \) orbital is below \( \pi^{*}_{b_1}(NO) \) in energy.\(^{1,44}\)

For four coordinate \( \{M(NO)_{2}\}_{10} \) complexes, the "attracto" conformer is characteristic of the first row while the "repulso" configuration occurs for the second and third row transition metals.

(ii) Alternatively, when non-equivalent nitrosyl groups are present, the pair of electrons may be localised in an \( sp^2 \) type orbital on one of the nitrosyl N atoms. This gives one linear and one bent nitrosyl group. For example, the TP complexes \([RuCl(P\phi_3)(NO)]_{52}\) and \([Os(OH)(P\phi_3)(NO)]_{53}\) have a bent axial nitrosyl and linear equatorial nitrosyl. The presence of an empty \( d_{xz} \) orbital may explain the preference for TP geometry rather than TBP.\(^1\)
A large number of six coordinate \( \{M(\text{NO})_2\}^6 \) complexes are known, but unfortunately, relatively little structural information is available on them. The structures determined to date all show nearly linear nitrosyl groups. MO schemes for these complexes will be discussed in chapters 2 and 3.

A Summary

Molecular orbital schemes such as those described in this section, for mono- and di-nitrosyl complexes, are useful for the rationalisation of observed nitrosyl geometries. As a predictive tool, however, they tend to suffer from the uncertainty in the relative energy orderings of some of the metal d orbitals and the \( \pi^*(\text{NO}) \) levels. This is particularly so in four and five coordinate complexes. At present the range of structural information on nitrosyl complexes is insufficient to indicate any definite trends.

1.3 The Reactivity of Coordinated Nitrosyls

In this section the various types of nitrosyl reactivity will be presented and it will be shown that the chemistry of coordinated NO may be understood if it is assumed that there are only two types of reactive nitrosyl. These are the linearly coordinated \( \text{NO}^+ \) with a high nitrosyl frequency (>1850 cm\(^{-1}\)) and the bent \( \text{NO}^- \). It follows that linear nitrosyls with low NO stretching frequencies should be unreactive.

If a pathway exists whereby a linear unreactive nitrosyl can be converted into a bent \( \text{NO}^- \) then nitrosyl reactivity may be observed. One well established way in
which a nitrosyl group may change its coordination geometry is by the coordination of another molecule to the metal. Enemark and Feltham\(^1\) have termed this type of reactivity as "Stereochemical Control of Valence". An example of this occurs in the reaction of \([\text{Co}(\text{das})_2\text{NO}]^{2+}\) with \(X^-\) (\(X^- = \text{mono-anion}\)) to give \([\text{CoX}(\text{das})_2\text{NO}]^{+}\). MO schemes are particularly useful in understanding the change in nitrosyl geometry.

The nitrosyl group in \([\text{Co}(\text{das})_2\text{NO}]^{2+}\) has been shown to be linear implying that the metal \(d_{z^2}\) orbital is lower in energy than the \(\pi^*(\text{NO})\) levels. However upon coordination of \(X^-\), the \(d_{z^2}\) orbital becomes higher in energy than \(\pi^*(\text{NO})\) and this latter level should now contain a pair of electrons; consequently, the nitrosyl group should bend. The Co-N-O angle in \([\text{CoNCS}(\text{das})_2\text{NO}]^{+}\) was found to be 134(2)\(^\circ\).

In this work, MO methods were found useful in the understanding of certain types of nitrosyl reactivity - see section 1.3.1 and chapters 2 and 3. Also, in the following discussions, the more traditional valence bond representations combined with 16-18 electron rule\(^88\), are used extensively.

When writing structural formulae the following "short-hand" notations will be used to depict the type of nitrosyl coordination:

\(a\)  "M-NO"

This represents the formal NO\(^+\) coordination where the odd electron of the NO resides in an orbital of principally metal \(d\) character.

\(b\)  "M-\(\text{\=N}O\)"

Here the odd NO electron occupies an orbital which is mainly \(\pi^*(\text{NO})\) in character, i.e. NO\(^\circ\).
This corresponds to the formal bent NO\textsuperscript{-} ligand. The nitrosyl group has accepted an electron from the metal and the N has a lone pair of electrons in an sp\textsuperscript{2} type hybrid orbital.

1.3.1 Some Reactions of Nitrosyl Complexes with CO

A number of nitrosyl complexes have been found to react with CO to yield N\textsubscript{2}O and CO\textsubscript{2} as products. Examples of this are given by the following equations:

\[
[M(P\text{OP}_3)_2(NO)_2]^+ + 4CO \rightarrow [M(P\text{OP}_3)_2(CO)_3]^+ + CO_2 + N_2O \quad 54, 55
\]

\[
[IrBr(P\text{OP}_3)_2(NO)_2]^- + 3CO \rightarrow [IrBr(P\text{OP}_3)_2(CO)_2]^+ + CO_2 + N_2O \quad 56
\]

\[
[RhCl_2(NO)_2]^- + 3CO \rightarrow [RhCl_2(CO)_2]^+ + CO_2 + N_2O \quad 57
\]

\[
[Ir(NO_2)Cl(P\text{OP}_3)_2(NO)] + 4CO \rightarrow [IrCl(P\text{OP}_3)_2(CO)_2] + 2CO_2 + N_2O \quad 56
\]

All of these reactions are clearly related. Reaction (1) has been studied in detail using \textsuperscript{15}NO labelled complex. When equimolar quantities of labelled and unlabelled complex were reacted under CO, the \textsuperscript{15}N in the N\textsubscript{2}O evolved was found to be completely scrambled. It was suggested that the coordination of a molecule of CO resulted in the formation of a labile \textit{cis}-dinitrogen dioxide species which reacted with CO to give N\textsubscript{2}O and CO\textsubscript{2}. The effects of coordination of a molecule of CO upon the M(NO)\textsubscript{2} moiety will now be discussed using a molecular orbital approach.

The structures of [Ir(P\text{OP}_3)_2(NO)_2]^+ and [Rh(P\text{OP}_3)_2(NO)_2]^+ have been determined and they were shown to be pseudotetrahedral
A MO scheme consistent with this structural information is shown in Figure 1.10. The contributions of the pi bonds of the NO group (e.g., $\pi_{b_1}$) to give a TBP species should result in the $2a_1$ orbital having moderately antibonding character.

The empty MO scheme Figure 1.11 (cf., [M(NO)$_2$] and 2b$_1$(yz) orbitals are now bonding in the geometry. The point $I$ directly toward the filled $d_x^2$ and $d_y^2$ level (cf., [M(NO)$_3$]) and the $2a_1$ (NO) level is antibonding in the nitrosyls; they should bond away from each other and show the MO scheme for $[\text{M(P} \text{O})_3 \text{NO}]$ system ($\text{M} = \text{Ir}, \text{Rh}$).

**Figure 1.10** An MO Scheme for $[\text{M(P} \text{O})_3 \text{NO}]^+$ - An $\{\text{M(NO)}_2\}^{10}$ system ($\text{M} = \text{Ir}, \text{Rh}$).

**Figure 1.11** MO Scheme for $\text{MX(PO} \text{)}_3 \text{(NO)}$ - an $\{\text{M(NO)}_2\}^{10}$ system ($\text{M} = \text{Rh}, \text{Ir}; \text{X} = \text{Br}^-, \text{CO}$).
with the \textit{cis} nitrosyl groups bending away from each other. A MO scheme consistent with this structural information is shown in Figure 1.10.\textsuperscript{1} The coordination of an additional group (e.g. Br\textsuperscript{-} or CO) to give a TBP species should result in the 2a\textsubscript{1}(d\textsubscript{z\textsuperscript{2}}-y\textsuperscript{2}) orbital becoming strongly antibonding. The expected MO scheme (Figure 1.11) shows that the 1b\textsubscript{1}(\pi\textsuperscript{*}b\textsubscript{1}(NO)) and 2b\textsubscript{1}(d\textsubscript{xz}) orbitals are now both filled. A distortion to TP geometry would point X directly toward the filled d\textsubscript{xz} level (cf. [RuCl(P\textsubscript{3})\textsubscript{2}(NO)\textsubscript{2}])\textsuperscript{1} and seems unlikely. As the \pi\textsuperscript{*}b\textsubscript{1}(NO) level is antibonding with respect to the two nitrosyls they should bend away from each other and show no tendency to couple to form a \textit{cis} dinitrogen dioxide species. The similarity of the two nitrosyl frequencies in [IrBr(P\textsubscript{3})\textsubscript{2}(NO)\textsubscript{2}] (1540, 1500 cm\textsuperscript{-1})\textsuperscript{56} suggests that the NO groups are equivalent and is therefore consistent with a TBP geometry for the complex.

The consequences of the coordination of an additional molecule of CO to [MX(P\textsubscript{3})\textsubscript{2}(NO)\textsubscript{2}] are now considered assuming that an octahedral species results.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure112.png}
\caption{MO scheme for M(P\textsubscript{3})\textsubscript{2}(NO)\textsubscript{2}(CO)\textsubscript{2} : a \{M(NO)\textsubscript{2}\}\textsuperscript{10} system.}
\end{figure}
The MO scheme (Figure 1.12) shows that two $\pi^*(\text{NO})$ orbitals are now fully occupied. One is bonding with respect to the two nitrosyls ($2b_2$) while the other is antibonding ($1b_2$). Alternatively, this situation may be viewed as two NO$^-$ ligands which, by analogy with the mononitrosyl systems, should be both bent. The coupling of the two NO$^-$ ligands would produce a $\sigma\pi$-hyponitrite species bound to the metal. This coupling reaction is clearly analogous to the reaction of NO with Na in liquid ammonia, where the product is thought to be sodium $\sigma\pi$-hyponitrite.$^8,9$

However, the scrambling of the $^{15}$N label observed in the reaction of equimolar quantities of $[\text{Rh}(\text{P}\Omega_3)_2(15\text{NO})_2]$ and $[\text{Rh}(\text{P}\Omega_3)_2(\text{NO})_2]$ has still to be accounted for. One possible explanation could be that the coordination of CO results in the labilisation of the Rh-NO bond. If equilibria such as those shown below are rapidly established on the reaction timescale then the $^{15}$N scrambling can be accounted for.

\[
[M(\text{P}\Omega_3)_2(\text{NO})_2]^+ + \text{CO} \rightleftharpoons [M(\text{P}\Omega_3)_2(\text{NO})_2\text{CO}]^+ + \text{NO} \quad (M = \text{Rh, Ir})
\]

There are two other pieces of evidence which support the presence of such equilibria and these are:
(i) $[\text{Ir}(\text{P}\Omega_3)_2(\text{NO})_2]^+$ reacts with CO in the presence of excess perchlorate anion (which acts as an oxidising agent) to give $[\text{IrCl}(\text{P}\Omega_3)_2(\text{CO})\text{NO}][\text{ClO}_4]$ and CO$_2$.\(^{56}\)
(ii) $[\text{Ir}(\text{P}\Omega_3)_2(\text{CO})(\text{solvent})]^+$ reacts with NO to give $[\text{Ir}(\text{P}\Omega_3)_2(\text{NO})_2]^+$, NO and solvent.\(^{56}\) The absence of CO$_2$ and N$_2$O suggests that a reasonable pressure of CO is required
for reaction. Interestingly, $[\text{RhCl}_2(\text{CO})_2]^-$ reacts with six molecules of NO to give CO$_2$ and N$_2$O according to the equation:

$$[\text{RhCl}_2(\text{CO})_2]^- + 6\text{NO} \rightarrow [\text{RhCl}_2(\text{NO})_2]^- + 2\text{CO}_2 + 2\text{N}_2\text{O}.57$$

Apparently, coordination of NO to $[\text{RhCl}_2(\text{CO})_2]^-$ does not labilise the Rh-CO bond. This reaction will be discussed in section 1.3.2.

The proposed mechanism for the reaction of $[\text{M(PØ}_3)_2(\text{NO})_2]^+$ ($\text{M} = \text{Rh}, \text{Ir}$) with CO has been summarised in Figure 1.13. Similar mechanisms are envisaged for the reactions of $[\text{IrBr(PØ}_3)_2(\text{NO})_2]$ and $[\text{Ir(NO}_2)\text{Cl(PØ}_3)_2\text{NO}]$ with CO, but the latter must first be converted into $[\text{IrCl(PØ}_3)_2(\text{NO})_2]$ (section 1.3.2).

1.3.2 The Reactions of Carbonyl and Nitrosyl Complexes with NO

In section 1.3.1 it was proposed that the N$_2$O evolved in the reactions of Rh and Ir dinitrosyl complexes with CO came from the decomposition of a cis-hyponitrite species formed by the coupling of two NO$^-$ ligands. This principle will now be extended to the reactions of some carbonyl and nitrosyl complexes with NO.

(a) The Reactivity of $[\text{RhCl}_2(\text{CO})_2]^-$ with NO and Mixtures of CO and NO

Eisenberg and coworkers$^{57,58}$ have studied the reaction of $[\text{RhCl}_2(\text{CO})_2]^-$ in aqueous acidic ethanol with NO and with mixtures of CO and NO. Under NO, the reaction stoichiometry was found to be: $[\text{RhCl}_2(\text{CO})_2]^- + 6\text{NO} \rightarrow [\text{RhCl}_2(\text{NO})_2]^- + 2\text{N}_2\text{O} + 2\text{CO}_2$. After two equivalents of CO$_2$ and N$_2$O had been evolved there was a much slower evolution
Figure 1.13. The proposed mechanism for the reaction of $[\text{M}(\text{P} \text{O}_3)_2(\text{NO})_2]^+$ with CO (M = Rh, Ir).
Using mixtures of NO and CO (usually a 4:3 ratio) the solution developed a green colouration which was thought to be due to an unstable reaction intermediate. It was shown that after approximately five hours the reaction started to follow first order kinetics with respect to the Rh complex concentration. In addition, the rate of reaction showed relatively little change on varying the partial pressure of NO but was very dependent on the CO partial pressure. Reactions have also been carried out using $^{18}\text{O}$ labelled water and the CO$_2$ evolved contained the $^{18}\text{O}$ label.

In order to account for the experimental results it was postulated that an intermediate carbonyldinitrosyl species was formed which reacted with CO in the rate determining step. A mechanism similar to that proposed by Eisenberg and coworkers is set out in Figure 1.14. However, an alternative mechanism can be suggested for the reaction of $\left[\text{RhCl}_2(\text{CO})_2\right]^-$ with NO and this has been included in the figure.

(b) Reactions of $[\text{MP}_2(\text{NO})_2]^+$ ($M = \text{Rh, Ir}; P = \text{P} \phi_3$ or $\text{P} \phi_2\text{Me}$) and $[\text{MBr}(\text{P} \phi_3)_2(\text{NO})_2]$ with NO.

The complexes $[\text{MP}_2(\text{NO})_2]^+$ undergo a slow reaction with NO to give $[\text{M(NO}_2)\text{P}_2(\text{NO})]^+$ and N$_2$O.\textsuperscript{54} Similarly, $[\text{MBr}(\text{P} \phi_3)_2(\text{NO})_2]$ gives $[\text{MBr(NO}_2)(\text{P} \phi_3)_2\text{NO}]$ and N$_2$O on reaction with NO although the rate of reaction was not mentioned.\textsuperscript{56} This type of reaction may be rationalised as shown in Figure 1.15.
The proposed mechanism for the reaction of $[\text{RhCl}_2(\text{CO})_2]^{-}$ with CO and NO ($\text{I} = \text{the dinitrosylcarbonyl intermediate}$)
In the reaction of $[\text{RhCl}_2(\text{CO})_2]^{-}$ with NO, after two equivalents of CO$_2$ and N$_2$O had been evolved, it was noted that a slow evolution of N$_2$O occurred. It was postulated that the N$_2$O came from the reaction $^{57}$: $4\text{NO} + 2\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{N}_2\text{O} + 2\text{CH}_3\text{CH}_2\text{ONO} + \text{H}_2\text{O}$. However, it could also arise from the reaction of $[\text{RhCl}_2(\text{NO})_2]^{-}$ with NO in a manner similar to that described above.

The reverse reaction which involves an O atom migration from a coordinated nitro group to CO is well known. $^{56}$ A mechanism for the reaction has been set out in Figure 1.16.
Figure 1.16. The reaction of nitro groups with carbon monoxide.

\((c)\) The Reaction of \(\text{CoP}_3\text{NO}\) with NO \((P = P\Phi_3)\)

Detailed kinetic studies have been made on the reaction of \(\text{CoP}_3\text{NO}\) with NO by Sacco and his coworkers\(^{59}\). The reaction was observed to be first order in cobalt complex but independent of the pressure of NO. The overall reaction stoichiometry was:

\[
\text{Co}(\text{P}\Phi_3)_3\text{NO} + 7\text{NO} \rightarrow \text{Co(NO}_2\text{)(P}\Phi_3\text{)(NO)}_2 + 2\text{Ph}_3\text{PO} + \frac{5}{2}\text{N}_2 + 2\text{N}_2\text{O}
\]

This reaction appears to be the first example of a transition metal complex catalysing the NO disproportionation reaction: \(4\text{NO} \rightarrow 2\text{NO}_2 + \text{N}_2\). The \(\text{N}_2\) was postulated to arise from the collapse of a bridging hyponitrite species which allowed the concerted migration of oxygen atoms from the Co-N(O)=N(O)-Co moiety to oxidisable ligands on the metal (NO). A mechanism similar to that proposed by Sacco is shown in Figure 1.17.

1.3.3 The Reactions of Bent Nitrosyls with Free NO

There appear to be some reactions in which a coordinated bent nitrosyl reacts with free NO. Clearly, this type of reaction is related to those of \(\text{R}_2\text{NH}\) and \(\text{SO}_3^=\) with NO (section 1.1). The "infamous" red and black isomers of
Figure 1.17. A mechanism similar to that proposed by Sacco and co-workers for the reaction of 
$[\text{Co(P}O_3\text{)}_3\text{NO}]$ with NO.
[Co(NH₃)₅NO]²⁺ provide an example of the reaction under discussion. The black isomer has been shown, by X-ray crystallography, to be monomeric and to have the nitrosyl bound as NO⁻. In contrast, the red isomer was found to be dimeric and to contain a σδ-hyponitrite bridge⁶⁰. Gans⁶¹ has discussed the chemistry involved in the formation of the red and black isomers and points out that the black isomer does not isomerise to the red isomer. In addition to the black isomer, both free NO and Co(NH₃)₆²⁺ are required to produce the red species. Figure 1.18 details the postulated mechanism for the formation of [Co(NH₃)₅]₂N₂O₂.

\[ \begin{align*}
\text{a}_5\text{Co} & \quad \text{N} \equiv \overset{\ddot{\text{O}}}{\text{O}} + \text{NO} \rightarrow \text{a}_5\text{Co} \quad \text{N} \equiv \text{N} \\
& \quad \overset{\ddot{\text{O}}}{\text{O}} \quad \text{Co}^{\text{II}} \quad \overset{\ddot{\text{O}}}{\text{O}} \quad \text{Co}_5^{\text{III}} \quad \text{N} \equiv \text{N} \\
& \quad (a = \text{NH}_3)
\end{align*} \]

Figure 1.18 The Formation of [Co(NH₃)₅]₂N₂O₂

The intermediate hyponitrite species is apparently stabilised by a further reaction with Co(II).

An intermediate "hyponitrite" species has also been postulated for the reactions of [CoCl₂(en)₂NO] and [Co(dmg)(CH₃OH)(NO)] with NO in which it reacts further with NO to give N₂O and NO₂⁻ according to the equations⁶²:

\[ \begin{align*}
\text{CoCl}_2(\text{en})_2\text{NO} + 2\text{NO} & \rightarrow \text{CoCl}_2(\text{NO}_2)(\text{en})_2 + \text{N}_2\text{O} \\
\text{Co(dmg)}_2(\text{CH}_3\text{OH})\text{NO} + 2\text{NO} + \text{Py} & \rightarrow \text{Co(dmg)}_2(\text{NO}_2)\text{Py} + \text{N}_2\text{O} + \text{CH}_3\text{OH}
\end{align*} \]

This type of reactivity is analogous to the high pressure disproportionation of NO to give N₂O and NO₂¹⁶.
Finally, it is worth pointing out the similarity in the reactions between coordinated NO$^-$ groups and NO or O$_2$ (section 1.3.4).

1.3.4 The Reaction of Nitrosyl Complexes with Dioxygen

The NO$^-$ ligand in certain nitrosyl complexes has been observed to react with O$_2$ to give nitro, nitrito or nitrato complexes. Clarkson and Basolo$^{63}$ have made a detailed kinetic study of the reactions between Co$_4$NO ($L_4^-$ = quadridentate dinegative Schiffs base or two bidentate dialkylidithiocarbamate ligands) and O$_2$ in the presence of various bases B (e.g. Py, Bu$_3$P) to yield the nitro compounds Co$_4$BNO$_2$. The rate of reaction was found to be dependent on the type of base and significantly, in the absence of base, no reaction occurred. The kinetic data obtained was in accord with the following reaction scheme.

\[
\begin{align*}
\text{K} & \quad \text{BCoL}_4\text{NO} + B \quad \xrightarrow{\text{fast}} \quad \text{BCoL}_4\text{NO} \\
\text{BCoL}_4\text{NO} + O_2 & \quad \xrightarrow{\text{slow}} \quad \text{BCoL}_4\text{N}^\circ \\
\text{BCoL}_4\text{N}^\circ & \quad + \text{BCoL}_4\text{NO} \quad \xrightarrow{\text{fast}} \quad \text{BCoL}_4\text{N}^\circ \text{NCoL}_4\text{B} \\
\text{BCoL}_4\text{N}^\circ \text{NCoL}_4\text{B} & \quad \xrightarrow{\text{fast}} \quad 2\text{CoL}_4(\text{NO}_2)\text{B}
\end{align*}
\]

The role of the coordinating base is presumably to increase the electron density on the nitrosyl group rendering it more susceptible to electrophilic attack by O$_2$. Consistent with this was the pmr study on the protonation of [Co(en)$_2$NO](ClO$_4$)$_2$ in "superacid" (SbF$_5$.HSO$_3$.F.SO$_2$) media$^{64}$ which suggested that in the absence of axial base, protonation
occurred at the oxygen of the nitrosyl group.

The formation of a coordinated NO$_3$ intermediate with a peroxy structure parallels the proposed mechanism for the reaction of gaseous NO and O$_2$. ESR evidence for the formation of a peroxy bridged intermediate was observed in the reaction of [NiCl(dppe)NO] with O$_2$, under UV irradiation, to yield [Ni(NO$_2$)Cl(dppe)]. As the reaction occurs only on photoirradiation or thermal excitation a formal charge transfer of the type shown below is implied.

\[
\text{Ni}^0 - \text{NO} \quad \xrightarrow{\text{hv or } \Delta} \quad \text{Ni}^{II} - \text{NO} \quad (\pm)
\]

In the presence of water and O$_2$ the complex [Co(dmg)$_2$NO] was transformed into the nitro complex [Co(NO$_2$)(dmg)$_2$H$_2$O]. However, if a base was present (e.g. t-Bu(Py), CNPy, Me(IMD), PØ$_3$) the major product was the O-bonded nitrato compound [Co(NO$_3$)(dmg)$_2$B] (>50%), in addition to a smaller amount of the nitro compound.

The complexes [IrClX(PØ$_3$)$_2$(CO)NO] were found to react with O$_2$ to yield the nitrato compounds [IrClX(NO$_3$)(PØ$_3$)$_2$CO]. Kinetic studies revealed that the reaction was pseudo first order with respect to the Ir complex and the rate of reaction was dependent on the nature of X. The order obtained was I$^-$ > Br$^-$ > Cl$^-$ > NCS$^-$ > NCO$^-$ > N$_3$ which can be roughly correlated with the degree of electron release. It was also found that [IrCl(PØ$_3$)$_2$(CO)NO] reacted with oxygen if pyridine or picoline was present, to give a mixture of nitro, nitrito and nitrato complexes.

It has not been established why nitrito or nitro
complexes are formed in some reactions while in others nitrato species result, but it does appear to be a function of the metal and the type of ligands present.

There is one reaction involving \([\text{Ru(P} O_3\text{)}_2(\text{NO})_2]\) in which the coordination of \(O_2\) may occur prior to a reaction with \(\text{NO}^+\). A possible reaction sequence has been set out in Figure 1.19.

![Figure 1.19](image)

Interestingly, \([\text{Ru(NO}_3\text{)(P} O_3\text{)}_2\text{NO}]\) reacts further with \(O_2\) to give the stable species \([\text{Ru(NO}_3\text{)}_2(O_2)(\text{P} O_3\text{)}_2\text{NO}]\) which will react further with CO to give \([\text{Ru(NO}_3\text{)}_2(\text{P} O_3\text{)}_2(\text{CO})_2]\). This reactivity is rationalised in Figure 1.20.

![Figure 1.20](image)

1.3.5 Nitrosyl Transfer Reactions

Intermolecular nitrosyl transfer reactions involve the migration of a coordinated NO from one metal to another. The nitrosyl in the donor complex is bent (i.e. \(\text{NO}^-\)) and the
reaction can be envisaged as a nucleophilic attack by \( \text{NO}^- \) on another metal. Only a small number of reactions of this type have been reported in the literature to date. However, the reaction may be quite general. In addition, if the metal to nitrosyl bonds are sufficiently strong then this type of reaction could also lead to the formation of stable bridged nitrosyl complexes.

The reactions of \([\text{Co(dmg)}_2\text{NO}]\) with a variety of acceptor metals (e.g. \([\text{FeCl}_2(\text{P}_3\text{O})_2]\), \([\text{CoCl}_2(\text{P}_3\text{O})_2]\) and \([\text{NiCl}_2(\text{P}_3\text{O})_2]\)) have been studied by Caulton and Ungerman\(^{70,71}\). Their results show that the nitrosyl transfer reaction proceeds more readily if the nitrosyl acceptor is coordinatively unsaturated. Halide or hydrogen transfer may accompany the nitrosyl transfer reaction.

The kinetics of the nitrosyl transfer reaction occurring between \([\text{Co(en)}_2(\text{H}_2\text{O})(\text{NOH})]^2+\) and \([\text{Cr(H}_2\text{O})_6]^2+\) has been studied in aqueous perchlorate media\(^{72}\) and the results were in accord with an associative process being the rate determining step. \([\text{Cr(H}_2\text{O})_6]^2+\) has also been found to react rapidly with \([\text{Co(NH}_3)_5\text{NO}]^2+\) to give \([\text{Cr(H}_2\text{O})_5\text{NO}]^2+\).\(^{73}\)

### 1.3.6 Protonation and Reduction Reactions Involving Nitrosyl Groups

A number of reactions have been reported which involve the protonation of either an \( \text{NO}^- \) or \( \text{NO}^\circ \) group. For example, \([\text{Fe(CN)}_5\text{NO}]^3-\), \([\text{CoX(das)}_2\text{NO}]^+\) and \([\text{OsCl}_2(\text{P}_3\text{O})_2(\text{CO})(\text{NO})]\) react with protons to yield products formulated as \([\text{Fe(CN)}_5(\text{NOH})]^2-\), \([\text{CoX(das)}_2(\text{NOH})]^2+\) and \([\text{OsCl}_2(\text{P}_3\text{O})_2(\text{CO})(\text{NOH})]^+\) respectively, where the site of protonation could be either the \( \text{N} \) or \( \text{O} \) of
the nitrosyl ligand. Some pmr studies on the protonation of 
\([\text{Co(en)}_2\text{NO}]^{2+}\) in non-aqueous "superacid" (SbF$_3$.HSO$_3$F.SO$_2$)
have suggested that the O of the NO$^-$ group may be the site
of protonation in this complex.

\([\text{Os}(\text{PO}_3)_2\text{NO}]\) and \([\text{Ir}(\text{PO}_3)_2\text{NO}]\) react with two and
three moles of HCl respectively to yield \([\text{OsCl}_2\text{(NH}_2\text{OH)}(\text{PO}_3)_2\text{NO}]\)
and \([\text{IrCl}_3(\text{PO}_3)_2(\text{NH}_2\text{OH})]\)$^{75}$. Mechanisms consistent with
these protonation reactions are suggested in Figure 1.21.

The ESR spectra of \([\text{OsCl}_2(\text{bipy})(\text{NO})]\)$^{2+}$ and \([\text{OsCl}_2(\text{en})(\text{NO})]\)$^{2+}$
show the expected hyperfine splittings but no metal hyper-
fine splittings are observed. These results are consistent
with the mechanism shown in Figure 1.21.

Figure 1.21. Protonation reactions involving NO$^-$ and NO$^\circ$.

The molecular orbital schemes which have been proposed
for six coordinate mononitrosyl complexes indicate that there
are three metal d orbitals of lower energy than the $\pi^*(\text{NO})$
levels. Consequently, if six coordinate \((\text{M(NO)})^6\) systems
can undergo reduction reactions they should be nitrosyl
based. Some examples are given in the following equations.
\[
[RuA(bipy)_2NO]^{3+} + e^- \rightarrow RuA(bipy)(NO)_{2+}^{3+} \quad (a)
\]
\[
\{Ru(NO)\}_6 \quad \{Ru(NO)\}_7
\]
\[
[Fe(CN)_5NO]^{2-} + e^- \rightarrow [Fe(CN)_5(NO)]^{3-} \quad (b)
\]
\[
\{Fe(NO)\}_6 \quad \{Fe(NO)\}_7
\]
\[
[Ru(NH_3)_5NO]^{3+} + e^- \rightarrow [Ru(NH_3)_5NO]^{2+} \quad (c)
\]
\[
\{Ru(NO)\}_6 \quad \{Ru(NO)\}_7
\]

The ESR spectra of \([RuCl(bipy)_2NO]^{2+}\) and \([Fe(CN)_5NO]^{3-}\) show the expected \(^1\)N hyperfine splittings but no metal hyperfine interactions were observed. These results are consistent with the unpaired electron occupying a nitrosyl based MO.

The one electron reduction product formed in reaction (c) was found to be extremely reactive and when \(Cr^{2+}\) was used as the reductant, the products isolated were \([Ru(NH_3)_6]^{2+}\) and \(Cr^{3+}\). The formation of \(Cr^{3+}\) indicates that the reduction involves six successive one electron steps with the overall reaction being:

\[
[(NH_3)_5Ru-NO]^{3+} + 6Cr^{2+} + 5H^+ \rightarrow [(NH_3)_5Ru-NH_3]^{2+} + 6Cr^{3+} + H_2O
\]

If \([Ru(NH_3)_5NO]^{2+}\) was generated by pulse radiolysis techniques in the presence of t-BuOH, the complex \([Ru(NH_3)_5{(NO)CH_2C(CH_3)_2OH}]^{2+}\) was formed.

Another related reaction occurs between \([Cr(H_2O)_5NO]^{2+}\) and \([Cr(H_2O)_6]^{2+}\) to give \(NH_3OH^+\) and the chromium dimer \((Cr_2(OH)_2)^{4+}\). The formation of the latter implies a simultaneous two electron reduction of \([Cr(H_2O)_5NO]^{2+}\).
1.3.7 Nitrosyls Acting as "Electron Sinks"

Basolo and Pearson have discussed the second order substitution reactions of the 18-electron \([\text{Co(CO)}_3\text{NO}]\) and \([\text{Fe(CO)}_2(\text{NO})_2]\) complexes with a variety of nucleophilic molecules \(L\) (e.g., tertiary phosphines)\(^8\). The reactions are shown in the following equations:

\[
\text{[Co(CO)}_3\text{NO}] + L \rightarrow \text{[CoL(CO)}_2\text{NO]} + \text{CO}
\]

\[
\text{[Fe(CO)}_2(\text{NO})_2] + L \rightarrow \text{[FeL(CO)(NO)}_2] + \text{CO}
\]

In order to account for the reactions being first order with respect to both metal complex and \(L\), it was suggested that the coordination of \(L\) to the metal caused a pair of electrons to be transferred to the NO group. The proposed intermediate would then be in accord with the 16-18 electron rule\(^8\). The charge transfer can be represented schematically as: \(\text{M-NO} + L \rightarrow \text{LM-NO}\); in this way, the nitrosyl group may be thought of as acting as an "electron sink". After elimination of CO, the electron pair may then return to the metal.

1.3.8 Reactions of \(\text{NO}^+\)

Nitrosyl complexes with relatively high NO stretching frequencies (>1850 cm\(^{-1}\)) behave chemically as \(\text{NO}^+\) and undergo a variety of reactions involving nucleophilic attack on the coordinated nitrosyl. Some examples of \(\text{NO}^+\) reactivity are given in the following equations.

\[
\text{Fe(CN)}_5(\text{NO})^{2-} + 2\text{OH}^- \rightarrow \text{Fe(CN)}_5(\text{NO}_2)^{4-} + \text{H}_2\text{O} \quad \text{\textsuperscript{81} (a)}
\]

\[
[\text{RuCl(das)}_2\text{NO}]^{2+} + 3\text{N}_2\text{H}_4 \rightarrow \text{RuN}_3\text{Cl(das)}_2 + 2\text{N}_2\text{H}_5\text{Cl} + \text{H}_2\text{O} \quad \text{\textsuperscript{82} (b)}
\]
The reactions involving coordinated nitrosyl groups have been discussed in considerable detail. The reported chemistry appears to be consistent with the hypothesis that there are two reactive forms of coordinated nitrosyl. These are the linearly coordinated (NO⁺) species with ν(NO) greater than 1850 cm⁻¹ and the bent nitrosyl. The former type of nitrosyl can undergo nucleophilic attack at the nitrosyl N while the latter may be reactive towards other bent nitrosyls, NO, O₂, protons and coordinatively unsaturated metal complexes. But it does not necessarily follow that a bent nitrosyl will undergo all of the mentioned reactions. The amount of electron density on the NO⁻ group seems to be an important factor in determining reactivity (e.g. in the reactions with O₂).

With some qualifications, the remaining vast majority of nitrosyl complexes contain unreactive NO groups (i.e. linear nitrosyls with low nitrosyl stretching frequencies).
It has been shown that the coordination of a molecule or ion to a nitrosyl complex can drastically alter the coordination mode of the nitrosyl. For example, [Co(das)_2(NO)]^{2+} has a linear nitrosyl group, but upon coordination of NCS⁻ the nitrosyl bends. So in this manner, "unreactive" nitrosyls may be converted into reactive bent species.

In chapters 3 and 4 the reactions occurring between [Mo(S₂CNEt₂)₂(NO)₂] and NaN₃ or KNCO will be discussed and the observed reactivity will be shown to be consistent with the above principles.

1.4 CO, NO and N₂

Enemark and Feltham¹, in their review on nitrosyl structure, bonding and reactivity, have suggested that the principles and procedures used for metal nitrosyl complexes should be applicable to a variety of other ligands - in particular CO, N₂ and O₂. The structure and reactions of dinitrogen complexes will be dealt with in chapter 5. In this section the discussion will centre on the similarities in bonding and reactivity of carbonyl, nitrosyl and dioxygen complexes.

Linear terminal (Figure 1.3(a)) and doubly and triply bridged (Figures 1.3(c) and 1.3(d), respectively) coordination are found in both nitrosyl and carbonyl chemistry¹⁹. The bent nitrosyl analogue for carbonyl complexes is not known, although complexes containing the protonated nitrosyl (nitroxyl, NHO) and the formyl group (-CH₂O)⁰⁹,⁰¹ are clearly related. The linear coordination of O₂ (formally O₂²⁺) has not been observed as yet, but it could arise in a situation
where one of the metal d orbitals is lower in energy than the \( \pi^*(O_2) \) levels (c/f NO\(^+\)). Figure 1.22 shows the principal types of metal-dioxygen bonding which are presently known.\(^ {92} \)

![Diagram of metal-dioxygen bonding types]

Figure 1.22 Known Types of Metal-Dioxygen Bonding. Bond Orders: \( = \) 1 single bond; \( \equiv \equiv \) bond order of 1.5.

The superoxo linkage I(a) is similar to the bent nitrosyl but the former contains an additional electron in the \( \pi^*(O_2) \) orbital. The biologically significant "Cobalt-Schiff-base-dioxygen-carrier" model complexes are thought to bind dioxygen in this way\(^ {93} \). However, the most common type of dioxygen coordination appears to involve the peroxo structure II(a).\(^ {92} \)

With respect to chemical reactivity, nitrosyl and carbonyl complexes bear the closest resemblance. For example, certain types of nitrosyl and carbonyl groups may react with a variety of nucleophiles, which include anions or bases such as \( N_3^-\), \( OH^-\), \( N_2H_4\), \( OR^-\) and \( OCOR^-\).\(^ {19} \) It has already been mentioned that bent carbonyls are not known, but the application of the concept of "Stereochemical Control of
Valence to a number of carbonyl reactions suggests that they may have a transient existence. A few examples will now be discussed.

In order to account for the enhanced rate of carbonyl exchange observed for [Mn H(CO)₅] under CO an intermediate species containing the formyl group was postulated:

\[ [\text{MnH(CO)}{\text{s}}] + \text{CO} \rightarrow [\text{Mn(HCO)}(\text{CO}){\text{s}}] \]

This reaction has been formalised in Figure 1.23.

Here, the coordination of CO to the metal is suggested to "activate" one of the carbonyl groups toward reaction by converting it into a carbene. Another closely related process is the carbonyl insertion reaction shown in Figure 1.24.
A similar type of mechanism may also be given for the carbonyl insertion reaction involving \([\text{Rh(CH}_2\text{CH}_2\text{R})(\text{P}0_3)_2(\text{CO})_2]\) under CO. This species is a postulated intermediate in the catalytic cycle for hydroformylation of alkenes by \([\text{RhH(P}0_3)_2(\text{CO})_2]\) - (ref. 19, page 792).

The purpose of this section has been to point out some of the similarities which exist in the chemistry of NO, CO and \(O_2\) bound to transition metals. This chapter will conclude with the following question: "Is it possible to insert the NO molecule into a metal-carbon bond?".
Chapter 2

The Preparation and Characterisation of

the Complexes \([M(S_2CNR_2)_2(NO)_2]\)
2.1 Introduction

Johnson, Al-Obaidi and McCleverty\textsuperscript{94} first prepared the complexes \([\text{M(S}_2\text{CNR}_2)_2(\text{NO})_2]\), \((\text{M} = \text{Mo}, \text{R} = \text{Me or Et}; \text{M} = \text{W}, \text{R} = \text{Me})\) by reacting \([\text{MBr}_2(\text{NO})_2]_n\text{ }^\text{95}\) with the appropriate dialkylthiocarbamate in acetone. On the basis of i.r., n.m.r. and mass spectral data it was proposed that the complexes were monomeric and had \(\text{cis-\text{octahedral}}\) structures with \(\text{C}_2\) symmetry. Figure 2.1 shows the probable structure of the complexes.

Green and Taylor\textsuperscript{96} have also prepared the molybdenum and tungsten diethyldithiocarbamate dinitrosyl complexes by reacting \([\text{M(CH}_3\text{CN})_4(\text{NO})_2]^{2+}\) with \(\text{NaS}_2\text{CNEt}_2.3\text{H}_2\text{O}\) in nitromethane \((\text{M} = \text{Mo})\) and acetonitrile \((\text{M} = \text{W})\).

Both of the above preparations utilise starting materials derived from \([\text{M(CO)}_6]\) as indicated in equations 2.1 and 2.2.

\[
[\text{M(CO)}_6] + 2\text{NOBr} \rightarrow [\text{MBr}_2(\text{NO})_2] + 6\text{CO} \tag{2.1}
\]

\[
[\text{M(CO)}_6] \xrightarrow{\Delta} [\text{M(CH}_3\text{CN})_3(\text{CO})_3] + 3\text{CO} \rightarrow [\text{M(CH}_3\text{CN})_4(\text{NO})_2][\text{PF}_6]_2 + 3\text{CO} \tag{2.2}
\]
A more convenient synthesis of the dinitrosyl complexes, partly developed during this work, is summarised in equations 2.3-2.5.\(^97\)

\[
[M(CO)_{6}] + Br_2 \rightarrow [MBr_2(CO)_4] + 2CO \quad (2.3)
\]

\[
[MBr_2(CO)_4] + 2NaS_2CNR_2 \rightarrow [M(S_2CNR_2)_2(CO)_2] + 2CO + 2NaBr \quad (2.4)
\]

\[
[M(S_2CNR_2)_2(CO)_2] + 2NO \rightarrow [M(S_2CNR_2)_2(NO)_2] + 2CO \quad (2.5)
\]

The advantages of this procedure are that it makes use of readily available starting materials, the apparatus required is simple and also, the intermediates in the preparation do not have to be isolated. However, by proceeding only as far as reaction 2.4, the synthetically important \([Mo(S_2CNR_2)_2(CO)_2]\) may be obtained\(^98\) - see chapter 6.

2.2 Preparation of Complexes

2.2.1 Materials

All solvents were A.R. grade and were used without purification. The reagents \([Mo(CO)_6]\), \(Br_2\), \(NaS_2CNEt_2\cdot3H_2O\), \(NaS_2CNMe_2\) and \(NO\) were used as obtained commercially. A sample of \(Na(acac)\) was obtained from Dr. A. Hendrickson of the Research School of Chemistry, Canberra.

The pyrrolidyl, di-n-butyl and dibenzyl dithiocarbamates were generated \(in situ\) by slowly adding the appropriate diamine \((1.91\times10^{-2}\) mole\) to 1.45 g of \(CS_2\) \((1.91\times10^{-2}\) mole, 1.45 g) in 40 ml of methanol. Solid \(NaOH\) \((1.91\times10^{-2}\) mole, 0.76 g) was then added and the solution stirred until the solid had dissolved.
NaS₂CN⁻⁰Pr₂ was prepared by slowly adding 20.24 g of NH⁻⁰Pr₂ (0.2 mole) to 15.22 g of CS₂ (0.2 mole) in 40 ml of 1:1 ethanol-water. Then 20 ml of 10 M NaOH was added dropwise and the product precipitated from solution during the addition. The precipitate was filtered off and washed with cold ethanol and dried under vacuum.

2.2.2 Analyses

C, H, N and S analyses were carried out by the Microanalytical Section of the John Curtin School of Medical Research, Canberra. Mo and halogen analyses were determined at the Research School of Chemistry, A.N.U., Canberra.

2.2.3 Bis(N,N-diethyldithiocarbamato)dinitrosylmolybdenum

[Mo(S₂CNEt₂)₂(NO)₂] was prepared by the literature method. However for completeness, the procedure, with some minor modifications has been included here.

As carbon monoxide was evolved during the preparation, work was carried out in a fume hood. Solutions used in the preparation were deoxygenated by purging with dinitrogen for 30 min.

[Mo(CO)₆] (5 g, 0.019 mole) was placed in a 250 ml two-necked round bottom flask fitted with a gas bubbler, dropping funnel and magnetic stirrer. Dichloromethane (100 ml) was added and then a stream of dinitrogen was passed through the solution and was maintained throughout the subsequent reaction procedure. The reaction solution was cooled to -78°C in an acetone-dry ice bath and Br₂ (3.0 g, 0.019 mole) in dichloromethane (10 ml) was slowly added.
When the addition was complete, the vessel was removed from the bath and the reaction solution turned dark brown on warming. The dichloromethane was evaporated off in the dinitrogen stream. Methanol (50 ml) was then added, followed by a solution of NaS₂CNEt₂·3H₂O in methanol (8.55 g, 50 ml). A mixture of the orange [Mo(CO)₃(S₂CNEt₂)₂] and purple [Mo(CO)₂(S₂CNEt₂)₂] precipitated. The precipitate was redissolved by adding dichloromethane (100 ml) and nitric oxide was bubbled through the solution for 30 min. During this time the colour changed to a deep brown. All subsequent work was carried out in the air; in addition vessels containing the complex were covered with aluminium foil to minimise exposure to light.

The dark brown solution was evaporated to dryness using a rotary evaporator and the residue extracted with chloroform (30 ml). Further purification was best effected by column chromatography. A 50 x 3 cm column was prepared by suspending silica-gel powder (70-325 mesh) in n-hexane. Aluminium foil was wrapped around the column to prevent any photochemical reactions involving the dinitrosyl complex. The chloroform solution containing the crude material was placed on the column and the product eluted with 1:1 chloroform-hexane. The green-brown solution was collected and the solvent

† Thin layer chromatography using a drop of reaction solution spotted onto a Bakerflex silica-gel strip and eluted with dichloromethane (in air) readily monitors the disappearance of the purple intermediate. Brown [Mo(NO)₂(S₂CNEt₂)₂] moves with the solvent front while the purple complex has an rf. of ~0.5.
evaporated off yielding an oily residue. The oil was taken up in hot methanol and the complex precipitated by slowly adding water to the stirred solution. The brown crystalline product was filtered off, washed with ice-cold methanol and dried over \( \text{P}_2\text{O}_5 \) under vacuum. (Yield 6.5 g; 75% based on \([\text{Mo(CO)}_6]\)). (Found: C, 26.52; H, 4.54; N, 12.29; S, 28.70. \( \text{C}_{10}\text{H}_{20}\text{MoN}_4\text{S}_4\text{O}_2 \) requires: C, 26.55; H, 4.46; N, 12.38; S, 28.36%).

2.2.4 Preliminary Note for Other Preparations (2.2.5-2.2.10)

In the following preparations the method used was essentially the same as that described for \([\text{Mo(S}_2\text{CNEt}_2)\text{N}_2\text{O}_2]\) but scaled down by a factor of two. That is, the quantities used were: \([\text{Mo(CO)}_6]\) (2.5 g, \(9.5\times10^{-3}\) mole), \(\text{Br}_2\) (1.5 g, \(9.5\times10^{-3}\) mole) and \(\text{NaS}_2\text{CNR}_2\) (1.9\times10^{-2} mole). The volumes of solvents were also halved.

The same \(50 \times 3\) cm silica-gel column was used for purification but the solvent mixtures employed to elute the complex were sometimes varied. Also different solvent mixtures have been used for recrystallisation of the complexes. In the following sections only the modifications to the \([\text{Mo(NO)}_2\text{(S}_2\text{CNEt}_2)\text{N}_2]\) procedure have been listed.

2.2.5 Bis(N,N-dimethylthiocarbamato)dinitrosylmolybdenum

(a) Chromatography: The complex was eluted with 3:1 chloroform-hexane.

(b) Crystallisation: hot acetone-water.

(c) The yield was 1.7 g (4.29\times10^{-3} mole, 45%).
2.2.6 Bis(N,N-di-n-butyldithiocarbamato)dinitrosylmolybdenum

(a) Crystallisation: The product was taken up in ethanol (100 ml) and distilled water was slowly added to the vigorously stirred solution. Oiling occurred if the water was added too quickly, or if the solution was not vigorously stirred.

(b) The yield was 4 g (7.1x10^-3 mole, 75%).

2.2.7 Bis(N,N-di-iso-propyldithiocarbamato)dinitrosylmolybdenum

The yield of complex was 3.2 g (66%). (Found: C, 32.94; H, 5.58; N, 11.12; S, 25.02. C_14H_35MoN_4S_4O_2 requires: C, 33.06; H, 5.55; N, 11.02; S, 25.22%).

2.2.8 Bis(pyrrolidyldithiocarbamato)dinitrosylmolybdenum

3.1 g of complex was obtained (73%). (Found: C, 26.74; H, 3.85; N, 12.61; S, 28.58.

C_{15}H_{16}MoN_4S_4O_2 requires: C, 26.78; H, 3.60; N, 12.50; S, 28.60%).
2.2.9 Bis(N,N-dibenzyldithiocarbamato)dinitrosylmolybdenum

The yield of complex was 3.2 g (48%).

(Found: C, 51.63; H, 4.35; N, 8.06; S, 18.48. C_{30}H_{28}MoN_4S_4O_2 requires C, 51.42; H, 4.03; N, 8.00; S, 18.30%).

2.2.10 Bis(N,N-diethyldithiocarbamato)dinitrosyltungsten

(a) 3.34 g of [W(CO)_{6}] was used (9.5\times10^{-3} mole).

(b) The yield was 1.4 g (27%).

(Found: C, 22.32; H, 3.72; N, 10.39; S, 23.55. C_{10}H_{20}WN_4S_4O_2 requires C, 22.23; H, 3.73; N, 10.37; S, 23.73%).

2.2.11 Bis(acetylacetone)dinitrosylmolybdenum

The preparation of [Mo(acac)_{2}(NO)_{2}] from [Mo(CO)_{6}] via [Mo(CO)_{4}Br_{2}] and [Mo(acac)_{2}(CO)_{2}] was attempted but only small yields of the dinitrosyl complex were obtained.

The method of preparation followed that described for [Mo(S_{2}CNEt_{2})_{2}(NO)_{2}] except that a chromatography column prepared with dichloromethane was used and the green complex was eluted with dichloromethane. The yield of complex was 15%.

The product was characterised by a comparison of the mass, ir and pmr spectra with those reported in the literature^{96} (Mass spectrum P, m/e 356; P-NO, m/e 326; P-2NO, m/e 296).

In view of the very low yield, the method described by Green and Taylor seems preferable^{96}. 
2.3 Preparation of Labelled Complexes

2.3.1 Materials

All solvents were A.R. grade and were used without further purification. Potassium nitrate (95 atom % $^{15}$N) was obtained from Bio-Rad, Richmond, California.

95 atom % $^{15}$N nitric oxide was prepared by reacting $K^{15}NO_3$ (0.090 g, $8.8 \times 10^{-4}$ mole) with Hg (2 g, 0.01 mole) and concentrated $H_2SO_4$ (2.5 cc, $4.5 \times 10^{-2}$ mole) under vacuum\(^99,100\).

Similarly, 48 atom % $^{15}$N nitric oxide was obtained from $KNO_3$ (0.0450 g, $4.45 \times 10^{-4}$ mole) and $K^{15}NO_3$ (0.0463 g, $4.44 \times 10^{-4}$ mole).

The nitric oxide prepared in the above manner contains no nitrogen dioxide as any that is formed is further reduced according to the equation\(^{101}\):

$$6NO_2 + 4Hg + 2H_2SO_4 \rightarrow 4NO + Hg_2(NO_3)_2 + 2HgSO_4 + 2H_2O$$

A mass spectrum on a freshly prepared sample indicated that the only impurity was a trace of dinitrogen oxide.

2.3.2 $[Mo(S_2CNEt_2)_2(15NO)_2]$  

$[Mo(CO)_6]$ (0.1 g, $3.78 \times 10^{-4}$ mole) was suspended in dichloromethane (10 ml) and dinitrogen bubbled through the solution. After cooling to $-78^\circ C$, $Br_2$ (0.06 g, $3.78 \times 10^{-4}$ mole) in dichloromethane (2 ml) was added. On warming, the solution became dark brown. The dichloromethane was evaporated off in the dinitrogen stream and the residue taken up in methanol (5 ml). A solution of $NaS_2CNEt_2.3H_2O$ (0.17 g, $7.56 \times 10^{-4}$ mole) in methanol (5 ml) was added and $[Mo(S_2CNEt_2)_2(CO)_3]$ precipitated. The vessel containing the
solution was connected to a vacuum line and the gas above the solution pumped off. The section of the line containing the reaction vessel and $^{15}$NO (see section 2.3.1) was isolated from the pump and the $^{15}$NO transferred to the reaction vessel by freezing it in liquid nitrogen. The solution was allowed to thaw and the mixture was stirred for ca 30 minutes.

All of the remaining work was carried out in the air. The methanol was removed using a rotary evaporator and the residue extracted with chloroform (5 ml). A 0.5 x 18 cm chromatography column was prepared by suspending silica-gel (70-230 mesh) in n-hexane. Aluminium foil was wrapped around the column to prevent photochemical reactions occurring during the chromatography. The crude reaction mixture was placed on the column and the product eluted with 1:1 chloroform-hexane. The complex was collected and the solvent removed. The oily residue was taken up in hot methanol and after filtering the solution, water was slowly added to precipitate the product. Further warming of the solution increased the particle size. On cooling, the product was filtered off, washed with ice-cold methanol (1 ml) and dried under vacuum over $\text{P}_2\text{O}_5$. The yield was 0.075 g.

2.3.3 Preparation of an Approximately 1:2:1 Mixture of $[\text{Mo(S}_2\text{CNEt}_2)_2(^{15}\text{NO})_2]$, $[\text{Mo(S}_2\text{CNEt}_2)_2(^{15}\text{NO})(\text{NO})]$ and $[\text{Mo(S}_2\text{CNEt}_2)_2(\text{NO})_2]$

The mixture was prepared in an identical manner to that described above using approximately 50% $^{15}$N nitric oxide (see section 2.3.1).
2.3.4 Calculation of Isotopic Distributions

The reaction under consideration is that of

\[ \text{[Mo(S}_2\text{CNET}_2\text{)]}_2(\text{CO})_3 \] with nitric oxide, i.e.

\[ \text{[Mo(S}_2\text{CNET}_2\text{)]}_2(\text{CO})_3 \] + 2NO \rightarrow \text{[Mo(S}_2\text{CNET}_2\text{)]}_2(\text{NO})_2 \] + 3CO.

To calculate the isotopic distribution in the product, the nitric oxide molecules are treated as being "identifiable". The total number of combinations giving \((^{15}\text{NO})_2\), \((^{15}\text{NO})(\text{NO})\) and \((\text{NO})_2\) can then be calculated and these are proportional to their respective probabilities of formation.

Let the total number of molecules in the sample be \(x\).

Then the total number of possible combinations of nitric oxide (labelled and unlabelled) is

\[
\frac{x!}{(x-2)!2!} = \frac{x(x-1)}{2} = \frac{x^2}{2} \text{ for } x \text{ very large.}
\]

The probability of formation is defined by the expression:

\[
\frac{\text{Total number of favourable combinations}}{\text{Total possible number of combinations}}
\]

The isotopic distributions for (a) 95% \(^{15}\text{N}\), (b) 99.6% \(^{14}\text{N}\) and (c) 48% \(^{15}\text{N}\) are summarised in Table 2.1.

So the compositions of the dinitrosyl complexes prepared in sections 2.3.2 and 2.3.3 correspond to those calculated in parts (a) and (c) respectively, of Table 2.1.

2.4 \(^1\text{H NMR Spectra}\)

\(^1\text{H nmr spectra were recorded on a Jeol MH-100 spectro-photometer at 100 MHz in various solvents; chemical shifts were relative to Me}_4\text{Si (60.00). Table 2.2 summarises the pmr data for the dinitrosyl complexes prepared.}
Table 2.1

Isotopic Distributions For $[\text{Mo(S}_2\text{CNEt}_2)_2(\text{NO})_2]$

<table>
<thead>
<tr>
<th>NO sample</th>
<th>Species</th>
<th>Total Number of Combinations</th>
<th>Probability ($\frac{x^2}{2}$)</th>
<th>% formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 95% $^{15}\text{N}$</td>
<td>$(^{15}\text{NO})_2$</td>
<td>$0.95x C_2 = \frac{0.9025x^2}{2}$</td>
<td>0.9025</td>
<td>90.25</td>
</tr>
<tr>
<td></td>
<td>$(^{15}\text{NO})(\text{NO})$</td>
<td>$(0.95x)(0.05x) = 0.0475x^2$</td>
<td>0.0950</td>
<td>9.50</td>
</tr>
<tr>
<td></td>
<td>$(\text{NO})_2$</td>
<td>$0.05x C_2 = \frac{0.0025x^2}{2}$</td>
<td>0.0025</td>
<td>0.25</td>
</tr>
<tr>
<td>(b) 99.6% $^{14}\text{N}$</td>
<td>$(^{15}\text{NO})_2$</td>
<td>$0.004x C_2 = \frac{1.6\times10^{-5}x^2}{2}$</td>
<td>1.6$\times10^{-5}$</td>
<td>0.0016</td>
</tr>
<tr>
<td></td>
<td>$(^{15}\text{NO})(\text{NO})$</td>
<td>$(0.996x)(0.004x) = 3.984\times10^{-3}x^2$</td>
<td>7.968$\times10^{-3}$</td>
<td>0.7968</td>
</tr>
<tr>
<td></td>
<td>$(\text{NO})_2$</td>
<td>$0.996x C_2 = \frac{0.992016x^2}{2}$</td>
<td>0.992016</td>
<td>99.2016</td>
</tr>
<tr>
<td>(c) 48% $^{15}\text{N}$</td>
<td>$(^{15}\text{NO})_2$</td>
<td>$0.48x C_2 = \frac{0.2304x^2}{2}$</td>
<td>0.2304</td>
<td>23.04</td>
</tr>
<tr>
<td></td>
<td>$(^{15}\text{NO})(\text{NO})$</td>
<td>$(0.52x)(0.48x) = 0.2496x^2$</td>
<td>0.4992</td>
<td>49.92</td>
</tr>
<tr>
<td></td>
<td>$(\text{NO})_2$</td>
<td>$0.52x C_2 = \frac{0.2704x^2}{2}$</td>
<td>0.2704</td>
<td>27.04</td>
</tr>
</tbody>
</table>
Table 2.2

'H NMR Data For [M(S2CNR2)2(NO)2] Complexes\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Resonance (δ±0.02 ppm)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo(S2CNMe2)2(NO)2]</td>
<td>ps 3.56</td>
<td>ne CH\textsubscript{3}'s of dtc</td>
</tr>
<tr>
<td>[Mo(S2CNEt2)2(NO)2]</td>
<td>pt 1.29</td>
<td>ne CH\textsubscript{3}'s of dtc</td>
</tr>
<tr>
<td></td>
<td>m 3.81</td>
<td>ne CH\textsubscript{2}'s of dtc; A\textsubscript{2}X\textsubscript{3} and ABX\textsubscript{3}</td>
</tr>
<tr>
<td>[Mo(S2CNEt2)2(NO)2]\textsuperscript{b}</td>
<td>pt 1.28</td>
<td>ne CH\textsubscript{3}'s of dtc</td>
</tr>
<tr>
<td></td>
<td>pq 3.85</td>
<td>ne CH\textsubscript{2}'s of dtc; A\textsubscript{2}X\textsubscript{3}</td>
</tr>
<tr>
<td>[Mo(S2CN{C\textsubscript{2}H\textsubscript{4}}\textsubscript{2})2(NO)2]</td>
<td>q 2.06</td>
<td>C-CH\textsubscript{2}-CH\textsubscript{2}-C of dtc; all protons equivalent N-CH\textsubscript{2}'s of dtc</td>
</tr>
<tr>
<td></td>
<td>sym.m 3.80</td>
<td></td>
</tr>
<tr>
<td>[Mo(S2CNn-Bu\textsubscript{2})2(NO)2]</td>
<td>m 0.96</td>
<td>CH\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td>m 1.36</td>
<td>γ-CH\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>m 1.68</td>
<td>β-CH\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>m 3.92</td>
<td>α-CH\textsubscript{2}</td>
</tr>
<tr>
<td>[Mo(S2CNi-Pr\textsubscript{2})2(NO)2]</td>
<td>pd 1.45</td>
<td>ne C(CH\textsubscript{3})\textsubscript{2}'s of dtc</td>
</tr>
<tr>
<td></td>
<td>s(br) 4.69</td>
<td></td>
</tr>
<tr>
<td>[Mo(S2CNBz\textsubscript{2})2(NO)2]</td>
<td>m 5.01</td>
<td>ne CH\textsubscript{2}'s of dtc; A\textsubscript{2} and AB</td>
</tr>
<tr>
<td></td>
<td>s 7.38</td>
<td>aromatic protons</td>
</tr>
<tr>
<td>[W(S2CNMe2)2(NO)2]\textsuperscript{c}</td>
<td>ps 3.33</td>
<td>ne CH\textsubscript{3}'s of dtc</td>
</tr>
<tr>
<td>[W(S2CNEt2)2(NO)2]</td>
<td>pt 1.33</td>
<td>ne CH\textsubscript{3}'s of dtc</td>
</tr>
<tr>
<td></td>
<td>m 3.77</td>
<td>ne CH\textsubscript{2}'s of dtc; A\textsubscript{2}X\textsubscript{3} and ABX\textsubscript{3}</td>
</tr>
<tr>
<td>[W(S2CNEt2)2(NO)2]\textsuperscript{b}</td>
<td>pt 1.34</td>
<td>ne CH\textsubscript{3}'s of dtc</td>
</tr>
<tr>
<td></td>
<td>pq 3.78</td>
<td>ne CH\textsubscript{2}'s of dtc; A\textsubscript{2}X\textsubscript{3}</td>
</tr>
<tr>
<td>[Mo(acac)\textsubscript{2}(NO)\textsubscript{2}]</td>
<td>s 2.00</td>
<td>CH\textsubscript{3} of acac</td>
</tr>
<tr>
<td></td>
<td>s 2.22</td>
<td>CH\textsubscript{3} of acac</td>
</tr>
<tr>
<td></td>
<td>s 5.65</td>
<td>CH of acac</td>
</tr>
</tbody>
</table>

\textsuperscript{a} In CDCl\textsubscript{3} unless otherwise stated; Abbreviations: d = doublet, t = triplet, s = singlet, q = quartet, p = pair of; m = multiplet; br = broad; ne = non equivalent, sym = symmetric

\textsuperscript{b} In acetone [D\textsubscript{6}]

\textsuperscript{c} Reference 94
2.5 Infrared Studies

2.5.1 Spectra in the 4000-650 cm\(^{-1}\) Region

The ir spectra between 4000 and 650 cm\(^{-1}\) were recorded on a Unicam SP200G spectrophotometer. Table 2.3 lists some of the characteristic absorption bands for the dinitrosyl compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(\text{NO}))</th>
<th>(\nu(\text{CN}))</th>
<th>(\nu(\text{CS}_2))</th>
<th>(\nu(\text{NC}_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mo(S}_2\text{CNMe}_2]_2(\text{NO})_2])</td>
<td>1646, 1753</td>
<td>1540</td>
<td>977</td>
<td>1151</td>
</tr>
<tr>
<td>([\text{Mo(S}_2\text{CNET}_2]_2(\text{NO})_2])</td>
<td>1636, 1747</td>
<td>1505</td>
<td>994</td>
<td>1151</td>
</tr>
<tr>
<td>([\text{Mo(S}_2\text{CNP}_2]_2(\text{NO})_2])</td>
<td>1644, 1754</td>
<td>1488</td>
<td>1039</td>
<td>1148</td>
</tr>
<tr>
<td>([\text{Mo(S}_2\text{CN(C}_2\text{H}_4]_2(\text{NO})_2])</td>
<td>1644, 1754</td>
<td>1494</td>
<td>1003</td>
<td>1164</td>
</tr>
<tr>
<td>([\text{Mo(S}_2\text{CN}^\text{Bu}_2]_2(\text{NO})_2])</td>
<td>1631, 1752</td>
<td>1500</td>
<td>?</td>
<td>1148</td>
</tr>
<tr>
<td>([\text{Mo(S}_2\text{CNBz}_2]_2(\text{NO})_2])</td>
<td>1650, 1762</td>
<td>1484 (?)</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>([\text{W(S}_2\text{CNET}_2]_2(\text{NO})_2])</td>
<td>1623, 1771</td>
<td>1514</td>
<td>997</td>
<td>1152</td>
</tr>
<tr>
<td>([\text{Mo(acac})(\text{NO})_2])</td>
<td>1657, 1770</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a KBr Discs
b Of dithiocarbamate

2.5.2 Far Infrared Spectra (500-200 cm\(^{-1}\))

The far infrared spectra were recorded in nujol mulls using a Grubb-Parsons DM4 spectrophotometer. Figure 2.2 shows some examples of the spectra obtained and Table 2.4 lists the bands observed.
Table 2.4
Far Infrared Spectra for [M(S$_2$CNMe$_2$)$_2$(NO)$_2$] Complexes (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(M-$S$)</th>
<th>$\nu$(OH-M-NO)</th>
<th>Other Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]</td>
<td>3722</td>
<td>465w</td>
<td>449w, 436sh, 375w, 345w, 253w, 385w</td>
</tr>
<tr>
<td>[Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]</td>
<td>3721</td>
<td>460w</td>
<td>469w, 397w, 329w, 232w</td>
</tr>
<tr>
<td>[Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]</td>
<td>3722</td>
<td>465w</td>
<td>449w, 436sh, 375w, 345w, 253w, 385w</td>
</tr>
<tr>
<td>[Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]</td>
<td>3721</td>
<td>460w</td>
<td>469w, 397w, 329w, 232w</td>
</tr>
<tr>
<td>[Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]</td>
<td>3722</td>
<td>465w</td>
<td>449w, 436sh, 375w, 345w, 253w, 385w</td>
</tr>
<tr>
<td>[Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]</td>
<td>3721</td>
<td>460w</td>
<td>469w, 397w, 329w, 232w</td>
</tr>
<tr>
<td>[Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]</td>
<td>3722</td>
<td>465w</td>
<td>449w, 436sh, 375w, 345w, 253w, 385w</td>
</tr>
<tr>
<td>[Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]</td>
<td>3721</td>
<td>460w</td>
<td>469w, 397w, 329w, 232w</td>
</tr>
<tr>
<td>[Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]</td>
<td>3722</td>
<td>465w</td>
<td>449w, 436sh, 375w, 345w, 253w, 385w</td>
</tr>
<tr>
<td>[Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]</td>
<td>3721</td>
<td>460w</td>
<td>469w, 397w, 329w, 232w</td>
</tr>
<tr>
<td>[Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]</td>
<td>3722</td>
<td>465w</td>
<td>449w, 436sh, 375w, 345w, 253w, 385w</td>
</tr>
<tr>
<td>[Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]</td>
<td>3721</td>
<td>460w</td>
<td>469w, 397w, 329w, 232w</td>
</tr>
</tbody>
</table>

2.3.3 Spectra of Labelled Complexes

Spectra in the range 2000-500 cm$^{-1}$ and 500-200 cm$^{-1}$ were recorded on Grubb-Parsons 254 and GCA spectrophotometers, respectively. The complexes were measured with benzene, (2000-650 cm$^{-1}$), 1,2,4-trichlorobenzene (450-5 cm$^{-1}$) and water vapour (500-200 cm$^{-1}$).

The complexes studied were [Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$], [Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$] and [Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]. Table 2.4 lists the peaks observed.

Figure 2.2. Far Infrared Spectra: A = [Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$], B = [Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$] and C = [Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]; Top scale: microns, Bottom scale: cm$^{-1}$.  

[Diagram of Far Infrared Spectra]

---

The diagram shows three spectra labeled A, B, and C, each representing different complexes. The spectra are plotted on a scale from 200 to 500 cm$^{-1}$.
Table 2.4

Far Infrared Spectra for \([\text{M}(\text{S}_2\text{CNR}_2)_2(\text{NO})_2]\) Complexes (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>M-S</th>
<th>(\delta(\text{ON-M-NO}))</th>
<th>Other Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2])</td>
<td>372s</td>
<td>465w</td>
<td>445m, 426sh, 326w, 256w, 233sh, 288m, 224sh</td>
</tr>
<tr>
<td>([\text{Mo}(\text{S}_2\text{CN}(\text{C}_2\text{H}_4)_2)_2(\text{NO})_2])</td>
<td>373s</td>
<td>460w</td>
<td>493w, 397w, 328w, 222w</td>
</tr>
<tr>
<td>([\text{Mo}(\text{S}_2\text{CNi-Pr}_2)_2(\text{NO})_2])</td>
<td>344s</td>
<td>459w</td>
<td>417m, 294m, 289sh</td>
</tr>
<tr>
<td>([\text{Mo}(\text{S}_2\text{CNn-Bu}_2)_2(\text{NO})_2])</td>
<td>385s</td>
<td>476w</td>
<td>412w, 333m, 313m</td>
</tr>
<tr>
<td>([\text{Mo}(\text{S}_2\text{CNBz}_2)_2(\text{NO})_2])</td>
<td>370s</td>
<td>461w</td>
<td>510m, 279w</td>
</tr>
<tr>
<td>([\text{W}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2])</td>
<td>375s</td>
<td>469w</td>
<td>490w, 397m, 326w</td>
</tr>
</tbody>
</table>

2.5.3 Spectra of Labelled Complexes

Spectra in the ranges 2000-500 cm\(^{-1}\) and 500-200 cm\(^{-1}\) were recorded on Grubb-Parsons GS4 and GM4 spectrophotometers, respectively. The spectra were calibrated using polystyrene (2000-650 cm\(^{-1}\)), 1,2,4-trichlorobenzene (650-500 cm\(^{-1}\)) and water vapour (500-200 cm\(^{-1}\)).

The complexes studied were \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]\), \([\text{Mo}(\text{S}_2\text{CNEt}_2)(^{15}\text{NO})_2]\), and a 1:2:1 mixture of \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]\), \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(^{15}\text{NO})(\text{NO})]\) and \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(^{15}\text{NO})_2]\). Table 2.5 lists the peaks observed to shift on \(^{15}\text{NO}\) substitution in \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]\) and the corresponding frequencies in the substituted products.
Table 2.5

I.r. Data: Bands Which Shift on $^{15}$NO Substitution in $[\text{Mo(S}_2\text{CNET}_2\text{)}_2\text{(NO)}_2]$ (in KBr Discs unless otherwise indicated)

<table>
<thead>
<tr>
<th>Compound</th>
<th>1:2:1 Mixture of (NO)$_2$, $^{15}$NO(NO) and $^{15}$NO$_2$</th>
<th>[Mo(S$_2$CNET$_2$)$_2$(1$^{15}$NO)$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo(S$_2$CNET$_2$)$_2$(NO)$_2$]</td>
<td>1747, 1729, 1711</td>
<td>1711</td>
</tr>
<tr>
<td></td>
<td>1636, 1615, 1604</td>
<td>1604</td>
</tr>
<tr>
<td></td>
<td>553, 547$^b$</td>
<td>544</td>
</tr>
<tr>
<td></td>
<td>528, 523$^b$</td>
<td>521</td>
</tr>
<tr>
<td></td>
<td>461$^b$, 454$^b$</td>
<td>449$^b$</td>
</tr>
</tbody>
</table>

a cm$^{-1}$; in KBr Discs unless otherwise indicated.
b 1% CsI disc.

2.6 Ultraviolet and Visible Spectra

All spectra were recorded on a Cary 14 spectrophotometer. Three bands in UV-visible region were characterised and Table 2.6 gives the observed absorptions and their extinction coefficients.

Table 2.6

UV-Visible Spectra ($\lambda$)$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption Maxima</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In Methanol</td>
</tr>
<tr>
<td>[Mo(S$_2$CNMe$_2$)$_2$(NO)$_2$]</td>
<td>2720 (2.35$\times$10$^4$, 2.39$\times$10$^4$)</td>
</tr>
<tr>
<td></td>
<td>4790 (2245, 2240)</td>
</tr>
<tr>
<td>[Mo(S$_2$CNET$_2$)$_2$(NO)$_2$]</td>
<td>2740 (2.44$\times$10$^4$, 2.43$\times$10$^4$)</td>
</tr>
<tr>
<td></td>
<td>4810 (2260, 2260)</td>
</tr>
<tr>
<td>[Mo(S$_2$CN(C$_2$H$_4$)$_2$(NO)$_2$]</td>
<td>2740 (2.61$\times$10$^4$, 2.67$\times$10$^4$)</td>
</tr>
<tr>
<td></td>
<td>4800 (2310, 2330)</td>
</tr>
</tbody>
</table>

cont.
### Table 2.6 (cont.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>In Methanol</th>
<th>In Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo(S&lt;sub&gt;2&lt;/sub&gt;CN&lt;sup&gt;iPr&lt;/sup&gt;)&lt;sub&gt;2&lt;/sub&gt;(NO)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>2780 (2.37×10&lt;sup&gt;4&lt;/sup&gt;, 2.38×10&lt;sup&gt;4&lt;/sup&gt;)&lt;br&gt;4850 (2230, 2230)</td>
<td>7220 (146, 147)</td>
</tr>
<tr>
<td>[Mo(S&lt;sub&gt;2&lt;/sub&gt;CN&lt;sup&gt;nBu&lt;/sup&gt;)&lt;sub&gt;2&lt;/sub&gt;(NO)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>2760 (2.50×10&lt;sup&gt;4&lt;/sup&gt;, 2.52×10&lt;sup&gt;4&lt;/sup&gt;)&lt;br&gt;4810 (2300, 2300)</td>
<td>7150 (138, 137)</td>
</tr>
<tr>
<td>[Mo(S&lt;sub&gt;2&lt;/sub&gt;CNBz)&lt;sub&gt;2&lt;/sub&gt;(NO)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>–</td>
<td>2830 (2.64×10&lt;sup&gt;4&lt;/sup&gt;, 2.65×10&lt;sup&gt;4&lt;/sup&gt;)&lt;br&gt;4770 (2410, 2420)&lt;br&gt;7140 (139, 142)</td>
</tr>
<tr>
<td>[W(S&lt;sub&gt;2&lt;/sub&gt;CNET)&lt;sub&gt;2&lt;/sub&gt;(NO)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>2720 (1.66×10&lt;sup&gt;4&lt;/sup&gt;, 1.66×10&lt;sup&gt;4&lt;/sup&gt;)&lt;br&gt;4610 (2920, 2930)</td>
<td>7140 (157, 158)</td>
</tr>
<tr>
<td>[Cr(S&lt;sub&gt;2&lt;/sub&gt;CNET)&lt;sub&gt;2&lt;/sub&gt;(NO)&lt;sub&gt;2&lt;/sub&gt;]&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2730 (3×10&lt;sup&gt;4&lt;/sup&gt;)&lt;br&gt;3000sh (1.3×10&lt;sup&gt;4&lt;/sup&gt;)&lt;br&gt;5120 (1.7×10&lt;sup&gt;3&lt;/sup&gt;)&lt;br&gt;7190 (80)</td>
<td></td>
</tr>
</tbody>
</table>

**a** Duplicate determinations of extinction coefficients in brackets.

**b** Reference 102

### 2.7 Cyclic Voltametry and Coulometry

#### 2.7.1 Experimental

Electrochemical measurements were made in acetone/0.1M Et<sub>4</sub>NClO<sub>4</sub> versus a Ag/AgCl/0.1M LiCl reference electrode with the assistance of Mrs Janet Hope. A three electrode, i.r. compensated system was used along with PAR instrumentation. Cyclic and ac voltammetry were performed at a platinum disc electrode with a geometrical area of ~0.27 cm<sup>2</sup>. Phase sensitive ac measurements were made at a scan rate of 10 mV/sec with a phase angle of 90° with respect to the applied potential and with an 80 Hz ac perturbation of 5 mV.
Solutions were deoxygenated with dinitrogen saturated with acetone and voltammetric measurements were performed under a blanket of dinitrogen at room temperature (−22°C). Electronic spectra were recorded on a Cary 14 spectrophotometer.

Controlled potential coulometry at -0.8 V was performed on 1.085×10⁻⁵ mole of \([\text{Mo(S}_2\text{CNET}_2\text{)(NO)}_2]\) in acetone/0.1M \(\text{Et}_4\text{NCIO}_4\) under dinitrogen.

2.7.2 Results

The cyclic and ac voltamograms of \([\text{Mo(S}_2\text{CNET}_2\text{)(NO)}_2]\) are shown in Figure 2.3. Similar voltamograms were obtained for the other dithiocarbamate complexes. Table 2.7 summarises the electrochemical parameters for the first reduction wave. The reductions occurring at lower potentials are clearly irreversible and were not studied in any detail. In addition, the complexes were not readily oxidised (scanned to +1.5 V).

2.8 The Infrared Spectrum of \([\text{Mo(S}_2\text{CNET}_2\text{)(NO)}_2]\)^−

A sample of \([\text{Mo(S}_2\text{CNET}_2\text{)(NO)}_2]\) was reduced electrochemically in dichloromethane saturated with \(\text{Et}_4\text{NCIO}_4\). For this solvent system, the infrared spectral region between 2000 and 1500 cm⁻¹ was found to be free of any strong absorptions.

The spectrum of the reduced anion showed a strong band at 1570 cm⁻¹ and absent were the nitrosyl bands at 1654 and 1762 cm⁻¹ due to \([\text{Mo(S}_2\text{CNET}_2\text{)(NO)}_2]\). Upon air oxidation of the solution, the 1570 cm⁻¹ peak disappeared.
### Table 2.7

Parameters for the Reduction of \([\text{M(S}_2\text{CNR}_2\text{)}_2\text{(NO)}_2]\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ac Voltametry(^a)</th>
<th>Cyclic Voltametry(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(E_p) (V)</td>
<td>(\Delta E/2) (mV)</td>
</tr>
<tr>
<td>([\text{Mo(S}_2\text{CNMe}_2\text{)}_2\text{(NO)}_2])</td>
<td>-0.626</td>
<td>98</td>
</tr>
<tr>
<td>([\text{Mo(S}_2\text{CNEt}_2\text{)}_2\text{(NO)}_2])</td>
<td>-0.646</td>
<td>98</td>
</tr>
<tr>
<td>([\text{Mo(S}_2\text{CN(C}_2\text{H}_4\text{)}_2\text{(NO)}_2])</td>
<td>-0.634</td>
<td>100</td>
</tr>
<tr>
<td>([\text{Mo(S}_2\text{CNI-Pr}_2\text{(NO)}_2])</td>
<td>-0.680</td>
<td>101</td>
</tr>
<tr>
<td>([\text{Mo(S}_2\text{Cn-Bu}_2\text{(NO)}_2])</td>
<td>-0.648</td>
<td>102</td>
</tr>
<tr>
<td>([\text{Mo(S}_2\text{CNBr}_2\text{(NO)}_2])</td>
<td>-0.566</td>
<td>98</td>
</tr>
<tr>
<td>([\text{W(S}_2\text{CNEt}_2\text{(NO)}_2])</td>
<td>-0.733</td>
<td>100</td>
</tr>
<tr>
<td>([\text{Mo(acac)}_2\text{(NO)}_2])</td>
<td>-0.653</td>
<td>105</td>
</tr>
</tbody>
</table>

\(^a\) (i) cyclic voltammetry: Scan rate 100 mV/sec.

(ii) Ac voltametry: Scan rate 10 mV/sec.

(iii) \(i_{p}^{f}/i_{p}^{b}\) calculated according to reference 104.
Figure 2.3. Cyclic and ac voltamograms for \([\text{Mo(S}^2\text{CNEt}_2)_2(\text{NO})_2]\).
and the 1654 and 1762 cm\(^{-1}\) bands returned.

The absorption of 1570 cm\(^{-1}\) can, on this basis, be assigned to \(\nu(\text{NO})\) in the reduced anion. However, there may also be another nitrosyl absorption below 1500 cm\(^{-1}\), but solvent and dithiocarbamate modes obscure this region.

2.9 E.S.R. Spectra

The e.s.r spectra were recorded at room temperature under an argon atmosphere in acetone/0.1M Et\(_4\)NCI0\(_4\). The anions [\(\text{M(S}_2\text{CNR}_2\text{)}_2(\text{NO})_2\)]\(^-\) and [\(\text{Mo(acac)}_2(\text{NO})_2\)]\(^-\) were generated \textit{in situ}, in the e.s.r tube, by electrolysing the neutral dinitrosyl complexes at -0.8 V using a gold coil working electrode.

\begin{table}[h]
\centering
\caption{Esr Data for Dinitrosyl Complexes}
\begin{tabular}{|c|c|c|}
\hline
\textbf{Compound} & \textbf{\(g_{av}\)} & \textbf{Nitrogen Hyperfine Coupling Constant (gauss)} \\
\hline
[\(\text{Mo(S}_2\text{CNET}_2\text{)}_2(\text{NO})_2\)]\(^-\) & 2.0075 & 7.6 \\
[\(\text{Mo(S}_2\text{CNET}_2\text{)}_2(\text{15NO})_2\)]\(^-\) & 2.0064 & 10.2 \\
[\(\text{Mo(S}_2\text{CNi-Pr}_2\text{)}_2(\text{NO})_2\)]\(^-\) & 2.0072 & 7.5 \\
[\(\text{Mo(S}_2\text{CNBz}_2\text{)}_2(\text{NO})_2\)]\(^-\) & 2.0071 & 7.4 \\
[\(\text{W(S}_2\text{CNET}_2\text{)}_2(\text{NO})_2\)]\(^-\) & 2.0191 & - \\
[\(\text{Mo(acac)}_2(\text{NO})_2\)]\(^-\) & 2.0095 & 7.9 \\
\hline
\end{tabular}
\end{table}

Figure 2.4 shows the e.s.r spectra obtained for [\(\text{Mo(S}_2\text{CNET}_2\text{)}_2(\text{NO})_2\)] and [\(\text{Mo(S}_2\text{CNET}_2\text{)}_2(\text{15NO})_2\)].
Figure 2.4. The esr spectra of: A \([\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2]\) and B \([\text{Mo}(S_2\text{CNET}_2)_2(^{15}\text{NO})_2]\).
The qualitative MO scheme suggested by Enemark and Feltham\(^1\) for a \(\{\text{M(NO)}_2\}\)\(^6\) system in octahedral \(\text{C}_2\text{V}\) symmetry is shown in Figure 2.5. Similar MO Schemes are expected for dinitrosyl complexes of lower than \(\text{C}_2\text{V}\) symmetry (\(\text{C}_2\), \(\text{C}_s\), \(\text{C}_1\)). The three filled MO's (\(1\text{a}_2\), \(1\text{a}_1\), \(1\text{b}_2\)) are all mainly metal in character while the LUMO (\(1\text{b}_1\)) is nitrosyl based.

![Figure 2.5 MO Scheme for \{Mo(NO)}_2\}^6 in octahedral \text{C}_2\text{V} symmetry.](image-url)
2.11 Discussion

The Nature of the Nitrosyl Groups in \([M(S_2CNR_2)_2(NO)_2]\)

The \([M(S_2CNR_2)_2(NO)_2]\) complexes (\(M=\text{Mo}, R=\text{Me, Et, n-Bu, i-Pr, Pyr, Bz}; M=\text{W, R=Me, Et}; M=\text{Cr, R=Et}\)), all possess two very strong nitrosyl absorptions at ~1650 and ~1750 cm\(^{-1}\) which imply a cis geometry for the two NO groups. Such low nitrosyl stretching frequencies are indicative of extensive electron delocalisation from the metal into the \(\pi^*(\text{NO})\) orbitals.

ESCA has been used to estimate the extent of electron delocalisation in the related complex, \([\text{MoCl}_2(\text{PO}_3)_2(\text{NO})_2]\), which has nitrosyl stretching frequencies at 1670 and 1790 cm\(^{-1}\).\(^{105}\) The results indicated that the molybdenum was probably nearer to the oxidation state II and that each of the nitrosyl groups possessed a small negative charge. The \(N(1s)\) binding energies of \([\text{MoCl}_2(\text{PO}_3)_2(\text{NO})_2]\) and \([\text{Mo(S}_2\text{CNET}_2)_2(\text{NO})_2]\) were found to be 230.3(2.0) and 229.6(1.9) eV\(^{106}\) respectively, suggesting that the nitrosyl groups in both complexes are similar. The crystal structure of \([\text{MoCl}_2(\text{PO}_3)_2(\text{NO})_2]\) shows a cis arrangement of the nitrosyl groups with M-N-O bond angles of 180 and 167°.\(^{107}\)

Both the MO schemes suggested by Enemark and Feltham\(^1\) and the empirical rules for predicting nitrosyl geometry given by Ibers and Haymore\(^{30}\), indicate that the nitrosyl groups should be linear in the \([M(S_2CNR_2)_2(NO)_2]\) complexes studied in this thesis.
The Infrared Spectra of \([\text{M(S}_2\text{CNR}_2\text{)}_2(\text{NO})_2]\) Complexes

The \([\text{M(S}_2\text{CNR}_2\text{)}_2(\text{NO})_2]\) complexes display the characteristic infrared bands expected for dithiocarbamate compounds (e.g. \(\nu(\text{CN})\) 1480-1540 cm\(^{-1}\), \(\nu(\text{CS}_2)\) 970-1040 cm\(^{-1}\) and \(\nu(\text{NC}_2)\) 1148-1152 cm\(^{-1}\))\(^{108}\). The relatively high \(\nu(\text{CN})\) frequencies reflect the partial double bond character of the dithiocarbamate CN bond.\(^{109}\) That is, canonical form (c) of Figure 2.6 contributes significantly to the overall structure of the coordinated dithiocarbamate.

![Figure 2.6](image)

**Figure 2.6** Canonical Forms for a Dithiocarbamate Ligand.

The electronic nature of \(R\) should affect the relative contributions of each canonical form to the total bonding with electron donating groups favouring structure (c). However, the observed CN stretch does not appear to be simply related to the electron donor capacity of \(R\) and this has been attributed to other "kinematic factors".\(^{109}\) For example, the CN stretching frequencies for \([\text{Mo(S}_2\text{CNMe}_2\text{)}_2(\text{NO})_2]\) and \([\text{Mo(S}_2\text{CNI-Pr}_2\text{)}_2(\text{NO})_2]\) are 1540 and 1488 cm\(^{-1}\), respectively.

The Mo-S stretch for dialkyldithiocarbamate complexes is suggested to occur around 370 cm\(^{-1}\)\(^{198}\) and for the dinitrosyl complexes, a strong band is observed in this region. If the one electron reduction potentials of the \([\text{Mo(S}_2\text{CNR}_2\text{)}_2(\text{NO})_2]\) complexes are taken as a guide to the relative electron donor
capacities of the dithiocarbamate ligands then the Mo-S stretch (like $v$(CN)) does not appear to be simply related to it. This can be seen in a comparison of

$[\text{Mo(S}_2\text{CNMe}_2\text{)}_2(\text{NO})_2] \ (E_{1/2} = -0.626 \text{ V}; \ v(\text{Mo-S}) = 372 \text{ cm}^{-1})$, $[\text{Mo(S}_2\text{CN(C}_2\text{H}_4\text{)}_2(\text{NO})_2] \ (E_{1/2} = -0.634 \text{ V}; \ v(\text{Mo-S}) = 344 \text{ cm}^{-1})$ and $[\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{NO})_2] \ (E_{1/2} = -0.646 \text{ V}; \ v(\text{Mo-S}) = 373 \text{ cm}^{-1})$. However, the more electron donating diisopropyl dithiocarbamate complex $[\text{Mo(S}_2\text{CNBz}_2\text{)}_2(\text{NO})_2] \ (E_{1/2} = -0.680 \text{ V})$ does have a higher Mo-S stretching frequency (385 cm$^{-1}$). For $[\text{Mo(S}_2\text{CNBz}_2\text{)}_2(\text{NO})_2]$, the position of the Mo-S stretch is uncertain. The spectrum shows a medium broad band at 370 cm$^{-1}$ in addition to a strong peak at 306 cm$^{-1}$ which could also be the Mo-S stretch. The dibenzyl dithiocarbamate ligand is one of the poorest electron donating dithiocarbamates known.

The assignment of bands due to the Mo(NO)$_2$ moiety was made by a comparison of the spectra of $[\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{NO})_2]$ and $[\text{Mo(S}_2\text{CNEt}_2\text{)}_2(15\text{NO})_2]$. Five bands were observed to shift upon isotopic substitution and these have been listed in Table 2.5. It is reasonable to assume that the Mo(NO)$_2$ moiety may be treated as if it were separated from the rest of the molecule. An Mo(NO)$_2$ species with $C_{2v}$ symmetry is predicted to have nine normal modes of vibration. Eight of these ($4A_1 + 3B_1 + B_2$) should be both infrared and raman active while the ninth ($A_2$) is raman active only. Figure 2.7 shows the expected normal modes of vibration.

For $[\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{NO})_2]$, the bands at 1747 cm$^{-1}$ and 1636 cm$^{-1}$ may be assigned to the symmetric ($A_1$, Figure 2.7(a)) and antisymmetric ($B_1$, Figure 2.7(e)) nitrosyl stretching modes, respectively. Using the simplified non-rigorous "Cotton and
Figure 2.7. IR and Raman Active Modes for Mo(NO)₂

(C₂ᵥ symmetry).
Kraihanzel's force field calculations\textsuperscript{112,113}, approximate NO stretching and interaction force constants have been obtained. Data for \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]\) was used to calculate the force constants and then these could be used to satisfactorily predict the nitrosyl stretching frequencies for \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(^{15}\text{NO})_2]\). Table 2.9 summarises the results of the above calculations. The NO stretching force constant obtained can be compared with those calculated for

\[\text{[Fe(CO)}_2(\text{NO})_2]\ (\nu(\text{NO}) = 1810, 1766 \text{ cm}^{-1}; k_{\text{NO}} = 14.1 \text{ mdyne/Å})^\text{23}
\]

\[\text{[RuCl(das)_2NO]}\text{Cl}_2\ (\nu(\text{NO}) = 1811.5 \text{ cm}^{-1}; k_{\text{NO}} = 13.84 \text{ mdyne/Å})^\text{111}
\]

and \([\text{Mo(NCO(S}_2\text{CNEt}_2)_2(dmso)NO]}\) (\(\nu(\text{NO}) = 1648 \text{ cm}^{-1}; k_{\text{NO}} = 9.88 \text{ mdyne/Å})^\text{.}

It can be seen from the valence bond representation

\[
\begin{array}{c}
+ \quad (+) \\
M \quad N \\
\end{array}
\]

for linear nitrosyl coordination \((M - N \equiv \bar{O}; \leftrightarrow M - N - \bar{O})\) that, to a first approximation, the weaker the NO bond, the stronger will be the MN bond\textsuperscript{111}. So, as the NO force constant in \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]\) is greater than in \([\text{MoNCO(S}_2\text{CNEt}_2)_2(dmso)NO]}\), the MN bond strength in the former should be less than in the latter. The Mo-NO stretch in \([\text{MoNCO(S}_2\text{CNEt}_2)_2(dmso)NO]}\) occurs at 623 \text{ cm}^{-1} (Chapter 3) and therefore in \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]\) it is expected at lower frequencies.

The bands at 553 and 528 \text{ cm}^{-1} for \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]\) have been tentatively assigned to the symmetric (A\textsubscript{1}, Figure 2.7(b)) and antisymmetric (B\textsubscript{1}, Figure 2.7(f)) Mo(NO\textsubscript{2}) stretches, respectively. The small shifts in the bands observed upon \(^{15}\text{NO} substitution (9 and 7 \text{ cm}^{-1}, respectively) support the assignment. In \([\text{MoNCO(S}_2\text{CNEt}_2)_2(dmso)NO]}\), \(\nu(\text{Mo-NO}) and \(\delta(\text{MoNO}) shift by 6 and 12 \text{ cm}^{-1}, respectively on \(^{15}\text{NO substitution (Chapter 3). Similar shifts were found for
### Table 2.9
Nitrosyl Force Constants in [Mo(S₂CNEt₂)₂(NO)₂]

<table>
<thead>
<tr>
<th></th>
<th>Force Constants Calculated (mdyne/Å)²</th>
<th>Observed NO Frequencies</th>
<th>Calcd. NO Frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kₜₜ, kₜₜInteraction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mo(S₂CNEt₂)₂(NO)₂]</td>
<td>12.6, 0.83</td>
<td>1636, 1747 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>[Mo(S₂CNEt₂)₂(¹⁵NO)₂]</td>
<td>-,-</td>
<td>1606, 1714 cm⁻¹</td>
<td>1604, 1715 cm⁻¹</td>
</tr>
</tbody>
</table>

* Using the [Mo(S₂CNEt₂)₂(NO)₂] nitrosyl stretching frequencies.
The remaining peak due to the Mo(NO)$_2$ moiety occurs at 461 cm$^{-1}$ and is below that expected for either $\nu$(Mo-NO) or $\delta$(M-N-O) modes. It has been assigned to the ON-Mo-NO bending mode (A$_1$, Figure 2.7(c)). The other nitrosyl modes expected for [Mo(S$_2$CNEt$_2$)$_2$(NO)$_2$] are not observed.

In a 1:2:1 mixture of [Mo(S$_2$CNEt$_2$)$_2$(NO)$_2$], [Mo(S$_2$CNEt$_2$)$_2$(NO)] and [Mo(S$_2$CNEt$_2$)$_2$(NO)$_2$], the nitrosyl stretching modes (i.e. Figure 2.7(a) and (e)) due to each of the species could be resolved. The nitrosyl stretching bands of [Mo(S$_2$CNEt$_2$)$_2$(NO)] were in between the corresponding bands for the other two complexes as shown in Figure 2.8. For the remaining Mo(NO)$_2$ absorptions only single peaks were resolvable but the peak centres must equate with the [Mo(S$_2$CNEt$_2$)$_2$(NO)] nitrosyl absorption frequencies.

$^1$H NMR Spectra

There are two factors which must be taken into consideration when interpreting the pmr spectra of the [M(S$_2$CNR)$_2$(NO)$_2$] complexes. These are: (1) The low symmetry of the [M(S$_2$CNR)$_2$(NO)$_2$] complexes (C$_2$), combined with the restricted rotation about the CN bond of the dithiocarbamate, result in the two R substituents being in different chemical environments$^{94}$. (2) The Mo atom is an asymmetric centre for the molecule. Some of the observed spectra will now be discussed with reference to the above two factors.
Figure 2.8. The infrared spectrum of a 1:2:1 mixture of 
\[\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{NO})_2\], \[\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{NO})(\text{NO})\] and \[\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{NO})_2\] showing the nitrosyl stretching modes.
[Mo(S₂CNMe₂)₂(NO)₂] gives the simplest spectrum consisting of a pair of singlets due to the non equivalent CH₃ groups. Each proton of the CH₃ group interacts equally with the asymmetric centre and hence no further splittings are observed. However, the spectrum of [Mo(S₂CNEt₂)₂(NO)₂] in deuterochloroform is somewhat more complicated. The CH₃ resonance appears as the expected pair of triplets (Figure 2.9), but clearly, the CH₂ absorption is not a pair of quartets as was implied by Johnson, McCleverty and Al-Obaidi.⁹⁴

The reason for this complexity arises from the fact that methylene groups near an asymmetric centre may not be chemically equivalent. As the methylene protons in [Mo(S₂CNBz₂)₂(NO)₂] are not coupled to any adjacent protons, the spectrum (Figure 2.10) is less complicated and will be discussed first. The CH₂ resonance consists of an overlapping singlet and AB quartet. The AB quartet must arise from the geminal coupling of non-equivalent CH₂ protons on one of the benzyl groups. The CH₂ protons on the other benzyl of the dithiocarbamate appear as a singlet implying that they have the same or very similar chemical shifts. It is interesting that the interaction with the asymmetric Mo centre causes inequivalence in only one of the methylene groups of the dithiocarbamate.

In view of the above results on [Mo(S₂CNBz)₂(NO)₂] a spin decoupling experiment was carried out on [Mo(S₂CNEt₂)₂(NO)₂]. Upon irradiation of the CH₂ resonance, the CH₃ absorption collapsed to a pair of singlets. The reverse decoupling was more difficult to achieve experimentally and only partial decoupling was obtained.
Figure 2.9. $^1$H nmr spectrum of $[\text{Mo(S}_2\text{CNEt}_2)_2(\text{NO})_2]$ in Deuterochloroform.
Figure 2.10. The $^1$H nmr spectrum of [Mo(S$_2$CNBz$_2$)$_2$(NO)$_2$] in Deuterochloroform
However, the CH$_2$ resonance did appear to be collapsing to an overlapping singlet and AB quartet. The CH$_2$ resonance has been computer simulated assuming that it consists of overlapping A$_2$X$_3$ and ABX$_3$ systems. Figure 2.11 compares the experimental and calculated spectra.

In acetone [D$_6$], the CH$_2$ resonance of [Mo(S$_2$CNEt$_2$)$_2$(NO)$_2$] appears as an overlapping pair of quartets whose centres are separated by approximately the CH$_3$-CH$_2$ coupling constant (Figure 2.12). This implies that a solvent interaction has caused the formally non-equivalent CH$_2$ protons to become chemically equivalent.

The spectrum of [Mo(S$_2$CNI-Pr$_2$)$_2$(NO)$_2$] contains a very broad singlet due to the CH protons and also a pair of doublets due to the non-equivalent -C(CH$_3$)$_2$ groups coupled to the CH protons. The latter resonance collapsed to a pair of singlets upon irradiation of the CH protons.

For [Mo(S$_2$CN(C$_2$H$_4$)$_2$(NO)$_2$] a quintet was observed at $\delta$2.06 in addition to a symmetric multiplet at $\delta$3.80. The quintet, on decoupling from the NCH$_2$ protons ($\delta$3.08), collapsed to a singlet implying that the protons in the (C-CH$_2$-CH$_2$-C) grouping have the same or very similar chemical shifts. The reverse decoupling, however, could not be completely achieved.

**Electrochemical Studies on [M(S$_2$CNR$_2$)$_2$(NO)$_2$]**

The electrochemical data obtained on the [M(S$_2$CNR$_2$)$_2$(NO)$_2$] complexes suggests that they are all similar and therefore, only one will be discussed in detail viz., [Mo(S$_2$CNEt$_2$)$_2$(NO)$_2$]. The reduction process for [Mo(S$_2$CNEt$_2$)$_2$(NO)$_2$] was found to have a half-wave potential
Figure 2.11. The theoretical and experimental spectra for the CH$_2$ resonance in the $^1$H nmr spectrum of [Mo(S$_2$CNEt$_2$)$_2$(NO)$_2$]. The spectrum was calculated assuming that it consisted of overlapping A$_2$X$_3$ ($A=374.7$ Hz, $X=118.4$ Hz; $J_{AX}=7.6$ Hz) and ABX$_3$ ($A=364.0$ Hz, $B=375.3$ Hz, $X=122.1$ Hz; $J_{AX}=7.1$ Hz, $J_{BX}=7.6$ Hz, $J_{AB}=-13.8$ Hz) spin systems.
Figure 2.12. The 'H nmr spectrum of $[\text{Mo(S}_2\text{CNET}_2)\text{NO}_2]$ in acetone[D$_6$].
(E½) of -0.646 V versus a Ag/AgCl/LiCl(0.1M) reference electrode; this value was obtained from the ac peak potential. The experimentally determined ac peak parameter, ΔE/2, was 95 mV implying a reversible one electron process (the expected theoretical value is 90 mV) 114.

In addition, cyclic voltamograms were obtained for potential scan rates of between 20 and 200 mV/sec and all of the voltamograms were centred at -0.643 V. The ratio of the cathodic to anodic sweep currents (i_p^f/i_p^b) was 1.06 suggesting that the reduction product was stable on the experimental timescale. The ΔE_p value of 64 mV at scan rates of up to 200 mV/sec indicates a relatively fast electron transfer.

The coulometric value for the number of moles of electrons consumed per mole of complex in the reduction process was 1.04. Figure 2.13 shows the changes which occur in the UV-visible spectrum at various stages in the exhaustive electrolysis of a solution of [Mo(S₂CNEt₂)₂(NO)₂] in acetone/0.1M Et₄NClO₄.

All of the electrochemical evidence discussed above has been consistent with the [Mo(S₂CNEt₂)₂(NO)₂] undergoing a reversible one electron reduction:

\[
\text{[Mo(S₂CNEt₂)₂(NO)₂] + e} \rightarrow \text{[Mo(S₂CNEt₂)₂(NO)₂]⁻}
\]

The paramagnetic reduction product can also be readily oxidised back to [Mo(S₂CNEt₂)₂(NO)₂] by atmospheric O₂. Infrared studies on [Mo(S₂CNEt₂)₂(NO)₂]⁻ have shown that it has a nitrosyl band at 1570 cm⁻¹ (section 2.8).

It is interesting to compare the spread in half wave reduction potentials for the various dithiocarbamate
Figure 2.13. The changes occurring in the UV-visible spectrum during the exhaustive electrolysis of
[Mo(S₂CNEt₂)₂(NO)₂] in acetone/Et₄NClO₄.

A = initial trace, with successive traces at 
-25%, 50%, 75% and 100% conversion to 
[Mo(S₂CNEt₂)₂(NO)₂]⁻.
substituents. On going from \([\text{Mo}(S_2\text{CNBz})_2(\text{NO})_2]\) to \([\text{Mo}(S_2\text{CNi-Pr}_2)_2(\text{NO})_2]\) the reduction potential decreases by 114 mV. In contrast, the metal based one electron reduction potentials of \([\text{Mn}(S_2\text{CNR})_3]\) decrease by 257 mV on going from the dibenzyl to the diisopropyl dithiocarbamate.\(^\text{110}\) The relatively small change in the \(E_k\) reduction potentials for \([\text{Mo}(S_2\text{CNR}_2)_2(\text{NO})_2]\) is consistent with the process being ligand based. Further evidence for this comes from the esr spectra of the anionic dinitrosyl complexes to be discussed next.

\([\text{Mo}(\text{acac})_2(\text{NO})_2]\) also appears to undergo a similar one electron reduction but the process is less reversible.

**ESR Spectra**

Esr spectra have been obtained on the one electron reduction products of a number of dinitrosyl complexes (section 2.9). The isotropic g values were all between 2.0064 and 2.0191, indicative of a complex with a ligand based odd electron.\(^\text{49}\) The unlabelled complexes, except for \([\text{W}(S_2\text{CNEt}_2)_2(\text{NO})_2]\), show a five line spectrum in accord with the coupling of the odd electron to two \(^{14}\text{N}\) nuclei \((S = 3/2)\). The spectrum of \([\text{Mo}(S_2\text{CNEt}_2)_2(^{15}\text{NO})_2]\) (see Figure 2.4) shows only three lines - since \(^{15}\text{N}\) has \(S = 1/2\) - and confirms that the observed hyperfine splitting is due to coupling to the nitrosoyl nitrogen atoms. The reason why \([\text{W}(S_2\text{CNEt}_2)_2(\text{NO})_2]\) shows no N hyperfine coupling is not known. In addition, no \(^{95}\text{Mo} - ^{97}\text{Mo} (S = 5/2)\) or \(^{163}\text{W} (S = 1/2)\) hyperfine couplings were observed. Figure 2.14 depicts the splitting patterns expected for coupling to two nitrogen nuclei.
Coupling to $1\,N$

Coupling to $2\,N$

Expected peak intensity ratio:

(a) $^{14}\text{N} (s=3/2)$

(b) $^{15}\text{N} (s=1/2)$

Figure 2.14  Hyperfine Coupling to Nitrogen

The $g$ values for the dinitrosyl complexes are surprisingly insensitive to the type of dithiocarbamate ligand and even with acetylacetone, the change in $g$ value is small. This, combined with the relatively high $g$-values, nitrogen hyperfine coupling and the absence of metal hyperfine interactions, strongly suggests that the odd electron is occupying a nitrosyl based MO.

The result is consistent with the MO diagram, suggested by Enemark and Feltham, for six coordinate $\{\text{M(NO)}_2\}_6$ systems (section 2.10). Here the LUMO has principally $\pi^*(\text{NO})$ character and a one electron reduction should result in an electron occupying this orbital.
UV-Visible Spectra

Three bands in the UV-visible have been characterised for the \([M(S_2CNR_2)_2(NO)_2]\) complexes and Table 2.6 summarises the data. Table 2.10 compares the spectral data for \([Cr(S_2CNEt_2)_2(NO)_2]\), \([Mo(S_2CNEt_2)_2(NO)_2]\) and \([W(S_2CNEt_2)_2(NO)_2]\).

Table 2.10
UV-Visible Spectra for the \([M(S_2CNEt_2)_2(NO)_2]\) (M=Cr,Mo,W)

<table>
<thead>
<tr>
<th>Complexes (Å)</th>
<th>([Cr(S_2CNEt_2)_2(NO)_2])</th>
<th>([Mo(S_2CNEt_2)_2(NO)_2])</th>
<th>([W(S_2CNEt_2)_2(NO)_2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>2730 (3\times10^4)</td>
<td>2720 (2.37\times10^4)</td>
<td>2720 (1.66\times10^4)</td>
<td></td>
</tr>
<tr>
<td>3000sh (1.3\times10^4)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>5120 (1.7\times10^3)</td>
<td>4810 (2.26\times10^3)</td>
<td>4610 (2.925\times10^3)</td>
<td></td>
</tr>
<tr>
<td>7190 (80)</td>
<td>7130 (133)</td>
<td>7140 (158)</td>
<td></td>
</tr>
</tbody>
</table>

a In EtOH (reference 102).
b In MeOH
c In CHCl₃

The most striking feature of the data is the insensitivity of the bands at ~2720 Å and ~7130 Å to the type of metal present and suggests that they are associated with the dithiocarbamate ligand. The free ligand has absorptions at 2570 Å and 2900 Å (logε = 4.1 and 4.2 respectively)\(^{109}\). However, the electronic spectra of dithiocarbamate complexes are not well understood and no assignments can be made at present\(^{109}\).

The bands at 5120, 4790 and 4610 Å for the Cr, Mo and W complexes respectively, are assigned to metal (\(d_{x^2}, d_{xy}, d_{yz}\))
\[ \pi^*_{b}(\text{NO}) \] transitions (see Figure 2.5). The trend towards shorter wavelengths (i.e. higher energies) on going from Cr to W is consistent with an increasing interaction between the \[ \pi^*(\text{NO})_2 \] and metal d-orbitals as shown in Figure 2.15.

Table 2.11 compares the reduction potentials of the Mo dinitrosyl complexes with the energies of the Mo \((d_{x^2}, d_{xy}, d_{yz}) \rightarrow \pi^*_b(\text{NO})\) transitions. If \([\text{Mo(S}_2\text{CNBz}_2)_2(\text{NO})_2]\) is excluded, it is apparent from Figure 2.16 that a linear correlation exists between the reduction potential and energy of the Mo \((d_{x^2}, d_{xy}, d_{yz}) \rightarrow \pi^*_b(\text{NO})\) transition. This correlation may be interpreted as follows:

(i) The reduction potentials for the complexes are a measure of the energies required to place an electron into the \[ \pi^*_b(\text{NO}) \] level, relative to a standard reference electrode. More electron donating dithiocarbamates raise the metal d orbital energies and thereby increase their interaction with the \[ \pi^*(\text{NO})_2 \] levels (see Figure 1.18). i.e. the electron density on the nitrosyl groups will increase. The \[ \pi^*_b(\text{NO}) \] level has a minimum of interaction with the metal d orbitals, but with more electron density on the nitrosyl groups an electron in this orbital will experience greater repulsive forces and the energy of the orbital will be greater. So, the energy of the \[ \pi^*_b(\text{NO}) \] level increases with the electron donor capacity of the dithiocarbamate ligand and this is reflected in more negative reduction potentials.

(ii) The wavenumber for the M \((d_{x^2}, d_{xy}, d_{yz}) \rightarrow \pi^*_b(\text{NO})\) transition is a measure of the energy required to transfer an electron from the metal into the \[ \pi^*_b(\text{NO}) \] level as shown in Figure 2.15. The metal d orbital and \[ \pi^*_b(\text{NO}) \] energies
Figure 2.15. Interaction diagrams for the $[\text{M(NO)}_2]$ moiety of the $[\text{M(S}_2\text{CNET}_2)_2\text{(NO)}_2]$ complexes; $\text{M} = \text{Cr}, \text{Mo}, \text{W}$.
The linear correlation between the energy of the $M(d_{x^2},d_{xy},d_{yz}) \rightarrow \pi^*_b$(NO) transition and the reduction potential for the $[Mo(S_2CNR_2)_2(NO)_2]$ complexes.

Figure 2.16.
increase with the electron donor capacity of the dithiocarbamate, but as can be seen in Table 2.11 the energy gap between the two levels is reduced. This simply implies that the metal d orbitals are raised more in energy than the $\pi^*_b$(NO) level.

The combined results of (1) and (2) are summarised in Figure 2.17.

Finally, one further piece of evidence which supports the assignment of the $M (d_{x^2}, d_{xy}, d_{yz}) \rightarrow \pi^*_b$(NO) transition is that on reduction of $[\text{Mo(S}_2\text{CNEt}_2)_2(\text{NO})_2]$ the $4810 \, \text{Å}$ band disappears (Figure 2.13).
Table 2.11

The Correlation Between the [Mo(S₂CN'R₂)₂(NO)₂] Reduction Potentials and Energy of the Metal → π*(NO) Charge Transfer Band

<table>
<thead>
<tr>
<th>Complex</th>
<th>E₀¹/² (reduction) (Volts)</th>
<th>M(dₓᵧ,dᵧz,x²)→π*(NO) Band (Å)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo(S₂CNi-Pr₂)₂(NO)₂]</td>
<td>-0.680</td>
<td>4850</td>
<td>20,610</td>
</tr>
<tr>
<td>[Mo(S₂CNn-Bu₂)₂(NO)₂]</td>
<td>-0.648</td>
<td>4810</td>
<td>20,790</td>
</tr>
<tr>
<td>[Mo(S₂CNEt₂)₂(NO)₂]</td>
<td>-0.646</td>
<td>4810</td>
<td>20,790</td>
</tr>
<tr>
<td>[Mo(S₂CN(C₂H₄)₂)₂(NO)₂]</td>
<td>-0.634</td>
<td>4800</td>
<td>20,830</td>
</tr>
<tr>
<td>[Mo(S₂CNMe₂)₂(NO)₂]</td>
<td>-0.626</td>
<td>4790</td>
<td>20,870</td>
</tr>
<tr>
<td>[Mo(S₂CNBz₂)₂(NO)₂]</td>
<td>-0.566</td>
<td>4770</td>
<td>20,960</td>
</tr>
</tbody>
</table>
Figure 2.17. A scheme explaining the correlation between the reduction potentials of \([\text{Mo}(S_2CNR_2)_2(\text{NO})_2]\) and the energies of the \(\text{Mo}(d_{xy},d_{yz},d_{x^2}) \rightarrow \pi^*_{b}(\text{NO})\) transition.
CHAPTER 3

The reactions of [M(S₂CNR₂)₂(NO)₂] (L = NO, Et) with azide or cyanate have been reported to give the anionic complexes [MOL₂(S₂CNR₂)₂(NO)]⁻ (L = N₃⁻ or NCS⁻) and dinitrogen oxide. These anionic complexes were also readily converted into the neutral species, [MOL(S₂CNR₂)₂(dmso)NO].

This chapter deals with the characterisation of the products from the reactions of [M(S₂CNR₂)(NO)]₂ (NO = NO₂, N₂O₅, Et, i-Pr, N=O, N≡O) with some or all of the following anions: N₃⁻, NCO⁻, NCS⁻ and S₂CNR₂⁻. In addition labelling studies dealing with the reactions of (NO(S₂CNR₂)₂(NO)₂) with N₇⁻, NCO⁻, CN⁻ and S₂CNR₂⁻ will be described.

The nitrooxy groups of [M(S₂CNR₂)₂(NO)]₂ are predicted to be nearly linear (Chapter 2) and the relatively low nitrooxy stretching frequencies suggest that the NO groups are

The Reactions of [M(S₂CNR₂)₂(NO)₂] with Azide, Cyanate, Thiocyanate, Cyanide and Diethylidithiocarbamate;

Characterisation of Products and Labelling Studies

3.1 Introduction

The dimethylsulphoxide used in the reactions was dried over 4Å molecular sieve, distilled under vacuum and stored over 4Å molecular sieve in a dinitrogen atmosphere.

The [M(S₂CNR₂)₂(NO)₂] complexes were prepared as described...
3.1 Introduction

The reactions of \([\text{Mo}(\text{S}_2\text{CNR}_2)\text{2(NO)}\text{2}] \) (R = Me, Et) with azide or cyanate have been reported to give the anionic complexes \([\text{MoL}_2(\text{S}_2\text{CNR}_2)\text{2(NO)}\text{2}]^{-} \) (L = N$_3$ or NCO$^-$) and dinitrogen oxide$^{116}$. These anionic complexes were also readily converted into the neutral species, \([\text{MoL}(\text{S}_2\text{CNR}_2)\text{2(dms)NO}] \).

This chapter deals with the characterisation of the products from the reactions of \([\text{M}(\text{S}_2\text{CNR}_2)\text{2(NO)}\text{2}] \) (M=Mo, R=Me, Et, i-Pr; M=W, R=Et) with some or all of the following anions: N$_3$-, NCO$^-$, NCS$^-$ and S$_2$CNEt$_2$-. In addition labelling studies dealing with the reactions of \([\text{Mo}(\text{S}_2\text{CNEt}_2)\text{2(15NO)}\text{2}] \) with N$_3$-, NCO$^-$, CN$^-$ and S$_2$CNEt$_2$- will be described.

The nitrosyl groups of \([\text{M}(\text{S}_2\text{CNR}_2)\text{2(NO)}\text{2}] \) are predicted to be nearly linear (Chapter 2) and the relatively low nitrosyl stretching frequencies suggest that the NO groups will be unreactive unless activated by the coordination of a suitable ligand to the metal (Chapter 1). The experimental results will be shown to be consistent with this proposal.

3.2 The Isolation of Products from the Reaction of \([\text{M}(\text{S}_2\text{CNR}_2)\text{2(NO)}\text{2}] \) with Azide, Cyanate and Thiocyanate

3.2.1 Materials

The dimethylsulphoxide used in the reactions was dried over 4A molecular sieve, distilled under vacuum and stored over 4A molecular sieve in a dinitrogen atmosphere. The \([\text{M}(\text{S}_2\text{CNR}_2)\text{2(NO)}\text{2}] \) complexes were prepared as described...
in section 2.2. All other chemicals and solvents were AR grade and were not further purified.

3.2.2 A Preliminary Note for the Syntheses

The reactions involving \([\text{Mo(S}_2\text{CNR}_2\text{)}_2(\text{NO})_2]\) were all carried out at either 60°C or 80°C in the absence of light and dioxygen. For \([\text{W(S}_2\text{CNET}_2\text{)}_2(\text{NO})_2]\), reactions were again done in the absence of dioxygen but it was necessary to irradiate the solutions with pyrex filtered light from a xenon lamp.

All of the work up procedures were performed in the air.

3.2.3 Analyses

See Section 2.2.2.

3.2.4 Cyanatobis(N,N-diethyldithiocarbamato)(dimethyl sulphoxide)nitrosylmolybdenum

\(\text{cis-}[\text{Mo(S}_2\text{CNET}_2\text{)}_2(\text{NO})_2]\) (0.8 g, 0.0018 mol) and potassium cyanate (0.29 g, 0.0036 mol) were dissolved in dimethyl sulphoxide (15 ml). The reaction mixture was heated at 60°C for 12 h, and dinitrogen oxide was evolved during this time.

The vessel was opened to the atmosphere and dichloromethane (60 ml) added. A brown solid precipitated and was filtered off. The dark brown filtrate was extracted with water (150 ml) for 5 min. The aqueous phase initially became yellow and then a fine yellow solid formed. The brown dichloromethane layer was removed. Dichloromethane (100 ml),
dimethyl sulfoxide (50 ml) and sodium persulphate (0.4 g) were added to the aqueous suspension and the mixture stirred magnetically for 1 h. The orange dichloromethane layer was separated, washed with water (2×200 ml), dried over anhydrous sodium sulphate and filtered. After evaporation of the solvent, the oily residue was dissolved in dichloromethane (10 ml) and carbon tetrachloride added until precipitation was just evident. The solution deposited yellow needles on standing overnight. The product was filtered off and washed with carbon tetrachloride/dichloromethane (90% v/v) and dried (7 h, 95°, vac.). The yield was 0.35 g (36%) (Found: C, 28.8; H, 4.9; Mo, 17.9; N, 10.4; S, 29.2; mol. wt. (osmometric), 493. \( \text{C}_{13}\text{H}_{25}\text{MoN}_{4}\text{O}_{3}\text{S}_{5} \) requires C, 28.8; H, 4.9; Mo, 17.7; N, 10.3; S, 29.5%; mol. wt., 543). The product was a non-electrolyte in dimethyl sulfoxide.

3.2.5 Azidobis(N,N-diethylthiocarbamato)(dimethyl sulfoxide)nitrosylmolybdenum

This complex may be prepared in a manner analogous to that described for the cyanato complex. However, the following procedure gives the best yields.

\[ \text{[MoNCO(S}_{2}\text{CNEt}_{2})_{2}(\text{dms})\text{NO}] \] (0.8 g, 0.0015 mol) was dissolved in dimethyl sulfoxide (15 ml) and excess sodium azide (1.9 g, 0.029 mol) added. The reaction vessel was placed in a water bath kept at 70°C and stirred by passage of dinitrogen for 48 h. No precautions were taken to exclude light. The solution was then cooled and dichloromethane (50 ml) was added; a white precipitate formed. This was filtered off and the filtrate extracted twice with 100 ml aliquots of aqueous
sodium sulphate solution (5% w/v). The dichloromethane solution was dried over magnesium sulphate for 2 h, filtered and evaporated to dryness. The product was recrystallized from dichloromethane/carbon tetrachloride and dried at 60°C under vacuum. The yield was 0.55 g (65%) (Found: C, 26.4; H, 4.8; Mo, 17.4; N, 15.1; S, 29.5. \( \text{C}_{12}\text{H}_{25}\text{MoN}_5\text{O}_2\text{S}_5 \) requires C, 26.6; H, 4.8; Mo, 17.7; N, 15.5; S, 29.5%).

3.2.6 Tetraethylammonium Dicyanatobis(N,N-diethyldithiocarbamato)nitrosylmolybdate

\( \text{cis-}[\text{Mo(S}_2\text{CNEt}_2]_2(\text{NO})_2] \) (0.104 g, 2.3×10^{-4} mol) and potassium cyanate (0.043 g, 5.3×10^{-4} mol) were dissolved in dimethyl sulphoxide (5 ml). The reaction was completed by heating at 80°C for 2 h. After cooling to room temperature, dichloromethane (50 ml) was added. A small amount of brown solid was filtered off and the filtrate placed in a separating funnel together with an aqueous solution of tetraethylammonium chloride (1 g in 30 ml \( \text{H}_2\text{O} \)). The two layers were swirled gently for about 2 min and the yellow-brown dichloromethane layer removed. This was dried over anhydrous sodium sulphate, filtered and carbon tetrachloride added until precipitation commenced. After several hours small yellow needle-like crystals had formed. These were filtered off and washed with carbon tetrachloride/dichloromethane (90%, v/v, 3×20 ml). The yield was 0.06 g (40%) (Found: C, 37.5; H, 6.1; Mo, 14.9; N, 13.3; S, 20.1. \( \text{C}_{20}\text{H}_{40}\text{MoN}_6\text{O}_3\text{S}_4 \) requires C, 37.7; H, 6.3; Mo, 15.1; N, 13.2; S, 20.1%). The product was a 1:1 electrolyte in dimethyl sulphoxide.
3.2.7 Tetraethylammonium Diazidobis(N,N-diethylidithiocarbamato)nitrosylmolybdate

\( \text{cis-}[\text{Mo(S}_2\text{CNET}_2]_2(\text{NO})_2] \) (0.2 g, \( 4.42 \times 10^{-4} \) mole) and sodium azide (0.1 g, \( 1.54 \times 10^{-3} \) mole) were dissolved in dimethylsulphoxide (5 ml). The reaction mixture was heated for 21 hours at 60°C. Dichloromethane (30 ml) was added and a brown precipitate formed. The solution was poured into a separating funnel containing aqueous tetraethylammonium chloride (1 g \( \text{Et}_4\text{NClH}_2\text{O} \) in 30 ml of \( \text{H}_2\text{O} \)). The two layers were swirled gently for a few minutes. The lower dichloromethane phase was drawn off and dried over anhydrous sodium sulphate. After filtering the solution, carbon tetrachloride was added until precipitation commenced. An orange crystalline product formed on standing and this was filtered off and washed with carbon tetrachloride-dichloromethane (90% v/v). The yield was 0.052 g (8.16 \times 10^{-5} \) mole, 18.5%) (Found: C, 33.47; H, 5.99; N, 21.06; S, 20.01; Cl, 0.78. \( \text{C}_{18}\text{H}_{40}\text{MoN}_{10}\text{S}_{4} \) requires C, 33.95; H, 6.33; N, 22.00; S, 20.14). For 0.04 molecules of carbon tetrachloride of crystallisation the calculated analysis is: C, 33.70; H, 6.28; N, 21.82; S, 19.97; Cl, 0.83.

3.2.8 Tetraethylammonium Dicyanatobis(N,N-dimethylidithiocarbamato)nitrosylmolybdate

\( \text{cis-}[\text{Mo(S}_2\text{CNMe}_2]_2(\text{NO})_2] \) (0.083 g, \( 2 \times 10^{-4} \) mole) and potassium cyanate (0.026 g, \( 3.2 \times 10^{-4} \) mole) were dissolved in dimethyl sulphoxide (5 ml). An identical procedure to that described in 3.2.6 was followed. The yield of complex was 0.042 g (36%) (Found: C, 33.0; H, 5.5; N, 14.4; S, 22.0. \( \text{C}_{16}\text{H}_{32}\text{MoN}_{6}\text{O}_{3}\text{S}_{4} \) requires C, 33.1; H, 5.6; N, 14.5; S, 22.1%).
3.2.9 Tetramethylammonium Dicyanatobis(N,N-dimethyldithiocarbamato)nitrosylmolybdate

cis-[Mo(S₂CNMe₂)₂(NO)₂] (0.182 g, 4.6×10⁻⁴ mole) and potassium cyanate (0.086 g, 1.1×10⁻³ mole) were dissolved in dimethyl sulfoxide (5 ml). A similar procedure to that described in 3.2.6 was employed, tetramethylammonium bromide being used in place of tetraethylammonium chloride. The yield of complex was 0.081 g (34%) (Found: C, 27.6; H, 4.9; N, 15.9; S, 24.2. C₁₂H₂₄MoN₆O₃S₄ requires C, 27.5; H, 4.6; N, 16.0; S, 24.5%).

3.2.10 Cyanatobis(N,N-dimethyldithiocarbamato)(dimethyl sulfoxide)nitrosylmolybdenum

The procedure used for the diethyldithiocarbamate analogue gives an impure product. However, the complex was readily obtained from (Me₄N)[Mo(NCO)₂(S₂CNMe₂)₂NO] by the following method.

(Me₄N)[Mo(NCO)₂(S₂CNMe₂)₂NO] (0.081 g, 1.54×10⁻⁴ mole) was dissolved in dimethyl sulfoxide (10 ml) and water (20 ml) added. Dichloromethane (30 ml) and sodium persulphate (0.1 g) were added and the solution stirred until the aqueous layer was colourless. The yellow dichloromethane layer was washed with distilled water (3×100 ml), dried over anhydrous sodium sulphate and filtered. The solvent was removed and the residue taken up in dichloromethane (5 ml). Carbon tetrachloride was added to deposit the yellow crystalline product which was filtered off and washed with carbon tetrachloride/dichloromethane (90%, v/v, 3×10 ml). The compound was dried under vacuum at 95°C for 13 h. The yield was 0.053 g (71%) (Found: C, 21.9; H, 3.7; Cl, 1.8; N, 11.3; S, 32.3.
The analysis is slightly low due to a small amount of carbon tetrachloride of crystallization being retained by the complex. For 0.06 molecules of carbon tetrachloride the calculated analysis is: C, 22.0; H, 3.7; Cl, 1.7; N, 11.3; S, 32.3%.

3.2.11 Tetraethylammonium Dicyanatobis(N,N-diisopropyl-dithiocarbamato)nitrosylmolybdate

\[ \text{cis-}[\text{Mo}(\text{S}_2\text{CNi-Pr}_2)_2(\text{NO})_2] \] (0.2 g, 3.93×10^{-4} mole) and potassium cyanate (0.064 g, 7.89×10^{-4} mole) were dissolved in dimethylsulphoxide (5 ml). The solution was heated at 80°C for 2 h and worked-up by a procedure similar to that described in 3.2.6. The yield was 0.064 g (9.23×10^{-5} mole, 23.5%). (Found C, 41.40; H, 6.98; N, 11.90; S, 18.38. \( \text{C}_{24}\text{H}_{48}\text{MoN}_6\text{S}_4\text{O}_3 \) requires C, 41.60; H, 6.98; N, 12.13; S, 18.51%).

3.2.12 Cyanatobis(N,N-diisopropyl-dithiocarbamato)(dimethylsulphoxide)nitrosylmolybdenum

\[ [\text{Et}_4\text{N}][\text{Mo(NCO)}_2(\text{S}_2\text{CNi-Pr}_2)_2\text{NO}] \] (0.16 g, 2.31×10^{-4} mole) was dissolved in dimethylsulphoxide (20 ml) and water (20 ml) added. A similar procedure to that described in section 3.2.10 was followed. The yield was 0.09 g (1.5×10^{-3} mole, 65%). (Found: C, 33.79; H, 6.05; N, 9.23; S, 26.45. \( \text{C}_{17}\text{H}_{34}\text{MoN}_4\text{S}_5\text{O}_3 \) requires C, 34.10; H, 5.74; N, 9.36; S, 26.77%).

3.2.13 Cyanatobis(N,N-diethyl-dithiocarbamato)(dimethylsulphoxide)nitrosyltungsten

\[ \text{cis-}[\text{W}(\text{S}_2\text{CNe}_2)_2(\text{NO})_2] \] (0.1 g, 1.85×10^{-4} mole) and potassium cyanate (0.03 g, 3.67×10^{-3} mole) were dissolved
in dimethylsulphoxide (3 ml) and the reaction mixture was irradiated for 7 h.

Dichloromethane (30 ml) was added and the solution filtered to remove a small amount of brown precipitate. The solution was then extracted with water (60 ml). The aqueous phase initially became yellow and then a fine yellow solid formed. The dichloromethane phase was removed. Dichloromethane (40 ml), dimethylsulphoxide (20 ml) and sodium persulphate (0.1 g) were added to the aqueous suspension which was then stirred magnetically until the aqueous layer was colourless (~1 h).

The yellow dichloromethane layer was separated, washed with water (2×100 ml) and dried over anhydrous sodium sulphate and filtered. The solvent was removed and the oily residue taken up in dichloromethane (3 ml) and carbon tetrachloride added to precipitate the complex. On standing yellow needles formed. The crystals were filtered off and washed with carbon tetrachloride/dichloromethane (90% v/v) and dried at 95°C under vacuum for 6 h. The yield was 0.02 g (3.17×10⁻⁵ mole, 17%) (Found: C, 24.62; H, 4.30; N, 9.12; S, 25.27. C₁₃H₂₆WN₄S₅O₃ requires C, 24.76; H, 4.16; N, 8.89; S, 25.42%).

3.2.14 Tetraethylammonium dicyanatobis(N,N-diethyldithiocarbamato)nitrosyltungstate

\[ \text{cis-[W(S₂CNEt₂)₂(0)₂]} (0.1 g, 1.85×10⁻³ mole) and potassium cyanate (0.1 g, 1.23×10⁻³ mole) were dissolved in dimethylsulphoxide (5 ml) and the reaction solution was irradiated for 10 h. A similar work-up procedure to that described in section 3.2.6 was used. The yield was 0.03 g
(4.13×10^{-5} \text{ mole}, 22\%) \text{ (Found: C, 32.92; H, 5.66; N, 11.74; S, 17.90. } \text{ C}_{20}\text{H}_{40}\text{WN}_6\text{S}_4\text{O}_3 \text{ requires C, 33.15; H, 5.56; N, 11.60; S, 17.70\%).}

The reaction may also be carried out in N,N-dimethylacetamide.

3.2.15 Cyanatobis(N,N-diethyldithiocarbamato)\textsuperscript{(N,N-dimethylacetamide)}nitrosyltungsten

\textit{cis-}[\text{W(NO)}_2(S_2CNET_2)_2] (0.1 g, \text{1.85x10^{-6} \text{ mole}}) and potassium cyanate (0.03 g, \text{3.7x10^{-4} \text{ mole}}) were dissolved in dimethylacetamide and irradiated for 7 h. The work-up procedure followed that described in section 3.2.13; N,N-dimethylacetamide being used in place of dimethylsulphoxide. The product was dried at room temperature, under vacuum, for 5 h yielding 0.029 g of product (3.8x10^{-5} \text{ mole}, 21\%). \text{ (Found: C, 25.04; H, 4.19; N, 8.8; S, 17.20; Cl, 14.75. } \text{ C}_{15.79}\text{H}_{29}\text{WN}_5\text{S}_4\text{O}_3\text{Cl}_{3.16} \text{ requires C, 24.95; H, 3.71; N, 9.22; S, 16.87; Cl, 14.74). The analysis was calculated for 0.79 molecules of carbon tetrachloride of crystallisation.}

3.2.16 Tetraethylammonium Diazidobis(N,N-diethyldithiocarbamato)\textsuperscript{(N,N-dimethylacetamide)}nitrosyltungstate

\textit{cis-}[\text{W(S}_2\text{CNET}_2)_2(\text{NO})_2] (0.1 g, \text{1.85x10^{-6} \text{ mole}}) and sodium azide (0.1 g, \text{1.54x10^{-3} \text{ mole}}) were dissolved in dimethylsulphoxide (5 ml). The solution was irradiated for 11.5 h. The work-up procedure followed that described in section 3.2.7. The yield of product was 0.037 g \text{ (Found: C, 30.63, 30.68; H, 5.49, 5.80; N, 19.02, 19.57; S, 16.94, 16.96; Cl, -, 0.46. } \text{ C}_{18}\text{H}_{40}\text{WN}_{10}\text{S}_4\text{O} \text{ requires }
C, 29.83; H, 5.56; N, 19.33; S, 17.70%). The two samples analysed were from independent preparations. The analysis gives the following atomic ratio:

\[
\begin{align*}
C : H : N : S : Cl \\
19.35 : 44 : 10.6 : 4 : 0.1
\end{align*}
\]

Both carbon and nitrogen are high and there is also a trace of CCl\(_4\) of crystallisation. The high carbon and nitrogen suggests coprecipitation of Et\(_4\)NN\(_3\).

For 0.15 Et\(_4\)NN\(_3\) and 0.025 CCl\(_4\) the calculated analysis is: C, 30.58; H, 5.75; N, 19.69; S, 17.01; Cl, 0.47.

3.2.17 Azidobis(N,N-diethyldithiocarbamato)(dimethylsulphoxide)nitrosyltungsten

\([Et_4N][W(N_3)_2(S_2CNEt_2)_2NO]\) (0.042 g) was dissolved in dimethylsulphoxide (10 ml) and water (20 ml) added. Sodium persulphate (0.1 g) and dichloromethane (10 ml) were then added and the solution was stirred until the aqueous layer was colourless. The dichloromethane phase was separated and washed with water (100 ml). After drying over anhydrous sodium sulphate, the solution was filtered and the solvent evaporated off. The oily residue was taken up in dichloromethane (2.5 ml) and carbon tetrachloride added to precipitate the complex. Yellow needles formed on standing. The product was filtered off and washed with carbon tetrachloride/dichloromethane (90% v/v) and dried (60°C, vac.). The yield was 0.02 g. (Found: C, 22.86; H, 4.45; N, 13.08; S, 25.67. \(C_{12}H_{26}WN_6S_5O_3\) requires C, 22.86; H, 4.16; N, 13.33; S, 25.42%). A sample not dried by heat was found to contain 1.07% Cl.
3.2.18 Tetraethylammonium Dithiocyanatobis(N,N-diethyl-dithiocarbamato)nitrosyltungstate

\[
cis-[W(S_2CNNEt_2)_2(NO)] (0.1 \text{ g, } 1.85 \times 10^{-4} \text{ mole}) \text{ and potassium thiocyanate (0.07 g, } 7.20 \times 10^{-4} \text{ mole) were dissolved in dimethylsulphoxide and the solution irradiated for 11 h. The product was isolated as described in section 3.2.6 and the yield was 0.03 g (3.93 \times 10^{-5} \text{ mole, } 21\%). A sample was recrystallised from carbon tetrachloride-dichloromethane and submitted for analysis. (Found: C, 31.24; H, 5.24; N, 10.89; S, 25.47; Cl, 0.70. }_{C_{20.04}H_{40}WN_6S_6OCl_{10.16}} \text{ requires C, 31.55; H, 5.29; N, 11.01; S, 25.21; Cl, 0.74). The analysis was calculated for 0.04 }_{CCl_4} \text{ of crystallisation.}
\]

3.3 N.M.R. Spectra

The proton n.m.r. spectra of the complexes prepared in section 3.2 have been summarised in Table 3.1. The instrumentation has been described in section 2.4.

3.4 Ir Spectra

The instrumentation and experimental techniques were as described in section 2.5.

3.4.1 Spectra in the 4000-650 cm\(^{-1}\) Region

Table 3.2 summarises some of the characteristic absorption bands observed in this region.
# Table 3.1

## N.m.r. Spectra

δ values ±0.02 ppm; correct proton counts were obtained in each case.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (δ±0.02 ppm)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MoNCO(S₂CNEt₂)₂(dmso)NO]²⁸</td>
<td>t 1.32, s 2.64, q 3.80</td>
<td>CH₃ of dtc, O-bonded dmso, CH₂ of dtc</td>
</tr>
<tr>
<td>[MoNCO(S₂CNEt₂)₂(dmso)NO]²⁸</td>
<td>t 1.32, s 2.64, s 2.53, q 3.80</td>
<td>CH₃ of dtc, O-bonded dmso, free dmso, CH₂ of dtc</td>
</tr>
<tr>
<td>[MoN₃(S₂CNEt₂)₂(dmso)NO]²⁸</td>
<td>pt 1.32, s 2.67, s 2.62, pq 3.82</td>
<td>CH₃ of dtc, O-bonded dmso, O-bonded dmso (?)</td>
</tr>
<tr>
<td>[Et₄N][Mo(NCO)₂(S₂CNEt₂)₂NO]²⁸</td>
<td>m 1.24, q 3.20, q 3.74</td>
<td>overlapping CH₃'s of Et₄N⁺ and dtc, CH₂ of Et₄N⁺, CH₂ of dtc</td>
</tr>
<tr>
<td>[Et₄N][Mo(N₃)₂(S₂CNEt₂)₂NO]²¹</td>
<td>m 1.33, q 3.39, q 3.85</td>
<td>overlapping CH₃'s of Et₄N⁺ and dtc, CH₂ of Et₄N⁺, CH₂ of dtc</td>
</tr>
<tr>
<td>[MoNCO(S₂CNMe₂)₂(dmso)NO]²⁸</td>
<td>s 2.63, s 2.51, ps 3.35</td>
<td>O-bonded dmso, free dmso, CH₃ of dtc</td>
</tr>
</tbody>
</table>

continued
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (±0.02 ppm)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Et}_4\text{N}])[Mo(NCO)(_2)(S(_2)CNMe(_2))(_2)NO](^C)</td>
<td>m 1.19</td>
<td>CH(_3) of \Et(_4\text{N})+</td>
</tr>
<tr>
<td></td>
<td>m 3.25</td>
<td>overlapping CH(_2) quarter of \Et(_4\text{N})+</td>
</tr>
<tr>
<td></td>
<td></td>
<td>and pair of CH(_3) singlets of dtc</td>
</tr>
<tr>
<td>([\text{Me}_4\text{N}])[Mo(NCO)(_2)(S(_2)CNMe(_2))(_2)NO](^B)</td>
<td>ps 3.29</td>
<td>CH(_3) of dtc</td>
</tr>
<tr>
<td></td>
<td>s 3.43</td>
<td>Me(_4\text{N})+</td>
</tr>
<tr>
<td>([\text{MoNCO}(S_2\text{CN}^{i}\text{Pr}_2)(_2(dmso)NO)](^A)</td>
<td>pd 1.49</td>
<td>(CH(_3))(_2) of dtc</td>
</tr>
<tr>
<td></td>
<td>s 2.68</td>
<td>0-bonded dmso</td>
</tr>
<tr>
<td></td>
<td>br.s 4.72</td>
<td>CH of dtc</td>
</tr>
<tr>
<td>([\text{Et}_4\text{N}])[Mo(NCO)(_2)(S(_2)CN^{i}\text{Pr}_2)(_2)NO](^B)</td>
<td>m 1.30</td>
<td>CH(_3) of \Et(_4\text{N})+</td>
</tr>
<tr>
<td></td>
<td>d 1.38</td>
<td>(CH(_3))(_2) of dtc</td>
</tr>
<tr>
<td></td>
<td>q 3.38</td>
<td>CH(_2) of \Et(_4\text{N})+</td>
</tr>
<tr>
<td></td>
<td>br.s 4.68</td>
<td>CH of dtc</td>
</tr>
<tr>
<td>([\text{WNCO}(S_2\text{CNEt}_2)(_2(dmso)NO)](^A)</td>
<td>t 1.33</td>
<td>CH(_3) of dtc</td>
</tr>
<tr>
<td></td>
<td>s 2.73</td>
<td>0-bonded dmso</td>
</tr>
<tr>
<td></td>
<td>q 3.74</td>
<td>CH(_2) of dtc</td>
</tr>
<tr>
<td>([\text{WN}_3(S_2\text{CNEt}_2)(_2(dmso)NO)](^A)</td>
<td>pt 1.28</td>
<td>CH(_3) of dtc</td>
</tr>
<tr>
<td></td>
<td>s 2.57(^D)</td>
<td>free dmso</td>
</tr>
<tr>
<td></td>
<td>s 2.71(^D)</td>
<td>0-bonded dmso</td>
</tr>
<tr>
<td></td>
<td>pq 3.71</td>
<td>CH(_2) of dtc</td>
</tr>
<tr>
<td>([\text{Et}_4\text{N}])[W(NCO)(_2)(S_2\text{CNEt}_2)(_2)NO](^B)</td>
<td>m 1.36</td>
<td>overlapping CH(_3)'s of \Et(_4\text{N})+ and dtc</td>
</tr>
<tr>
<td></td>
<td>q 3.50</td>
<td>CH(_2) of \Et(_4\text{N})+</td>
</tr>
<tr>
<td></td>
<td>q 3.75</td>
<td>CH(_2) of dtc</td>
</tr>
<tr>
<td>([\text{Et}_4\text{N}])[W(N_3)(_2)(S_2\text{CNEt}_2)(_2)NO](^A)</td>
<td>m 1.27</td>
<td>overlapping CH(_3)'s of \Et(_4\text{N})+ and dtc</td>
</tr>
<tr>
<td></td>
<td>q 3.35</td>
<td>CH(_2) of \Et(_4\text{N})+</td>
</tr>
<tr>
<td></td>
<td>q 3.70</td>
<td>CH(_2) of dtc</td>
</tr>
</tbody>
</table>

continued
Table 3.1 (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (δ±0.02 ppm)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Et₄N][W(NCS)₂(S₂CNET₂)₂NO]²⁺</td>
<td>m 1.38</td>
<td>overlapping CH₃'s of Et₄N⁺ and dtc</td>
</tr>
<tr>
<td></td>
<td>q 3.55</td>
<td>CH₂ of Et₄N⁺</td>
</tr>
<tr>
<td></td>
<td>q 3.81</td>
<td>CH₂ of dtc</td>
</tr>
<tr>
<td>[W(NCO)(S₂CNET₂)₂(dmac)NO]⁻</td>
<td>t 1.31</td>
<td>CH₃ of dtc</td>
</tr>
<tr>
<td></td>
<td>s (2.09, 3.04, 2.96)</td>
<td>free and coordinated dmac</td>
</tr>
<tr>
<td></td>
<td>s (2.28, 3.08)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>q 3.74</td>
<td>CH₂ of dtc</td>
</tr>
</tbody>
</table>

Abbreviations: See table 2.2 footnote; A = In CDCL₃; B = In (CD₃)₂CO; C = In (CD₃)₂SO; D = these two peaks gave a proton count of 6H.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$v_3 (N_3)$</th>
<th>$v_1 (NCO)$</th>
<th>$v_1 (NCS)$</th>
<th>$v (NO)$</th>
<th>$v (CN)^A$</th>
<th>$v (CS_2)^A$</th>
<th>$v (NC_2)^A$</th>
<th>$v (SO)^B$</th>
<th>$v_r (CH_3)^B$</th>
<th>OTHER BANDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{MoNCO} (S_2\text{CNET}_2) _2 (\text{dmso}) \text{NO}]$</td>
<td>-</td>
<td>2224s</td>
<td>-</td>
<td>1648s</td>
<td>1516s</td>
<td>1507s sh</td>
<td>996m</td>
<td>1152m</td>
<td>C</td>
<td>964m</td>
</tr>
<tr>
<td>$[\text{MoN}_3 (S_2\text{CNET}_2) _2 (\text{dmso}) \text{NO}]$</td>
<td>2049s</td>
<td>-</td>
<td>-</td>
<td>1648s</td>
<td>1515s</td>
<td>1505s sh</td>
<td>994m</td>
<td>1152m</td>
<td>C</td>
<td>952m</td>
</tr>
<tr>
<td>$[\text{Et}_4 \text{N}] [\text{Mo(NCO)} _2 (S_2\text{CNET}_2) _2 \text{NO}]$</td>
<td>-</td>
<td>2220s</td>
<td>-</td>
<td>1634s</td>
<td>1515s</td>
<td>1505s sh</td>
<td>1001m</td>
<td>1150m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Et}_4 \text{N}] [\text{Mo(N}_3) _2 (S_2\text{CNET}_2) _2 \text{NO}]$</td>
<td>2050s</td>
<td>-</td>
<td>-</td>
<td>1626s</td>
<td>1503s</td>
<td>1513s sh</td>
<td>1001m</td>
<td>1151m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{MoNCO} (S_2\text{CMMMe}_2) _2 (\text{dmso}) \text{NO}]$</td>
<td>-</td>
<td>2228s</td>
<td>-</td>
<td>1633s</td>
<td>1538s</td>
<td>992m</td>
<td>1158m</td>
<td>1024m</td>
<td>955m</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Et}_4 \text{N}] [\text{Mo(NCO)} _2 (S_2\text{CMMMe}_2) _2 \text{NO}]$</td>
<td>-</td>
<td>2220s</td>
<td>-</td>
<td>1634s</td>
<td>1539s</td>
<td>1000m</td>
<td>1148m</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Me}_4 \text{N}] [\text{Mo(NCO)} _2 (S_2\text{CMMMe}_2) _2 \text{NO}]$</td>
<td>-</td>
<td>2215s</td>
<td>-</td>
<td>1639s</td>
<td>1540s</td>
<td>1004m</td>
<td>1154m</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{MoNCO} (S_2\text{CN}^i\text{Pr}_2) _2 (\text{dmso}) \text{NO}]$</td>
<td>-</td>
<td>2225s</td>
<td>-</td>
<td>1647s</td>
<td>1494s</td>
<td>994m</td>
<td>1148m</td>
<td>1024m</td>
<td>957m</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Et}_4 \text{N}] [\text{Mo(NCO)} _2 (S_2\text{CN}^i\text{Pr}_2) _2 \text{NO}]$</td>
<td>-</td>
<td>2225s</td>
<td>-</td>
<td>1633s</td>
<td>1488s</td>
<td>1000m</td>
<td>1150m</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{WNCO} (S_2\text{CNET}_2) _2 (\text{dmso}) \text{NO}]$</td>
<td>-</td>
<td>2240s</td>
<td>-</td>
<td>1608s</td>
<td>1520s</td>
<td>1507s sh</td>
<td>989m</td>
<td>1151m</td>
<td>C</td>
<td>960m</td>
</tr>
<tr>
<td>$[\text{WN}_3 (S_2\text{CNET}_2) _2 (\text{dmso}) \text{NO}]$</td>
<td>2062s</td>
<td>-</td>
<td>-</td>
<td>1606s</td>
<td>1518s</td>
<td>1505s sh</td>
<td>986m</td>
<td>1152m</td>
<td>C</td>
<td>954m</td>
</tr>
</tbody>
</table>

continued
### Table 3.2 (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu_1(\text{N}_3))</th>
<th>(\nu_1(\text{NCO}))</th>
<th>(\nu_2(\text{NCS}))</th>
<th>(\nu(\text{NO}))</th>
<th>(\nu(\text{CN})^A)</th>
<th>(\nu(\text{CS}_2)^A)</th>
<th>(\nu(\text{NC}_2)^A)</th>
<th>(\nu(\text{SO})^B)</th>
<th>(\nu_r(\text{CH}_3)^B)</th>
<th>OTHER BANDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Et}_4\text{N}][\text{W(NCO)}_2(\text{S}_2\text{CNET}_2)_2\text{NO}])</td>
<td>-</td>
<td>2235s</td>
<td>-</td>
<td>1599s</td>
<td>1515s</td>
<td>1505sh</td>
<td>1002m</td>
<td>1152m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Et}_4\text{N}][\text{W(N}_3)_2(\text{S}_2\text{CNET}_2)_2\text{NO}])</td>
<td>2065s</td>
<td>-</td>
<td>-</td>
<td>1592s</td>
<td>1517s</td>
<td>1506sh</td>
<td>1001m</td>
<td>1151m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Et}_4\text{N}][\text{W(NCS)}_2(\text{S}_2\text{CNET}_2)_2\text{NO}])</td>
<td>-</td>
<td>-</td>
<td>2085s</td>
<td>1613s</td>
<td>1516s</td>
<td>1505sh</td>
<td>1003m</td>
<td>1151m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>([\text{WNCO}(\text{S}_2\text{CNET}_2)_2(\text{dmac})\text{NO}])</td>
<td>-</td>
<td>2240s</td>
<td>-</td>
<td>1604s</td>
<td>1514s</td>
<td>1505sh</td>
<td>1004sh</td>
<td>1152m</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

A In dithiocarbamate

B for dmsso

C Overlapping dithiocarbamate bands make assignment difficult.

D 2032 cm\(^{-1}\) and 2043 cm\(^{-1}\) for the complex prepared using \(^{15}\text{NN}_2\) labelled azide.
3.4.2 Far Infrared Spectra of Molybdenum Complexes (500-200 cm\(^{-1}\))

An exhaustive list of peaks in the 500-200 cm\(^{-1}\) region has been presented in Table 3.3 along with some tentative assignments. Some of the spectra have been reproduced in Figure 3.1.

**Table 3.3**

Far Infrared Spectra

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mo-S</th>
<th>Mo-OS(CH(_3))(_2)</th>
<th>Other bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MoNCO(S(_2)CNEt(_2))(_2) (dmos)NO]</td>
<td>367s</td>
<td>442s</td>
<td>487w, 480vw, 308m</td>
</tr>
<tr>
<td>[Mo(_3)(S(_2)CNEt(_2))(_2) (dmos)NO]</td>
<td>372s</td>
<td>447s</td>
<td>320m</td>
</tr>
<tr>
<td>[Et(_4)N] [Mo(NCO)(_2)(S(_2)CNEt(_2))(_2)NO]</td>
<td>364s</td>
<td>-</td>
<td>329w, 308w, 291w</td>
</tr>
<tr>
<td>[Et(_4)N] [Mo(N(_3))(_2)(S(_2)CNEt(_2))(_2)NO]</td>
<td>364s</td>
<td>-</td>
<td>327sh, 313m</td>
</tr>
<tr>
<td>[MoNCO(S(_2)CNMe(_2))(_2) (dmos)NO]</td>
<td>370s</td>
<td>446s(^{+})</td>
<td>304w, 280w, 255w, 224w</td>
</tr>
<tr>
<td>[Et(_4)N] [Mo(NCO)(_2)(S(_2)CNMe(_2))(_2)NO]</td>
<td>370s</td>
<td>-</td>
<td>452m, 422w, 318m, 285m, 255w</td>
</tr>
<tr>
<td>[Me(_4)N] [Mo(NCO)(_2)(S(_2)CNMe(_2))(_2)NO]</td>
<td>370s</td>
<td>-</td>
<td>456m, 420w, 313m, 287m, 256w</td>
</tr>
<tr>
<td>[MoNCO(S(_2)CN(_i)Pr(_2))(_2) (dmos)NO]</td>
<td>382s</td>
<td>445m</td>
<td>525vw, 473w, 340m, 326vw, 308m</td>
</tr>
<tr>
<td>[Et(_4)N] [Mo(NCO)(_2)(S(_2)CN(_i)Pr(_2))(_2)NO]</td>
<td>381s</td>
<td>368msh</td>
<td>475w, 330m</td>
</tr>
<tr>
<td>[Mo(S(_2)CNEt(_2))(_3)NO]</td>
<td>371sh</td>
<td>-</td>
<td>392m, 319w</td>
</tr>
</tbody>
</table>

\(^{+}\) Probably, this peak contains two absorption bands.

c/f [Me\(_4\)N]\(^{+}\) and [Et\(_4\)N]\(^{+}\) [Mo(NCO)\(_2\)(S\(_2\)CNMe\(_2\))\(_2\)NO]
Figure 3.1. Far Infrared Spectra of:

A = [MoNCO(S₂CNCH₂)₂(dmso)NO];
B = (Et₄N)[Mo(N₃)₂(S₂CNCH₂)₂NO];
C = [MoNCO(S₂CNEt₂)₂(dmso)NO];
D = (Et₄N)[Mo(NCO)₂(S₂CNEt₂)₂NO].

The top scale is in microns while the lower scale is in cm⁻¹.
3.4.3 $[\text{MoNCO(S}_2\text{CNEt}_2)_2\text{(dmsO)NO}]$ and $[\text{MoNCO(S}_2\text{CNEt}_2)_2\text{(dmsO)}^{15}\text{NO}]$

$[\text{MoNCO(S}_2\text{CNEt}_2)_2\text{(dmsO)NO}]$ was prepared as described in section 3.2.4, while $[\text{MoNCO(S}_2\text{CNEt}_2)_2\text{(dmsO)}^{15}\text{NO}]$ was prepared in a similar (but scaled down) manner from the reaction given in footnote (e) of Table 3.5.

Spectra in the range 4000-650 cm$^{-1}$ were recorded as KBr discs on a Unicam SP200G spectrophotometer. For the ranges 650-500 cm$^{-1}$ and 500-200 cm$^{-1}$ 1% CsI were employed and spectra were recorded on Grubb-Parsons DS4 and DM4 instruments respectively. Three bands were observed to shift upon isotopic N-15 substitution and these are listed in Table 3.4. In addition force constants for the Mo-N-O moiety have been calculated using the three-body model and valence force field approximation described by Herzberg. Although the separation of the Mo-N-O moiety from the rest of the molecule is not strictly correct, it has been shown to be a valid approximation. In addition errors of as much as 10° in the Mo-N-O bond angle and 0.1 Å in the bond lengths give rise to differences which are within the experimental uncertainties ($\pm$1 cm$^{-1}$).

The equations used for the calculation of force constants and expected frequencies are listed below in general form for the linear $xyz$ molecule.

$$\lambda_1 + \lambda_3 = 4\pi^2(\nu_1^2 + \nu_3^2) = k_1(1/m_x + 1/m_y) + k_2(1/m_y + 1/m_z)$$

$$\lambda_1\lambda_3 = 16\pi^4\nu_1^2\nu_3^2 = (m_x + m_y + m_z)k_1k_2/m_xm_ym_z$$

$$\lambda_2 = 4\pi^2\nu_2^2 = (\nu_1^2/m_z + \nu_2^2/m_x + (\nu_1\nu_2)^2/m_y)k_\delta/\nu_1^2\nu_2^2$$
where: \(v_1, v_2\) and \(v_3\) are the observed frequencies in cm\(^{-1}\) units.

\(\ell_1\) and \(\ell_2\) are the \(xy\) and \(yz\) bond lengths, respectively, in cm units.

\(k_1\) and \(k_2\) are the \(xy\) and \(yz\) bond force constants, respectively, in dyne/cm units.

\(k_0\) is the \(xyz\) bending force constant in dyne.cm/radian units.

\(m_x, m_y\) and \(m_z\) are the masses of atoms \(x, y\) and \(z\) respectively in grams.

For the Mo-N-O moiety, \(v_1\) corresponds to the Mo-N stretch, \(v_2\) to the MNO bending modes and \(v_3\) to the NO stretch. In addition, \(\ell_1\) equals the Mo-N bond length of 1.73 Å while \(\ell_2\) is the N-O bond length of 1.20 Å - see section 3.12.

Using the above equations and the observed frequencies, the force constants for both the labelled and unlabelled complexes have been calculated. The averaged force constants have been used to calculate the expected frequencies and these are compared to those observed (Table 3.4).

### Table 3.4

<table>
<thead>
<tr>
<th>MoNO Moieto</th>
<th>(v_1) (MoN)</th>
<th>(v_2) ((\delta)MoNO)</th>
<th>(v_3) (NO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{MoNCO(S}_2\text{CNEt}_2]_2(\text{dmsso})\text{NO}])</td>
<td>(14\text{N}^{15}\text{N})</td>
<td>(14\text{N}^{15}\text{N})</td>
<td>(14\text{N}^{15}\text{N})</td>
</tr>
<tr>
<td>Observed frequencies (cm(^{-1}))</td>
<td>623</td>
<td>581</td>
<td>1648</td>
</tr>
<tr>
<td>Calculated frequencies(^a) (cm(^{-1}))</td>
<td>622</td>
<td>582</td>
<td>1651</td>
</tr>
<tr>
<td>Calculated force constants ((\text{mdynes/Å}))</td>
<td>6.47</td>
<td>0.51(^b)</td>
<td>9.82</td>
</tr>
<tr>
<td>Averaged force constants ((\text{mdynes/Å}))</td>
<td>6.44</td>
<td>0.515</td>
<td>9.88</td>
</tr>
</tbody>
</table>

\(^a\) Using averaged force constants. \(^b\) \(k_0/\ell_1\ell_2\)
3.5 Labelling Experiments: Some Reactions Involving $[\text{Mo}(\text{S}_2\text{CNEt}_2)_2(^{15}\text{NO})_2]$ and $[\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]$ With Various Anions in Dimethylsulphoxide

The preparation of $[\text{Mo}(\text{S}_2\text{CNEt}_2)_2(^{15}\text{NO})_2]$ has been described in section 2.3.2 and its isotopic composition calculated in section 2.3.4.

The dimethylsulphoxide used in the reactions was distilled from calcium hydride and thoroughly degassed prior to use. The reactions described in this section were either carried out under vacuum or under nitric oxide (20 mm Hg); the one exception being reaction (6) of Table 3.5 which was done under dioxygen.

The nitric oxide was prepared as described in section 2.3 and freshly prepared samples contained no nitrogen dioxide and only a trace of dinitrogen oxide. The dioxygen was obtained directly from a cylinder.

Using vacuum line techniques, the gaseous reaction products were distilled into a vessel immersed in liquid dinitrogen. Prior to analysing the gases evolved on an A.E.I.-MS10-C2 mass spectrometer, the gas vessel was cooled to -76°C to freeze out a small amount of dimethylsulphoxide distillate. ($\text{N}_2\text{O}$, NO and NO$_2$ are not condensed at this temperature.) For reaction (6) of Table 3.5, the dioxygen was first pumped off - the reaction solution being frozen in liquid dinitrogen - and then the gaseous reaction products were analysed as described above.

3.5.1 Reactions with potassium cyanate at 60°C

In the reactions of $[\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]$ with potassium cyanate, dinitrogen oxide was the only gas evolved. Table
3.5 details the labelling experiments which were carried out on this reaction. Also included are a number of "blank reactions" relevant to the understanding of the reaction system.

For two of the reactions described in Table 3.5, the dinitrosyl complexes were recovered and their ir spectra recorded. The experimental procedures and results are now described:

**Reaction 3**

After heating for 12 h it was apparent from the colour of the reaction solution that a reasonable amount of starting material was present. That is, the nitric oxide (like O₂ - chapter 4) appears to be retarding the rate of reaction.

The solution was opened to the air and dichloromethane (20 ml) added. The dimethylsulphoxide was removed by washing with water (3×100 ml) and the resulting dichloromethane solution was dried over anhydrous sodium sulphate. After filtering the solution, the dichloromethane was evaporated off. The residue was taken up in chloroform (1-2 ml) and placed on an 18×0.5 cm silica-gel column (70-230 mesh) prepared using n-hexane and the dinitrosyl complex eluted with 1:1 n-hexane-chloroform. The product was collected, the solvent removed and the material recrystallised from methanol-water and dried over P₂O₅ under vacuum.

The infrared spectrum of the product showed that it consisted mainly of [Mo(S₂CNEt₂)₂(¹⁵NO)₂], but much weaker bands due to [Mo(S₂CNEt₂)₂(¹⁵NO)NO] and [Mo(S₂CNEt₂)₂(NO)₂] were also present. Hence under the reaction conditions a slow exchange of free with coordinated nitric oxide does occur.
Table 3.5
Reactions of \([\text{Mo(S}_2\text{CNET}_2\text{)}_2(\text{NO})_2]\) and \([\text{Mo(S}_2\text{CNET}_2\text{)}_2(\text{NO})_2]\) with Potassium Cyanate

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Quantities Used</th>
<th>Dinitrogen Oxide Evolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) ([\text{Mo(dtct)}_2(\text{NO})_2]) + KNCO</td>
<td>[Mo(dtct)_2(NO)_2]</td>
<td>[Mo(dtct)_2(NO)_2]</td>
</tr>
<tr>
<td>(2) ([\text{Mo(dtct)}_2(\text{NO})_2]) + ([\text{Mo(dtct)}_2(\text{NO})_2]) + KNCO</td>
<td>5 mg (1.1x10^-5 mole)</td>
<td>4.97 mg (1.1x10^-5 mole)</td>
</tr>
<tr>
<td>(3) ([\text{Mo(dtct)}_2(\text{NO})_2]) + KNCO under NO (20 mm Hg)</td>
<td>4.8 mg (1.05x10^-5 mole)</td>
<td>-</td>
</tr>
<tr>
<td>(4) KNCO under NO (20 mm Hg)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(5) ([\text{Mo(dtct)}_2(\text{NO})_2]) under NO (20 mm Hg)</td>
<td>5.6 mg (1.23x10^-5 mole)</td>
<td>-</td>
</tr>
<tr>
<td>(6) ([\text{Mo(dtct)}_2(\text{NO})_2]) + KNCO under dioxygen (300 mm Hg)</td>
<td>-</td>
<td>50 mg (1.1x10^-4 mole)</td>
</tr>
<tr>
<td>(7) ([\text{Mo(dtct)}_2(\text{NO})_2]) + ([\text{Mo(dtct)}_2(\text{NO})_2])</td>
<td>10 mg (2.2x10^-5 mole)</td>
<td>9.8 mg (2.16x10^-5 mole)</td>
</tr>
</tbody>
</table>

continued
Table 3.5 (continued)

<table>
<thead>
<tr>
<th>Reaction&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Quantities Used&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Dinitrogen Oxide Evolved&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>(8) [Mo(dtc)&lt;sub&gt;2&lt;/sub&gt;(&lt;sup&gt;15&lt;/sup&gt;NO)&lt;sub&gt;2&lt;/sub&gt;] + KNCO under &lt;sup&gt;15&lt;/sup&gt;N&lt;sub&gt;2&lt;/sub&gt;O (~2.13×10&lt;sup&gt;-5&lt;/sup&gt; mole) and &lt;sup&gt;15&lt;/sup&gt;NNO (~0.2×10&lt;sup&gt;-5&lt;/sup&gt; mole)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>[Mo(dtc)&lt;sub&gt;2&lt;/sub&gt;(&lt;sup&gt;15&lt;/sup&gt;NO)&lt;sub&gt;2&lt;/sub&gt;] - 20.3 mg (4.49×10&lt;sup&gt;-5&lt;/sup&gt; mole)</td>
<td>&lt;sup&gt;15&lt;/sup&gt;N&lt;sub&gt;2&lt;/sub&gt;O: &lt;sup&gt;15&lt;/sup&gt;NNO:N&lt;sub&gt;2&lt;/sub&gt;O&lt;sup&gt;c&lt;/sup&gt; 1:0.1:1 (1:0.1:1.1)</td>
</tr>
<tr>
<td></td>
<td>[Mo(dtc)&lt;sub&gt;2&lt;/sub&gt;(NO)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>KNCO 7.7 mg (9.5×10&lt;sup&gt;-5&lt;/sup&gt; mole)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction time 12-14 h.; dtc = S<sub>2</sub>CNEt<sub>2</sub>

<sup>b</sup> In dimethylsulphoxide (3 ml).

<sup>c</sup> Observed ratios with calculated ratios in parentheses (see section 3.6).

<sup>d</sup> This result confirms that the labelled complex contains 95% <sup>15</sup>N. The high amount of "N<sub>2</sub>O" is probably due to a trace of CO<sub>2</sub> (NCO<sup>-</sup> + H<sub>2</sub>O <sup>dmsO</sup> NH<sub>3</sub> + CO<sub>2</sub>) which also has m/e 44.

<sup>e</sup> Prepared by reacting [Mo(dtc)<sub>2</sub>(<sup>15</sup>NO)<sub>2</sub>] (21.3 mg, 4.68×10<sup>-5</sup> mole) and KNCO (7.7 mg, 9.49×10<sup>-5</sup> mole) in dmso (3 ml). The dinitrogen oxide evolved was transferred using vacuum line techniques to the reaction vessel for (8).
Reaction 7

The dinitrosyl complexes were recovered as follows: Dichloromethane (10 ml) was added to the reaction solution and the dimethylsulphoxide was removed by washing with water (3×50 ml). The dichloromethane was evaporated off and the product recrystallised from methanol-water and dried over $\text{P}_2\text{O}_5$ under vacuum.

The nitrosyl region of the infrared spectrum of the product is shown in Figure 3.2. Clearly no scrambling of the nitrosyl groups occurs under the reaction conditions (c/f Figure 2.8).

3.5.2 Reactions with Sodium Azide at 60°C

The reaction of [Mo(S$_2$CNEt$_2$)$_2$(NO)$_2$] with $^{15}$N$_2$N$^-$ labelled azide has already been reported to give unlabelled dinitrogen oxide$^{128}$. Labelling studies similar to those for cyanate are described in Table 3.6.

3.5.3 Reactions with NaS$_2$CNEt$_2$.3H$_2$O at 70°C

[Mo(S$_2$CNEt$_2$)$_2$(NO)$_2$] was found to react with NaS$_2$CNEt$_2$.3H$_2$O at 70°C in dimethylsulphoxide to give, *inter alia*, dinitrogen oxide and the known complex [Mo(S$_2$CNEt$_3$)$_3$NO]$^{94}$. The labelling experiments carried out are summarised in Table 3.7.

3.5.4 Reactions with Potassium Cyanide at Room Temperature (-22°C)

The reaction of [Mo(S$_2$CNEt$_2$)$_2$(NO)$_2$] with cyanide gave dinitrogen oxide and what appeared to be a mixture of yellow
Figure 3.2. Infrared Spectrum of the product from the reaction:

\[
\text{dms} \quad \text{[Mo(S\text{\textsubscript{2}}\text{CNEt}\text{\textsubscript{2}})(\text{NO})\text{\textsubscript{2}}] + [Mo(S\text{\textsubscript{2}}\text{CNEt}\text{\textsubscript{2}})(^{15}\text{NO})\text{\textsubscript{2}}]} \rightarrow \text{60°C} \quad \text{12 hr.}
\]
Table 3.6
Reactions of \([\text{Mo(S}_2\text{CNET}_2\text{)}_2 (^{15}\text{NO})_2]\) and \([\text{Mo(S}_2\text{CNET}_2\text{)}_2 (\text{NO})_2]\) with Sodium Azide

<table>
<thead>
<tr>
<th>Reaction(^a)</th>
<th>Quantities Used(^b)</th>
<th>Dinitrogen Oxide Evolved (^{15}\text{N}_2\text{O}:^{15}\text{NNO}:\text{N}_2\text{O})(^c)</th>
</tr>
</thead>
</table>
| (1) \([\text{Mo(dtc)}_2 (^{15}\text{NO})_2]\) + \([\text{Mo(dtc)}_2 (\text{NO})_2]\) + \(\text{NaN}_3\) | \[\begin{array}{c}
3.56 \text{ mg} \\
(7.84 \times 10^{-6} \text{ mole})
\end{array}\] \[\begin{array}{c}
3.54 \text{ mg} \\
(7.82 \times 10^{-6} \text{ mole})
\end{array}\] \[3 \text{ mg} \\
(4.61 \times 10^{-6} \text{ mole})\] | 1:2.1:1.1 \(\text{(1:2.2:1.2)}\) |
| (2) \([\text{Mo(dtc)}_2 (^{15}\text{NO})_2]\) + \(\text{NaN}_3\) under \(\text{NO (20 mm Hg)}\) | \[6.9 \text{ mg} \\
(1.52 \times 10^{-6} \text{ mole})\] \(-\) \[3.2 \text{ mg} \\
(4.92 \times 10^{-6} \text{ mole})\] | 1:0.84:0.2 |
| (3) \(\text{NaN}_3\) under \(\text{NO (20 mm Hg)}\) | \(-\) \(-\) \[3 \text{ mg} \\
(4.61 \times 10^{-6} \text{ mole})\] | Trace \(\text{N}_2\text{O}\) |

\(^a\) Reaction time 12-14 h; dtc = \(\text{S}_2\text{CNET}_2^-\)

\(^b\) In dimethylsulphoxide (3 ml)

\(^c\) Observed ratios with calculated ratios in parentheses (see section 3.6).
Table 3.7
Reactions of \([\text{Mo}(\text{S}_2\text{CNET})_2]^{[15}\text{NO}]_2\) and \([\text{Mo}(\text{S}_2\text{CNET})_2]^{(\text{NO})}_2\) with \(\text{NaS}_2\text{CNET}_2\cdot 3\text{H}_2\text{O}\)

<table>
<thead>
<tr>
<th>Reaction(^a)</th>
<th>Quantities Used(^b)</th>
<th>Dinitrogen Oxide Evolved</th>
<th>(^{15}\text{N}_2\text{O}:^{15}\text{NO}:\text{N}_2\text{O})(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) ([\text{Mo}(\text{dtc})_2]^{(\text{NO})}_2) + (\text{NaS}_2\text{CNET}_2\cdot 3\text{H}_2\text{O})</td>
<td>([\text{Mo}(\text{dtc})_2]^{[15}\text{NO}]_2)</td>
<td>([\text{Mo}(\text{dtc})_2]^{(\text{NO})}_2)</td>
<td>(\text{NaS}_2\text{CNET}_2\cdot 3\text{H}_2\text{O})</td>
</tr>
<tr>
<td>(2) ([\text{Mo}(\text{dtc})_2]^{[15}\text{NO}]_2) + ([\text{Mo}(\text{dtc})_2]^{(\text{NO})}_2) + (\text{NaS}_2\text{CNET}_2\cdot 3\text{H}_2\text{O})</td>
<td>6.96 mg (1.53\times 10^{-5} \text{ mole})</td>
<td>6.97 mg (1.54\times 10^{-5} \text{ mole})</td>
<td>68.9 mg (3.06\times 10^{-4} \text{ mole})</td>
</tr>
<tr>
<td>(3) ([\text{Mo}(\text{dtc})_2]^{[15}\text{NO}]_2) + (\text{NaS}_2\text{CNET}_2\cdot 3\text{H}_2\text{O}) under NO (20 mm Hg)</td>
<td>5 mg (1.1\times 10^{-5} \text{ mole})</td>
<td>-</td>
<td>54.7 mg (2.43\times 10^{-4} \text{ mole})</td>
</tr>
</tbody>
</table>

\(^a\) Reaction time 12-14 h; dtc = \(\text{S}_2\text{CNET}_2\)\(^-\)

\(^b\) In dimethylsulphoxide (3 ml)

\(^c\) Observed ratios with calculated ratios in parentheses (see section 3.6).
mononitrosyl dithiocarbamate complexes. The infrared spectrum of the material isolated, showed a strong band at ~1630 cm\(^{-1}\) and the expected dithiocarbamate modes. But surprisingly, only a weak peak was found in the 2000 cm\(^{-1}\) region at ~2160 cm\(^{-1}\) and this is probably due to a minor cyanide containing product.

The labelling experiments carried out are listed in Table 3.8.

3.6 The calculation of the isotopic \(^{15}\text{N}\) distribution in the dinitrogen oxide evolved from the reactions of [Mo(S\(_2\)CNEt\(_2\))\(_2\)(\(^{15}\text{NO})\(_2\))] and [Mo(S\(_2\)CNEt\(_2\))\(_2\)(NO)\(_2\)] with various anions

In the calculations it is assumed that one nitrosyl group per molecule reacts via an associative mechanism to give dinitrogen oxide. A combination of two molecules of dinitrosyl complex has four "sub-combinations" for the production of dinitrogen oxide and the various possibilities are given in Table 3.9.

Let the respective mole fractions of [Mo(S\(_2\)CNEt\(_2\))\(_2\)(\(^{15}\text{NO})\(_2\))] , [Mo(S\(_2\)CNEt\(_2\))\(_2\)(\(^{15}\text{NO} \text{NO})\)] and [Mo(S\(_2\)CNEt\(_2\))\(_2\)(\text{NO})\(_2\)] be 'a', 'b' and 'c'. In Table 3.10 the number of combinations giving rise to \(^{15}\text{N}_2\text{O}, \(^{15}\text{NNO}\) and \(\text{N}_2\text{O}\) are calculated and these are assumed to be proportional to their respective probabilities of formation. A ratio relative to \(^{15}\text{N}_2\text{O}\) is then taken.

For the calculated ratios of \(^{15}\text{N}_2\text{O}:^{15}\text{NNO:N}_2\text{O}\) appearing in Tables 3.5-3.8, the appropriate mole fractions (a, b and c) were inserted into the formulae given in Table 3.10.
<table>
<thead>
<tr>
<th>Reaction(^a)</th>
<th>Quantities Used(^b)</th>
<th>Dinitrogen Oxide Evolved</th>
<th>(^{15}N_2O:^{15}NNO:N_2O(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) [Mo(dtc)(_2)(NO)(_2)] + KCN</td>
<td>-</td>
<td>-</td>
<td>N(_2O) evolved</td>
</tr>
<tr>
<td>(2) [Mo(dtc)(_2)((^{15})NO)(_2)] + [Mo(dtc)(_2)(NO)(_2)] + KCN</td>
<td>5.07 mg (1.12×10(^{-5}) mole)</td>
<td>6.07 mg (1.34×10(^{-5}) mole)</td>
<td>6 mg (9.21×10(^{-6}) mole)</td>
</tr>
<tr>
<td>(3) [Mo(dtc)(_2)((^{15})NO)(_2)] + KCN under NO (20 mm Hg)</td>
<td>5.2 mg (1.14×10(^{-5}) mole)</td>
<td>-</td>
<td>6.6 mg (1.01×10(^{-6}) mole)</td>
</tr>
<tr>
<td>(4) KCN under NO (20 mm Hg)</td>
<td>-</td>
<td>-</td>
<td>8.4 mg (1.29×10(^{-6}) mole)</td>
</tr>
</tbody>
</table>

\(^a\) Reaction time 2-3 hrs; dtc = S\(_2\)CNET\(_2\)\(^-\)

\(^b\) In dimethylsulphoxide (3 ml)

\(^c\) Observed ratios with calculated ratios in parentheses (see section 3.6)

\(^d\) This presumably comes from the reaction CN\(^-\) + 2NO → N\(_2O\) + NCO\(^-\)
Table 3.9

Various combinations and sub-combinations to give Dinitrogen Oxide

<table>
<thead>
<tr>
<th>Combination</th>
<th>&quot;Sub-combinations&quot; resulting in:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{15}\text{N}_2\text{O}$</td>
</tr>
<tr>
<td>Mo $^{15}\text{NO}$ ON $^{15}\text{Mo}$</td>
<td>4</td>
</tr>
<tr>
<td>Mo $^{15}\text{NO}$ ON $^{15}\text{Mo}$</td>
<td>-</td>
</tr>
<tr>
<td>Mo $^{15}\text{NO}$ ON $^{15}\text{Mo}$</td>
<td>-</td>
</tr>
<tr>
<td>Mo $^{15}\text{NO}$ ON $^{15}\text{Mo}$</td>
<td>2</td>
</tr>
<tr>
<td>Mo $^{15}\text{NO}$ ON $^{15}\text{Mo}$</td>
<td>-</td>
</tr>
<tr>
<td>Mo $^{15}\text{NO}$ ON $^{15}\text{Mo}$</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 3.10

The Calculation of the Ratio $^{15}\text{N}_2\text{O}:^{15}\text{NNO}:\text{N}_2\text{O}$

<table>
<thead>
<tr>
<th></th>
<th>$^{15}\text{N}_2\text{O}$</th>
<th>$^{15}\text{NNO}$</th>
<th>$\text{N}_2\text{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of</td>
<td>$4(axC_2)+bxC_2+2abx^2$</td>
<td>$2(bxC_2)+2abx^2+2bcx^2+4acx^2$</td>
<td>$bxC_2+4(cxC_2)+2bcx^2$</td>
</tr>
<tr>
<td>Combinations$^a$</td>
<td>$x^2(2a^2+2ab+b^2/2)$</td>
<td>$x^2(b^2+2ab+2bc+4ac)$</td>
<td>$x^2(b^2/2+2c^2+2bc)$</td>
</tr>
<tr>
<td>Ratio $^{15}\text{N}_2\text{O}:^{15}\text{NNO}:\text{N}_2\text{O}$</td>
<td>1</td>
<td>$b^2+2ab+2bc+4ac$</td>
<td>$b^2/2+2c^2+2bc$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2a^2+2ab+b^2/2$</td>
<td>$2a^2+2ab+b^2/2$</td>
</tr>
</tbody>
</table>

$^a$ $x$ = Total number of molecules of dinitrosyl complex present;

$yx^2 = \frac{(yx)(yx-1)}{2} = \frac{y^2x^2}{2}$ for $x$ very large ($y = a, b$ or $c$).
3.7 The Measurement of the Volume of Dinitrogen Oxide Evolved in the Reaction of [Mo(S₂CNEt₂)₂(NO)₂] with Potassium Cyanate

The determination of the volume of dinitrogen oxide evolved was made in duplicate using a thermostatted gas burette system operated under vacuum.† Table 3.11 gives the quantities of reactants used.

Table 3.11
Details of the Reaction Solutions

<table>
<thead>
<tr>
<th></th>
<th>Weight of [Mo(S₂CNEt₂)₂(NO)₂]</th>
<th>Weight of KNCO</th>
<th>Volume of dmsO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number 1</td>
<td>0.2000 g (4.423x10⁻⁴ mole)</td>
<td>0.0726 g (8.950x10⁻⁴ mole)</td>
<td>5 ml</td>
</tr>
<tr>
<td>Number 2</td>
<td>0.2012 g (4.449x10⁻⁴ mole)</td>
<td>0.0729 g (8.987x10⁻⁴ mole)</td>
<td>6 ml</td>
</tr>
</tbody>
</table>

The reaction solutions were thoroughly degassed and then heated at 60°C for 13 hr. The dinitrogen oxide evolved was transferred on a vacuum line by eight applications of a freeze (pentane slush, -130°C)-distill-thaw cycle into a vessel cooled to -176°C.

The gas vessel was connected to the left arm of the burette and then both arms were evacuated. After isolating the left arm from the pump, the gas vessel was opened and the

† Details of the design and use of the gas burette system were provided by Dr. A. Diamantis of the University of Adelaide.
pressure head due to the dinitrogen oxide measured using a cathetometer.

The volume occupied by the dinitrogen oxide is equal to $B_L + V_0$, where $V_0$ is the volume of the apparatus (including gas vessel) to the zero mark of the left burette and $B_L$ is the left burette reading. $V_0$ was determined at atmospheric pressure (right-hand burette open to the air) by trapping a volume of air in the left side of the apparatus and expanding this volume by lowering the mercury reservoir. Then $V_0$ is given by the formula:

$$V_0 = \frac{P(B_f - B_i)}{h} - B_f$$

where $B_i, B_f = \text{initial and final readings respectively of the left burette; } P = \text{atmospheric pressure (in mm) } h = \text{pressure head of mercury (in mm)}$. The details of the measurements are summarised in Table 3.12.

### Table 3.12

<table>
<thead>
<tr>
<th>Measurements for the Volume of Dinitrogen Oxide at 24.3°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Number 1</strong></td>
</tr>
<tr>
<td>(a) Determination of $V_0$</td>
</tr>
<tr>
<td>(b) Volume of $N_2O$</td>
</tr>
<tr>
<td>$B_L$</td>
</tr>
<tr>
<td>$P_{N_2O} = h$</td>
</tr>
<tr>
<td>$V_{N_2O} = B_L + V_0$</td>
</tr>
<tr>
<td>moles of $N_2O = \frac{P_{N_2O} \cdot V_{N_2O}}{RT}$</td>
</tr>
<tr>
<td>% $N_2O$ evolved based on $[\text{Mo(S}_2\text{CNET}_2\text{)}_2(\text{NO})_2]$</td>
</tr>
</tbody>
</table>
3.8 A Molybdenum Balance

In the preparation of [MoNCO(S₂CNEt₂)₂(dmso)NO] described in section 3.2.4, various products were obtained. The preparative reaction was repeated according to the following and the products analysed for their Mo content.

[Mo(S₂CNEt₂)₂(NO)₂] (0.1998 g, 4.418×10⁻⁴ mole) and potassium cyanate (0.089 g, 9.86×10⁻⁴ mole) were dissolved in dimethylsulphoxide (6 ml) and the solution degassed. The reaction was completed by heating at 60°C for 12 h, in the dark. On cooling to room temperature, the reaction vessel was opened to the air and dichloromethane (20 ml) added. The brown precipitate which formed was collected by filtration through a sintered glass funnel (porosity 4) and washed with dichloromethane (3×1 ml). This product will be referred to as fraction A.

The filtrate (plus washings) was placed in a separating funnel and water (40 ml) was added. A yellow species was extracted into the water. After gently swirling the two layers for a few minutes, the lower dichloromethane phase was removed and the solvent evaporated off. The residue obtained will be termed fraction B.

Dichloromethane (40 ml), dimethylsulphoxide (10 ml) and sodium persulphate (0.2 g) were added to the aqueous suspension and the mixture was stirred magnetically until the aqueous layer was colourless (~1 h). The dichloromethane phase was separated, washed with water (50 ml) and the solvent evaporated off. The remaining residue - fraction C - consists of impure [MoNCO(S₂CNEt₂)₂(dmso)NO].
Aqua-regia (10 ml) was added to each of the fractions A, B and C and the solutions were evaporated to near dryness. The Mo content was then determined gravimetrically by precipitation with 8-hydroxyquinoline\textsuperscript{119}. The results given below are expressed as percentages of the total Mo present.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>% Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (brown precipitate)</td>
<td>18.1</td>
</tr>
<tr>
<td>B (dichloromethane phase)</td>
<td>33.5</td>
</tr>
<tr>
<td>C (aqueous extract)</td>
<td>47.4</td>
</tr>
</tbody>
</table>

Total Mo accounted for = 99.0%

3.9 Substitution Reactions Involving [MoNCO(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{2}(dmso)NO]

[MoNCO(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{2}(dmso)NO] was found to undergo a variety of substitution reactions in which the dimethylsulphoxide is replaced. This section describes the preparations of the substitution products and their ir and 'H nmr spectra.

3.9.1 Tetraethylammonium Cyanatoazidobis(N,N-diethylthiocarbamato)nitrosylmolybdate

A mixture of [MoNCO(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{2}(dmso)NO] (0.08 g, 1.47×10\textsuperscript{-5} mole) and sodium azide (0.1 g, 1.54×10\textsuperscript{-3} mole) in dimethylsulphoxide (3 ml) was stirred for 10 minutes. Dichloromethane (30 ml) was added and the precipitated NaN\textsubscript{3} filtered off. The solution was washed with aqueous tetraethylammonium chloride (1 g Et\textsubscript{4}NCl.H\textsubscript{2}O in 30 ml of H\textsubscript{2}O) and dried over anhydrous sodium sulphate. After filtering, carbon tetrachloride was added to deposit a yellow crystalline
product which was filtered off, washed with carbon tetrachloride-dichloromethane (90% v/v) and dried at room temperature under vacuum. The yield was 0.059 g (63%).

(Found: C, 36.16; H, 6.53; N, 17.94; S, 19.74. \( \text{C}_{19}\text{H}_{49}\text{MoN}_{8}\text{S}_{4}\text{O}_{2} \) requires C, 35.84; H, 6.33; N, 17.60; S, 20.14%).

3.9.2 Tetraethylammonium Cyanatothiocyanatobis(N,N-diethyl-dithiocarbamato)nitrosylmolybdate

To a solution of [MoNCO(S\(_2\text{CNET}_2\)]\(_2\)(dms)NO] (0.09 g, 1.66\times10^{-5} \text{ mole}) in dimethylsulphoxide (3 ml) was added potassium thiocyanate (0.06 g, 6.17\times10^{-4} \text{ mole}) and the mixture was stirred for 10 minutes. The product was isolated as described in section 3.9.1. (Found: C, 37.07; H, 6.10; N, 12.90; S, 24.48. \( \text{C}_{20}\text{H}_{40}\text{MoN}_{5}\text{S}_{5}\text{O}_{2} \) requires C, 36.79; H, 6.18; N, 12.88; S, 24.56%).

3.9.3 Tetraethylammonium Cyanatochlorobis(N,N-diethyl-dithiocarbamato)nitrosylmolybdate Hemihydrate

Tetraethylammonium chloride monohydrate (0.030 g, 1.63\times10^{-4} \text{ mole}) was added to a solution of [MoNCO(S\(_2\text{CNET}_2\)]\(_2\)(dms)NO] in dichloromethane (15 ml) and the mixture was stirred until the solid had dissolved. The solution was filtered and carbon tetrachloride added to deposit a yellow crystalline product. This was filtered off, washed with carbon tetrachloride-dichloromethane (90% v/v) and dried at room temperature under vacuum. (Found: C, 35.63; H, 6.33; N, 10.92; S, 20.23; Cl, 5.66. \( \text{C}_{19}\text{H}_{41}\text{MoN}_{5}\text{S}_{4}\text{O}_{2} \cdot \text{SCl} \) requires C, 35.70; H, 6.47; N, 10.96; S, 20.06; Cl, 5.55%).
3.9.4 Cyanatobis(N,N-diethylthiocarbamato)amminenitrosylmolybdenum

\[\text{MoNCO(S}_2\text{CNEt}_2\text{)}_2(\text{dmsO})\text{NO}}\] (ca 0.1 g) was dissolved in dichloromethane (3 ml) and ammonia bubbled through the solution for about 1 minute. The solution was filtered and carbon tetrachloride added to deposit a yellow crystalline complex. The product was filtered off, washed with carbon tetrachloride-dichloromethane (90% v/v) and dried at room temperature under vacuum. (Found: C, 27.10; H, 4.85; N, 14.58; S, 26.62. \(\text{C}_{11}\text{H}_{23}\text{MoN}_{5}\text{S}_{4}\text{O}_{2}\) requires C, 27.44; H, 4.81; N, 14.55; S, 26.63%).

3.9.5 \(\mu\)-Hydrazinebis{cyanatobis(N,N-diethylthiocarbamato)nitrosylmolybdenum}

A solution of hydrazine in dichloromethane was prepared as follows: Hydrazine hydrate (0.1 g, \(\approx 2\times10^{-3}\) mole) was added to dichloromethane (10 ml) and the solution was dried over anhydrous sodium sulphate.

The hydrazine solution (1 ml, \(\approx 2\times10^{-4}\) mole) was added dropwise to a stirred dichloromethane solution of \[\text{MoNCO(S}_2\text{CNEt}_2\text{)}_2(\text{dmsO})\text{NO}}\] (0.11 g, \(2\times10^{-4}\) mole; in 2 ml \(\text{CH}_2\text{Cl}_2\)). The resulting solution was filtered and carbon tetrachloride added to give a yellow crystalline material. This was filtered off and washed with carbon tetrachloride-dichloromethane (90% v/v). The material was dried at room temperature under vacuum. (Found: C, 25.89; H, 4.56; N, 13.50; S, 24.88; Cl, 6.59. \(\text{C}_{22.5}\text{H}_{44}\text{Mo}_2\text{N}_{10}\text{S}_{8}\text{O}_{4}\text{Cl}_2\) requires C, 26.04; H, 4.27; N, 13.50; S, 24.71; Cl, 6.83%). The analysis was calculated for 0.5 molecules of carbon tetrachloride of crystallisation.
3.9.6 Cyanatobis(N,N-diethylidithiocarbamato)pyridinenitrosyl-
molybdenum

\[
[\text{MoNCO(S}_2\text{CNET}_2\text{)}_2(\text{dms})\text{NO}] \quad (0.1 \text{ g, } 1.84 \times 10^{-4} \text{ mole})
\]
dissolved in dichloromethane (3 ml) and pyridine (0.05 g, 
\[6.3 \times 10^{-4} \text{ mole})
\] was added. The solution was filtered and on
addition of carbon tetrachloride, a yellow crystalline
compound was obtained. This was filtered off and washed
with carbon tetrachloride-dichloromethane (90% v/v) and
dried at room temperature under vacuum. (Found: C, 34.95;
H, 5.17; N, 12.74; S, 23.23; Cl, 1.22. \(C_{16.85}H_{25}MoN_{5}S_{4}O_{2}Cl_{0.2}\)
requires C, 34.97; H, 4.57; N, 12.71; S, 23.26; Cl, 1.29%).
The analysis was calculated for 0.05 molecules of carbon
tetrachloride of crystallisation.

3.10 Infrared Spectra of the Substitution Products of
[MoNCO(S₂CNET₂)₂(dms)NO]

The infrared spectral data for the complexes prepared
in section 3.9 has been summarised in Table 3.13.

3.11 The 'H NMR Spectra of the Substitution Products of
[MoNCO(S₂CNET₂)₂(dms)NO]

The details of the 'H nmr spectra of the complexes
described in section 3.9 are given in Table 3.14.

3.12 The Crystal Structure of [MoNCO(S₂CNET₂)₂(dms)NO]

The crystallographic work on [MoNCO(S₂CNET₂)₂(dms)NO]
was carried out by Dr. M. Sterns of the Department of
Chemistry, Australian National University, Canberra.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_1$(NCO)</th>
<th>$\nu_3$(N$_3$)</th>
<th>$\nu$(NCS)</th>
<th>$\nu$(NO)</th>
<th>$\nu$(CN)$^b$</th>
<th>$\nu$(NH)</th>
<th>$\nu$(NC$_2$)</th>
<th>$\nu$(CS$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Et}_4\text{N}][\text{MoN}_3(\text{NCO})(\text{S}_2\text{CNET}_2)_2\text{NO}]$</td>
<td>2215s</td>
<td>2050s</td>
<td>-</td>
<td>1630s</td>
<td>1505sh 1515s</td>
<td>-</td>
<td>1152m</td>
<td>1001m</td>
</tr>
<tr>
<td>$[\text{Et}_4\text{N}][\text{Mo(}\text{NCO})(\text{NCS})(\text{S}_2\text{CNET}_2)_2\text{NO}]$</td>
<td>2220s</td>
<td>-</td>
<td>2090s</td>
<td>1641s</td>
<td>1505sh 1515s</td>
<td>-</td>
<td>1152m</td>
<td>1000m</td>
</tr>
<tr>
<td>$[\text{Et}_4\text{N}][\text{Mo(}\text{NCO})\text{Cl}(\text{S}_2\text{CNET}_2)_2\text{NO}]$</td>
<td>2225s</td>
<td>-</td>
<td>-</td>
<td>1633s</td>
<td>1505s</td>
<td>-</td>
<td>1150m</td>
<td>1004m</td>
</tr>
<tr>
<td>$[\text{MoNCO(}\text{S}_2\text{CNET}_2)(\text{NH}_3)\text{NO}]$</td>
<td>2230s</td>
<td>-</td>
<td>-</td>
<td>1645s</td>
<td>1505sh 1515s</td>
<td>3333m 3242m 3196w 3164w</td>
<td>1152m</td>
<td>1014m</td>
</tr>
<tr>
<td>$[\text{MoNCO(}\text{S}_2\text{CNET}_2)_2\text{NO}]-\mu-\text{N}_2\text{H}_4$</td>
<td>2220s</td>
<td>-</td>
<td>-</td>
<td>1661s</td>
<td>1519s</td>
<td>3291w 3278w 3213w 3140vw</td>
<td>1153m</td>
<td>1014m</td>
</tr>
<tr>
<td>$[\text{MoNCO(}\text{S}_2\text{CNET}_2)_2\text{PyNO}]$</td>
<td>2210s</td>
<td>-</td>
<td>-</td>
<td>1651s</td>
<td>1505sh 1517s</td>
<td>-</td>
<td>1151m</td>
<td>1013m</td>
</tr>
</tbody>
</table>

---

**Table 3.13**

**Infrared Data (cm$^{-1}$)$^a$**

---

a As KBr Discs; See section 2.5.1 for the instrumentation used.

b In dithiocarbamate.
Table 3.14
'H NMR Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (δ±0.02 ppm)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Et₄N][MoN₃(NCO)(S₂CNET₂)₂NO]ᵇ</td>
<td>m 1.32</td>
<td>overlapping CH₃'s of Et₄N⁺ and dtc</td>
</tr>
<tr>
<td></td>
<td>q 3.45</td>
<td>CH₂ of Et₄N⁺</td>
</tr>
<tr>
<td></td>
<td>q 3.77</td>
<td>CH₂ of dtc</td>
</tr>
<tr>
<td>[Et₄N][MoNCO(NCS)(S₂CNET₂)₂NO]ᵇ</td>
<td>m 1.35</td>
<td>overlapping CH₃'s of Et₄N⁺ and dtc</td>
</tr>
<tr>
<td></td>
<td>q 3.50</td>
<td>CH₂ of Et₄N⁺</td>
</tr>
<tr>
<td></td>
<td>q 3.82</td>
<td>CH₂ of dtc</td>
</tr>
<tr>
<td>[Et₄N][Mo(NCO)Cl(S₂CNET₂)₂NO]ᵃ</td>
<td>m 1.32</td>
<td>overlapping CH₃'s of Et₄N⁺ and dtc</td>
</tr>
<tr>
<td></td>
<td>q 3.39</td>
<td>CH₂ of Et₄N⁺</td>
</tr>
<tr>
<td></td>
<td>q 3.81</td>
<td>CH₂ of dtc</td>
</tr>
<tr>
<td></td>
<td>s 1.84</td>
<td>H₂O (position concentration dependent)</td>
</tr>
<tr>
<td>[MoNCO(S₂CNET₂)₂(NH₃)NO]ᶜ</td>
<td>t 1.26</td>
<td>CH₃ of dtc</td>
</tr>
<tr>
<td></td>
<td>s 2.22</td>
<td>NH₃</td>
</tr>
<tr>
<td></td>
<td>q 3.80</td>
<td>CH₂ of dtc</td>
</tr>
<tr>
<td>[MoNCO(S₂CNET₂)₂NO]₂N₂H₄ᶜ</td>
<td>t 1.27</td>
<td>CH₃ of dtc</td>
</tr>
<tr>
<td></td>
<td>q 3.81</td>
<td>CH₂ of dtc</td>
</tr>
<tr>
<td></td>
<td>s 4.30 (1.5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>s 4.59 (2.5)</td>
<td>N₂H₄</td>
</tr>
<tr>
<td>[MoNCO(S₂CNET₂)₂PyNO]ᵃ</td>
<td>pt 1.26</td>
<td>CH₃ of dtc, symmetry split</td>
</tr>
<tr>
<td></td>
<td>m 3.76</td>
<td>CH₂'s of dtc, symmetry split</td>
</tr>
<tr>
<td></td>
<td>m 7.56</td>
<td>3,5 protons of Py</td>
</tr>
<tr>
<td></td>
<td>m 7.80</td>
<td>4 proton of Py</td>
</tr>
<tr>
<td></td>
<td>m 9.10</td>
<td>2,6 protons of Py</td>
</tr>
</tbody>
</table>

⁺ a = In CDCl₃; b = In (CD₃)₂CO; c = In (CD₃)₂SO; For other abbreviations see Table 2.2.
A suitable crystal was selected from a batch grown by the slow evaporation of a dichloromethane-hexane solution of the complex. Preliminary single crystal X-ray diffraction photographs indicated that the unit cell was monoclinic and belonged to the space group P2₁/C. The calculated cell parameters were \( a = 8.62 \) Å, \( b = 19.48 \) Å and \( c = 14.28 \) Å with \( \beta = 103^\circ \). For four molecules of \([\text{MoNCO}(S₂\text{CNEt₂})₂(\text{dms})\text{NO}] \) per unit cell the calculated density of \( 1.54 \text{ g cm}^{-3} \) compares well with the experimental value of \( 1.52 \text{ g cm}^{-3} \).

The single crystal X-ray structural determination has been complicated by considerable disorder in the dimethylsulphoxide moiety and at present the crystallographic R factor is 10%. The molecular structure of \([\text{MoNCO}(S₂\text{CNEt₂})₂(\text{dms})\text{NO}] \) is shown in Figure 3.3 and Table 3.15 gives the bond distances and angles at the present state of refinement.

**Table 3.15**

Selected Bond Distances and Angles in \([\text{MoNCO}(S₂\text{CNEt₂})₂(\text{dms})\text{NO}] \)

<table>
<thead>
<tr>
<th>Bond Distances (in Å)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-S(1) 2.535</td>
<td>C(1)-S(1) 1.71</td>
<td>C(3)-C(10) 1.48</td>
<td>S(1)--S(2) 2.81</td>
</tr>
<tr>
<td>Mo-S(2) 2.526</td>
<td>C(1)-S(2) 1.68</td>
<td>C(4)-C(9) 1.50</td>
<td>S(1)--S(4) 2.96</td>
</tr>
<tr>
<td>Mo-S(3) 2.528</td>
<td>C(2)-S(3) 1.70</td>
<td>C(5)-C(7) 1.54</td>
<td>S(4)--S(3) 2.82</td>
</tr>
<tr>
<td>Mo-S(4) 2.514</td>
<td>C(2)-S(4) 1.73</td>
<td>C(6)-C(8) 1.51</td>
<td>S(2)--N(3) 2.87</td>
</tr>
<tr>
<td>Mo-N(3) 2.11</td>
<td>C(1)-N(1) 1.31</td>
<td>N(3)-C(11) 1.04</td>
<td>S(3)--N(3) 2.87</td>
</tr>
<tr>
<td>Mo-N(4) 1.73</td>
<td>C(2)-N(2) 1.31</td>
<td>C(11)-O(1) 1.25</td>
<td></td>
</tr>
<tr>
<td>Mo-O(3) 2.17</td>
<td>C(3)-N(1) 1.50</td>
<td>N(4)-O(2) 1.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C(4)-N(1) 1.49</td>
<td>O(3)-S(5) 1.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C(5)-N(2) 1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C(6)-N(2) 1.49</td>
<td></td>
<td></td>
</tr>
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</table>

continued
### Table 3.15 (continued)

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)-Mo-S(2)</td>
<td>67.5°</td>
</tr>
<tr>
<td>S(3)-Mo-S(4)</td>
<td>68.0°</td>
</tr>
<tr>
<td>S(1)-Mo-S(4)</td>
<td>71.9°</td>
</tr>
<tr>
<td>S(2)-Mo-N(3)</td>
<td>75.9°</td>
</tr>
<tr>
<td>S(3)-Mo-N(3)</td>
<td>75.9°</td>
</tr>
<tr>
<td>N(4)-Mo-S(1)</td>
<td>93.4°</td>
</tr>
<tr>
<td>N(4)-Mo-S(2)</td>
<td>95.4°</td>
</tr>
<tr>
<td>N(4)-Mo-S(3)</td>
<td>96.1°</td>
</tr>
<tr>
<td>N(4)-Mo-S(4)</td>
<td>91.1°</td>
</tr>
<tr>
<td>N(4)-Mo-N(3)</td>
<td>94.2°</td>
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<tr>
<td>N(1)-C(3)-C(10)</td>
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</tr>
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</tr>
<tr>
<td>N(2)-C(5)-C(7)</td>
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</tr>
<tr>
<td>N(2)-C(6)-C(8)</td>
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#### 3.13 Preliminary Crystallographic Studies on

**[Et₄N][Mo(NCO)₂(S₂CNEt₂)₂NO]**

A suitable crystal for the study was obtained by the slow evaporation of a dichloromethane-carbon tetrachloride solution of **[Et₄N][Mo(NCO)₂(S₂CNEt₂)₂NO]**.

Single crystal X-ray photographs taken by Dr. M. Sterns indicated that the unit cell belonged to the space group **P222₁**. The unit cell dimensions were: a = 13.08 Å, b = 11.31 Å and c = 10.28 Å.

For two molecules of **[Et₄N][Mo(NCO)₂(S₂CNEt₂)₂NO]** per unit cell, the calculated density is 1.39 g cm⁻³ compared with the observed density of ~1.38 g cm⁻³.
Figure 3.3. The Molecular Structure of \([\text{MoNCO(S}_2\text{CNEt}_2)_2(\text{dms})\text{NO}]\).
3.14 Discussion

Labelling Experiments

The most significant contribution to the understanding of the mechanism of the reaction between $[M(S_2CNR_2)_2(NO)_2]$ and various anions has come from a study of the dinitrogen oxide evolved in the reactions. In particular, the reaction of $[Mo(S_2CNEt_2)_2(NO)_2]$ with azide, cyanate, cyanide and diethylidithiocarbamate were looked at in detail.

There are three possible pathways for the formation of dinitrogen oxide and these are shown in Figure 3.4.

The aim of the labelling experiment described in section 3.5,

![Figure 3.4 Pathways for the formation of \( N_2O \)](image)

has been to establish the nature of the nitrosyl reaction. The first part of this discussion will be restricted to the reactions of $[Mo(S_2CNEt_2)_2(NO)_2]$ with azide and cyanate.
When equimolar quantities of \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2\text{(NO)}_2]\) and \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{NO})_2]\) react with either azide or cyanate in dimethylsulphoxide at 60°C, the dinitrogen oxide evolved contains \(^{15}\text{N}_2\text{O}, \ 15\text{NNO}\) and \(\text{N}_2\text{O}\) in the ratio of 1:2:1. This indicates that a complete scrambling of the \(^{15}\text{N}\) label has occurred in the production of the dinitrogen oxide. In order to further clarify the situation, a number of additional experiments were carried out and the results are summarised below:

(i) \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{15NO)}_2]\) reacted with azide or cyanate to produce \(^{15}\text{N}_2\text{O}\).

(ii) No nitrosyl scrambling occurred when a 1:1 mixture of \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2\text{(NO)}_2]\) and \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{15NO)}_2]\) was heated at 60°C for 12 h in dimethylsulphoxide (see Figure 3.2).

(iii) The reaction of \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2\text{(NO)}_2]\) and cyanate under dioxygen gave only \(\text{N}_2\text{O}\). No \(\text{NO}_2\) was detected.

(iv) When the reactions of \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{15NO)}_2]\) with azide and cyanate were done under nitric oxide the ratios of \(^{15}\text{N}_2\text{O}:^{15}\text{NNO}:\text{N}_2\text{O}\) were 1:0.84:0.2 and 1:0.4:0.2, respectively. These results indicate that a slow exchange of free with coordinated nitric oxide does occur under the reaction conditions. The presence of nitric oxide also appears to retard the rates of reaction with azide and cyanate but the reasons for this are not clear.

The first result establishes that the dinitrogen oxide evolved comes from a reaction of nitrosyl groups and thereby eliminates mechanism (a) of Figure 3.4. Results (iii) and (iv) show that a dissociative mechanism involving NO is not present under the reaction conditions and therefore cannot account for the observed \(^{15}\text{N}\) scrambling. When this is
combined with result (ii), mechanism (b) of Figure 3.4 is dismissed leaving (c) as the only process consistent with the labelling experiments. Mechanism (c) entails the reaction of one nitrosyl group only, per molecule of $[\text{Mo(S}_2\text{CNET}_2)_2(\text{NO})_2]$ via an associative mechanism (see later).

Similar labelling experiments to those described for azide and cyanate have been carried out for the reactions with cyanide and diethyldithiocarbamate. When the latter two anions were reacted with equimolar quantities of $[\text{Mo(S}_2\text{CNET}_2)_2(\text{^{15}NO})_2]$ and $[\text{Mo(S}_2\text{CNET}_2)_2(\text{NO})_2]$ the ratio of $^{15}\text{N}_2\text{O}:^{15}\text{NNO}:\text{N}_2\text{O}$ was 1:2:1 in both cases. However, the reactions of $[\text{Mo(S}_2\text{CNET}_2)_2(\text{^{15}NO})_2]$ under nitric oxide resulted in a considerable dilution of the $^{15}\text{N}$ label in the dinitrogen oxide evolved; the ratios of $^{15}\text{N}_2\text{O}:{^{15}\text{NNO}}:\text{N}_2\text{O}$ being 1:1.7:2.3 and 1:1.4:0.6 for the cyanide and diethyldithiocarbamate reactions, respectively. The large amount of dinitrogen oxide obtained with cyanide is due, in part, to the parallel reaction: $\text{CN}^- + 2\text{NO} \rightarrow \text{N}_2\text{O} + \text{NCO}^-$. Clearly, the exchange of free with coordinated nitric oxide occurs in these reactions but the mechanism of exchange does not involve a prior dissociation of nitric oxide. This follows from the fact that the reactions may be carried out in the air with no apparent formation of nitrogen dioxide. In view of the above results it would appear that the cyanide and diethyldithiocarbamate reactions are mechanistically similar to those involving azide and cyanate.

The Stoichiometry of the Reactions of $[\text{Mo(S}_2\text{CNET}_2)_2(\text{NO})_2]$ with Azide and Cyanate Relevant to the discussion on reaction stoichiometry
are the following experimental observations:

(a) No dinitrogen oxide is evolved in the absence of anion.

(b) One mole of dinitrogen oxide is evolved for every two moles of \([\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]\) in the reactions with cyanate (Table 3.12) and azide

(c) All of the solution reaction products have one nitrosyl band in their infrared spectra.

(d) The brown precipitate obtained on addition of dichloromethane to the \([\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]\)-cyanate reaction solution contained 18.1% of the total Mo (section 3.8).

(e) The brown precipitates obtained (as above) in both the azide and cyanate reactions show no dithiocarbamate modes in their infrared spectra.

(f) The complexes \([\text{Et}_4\text{N}][\text{Mo}(\text{NCO})_2(\text{S}_2\text{CNET}_2)_2\text{NO}]\) and \([\text{Et}_4\text{N}][\text{Mo}(\text{N}_3)_2(\text{S}_2\text{CNET}_2)_2\text{NO}]\) are obtained in yields of 40% and 18.5%, respectively, based on \([\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]\).

(g) The known 7 coordinate complex, \([\text{Mo}(\text{S}_2\text{CNET}_2)_3\text{NO}]\), has been identified as a reaction product.

When the above results are combined with the labelling studies discussed previously, the following reaction scheme may be proposed:

\[
[\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2] + L^- \rightarrow [\text{MoL}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]^-(1)
\]

\[
\{L = \text{N}_3^- \text{ or NCO}^-\}
\]

\[
2[\text{MoL}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]^- \rightarrow \{[\text{MoL}(\text{S}_2\text{CNET}_2)_2\text{NO}]_2 \mu - \text{N}_2\text{O}_2\}^2^- (2)
\]

\[
\text{dmso} \quad [\{\text{MoL}(\text{S}_2\text{CNET}_2)_2\text{NO}\}_2 \mu - \text{N}_2\text{O}_2\}^2^- \rightarrow [\text{MoL}(\text{S}_2\text{CNET}_2)_2\text{NO}] + \text{N}_2\text{O} + (\text{CH}_3)_2\text{SO}_2 + \"[\text{MoL}(\text{S}_2\text{CNET}_2)_2\text{NO}]^2\" (3)
\]

\[
[\text{MoL}(\text{S}_2\text{CNET}_2)_2\text{NO}] + L^- \rightarrow [\text{MoL}_2(\text{S}_2\text{CNET}_2)_2\text{NO}]^- (4)
\]
Equation (1) suggests that the initial step in the reaction is the coordination of \( \text{L}^- \) to \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]\) in accord with observation (a). The anionic complex formed then undergoes a dimerisation which involves the coupling of two nitrosyl groups - one on each complex - to form a bridged hyponitrite species (labelling experiments). The nitrosyl reactivity will be analysed further in the next section of this discussion.

In equation (3), the bridged complex is envisaged as breaking down to give \([\text{MoL}(\text{S}_2\text{CNEt}_2)_2\text{NO}]\) (which reacts further with \( \text{L}^- \), \( \text{N}_2\text{O}, (\text{CH}_3)_2\text{SO}_2 \) and "\([\text{MoL}(\text{S}_2\text{CNEt}_2)_2\text{NO}]^2^-\)." Thus, observations (b) and (c) in addition to part of (f) may be explained. The 40% yield of \([\text{Et}_4\text{N}][\text{Mo}(\text{NCO})_2(\text{S}_2\text{CNEt}_2)_2\text{NO}]\) provides good evidence for the breakdown of a dimeric species but the low yield obtained for the azido analogue requires further explanation and will be discussed later. The oxygen atom left after the breakdown of the hyponitrite bridge to give dinitrogen oxide could be transferred to a molecule of dimethylsulphoxide to form dimethylsulphone. Such reactions involving dimethylsulphoxide are well known\(^{120-124}\).

Alternatively the oxygen atom could be associated with the "\([\text{MoL}(\text{S}_2\text{CNEt}_2)_2\text{NO}]^2^-\)" fragment. No direct experimental evidence, infrared or otherwise, has been found which would indicate the fate of the oxygen atom.

The purpose of the inverted commas around the Mo fragment is to emphasise that this product has not been isolated and moreover, that it is probably unstable under the reaction conditions. For example, it may be involved in a dithiocarbamate transfer reaction, with \([\text{MoL}_2(\text{S}_2\text{CNEt}_2)_2\text{NO}]^-\) as the acceptor, to give the brown, ionic, water soluble
product described in (d) and (e) and \([\text{Mo}(S_2\text{CNEt}_2)_3\text{NO}]^{-}\) - observation (g). Although no quantitative measurements have been made, it is apparent that considerably more \([\text{Mo}(S_2\text{CNEt}_2)_3\text{NO}]^{-}\) and "brown precipitate" are formed in the reaction with azide and this may reflect the greater lability of azide compared with cyanate\(^{125}\).

Evidence for the lability of azide can be seen in the preparation of \([\text{MoN}_3(S_2\text{CNEt}_2)_2(\text{dms})\text{NO}]^{-}\) described in section 3.2.5. Here a dichloromethane-dimethylsulphoxide solution containing \([\text{Mo}(\text{N}_3)_2(S_2\text{CNEt}_2)_2\text{NO}]^{-}\) is allowed to stand over anhydrous magnesium sulphate for two hours and during this time a fine precipitate of sodium azide forms. The reaction involved is: \(\text{Na}[\text{Mo}(\text{N}_3)_2(S_2\text{CNEt}_2)_2\text{NO}] + \text{dms} \rightarrow [\text{MoN}_3(S_2\text{CNEt}_2)_2(\text{dms})\text{NO}] + \text{NaN}_3\). Interestingly, no "brown precipitate" is formed during the preparation and this supports the hypothesis that it comes from a breakdown of an unstable species formulated as "[\text{MoL}_2(S_2\text{CNEt}_2)_2\text{NO}]^{2-}\".

Finally, the low yield of \([\text{Et}_4\text{N}][\text{Mo}(\text{N}_3)_2(S_2\text{CNEt}_2)_2\text{NO}]\) mentioned in (f) (and also section 3.2.7) may be attributed to two factors:

(i) The formation of \([\text{MoN}_3(S_2\text{CNEt}_2)_2(\text{dms})\text{NO}]^{-}\) according to the equilibrium reaction \([\text{Et}_4\text{N}][\text{Mo}(\text{N}_3)_2(S_2\text{CNEt}_2)_2\text{NO}] + \text{dms} \rightarrow [\text{MoN}_3(S_2\text{CNEt}_2)_2(\text{dms})\text{NO}] + \text{Et}_4\text{NN}_3\)

(ii) Significantly more dithiocarbamate transfer from "[\text{Mo}(\text{N}_3)_2(S_2\text{CNEt}_2)_2\text{NO}]^{2-}\" to \([\text{Mo}(\text{N}_3)_2(S_2\text{CNEt}_2)_2\text{NO}]^{-}\) (resulting in the formation of \([\text{Mo}(S_2\text{CNEt}_2)_3\text{NO}]^{-}\) and "brown precipitate") than in the corresponding reaction with cyanate.

The Application of MO Schemes to Nitrosyl Reactivity

In chapter 1 it was shown that MO schemes for nitrosyl
complexes could be useful in the rationalisation of observed nitrosyl reactivity and they will now be applied to the reactions of \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]\) with azide and cyanate. Figure 3.5 shows two MO diagrams; one for \(\text{cis-[Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]\) and the other for the postulated intermediate \([\text{MoL}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]^-\), assuming it has a PBP geometry.

Upon coordination of \(L\) to \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]\), the \(d_{x^2}\) orbital (see chapter 1) becomes strongly antibonding and consequently a pair of electrons now occupy the \(\pi^*_{a}(\text{NO})\) orbital \((\pi^*_{b_1}(\text{NO})\) in \(C_{2v}\) symmetry). If the nitrosyl groups are non-equivalent - as shown in Figure 3.5 - then the electron pair may be localised in an \(\text{sp}^2\) type orbital on one of the nitrosyl N atoms. That is, one nitrosyl bends and the other remains linear (c/f \(\text{RuCl}(\text{P}0_3)_2(\text{NO})_2\)). In addition, these two nitrosyl groups should show no tendency to couple because the \(\pi^*_{a}(\text{NO})\) level is antibonding between them.

The coupling of two \(\text{NO}^-\) ligands on different complexes would produce a bridged hyponitrite species which could break down to give dinitrogen oxide, \([\text{MoL}_2(\text{S}_2\text{CNEt}_2)_2\text{NO}]^-\) and the unstable Mo complex "\([\text{MoL}(\text{S}_2\text{CNEt}_2)_2\text{NO}]^2-\)".

Support for the formation of a hyponitrite bridged intermediate comes from a reaction of the related complexes \([\text{MoCl}_2(\text{en})(\text{NO})_2]\) and \([\text{MoCl}_2(\text{das})(\text{NO})_2]\). These complexes were found to isomerise in methanolic solutions in the absence of air to give species formulated as containing bridging hyponitrite groups viz., \([\{\text{MoCl}(\text{das})\text{NO}\}_2-\mu-\text{N}_2\text{O}_2\}^2\text{Cl}_2\) and \([\{\text{MoCl}(\text{en})\text{NO}\}_2-\mu-\text{N}_2\text{O}_2\}^2\text{Cl}_2\). A possible structure for the complexes is shown in Figure 3.6 but the type of hyponitrite
Figure 3.5. MO schemes for the \{\text{Mo(NO)}_2\}_6\) systems:

(a) \([\text{Mo(S}_2\text{CNR}_2)_2(\text{NO})_2]\)  
(b) \([\text{MoL(S}_2\text{CNR}_2)_2(\text{NO})_2]\)^-  
\((L = \text{anion}).\)
Figure 3.6. A possible structure for the cation in 

\[[\text{MoCl(das)NO}_2 \mu - \text{N}_2\text{O}_2]\text{Cl}_2 \text{ and} \]

\[[\text{MoCl(en)NO}_2 \mu - \text{N}_2\text{O}_2]\text{Cl}_2.\]

bridge differs from that originally suggested. The activating step in these isomerisation reactions could be coordination of a molecule of methanol which causes one of the nitrosyl groups to bend and then couple with another bent nitrosyl. The molecule of methanol and also a chloride ion are subsequently displaced to produce the observed product.

Interestingly, when methanolic solutions of 

\[[\text{Mo(S}_2\text{CNEt}_2)_2(\text{NO})_2]\] are irradiated with light from a xenon lamp, dinitrogen oxide is readily evolved. However, in dimethylsulphoxide the reaction is extremely slow and suggests that the solvent is playing more than a "spectator" role in the reaction. Indeed, the relative reaction rates may reflect the ability of the solvent to coordinate to the Mo. The reaction in both solvents gave a yellow
"mononitrosyldiethyldithiocarbamate" complex whose mass spectrum displayed a parent peak at m/e 1054, but the Mo isotope pattern did not correspond to either a mono- or di-molybdenum species. The breakdown pattern was consistent with the loss of nitric oxide and fragments of the diethyl-dithiocarbamate ligands. The product could not be further characterised as suitable crystals for an X-ray structural determination were unobtainable\textsuperscript{127}.

**Other Reactions Involving the \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2\text{(NO)}_2]\) System**

The preceding discussions have dealt with the reactions of \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2\text{(NO)}_2]\) with a variety of anions which include azide, cyanate, diethyldithiocarbamate and cyanide. In addition a photochemical reaction of \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2\text{(NO)}_2]\) in methanol or dimethylsulphoxide has been described. \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2\text{(NO)}_2]\) was also found to react with thiocyanate and iodide under UV irradiation in dimethylsulphoxide to give dinitrogen oxide and mononitrosyl diethyldithiocarbamate complexes.

The reactions of \([\text{W(S}_2\text{CNEt}_2\text{)}_2\text{(NO)}_2]\) with azide, cyanate and thiocyanate under thermal conditions (60°C in dimethylsulphoxide) were found to be extremely slow and irradiation with light from a xenon lamp was required. Dinitrogen oxide was again evolved and complexes of the type \([\text{Et}_4\text{N}]\text{[WL}_2\text{(S}_2\text{CNEt}_2\text{)}\text{NO]}\) (\(L = \text{N}_3^-, \text{NCO}^-, \text{NCS}^\)) analogous to those obtained for Mo, have been fully characterised. These reactions could also be carried out in dimethylacetamide.

Since the types of product obtained in both the thermal and photochemical processes are similar, it tends to suggest
that a common type of nitrosyl reactivity is involved. In the reactions involving light, a charge transfer of the type \( \text{hv} \) is probably involved and this will facilitate the coordination of an anion. An intermediate, identical to that obtained under thermal conditions results and therefore the type of nitrosyl reaction involved should be the same.

The Characterisation of Products

In the reactions of \([\text{M(S}_2\text{CNR}_2)(\text{NO})_2]\) with azide, cyanate and thiocyanate, products of the type \([\text{NR}']_4\text{[ML}_2(\text{S}_2\text{CNR}_2)_2\text{NO}]\) (\(\text{M} = \text{Mo}, \text{R} = \text{R}' = \text{Et}, \text{L} = \text{N}_3^-\) or \(\text{NCO}^-\); \(\text{M} = \text{Mo}, \text{R} = \text{Me}, \text{R}' = \text{Me or Et}, \text{L} = \text{NCO}^-\); \(\text{M} = \text{Mo}, \text{R} = \text{i-Pr}, \text{R}' = \text{Et}, \text{L} = \text{NCO}^-\); \(\text{M} = \text{W}, \text{R} = \text{R}' = \text{Et}, \text{L} = \text{N}_3^-, \text{NCO}^-\) or \(\text{NCS}^-\) have been isolated. These complexes, with the exception of \([\text{Et}_4\text{N}]_2(\text{W(NCS)}_2(\text{S}_2\text{CNEt}_2)_2\text{NO}),\) are converted in water/dimethylsulphoxide/sodium persulphate to the neutral species \([\text{ML}(\text{S}_2\text{CNEt}_2)_2(\text{dmsso})\text{NO}]\). Also, \([\text{MoNCO}(\text{S}_2\text{CNEt}_2)_2(\text{dmsso})\text{NO}]\) has been found to undergo a variety of substitution reactions in which the dimethylsulphoxide is replaced by certain anionic and neutral ligands. This type of reaction has yielded the complexes \([\text{Et}_4\text{N}][\text{Mo(NCO)}_2(\text{S}_2\text{CNEt}_2)_2\text{NO}]\) (\(\text{L} = \text{NCO}^-, \text{N}_3^-, \text{NCS}^-\) and \(\text{Cl}^-\)), \([\text{MoNCO}(\text{S}_2\text{CNEt}_2)_2\text{Y(NO)}]\) (\(\text{Y} = \text{Py}, \text{NH}_3\)) and \([\text{MoNCO}(\text{S}_2\text{CNEt}_2)_2\text{NO}]_2-\mu-\text{N}_2\text{H}_4\). Substitution reactions were also attempted using the bromide or nitrate ions and also acetonitrile but the starting material was recovered in each case.

The complexes mentioned above have all been formulated as seven coordinate species based on evidence from analyses,
infrared and $^1$H nmr spectra and crystallographic studies for [MoNCO(S$_2$CNEt$_2$)$_2$(dmso)NO] and [Et$_4$N][Mo(NCO)$_2$(S$_2$CNEt$_2$)$_2$NO].

A single crystal X-ray structural determination of [MoNCO(S$_2$CNEt$_2$)$_2$(dmso)NO] has been partly completed and the details are given in section 3.12. Figure 3.3 shows the molecular structure of the complex. It consists of discrete monomeric molecules each composed of two bidentate diethyl-dithiocarbamate ligands, a nitrosyl group and a cyanate group, in a pentagonal bipyramidal arrangement about the Mo. The Mo is slightly displaced from the plane formed by the four S atoms of the two bidentate diethyl-dithiocarbamate ligands and the cyanate group. Both the (MoNO) and (MoNCO) moieties deviate only slightly from linearity.

The [Mo(S$_2$CNEt$_2$)$_2$NO] fragment is well defined and the bond length and angles compare favourably with those found in the related complex [Mo(S$_2$CNn-Bu$_2$)$_3$NO]$_{129}$. However, for the cyanate group the situation is less clear as the bond lengths differ significantly from those observed in other isocyanato complexes$_{130-132}$ and are suspect. Presumably this problem arises from the disorder in the dimethylsulphoxide moiety. It was not possible to establish crystallographically whether the cyanate was O or N bound. Unfortunately, no structural information is available on O-bonded cyanates except for the complex [BØ$_4$][Ni$_2$(tren)$_2$(NCO)$_2$] which contains bridging cyanate groups.

Figure 3.7 shows the resonance hybrid structures for O and N bound cyanate:
The crystal structures to date on isocyanato complexes have all shown the MNCO moiety to be nearly linear. When this is combined with the high CN stretching frequencies observed for metal isocyanates (2240-2170 cm\(^{-1}\)) it suggests that structure III of Figure 3.7(a) is the most important. In addition, O-bonded cyanates should be bent (Figure 3.7(b)). Therefore, the nearly linear MoNCO moiety found in the structure of \([\text{MoNCO}(S_2\text{CNEt}_2)_2(\text{dms})\text{NO}]\) suggests that the cyanate is N-bound.

Single crystal X-ray photographs of \([\text{Et}_4\text{N}][\text{Mo(NCO)}_2(S_2\text{CNEt}_2)_2\text{NO}]\) have indicated that the complex
must have a $C_2$ axis of symmetry. In addition, the infrared spectrum of the complex contains only one CN stretch for the cyanato ligands and therefore implies a trans configuration. The proposed structure for the anion in $[\text{Et}_4\text{N}][\text{Mo(NCO)}_2(S_2\text{CNR}_2)_2\text{NO}]$ is shown in Figure 3.8.

In contrast to isocyanate coordination, azide binds to metals in a non-linear arrangement and the M-N-N bond angle is generally around 120°. Hybrid structures II and IV of Figure 3.9 are considered to contribute most to the coordination of thiocyanate in $[\text{Et}_4\text{N}][\text{M(NCS)}_2(S_2\text{CNR}_2)_2\text{NO}]$ and $[\text{Et}_4\text{N}][\text{Mo(NCO)(NCS)}(S_2\text{CNR}_2)_2\text{NO}]$ could be either through N or S. Both electronic and steric factors are considered to be important in determining how the thiocyanate coordinates and for the above two reasons the N-S bond angles are expected to be around 90° ± 5°.
The total structure\textsuperscript{133} \([\text{MoN}_3(S_2\text{CNEt}_2)_2(\text{dms})\text{NO}]\) and \([\text{MoNCO}(S_2\text{CNEt}_2)_2(\text{dms})\text{NO}]\) were found to be isomorphous indicating a similar stereochemistry\textsuperscript{116}. However, the two structures will differ in that the MoNCO and MoNNN moieties are linear and bent, respectively.

The mode of coordination of thiocyanate in \([\text{Et}_4\text{N}][\text{W(NCS)}_2(S_2\text{CNEt}_2)_2\text{NO}]\) and \([\text{Et}_4\text{N}][\text{Mo(NCO)(NCS)}(S_2\text{CNEt}_2)_2\text{NO}]\) could be either through N or S. Both electronic and steric factors are considered to be important in determining how the thiocyanate coordinates\textsuperscript{134} and for the above two seven coordinate complexes steric factors should be quite significant. Crystal structures of complexes containing S-bonded thiocyanates have shown the M-S-C bond angles to be around 110° and therefore this type of coordination makes far greater steric demands than the near linear N-bonded form\textsuperscript{134}. Thus, N-bonded thiocyanates are expected for these two complexes (see also ir discussion).

It is interesting to compare the seven coordinate
geometries of \([\text{MoNCO}(\text{S}_2\text{CNEt}_2)_2(\text{dmso})\text{NO}]\) and 
\([\text{Mo(NCO)}_2(\text{S}_2\text{CNEt}_2)_2\text{NO}]^{-}\). In the former, the nitrosyl group 
occupies an axial position while in the latter it is 
equatorial. It is reasonable to expect that the complexes 
\([\text{ML}(\text{S}_2\text{CNEt}_2)_2(\text{dmso})\text{NO}] (\text{M} = \text{Mo or W, R} = \text{Et}; \text{M} = \text{Mo, R} = \text{Me}
\text{or i-Pr})\) and \([\text{MLL'}(\text{S}_2\text{CNEt}_2)_2\text{NO}]^{-} (\text{M} = \text{Mo, L} = \text{L'} = \text{N}_3^{-};
\text{M} = \text{Mo, L} = \text{NCO}^{-}, \text{L'} = \text{N}_3^{-} \text{or NCS}^{-}; \text{M} = \text{W, L} = \text{L'} = \text{NCO}^{-},
\text{N}_3^{-} \text{and NCS}^{-})\) should have the same types of stereochemistry 
as \([\text{MoNCO}(\text{S}_2\text{CNEt}_2)_2(\text{dmso})\text{NO}]\) and \([\text{Mo(NCO)}_2(\text{S}_2\text{CNEt}_2)_2\text{NO}]^{-}\), 
respectively. However, for complexes such as 
\([\text{Mo(NCO)}\text{Cl}(\text{S}_2\text{CNEt}_2)_2\text{NO}]\), \([\text{MoNCO}(\text{S}_2\text{CNEt}_2)_2(\text{NH}_3)\text{NO}]\) and 
\([\text{[MoNCO}(\text{S}_2\text{CNEt}_2)_2\text{NO}]_2-\text{u-N}_2\text{H}_4\]), the nitrosyl group could be 
either axial or equatorial. Indeed, for the latter complex 
there is 'H nmr evidence to suggest that a mixture of isomers 
is present and the isomerism could arise from the nitrosyl 
occupying either an axial or equatorial site (see nmr 
discussion).

'\text{H NMR Spectra}

The pmr spectra of the complexes prepared in this 
chapter are similar to those reported for other dialkyl-
dithiocarbamate complexes\(^94\) (see also chapter 2). The solid 
state structures of the new compounds imply splitting of the 
dithiocarbamate resonances owing to restricted rotation 
about the CN bond of the dithiocarbamate. The predicted 
splitting was observed for some of the complexes but not in 
others. Figures 3.10-3.13 show spectra in which dithio-
carbamate splitting is observed. This may be compared with 
the spectrum of \([\text{MoNCO}(\text{S}_2\text{CNEt}_2)_2(\text{dmso})\text{NO}]\) in deuterochloroform 
(Figure 3.14); here no splittings are observed.
Figure 3.10. 'H nmr Spectrum of \([\text{MoN}_3(S_2\text{CNET}_2)_2(\text{dmso})\text{NO}]\) in Deuterochloroform.
Figure 3.11. $^1$H nmr spectrum of [MoNCO(S$_2$CNMe$_2$)$_2$(dmsO)NO] in acetone [D$_6$].
Figure 3.12. $^1$H nmr spectrum of $\text{[Me}_4\text{N}]\text{[Mo(NCO)}_2\text{(S}_2\text{CNMe}_2\text{)}_2\text{NO]}$ in acetone $[D_6]$. 

Figure 3.13. $^1$H nmr spectrum of $\text{[Mo(NCO)}_2\text{(S}_2\text{CNMe}_2\text{)}_2\text{NO]}$ in deuterochloroform.
Figure 3.13. $^1H$ nmr spectrum of [MoNCO(S$_2$Ni-Pr$_2$)$_2$(dmsO)NO] in deuterochloroform.
Figure 3.14. \(^1\)H nmr spectrum of [MoNCO(S\(^2\)CNEt\(_2\))(dmsO)NO] in deuterochloroform.
Figure 3.15. $^1$H nmr spectrum of [MoNCO(S$_2$CNEt$_2$)$_2$][dmsO]NO] in acetone [D$_6$].
With the exception of $[\text{WN}_3(S_2\text{CNEt}_2)_2(\text{dmso})\text{NO}]$, the pmr spectra of the $[\text{ML}(S_2\text{CNR}_2)_2(\text{dmso})\text{NO}]$ complexes in deuterochloroform show absorptions due to O-bonded dimethylsulphoxide only (Figures 3.10, 3.13 and 3.14). For the above tungsten complex in deuterochloroform and for all $[\text{ML}(S_2\text{CNR}_2)_2(\text{dmso})\text{NO}]$ complexes in acetone $[\text{D}_6]$, partial dissociation of the dimethylsulphoxide occurs and peaks due to free and O-bonded species are observed\textsuperscript{135} (Figures 3.11 and 3.15).

The dimethylsulphoxide resonance in the spectrum of $[\text{MoN}_3(S_2\text{CNEt}_2)_2(\text{dmso})\text{NO}]$ (Figure 3.10) consists of a large peak at $\delta 2.67$ in addition to a much smaller peak at $\delta 2.62$. The latter peak is not due to free dimethylsulphoxide and cannot be assigned with certainty.

Similarly, in the spectrum of $[{\text{MoNCO}}(S_2\text{CNEt}_2)_2\text{NO}]_2$-$\mu$-N$_2$H$_4$, two NH resonances are observed at $\delta 4.30$ and $\delta 4.59$ which integrate in the ratio 1.5:2.5. The diethyldithiocarbamate resonances are also broad and this tends to suggest that isomers are present. The isomerism could arise from the NH$_2$ or NO groups occupying either axial or equatorial positions as shown in Figure 3.16. The unassigned dimethylsulphoxide resonance in the spectrum of $[\text{MoN}_3(S_2\text{CNEt}_2)_2(\text{dmso})\text{NO}]$ could also be due to a small amount of an isomeric species.

Infrared Spectra

The infrared spectra (Tables 3.2 and 3.13) are particularly useful for identification purposes owing to the strong characteristic absorption bands of each ligand type present\textsuperscript{108}. 
The assignment of bands due to the coordinated dmsO has been aided by comparison with the corresponding anionic complexes \([\text{ML}_2(\text{S}_2\text{CNR}_2)_2\text{NO}]^-\). For the complexes containing dimethylsulphoxide, the band occurring between 950 and 960 cm\(^{-1}\) is assigned to the \(\text{CH}_3\) rocking modes of the ligand\(^\text{136}\). The SO stretch for O-bonded dimethylsulphoxide is reported to occur in the range 1025-985 cm\(^{-1}\),\(^\text{136}\) but is difficult to assign in the diethylidithiocarbamate complexes due to overlapping dithiocarbamate modes. However, the spectra of \([\text{MoNCO(S}_2\text{CNe}_2)_2(\text{dmsO})\text{NO}]\) and \([\text{MoNCO(S}_2\text{CNi-Pr})_2-(\text{dmsO})\text{NO}]\) are sufficiently simplified in this region to enable the assignment of the peak at 1024 cm\(^{-1}\) to the SO stretch. Metal-oxygen (of dmsO) stretching frequencies are expected in the range 400-500 cm\(^{-1}\) and the band around 460 cm\(^{-1}\) is attributed to this mode (Table 3.2 and Figure 3.11). For \([\text{MoNCO(S}_2\text{CNMe}_2)_2(\text{dmsO})\text{NO}]\) the strong peak at 446 cm\(^{-1}\) probably consists of two peaks as bands \([\text{Mo(S}_2\text{CNMe}_2)_2(\text{NO})_2]\) and \([\text{R}^\_\text{N}[\text{Mo(\text{S}_2\text{CNR}_2)_2(\text{NO})_2}]\) have strong peaks around 450 cm\(^{-1}\). The NO stretching region have been discussed in Chapter 3 and will not be repeated here.

The absorption bands associated with the MoNO moiety in \([\text{MoNCO(S}_2\text{CNMe}_2)_2(\text{dmsO})\text{NO}]\) have been assigned by preparing the \(^\text{15}\text{N}\)-labelled complex and comparing the spectra. Table 3.4 lists the bands which were observed to shift upon deuteration. The agreement between observed and calculated force constants and frequencies is good.
stretch. Metal-oxygen (of dms0) stretching frequencies are expected in the range 400-500 cm\(^{-1}\) and the band around 450 cm\(^{-1}\) is attributed to this mode (Table 3.3 and Figure 3.1). For \([\text{MoNCO(S}_2\text{CNMe}_2)_2\text{(dms0)NO]}\) the strong peak at 446 cm\(^{-1}\) probably consists of two peaks as both \([\text{Mo(S}_2\text{CNMe}_2)_2\text{(NO)}_2]\) and \([\text{R}_h\text{N}[\text{Mo(NCO)}_2\text{(S}_2\text{CNMe}_2)_2\text{(NO)}]\) have a band around 450 cm\(^{-1}\). The Mo-S stretching region has been described in chapter 2.

The infrared spectra of dithiocarbamate complexes have already been discussed in chapter 2 and will not be repeated here.

The absorption bands associated with the MoNO moiety in \([\text{MoNCO(S}_2\text{CNEt}_2)_2\text{(dms0)NO]}\) have been assigned by preparing the \(^{15}\text{NO}-\text{labelled complex and comparing the spectra. Table 3.4 lists the bands which were observed to shift upon isotopic substitution, their assignments and the calculated force constants and frequencies. The agreement between observed and calculated frequencies upon isotopic substitution confirms the assignments.}

The low nitrosyl stretching force constant (9.88 mdyne/Å; \(\nu(\text{NO}) = 1648\) cm\(^{-1}\)) reflects a considerable weakening of the NO bond due to back donation from the metal into the \(\pi^*(\text{NO})\) orbitals. A comparison of force constants has already been made in chapter 2.

The approximate frequency ranges for the CN stretch of O and N bonded cyanates are 2240-2200 and 2240-2170 cm\(^{-1}\), respectively. For the cyanato complexes prepared in this work, the CN stretch for the ligand occurs between 2240 and 2210 cm\(^{-1}\) making any distinction between O and N bonded groups difficult.
The CN stretching frequencies for N and S bonded thiocyanates are suggested to fall into the ranges 2100-2050 cm\(^{-1}\) and 2130-2085 cm\(^{-1}\), respectively\(^{134}\). Bands are observed at 2090 cm\(^{-1}\) and 2085 cm\(^{-1}\) for 
\([\text{Et}_4\text{N}][\text{MoNCO(NCS)}(\text{S}_2\text{CNET}_2)_2\text{NO}]\) and 
\([\text{Et}_4\text{N}][\text{Mo(NCS)}_2(\text{S}_2\text{CNET}_2)_2\text{NO}]\), respectively, suggesting an N-bonded thiocyanate.

However, these frequency ranges for N and S bonded thiocyanates and O and N bond cyanates are only a guide to the type of coordination and are not to be taken as conclusive proof.

**Protonation Reactions Involving** 
\([\text{MoL}(\text{S}_2\text{CNET}_2)_2(\text{dmsO})\text{NO}]\) 
and 
\([\text{MoL}_2(\text{S}_2\text{CNET}_2)_2\text{NO}]^-; \text{L} = \text{N}_3^- \text{or NCO}^-\)

Both \([\text{MoL}(\text{S}_2\text{CNET}_2)_2(\text{dmsO})\text{NO}]^-\) and \([\text{MoL}_2(\text{S}_2\text{CNET}_2)_2\text{NO}]^-\) react with dry HCl in dichloromethane; the cyanato complexes giving carbon dioxide but no dinitrogen is evolved in the azide reactions. Evaporated film infrared spectra of the reaction solutions show bands due to the nitrosyl and diethyldithiocarbamate groups but the bands due to azide and cyanate are absent. The solution infrared spectra, immediately after the azide reactions, showed a sharp band at 2140 cm\(^{-1}\) indicative of hydrazoic acid. The proton assisted dissociation of coordinated azide as hydrazoic acid is well known\(^{138}\) as is the reaction of cyanate with acid to give carbon dioxide.\(^{139}\)

\([\text{MoN}_3(\text{S}_2\text{CNET}_2)_2(\text{dmsO})\text{NO}]\) has also been reported to give ammonia and dinitrogen on reaction with concentrated sulphuric acid.\(^{116}\)
A Summary

This chapter has presented an account of the reactivity of the complexes \([M(S_2CNR_2)_2(NO)_2]\) toward a variety of anions. From the type of products isolated and studies employing \(^{15}\text{NO}\) labelled complex it would appear that a common type of nitrosyl reactivity is involved in all of the reactions.

The dinitrogen oxide produced comes from a reaction of nitrosyl groups only, and moreover, only one nitrosyl per molecule reacts. MO arguments have been advanced to account for the observed nitrosyl reactivity.

Complexes of the type \([ML_2(S_2CNR_2)_2NO]^-\), \([ML(S_2CNR_2)_2(dmso)NO]\) and \([MLL'(S_2CNR_2)_2NO]^n (n = 0, -1)\) have been prepared and fully characterised.
CHAPTER 4

2.1. Introduction

This chapter deals with the kinetic studies which were carried out on the reactions of the \([\text{Mo}(S_2\text{CNR}_2)_2(\text{NO})_2]\) complexes with azide and cyanate in dimethylsulfoxide. The labelling experiments using \([\text{Mo}(S_2\text{CNR}_2)_2(\text{NO})_2]^{14}\text{NO}_2\), described in chapter 1, indicated that the same nitrosyl reactivity was involved in both the azide and cyanate reactions and a mechanism was proposed based on the data available.

The aim of this work has been to obtain the rate expressions for the reactions with the hope of further clarifying the mechanism.

4.2 Experimental Details

4.2.1 Materials

The dimethylsulfoxide used in these studies was freshly distilled and then thoroughly degassed prior to use. NaN₃ (A.R., Laboratory reagent) and KN₃ (Eastman Organic Chemicals) were of high purity and were used as obtained.

However, NaNCO and KNCOC (A.R., technical and laboratory grades, respectively) were found to contain large amounts of carbonate (10%) and had to be purified by recrystallisation from water as follows:

- NaNCO: 5 g of NaNCO was dissolved in 100 ml of water and the solution was heated to about 90°C, NaOH was added dropwise until it was neutral to phenol-phthalein.
- KNCOC: 100 ml of water was added to 5 g of KNCOC and the mixture was heated to about 90°C and NaOH was added dropwise until it was neutral to phenol-phthalein.

Kinetic Studies on the Reactions of \([\text{Mo}(S_2\text{CNR}_2)_2(\text{NO})_2]\) with Azide and Cyanate
4.1 Introduction

This chapter deals with the kinetic studies which were carried out on the reactions of the $[^{15} \text{NO}]_2$ complexes with azide and cyanate in dimethylsulphoxide. The labelling experiments using $[^{15} \text{NO}]_2$, described in chapter 3, indicated that the same nitrosyl reactivity was involved in both the azide and cyanate reactions and a mechanism was proposed based on the data available.

The aim of this work has been to obtain the rate expressions for the reactions with the hope of further clarifying the mechanism.

4.2 Experimental Details

4.2.1 Materials

The dimethylsulphoxide used in the kinetic studies was freshly distilled under vacuum from calcium hydride and then thoroughly degassed prior to use. NaN$_3$ (B.D.H. Laboratory reagent) and KN$_3$ (Eastman Organic Chemicals) were of high purity and were used as obtained.

However, NaNCO and KNCO (B.D.H. technical and laboratory grades, respectively) were found to contain large amounts of carbonate (~10%) and had to be purified by recrystallisation from water as follows:

(a) NaNCO

The crude NaNCO (30 g) in water (200 ml) was warmed with stirring to about 40°C. Glacial acetic acid was then added dropwise until the solution was neutral to phenol-
phenolphthalein. The mixture was then quickly filtered and the filtrate cooled in an ice-bath for 20 minutes. The precipitated NaNCO was filtered off and washed with ethanol, then ether and finally dried under vacuum.

(b) **KNCO**

KNCO (50 g) in water (50 ml) was warmed with stirring to ~30°C. The solution was made neutral to phenolphthalein by slowly adding glacial acetic acid and was then quickly filtered. After cooling the filtrate in an ice-bath for five minutes, the precipitate was quickly filtered off and washed with ethanol and then ether and dried under vacuum.

The NaNCO and KNCO were analysed gravimetrically by precipitation with semicarbazide\(^\text{140}\); the reaction involved is:

\[
\text{NH}_2\text{CONHNH}_3^+ + \text{NCO}^- \rightarrow \text{NH}_2\text{CONHNHCONH}_2^+ \quad \text{(hydrazodicarbamide)}
\]

Using this method the purities of KNCO and NaNCO were estimated to be 98.7% and 99.3%, respectively.

The [Mo(S\(_2\)CNR\(_2\))\(_2\)(NO)\(_2\)] complexes were prepared as described in chapter 2 and all other chemicals were of reagent grade quality.

4.2.2 **Preparation of Solutions**

The hygroscopic nature of dimethylsulphoxide and the retardatory effect of dioxygen on the reaction rates (section 4.10) made it necessary to prepare the solutions in a dry dinitrogen glove-box. The relative humidity in the box was estimated to be less than 4% using a Lambrecht hygrometer.
4.2.3 Instrumentation

The reactions were followed spectrophotometrically using a Cary 14 instrument fitted with a cell holder thermostatted to ±0.1°C. An electronic timing device was also installed in the Cary which turned the spectrometer lamp and recorder on for 1 minute at hourly intervals. This was purely an economy measure as reactions were monitored for about five half lives and this corresponded to periods of between 10 and 40 hours in most cases. It also provided the essential information in a condensed form.

4.2.4 Techniques

Two types of spectrophotometer cell were used in the kinetics studies and these are illustrated in figure 4.1. Both cells were 1 cm in width and were fitted with air-tight seals.

For the reactions involving NaN₃ cell (a) was used. After filling the cell with reaction solution in the dinitrogen glove-box it was then sealed and placed in the heated cell holder of the Cary. The reactions with half-lives greater than 2 hours were monitored hourly with the first reading being taken 10-15 minutes after placing the cell in the heated compartment. The faster reactions were monitored continuously with the chart recorder set at an appropriate speed. The light from the spectrophotometer did not affect the rate of reaction.

The reactions with KNCO and NaNCO were carried out using cell (b). A weighed sample of $\text{[Mo(S}_2\text{CNEt}_2\text{)(NO)}_2\text{]}$ was placed in cuvette B and the cyanate solution (5 ml) was syringed into
Figure 4.1. Spectrophotomer cells which were used in the kinetic studies.
bulb A. After heating the cell to the reaction temperature, the reactants were allowed to mix and it was placed immediately in the heated compartment of the Cary. The reaction was then monitored continuously.

4.3 The Treatment of Rate Data

4.3.1 Calculation of Observed Rate Constants

All of the reactions were carried out using at least a 10-fold excess of anion. Under these conditions, the reactions with azide were observed to follow first order kinetics with respect to the molybdenum complex. As the absorbance values at infinite time were not constant, Guggenheim plots using time intervals of greater than two half lives were used to evaluate the rate constants.

However, the reactions involving cyanate were far more complicated and appeared to be autocatalytic in nature. A satisfactory interpretation of the cyanate kinetics has not been achieved and only a descriptive account of the reactions will be given in this thesis.

4.3.2 The Temperature Dependence of Rate Data

The empirical Arrhenius equation for the variation of rate constant with temperature is

\[ k_r = A \cdot e^{-\frac{E_A}{RT}} \]

where

- \( k_r \) = rate constant
- \( A \) = frequency factor
- \( E_A \) = Arrhenius activation energy; this quantity represents the minimum energy a molecule must possess in order to partake in a chemical reaction
- \( T \) = absolute temperature
R = gas constant = 8.3143 joules deg⁻¹ mole⁻¹
= 1.9872 cal deg⁻¹ mole⁻¹

The Arrhenius equation is clearly similar in form to the Van't Hoff equation \( \frac{d}{dT} \ln K = \frac{\Delta H^°}{RT^2} \) which relates the equilibrium constant for a reaction with the absolute temperature.

Using collision theory an expression for the variation in rate constant with temperature can be derived and it is identical to the Arrhenius equation, viz.

\[ k_r = PZ e^{-E/RT} \]

where \( P \) = probability or steric factor of the reaction
\( Z \) = frequency of collision.

The P factor was introduced because many reaction rates tended to be smaller than predicted by theory and it was originally supposed that the molecules had to collide in a particular configuration to produce a reaction.

The theory of absolute reaction rates, developed by Eyring, has the advantage that it takes into account, in principle, the internal motions of the reacting species. The fundamental postulate of the theory is that reactants are in equilibrium with an activated complex or transition state:

\[ aA + bB + ... \underset{\text{M}^\#}{\rightarrow} \text{products} \]

where \( \text{M}^\# \) = activated complex
\( A, B, ... \) = reactants
\( a, b, ... \) = stoichiometric coefficients.

The equilibrium constant \( K \) is equal to \( \frac{C^\#}{C_A^a C_B^b} \), where concentration units have been employed. The transition state is illustrated on the potential energy curve shown below:
The activated complex is treated as being a normal molecule except for motion along one direction - the reaction coordinate - which leads to decomposition and product formation. For convenience, the activated complex has been defined as being in a potential box of arbitrary length \( \delta \) at the top of the potential energy curve. The theory predicts that the rate constant is given by the formula:

\[
K = \frac{kT}{h} K_t = \frac{kT}{h} \left( \frac{K \hbar}{(2\pi \hbar M \delta)} \right)
\]

where \( K = \) transmission coefficient, which represents the fraction of crossing of the energy barrier that successfully led to product formation

\( k = \) Boltzmann's constant

\( \hbar = \) Planck's constant

\( M = \) effective mass of the activated complex along the reaction coordinate.

In as much as \( \delta \) is an arbitrary, but small distance, it can be set equal to \( \hbar/(2\pi M \delta) \approx 10^{-8} \text{ cm} \), making \( K_t = K \). So as \( K_t \) is analogous to an equilibrium constant it can be related to the usual thermodynamic parameters:
(a) Free energy of activation: \( \Delta G^\# = -RT\ln K' \)  

(b) Enthalpy of activation: \( \Delta H^\# = RT \frac{d(\ln K')}{dT} \)  

(c) Entropy of activation: \( \Delta S^\# = \frac{\Delta H^\# - \Delta G^\#}{T} \)  

In equation (1) the transmission coefficient is usually set equal to 1 but it may vary between 0.9 and 1. With this simplification the rate expression becomes:

\[
k_r = \frac{kT}{h} e^{-\Delta G^\#/RT} = \left( \frac{kT}{h} e^{\Delta S^\#/RT} \right) e^{-\Delta H^\#/RT}
\]

The quantity \( \Delta H^\# \) is equal to \( E_A - RT \), but since \( RT \approx 2.5 \text{ kJ} \) (\( T = 300K \)) and \( E_A \) is generally between 42 and 126 \text{ kJ mole}^{-1}, then \( E_A \approx \Delta H^\# \). The PZ factor of collision theory is then approximately equal to \( \frac{kT}{h} e^{\Delta S^\#/RT} \). The entropy of activation, \( \Delta S^\# \), is a measure of the randomness or probability of the transition state complex compared to the reactants.

Equation (5) may be rearranged to give equation (6)

\[
-\log_{10} k_r = \frac{\Delta H^\#}{2.303RT} - \left( \log_{10} \frac{kT}{h} + \frac{\Delta S^\#}{2.303R} \right)
\]

In this work, equation (6) was used to obtain the thermodynamic parameters. A plot of \( -\log_{10} \frac{k_r}{T} \) versus \( 1/T \) has a slope equal \( \frac{\Delta H^\#}{2.303RT} \) and intercept I of \( \left( \log_{10} \frac{k}{h} + \frac{\Delta S^\#}{2.303R} \right) \). Thus:

\[
\Delta H^\# = \text{slope} \times 2.303R
\]

\[
\Delta S^\# = -2.303R \left[ I + \log_{10} \frac{k}{h} \right] = -2.303R \left[ I + 10.32 \right]
\]

Reactions in Solution

For solution reactions the equilibrium constant is more correctly expressed in terms of activities, i.e.
\[ K_S = \frac{a^\gamma}{a_A a_B^\gamma} = \frac{c^\gamma}{c_A c_B^\gamma} \times \frac{\gamma}{\gamma_A \gamma_B} \]

where \( \gamma, \gamma_A, \gamma_B \ldots \) are the activity coefficients. The Debye-Hückle limiting law gives the variation of activity coefficient with ionic strength as

\[ \log_{10} \gamma_i = CZ_i^2 \sqrt{\mu} \quad \text{(9)} \]

where \( \mu = \text{ionic strength} \) and \( C = \text{constant} \).

Now, for a reaction of the type \( A + B \rightarrow M^\# \), the rate expression becomes

\[ \log_{10} k_r = \log_{10} k_0 + 2CZ_A Z_B \sqrt{\mu} \quad \text{(10)} \]

where \( k_0 \) is the rate constant at infinite dilution and \( Z_A \) and \( Z_B \) are the ionic charges on the reacting species.

If one of the reacting species is neutral then \( k_r = k_0 \), implying that there are no first order ionic strength effects on the reaction rate. Alternatively, if ionic strength effects are significant the value of \( \Delta H^\# \) obtained using equation (6) will be unaffected but the \( \Delta S^\# \) value will not coincide with the true entropy of activation.

For the reaction of \([\text{Mo(S}_2\text{CNR}_2)_2(\text{NO})_2]\) with azide, the kinetic studies to be presented, suggest that the rate determining step is the coordination of azide to the metal. In addition, as \([\text{Mo(S}_2\text{CNR}_2)_2(\text{NO})_2]\) is neutral, ionic strength effects on the rate constant should be small as dilute solutions were employed (\([\text{NaN}_3] < 0.05 \, \text{M}\)). In view of this, no background electrolyte has been added.
4.4 Preliminary Kinetic Studies

4.4.1 The Stability of \([\text{Mo(S}_2\text{CNR}_2)_2(\text{NO})_2]\) Complexes in Dimethylsulphoxide at 63.7°C

Dimethylsulphoxide solutions of \([\text{Mo(S}_2\text{CNR}_2)_2(\text{NO})_2]\) \((R = \text{Me, Et, }\frac{3}{4}\text{Pyr, i-Pr, n-Bu and Bz})\) at 63.7°C showed negligible changes in optical density over a 20 hour period.

4.4.2 Check on Beer's Law

\([\text{Mo(S}_2\text{CNEt}_2)_2(\text{NO})_2]\) was found to obey Beer's Law in dimethylsulphoxide at 63.7°C over the concentration range \(1-8 \times 10^{-4}\) M. Figure 4.3 shows the absorbance versus concentration plot obtained.

4.4.3 The Changes Occurring in the UV-Visible Spectra with Time

The UV-visible spectral changes for the reactions of \([\text{Mo(S}_2\text{CNR}_2)_2(\text{NO})_2]\) with sodium azide and \([\text{Mo(S}_2\text{CNEt}_2)_2(\text{NO})_2]\) with sodium cyanate were obtained by repetitive scanning of the spectral region. Typical spectral changes for the \([\text{Mo(S}_2\text{CNEt}_2)_2(\text{NO})_2]\)-\(\text{NaN}_3\) reaction are shown in Figure 4.4 and Table 4.1 lists the various peak maxima and isosbestic points found for the reactions.

4.5 Units and Notation

In this thesis all concentrations will be expressed in mole litre\(^{-1}\). The square bracket, [], will be used to denote the concentration of a species; however, since metal complexes have been contained in square brackets a "double"
Figure 4.3. The absorbance versus concentration plot for a \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2] \times 10^4\) solution in dimethylsulphoxide at 63.7°C.
Figure 4.4. Absorption spectral time scans for the reaction of cis-[Mo(S₂CNMe₂)₂(NO)₂] (4.4×10⁻⁴ M) with NaN₃ (4.94×10⁻² M) at 63.7°C in dimethylsulphoxide. Curve A is the initial trace followed successively by traces at 55, 115, 245, 475, 1405 and 2855 min reaction.
Table 4.1

Absorption Maxima and Isosbestic Points Found for the

$[\text{Mo}(\text{S}_2\text{CNR}_2)_2(\text{NO})_2]$-$\text{NaN}_3$ and $[\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]$-$\text{NaNCO}$

Reactions in Dimethylsulphoxide at 63.7°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak Maxima (nm)</th>
<th>Isosbestic Points (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) with NaN₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Mo}(\text{S}_2\text{CNMe}_2)_2(\text{NO})_2]$</td>
<td>484.5</td>
<td>370, 562, 603</td>
</tr>
<tr>
<td>$[\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]$</td>
<td>484</td>
<td>370, 578</td>
</tr>
<tr>
<td>$[\text{Mo}(\text{S}_2\text{CN(C}_2\text{H}_4)_2(\text{NO})_2]$</td>
<td>485</td>
<td>373, 563, 604</td>
</tr>
<tr>
<td>$[\text{Mo}(\text{S}_2\text{CN}^{\text{iPr}})_2(\text{NO})_2]$</td>
<td>489.5</td>
<td>375</td>
</tr>
<tr>
<td>$[\text{Mo}(\text{S}_2\text{CNn-Bu}_2)_2(\text{NO})_2]$</td>
<td>486</td>
<td>370, 584</td>
</tr>
<tr>
<td>$[\text{Mo}(\text{S}_2\text{CNbz}_2)_2(\text{NO})_2]$</td>
<td>483</td>
<td>390, 553, 612</td>
</tr>
<tr>
<td>(2) with NaNCO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]$</td>
<td>484.5</td>
<td>355</td>
</tr>
</tbody>
</table>

square bracket will be used for them, e.g. $[[\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]]$. Observed rate constants are quoted in sec⁻¹ units while energies are given in both kj mole⁻¹ and kcal mole⁻¹.

4.6 Rate Measurements on the Reactions of $[\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]$ with NaN₃ and KN₃

In this section the dependence of the rates of reaction on the azide concentration are described for the reactions of $[\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]$ with NaN₃ at 63.7°C and 73.1°C and KN₃ at 63.7°C. A typical Guggenheim plot for the evaluation of rate
Figure 4.5. A typical Guggenheim plot ($\Delta = 7$ hr) for the reaction of $cis$-$[\text{Mo(S}_2\text{CNEt}_2)_2(\text{NO})_2]$ (5.79$ \times 10^{-4}$ M) with $\text{NaN}_3$ (3.02$ \times 10^{-2}$ M) in dimethylsulphoxide at 63.7°C. The reaction half life is 3.03 hours and this corresponds to an observed rate constant of 6.35$ \times 10^{-5}$ sec$^{-1}$.
<table>
<thead>
<tr>
<th>[NaN₃]×10²</th>
<th>[[Mo(S₂CNEt₂)₂(NO)₂]]×10⁻⁶</th>
<th>[NaN₃]</th>
<th>[Mo(S₂CNEt₂)₂(NO)₂]</th>
<th>k_{observed}×10⁵ (sec⁻¹)</th>
<th>τ_{½} (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.83</td>
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<td>49</td>
<td>9.72</td>
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<td>76</td>
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<td>90</td>
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<td>2.30</td>
<td></td>
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<tr>
<td>4.08</td>
<td>5.60</td>
<td>73</td>
<td>8.37</td>
<td>2.30</td>
<td></td>
</tr>
<tr>
<td>3.02</td>
<td>5.79</td>
<td>52</td>
<td>6.35</td>
<td>3.03</td>
<td></td>
</tr>
<tr>
<td>3.02</td>
<td>6.77</td>
<td>45</td>
<td>6.35</td>
<td>3.03</td>
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</tr>
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<td>4.58</td>
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</tr>
<tr>
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<td>4.42</td>
<td>27</td>
<td>3.10</td>
<td>6.22</td>
<td></td>
</tr>
<tr>
<td>$[\text{NaN}_3] \times 10^2$</td>
<td>$[[\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]] \times 10^4$</td>
<td>$[[\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]]$</td>
<td>$k_{\text{observed}} \times 10^5 \text{ (sec}^{-1})$</td>
<td>$\tau_{\frac{1}{2}} \text{ (hrs)}$</td>
<td></td>
</tr>
<tr>
<td>----------------</td>
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<td>----------------</td>
<td>-----------------</td>
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<tr>
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<td>103</td>
<td>9.43</td>
<td>2.04</td>
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<tr>
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<td>10.43</td>
<td>38</td>
<td>19.8</td>
<td>0.973</td>
<td></td>
</tr>
<tr>
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<td>0.968</td>
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<td>15.8</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
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<td>1.17</td>
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<td>1.68</td>
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<td>11.8</td>
<td>1.63</td>
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<td>4.81</td>
<td></td>
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<tr>
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<td>8.90</td>
<td>14</td>
<td>6.70</td>
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<td>16</td>
<td>7.18</td>
<td>2.68</td>
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<td>1.21</td>
<td>4.74</td>
<td>26</td>
<td>7.47</td>
<td>2.58</td>
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</table>
Table 4.4
Rate Data at 63.7°C for the Reaction of [Mo(S₂CNEt₂)₂(NO)₂] and KN₃

<table>
<thead>
<tr>
<th>[KN₃] x 10²</th>
<th>[[Mo(S₂CNEt₂)₂(NO)₂]] x 10⁴</th>
<th>[KN₃]</th>
<th>k_{observed} x 10⁵ (sec⁻¹)</th>
<th>τ_{½} (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.62</td>
<td>10.39</td>
<td>44</td>
<td>9.63</td>
<td>2.00</td>
</tr>
<tr>
<td>4.62</td>
<td>6.51</td>
<td>71</td>
<td>9.63</td>
<td>2.00</td>
</tr>
<tr>
<td>4.64</td>
<td>4.49</td>
<td>103</td>
<td>9.43</td>
<td>2.04</td>
</tr>
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<td>3.63</td>
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<td>8.02</td>
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<td>7.95</td>
<td>2.42</td>
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<td>87</td>
<td>7.70</td>
<td>2.50</td>
</tr>
<tr>
<td>2.62</td>
<td>8.94</td>
<td>29</td>
<td>6.05</td>
<td>3.18</td>
</tr>
<tr>
<td>2.62</td>
<td>6.04</td>
<td>43</td>
<td>6.02</td>
<td>3.20</td>
</tr>
<tr>
<td>2.62</td>
<td>4.18</td>
<td>63</td>
<td>5.97</td>
<td>3.23</td>
</tr>
<tr>
<td>1.24</td>
<td>6.99</td>
<td>18</td>
<td>3.25</td>
<td>5.93</td>
</tr>
<tr>
<td>1.24</td>
<td>6.55</td>
<td>19</td>
<td>3.53</td>
<td>5.45</td>
</tr>
<tr>
<td>1.24</td>
<td>4.34</td>
<td>29</td>
<td>3.32</td>
<td>5.81</td>
</tr>
</tbody>
</table>
It is apparent from figure 4.6 that the observed rate constant, $k_{obs}$, is related to the azide concentration as follows:

$$k_{obs} = k_1 [N_3^-] + k_2$$

where $k_1$ and $k_2$ are constants for the reaction involved.

Table 4.6 gives the values of $k_1$ and $k_2$ for the three reactions obtained from a least-squares analysis of the data.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_1 \times 10^4$ (sec$^{-1}$)</th>
<th>$k_2 \times 10^4$ (mole$^{-1}$ litre sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A $[\text{Mo(S}_2\text{CNEt}_2]_2(\text{NO})_2]$ + NaN$_3$ at 73.1°C.</td>
<td>1.86 ± 0.10</td>
<td>0.74 ± 0.69</td>
</tr>
<tr>
<td>B $[\text{Mo(S}_2\text{CNEt}_2]_2(\text{NO})_2]$ + KN$_3$ at 63.7°C.</td>
<td>1.12 ± 0.24</td>
<td>1.19 ± 0.67</td>
</tr>
<tr>
<td>C $[\text{Mo(S}_2\text{CNEt}_2]_2(\text{NO})_2]$ + NaN$_3$ at 63.7°C.</td>
<td>4.55 ± 0.54</td>
<td>3.09 ± 1.14</td>
</tr>
</tbody>
</table>

4.6 Temperature Dependence Studies on the $[\text{Mo(S}_2\text{CNEt}_2]_2(\text{NO})_2]$-NaN$_3$ Reaction

The rates of reaction have been measured over the temperature range 32.8°C to 74.3°C using $[\text{Mo(S}_2\text{CNEt}_2]_2(\text{NO})_2]$ at 9.84 ± 0.1 M. Rate data at 63.7°C and 73.1°C have already been given in Tables 4.3 and 4.4 while Table 4.6 gives rate constants obtained for reactions in the range 32.8°C to 74.3°C.

Figure 4.6. $k_{obs}$ vs azide concentration plots for the reactions:

A $[\text{Mo(S}_2\text{CNEt}_2]_2(\text{NO})_2]$ + NaN$_3$ at 73.1°C.

B $[\text{Mo(S}_2\text{CNEt}_2]_2(\text{NO})_2]$ + KN$_3$ at 63.7°C.

C $[\text{Mo(S}_2\text{CNEt}_2]_2(\text{NO})_2]$ + NaN$_3$ at 63.7°C.
It is apparent from figure 4.6 that the observed rate constant, $k_{\text{obs}}$, is related to the azide concentration as follows:

$$k_{\text{obs}} = k_1[N_3^-] + k_2$$

(11)

where $k_1$ and $k_2$ are constants for the reaction involved. Table 4.5 gives the values of $k_1$ and $k_2$ for the three reactions obtained from a least squares analysis of the data.

### Table 4.5

Values of $k_1$ and $k_2$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_1 \times 10^3$ (mole$^{-1}$ litre sec$^{-1}$)</th>
<th>$k_2 \times 10^5$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Mo(S}_2\text{CNET}_2\text{)(NO)}_2\text{]} + \text{NaN}_3$ at 63.7°C</td>
<td>1.86±0.22</td>
<td>0.78±0.59</td>
</tr>
<tr>
<td>$[\text{Mo(S}_2\text{CNET}_2\text{)(NO)}_2\text{]} + \text{KN}_3$ at 63.7°C</td>
<td>1.84±0.24</td>
<td>1.15±0.62</td>
</tr>
<tr>
<td>$[\text{Mo(S}_2\text{CNET}_2\text{)(NO)}_2\text{]} + \text{NaN}_3$ at 73.1°C</td>
<td>4.55±0.54</td>
<td>2.00±1.14</td>
</tr>
</tbody>
</table>

4.7 Temperature Dependence Studies on the $[\text{Mo(S}_2\text{CNET}_2\text{)(NO)}_2\text{]} - \text{NaN}_3$ Reaction

The rates of reaction have been measured over the temperature range 52.8°C-73.1°C using a $[\text{NaN}_3] = 4.84 \times 10^{-2}$ M. Rate data at 63.7°C and 73.1°C have already been given in Tables 4.2 and 4.3 while Table 4.6 gives rate constants obtained at other temperatures in the range.
<table>
<thead>
<tr>
<th>Temperature (±0.1°C)</th>
<th>([\text{Mo}({\text{S}_2\text{CNET}_2})_2({\text{NO}})_2]) \times 10^4</th>
<th>([\text{NaN}_3])</th>
<th>(k_{\text{observed}}\times10^5) (sec(^{-1}))</th>
<th>(\tau_{1/2}) (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>68.0</td>
<td>8.92</td>
<td>54</td>
<td>15.2</td>
<td>1.27</td>
</tr>
<tr>
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<td>6.68</td>
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<td>15.2</td>
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<td>4.26</td>
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<td>15.5</td>
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<td>3.93</td>
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<td>4.14</td>
<td>117</td>
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</table>
Table 4.7 summarises the temperature dependence data for the Eyring plot shown in figure 4.7.

Table 4.7
Eyring Plot Data

<table>
<thead>
<tr>
<th>t°C</th>
<th>T (K)</th>
<th>1/Tx10³ (K⁻¹)</th>
<th>Average k_{obs} x 10⁷ (sec⁻¹)</th>
<th>-log₁₀(T⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>346.25</td>
<td>2.8880</td>
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<td>6.164</td>
</tr>
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<td>6.348</td>
</tr>
<tr>
<td>63.7</td>
<td>336.85</td>
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<td>2.90</td>
<td>6.538</td>
</tr>
<tr>
<td>60.2</td>
<td>333.35</td>
<td>2.9998</td>
<td>2.11</td>
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<td>325.95</td>
<td>3.0679</td>
<td>0.979</td>
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</table>

A least squares analysis of the data in Table 4.7 gave a slope of 4740 K and intercept of -7.53 for the Eyring plot.

Using equation (11), the following expressions for log \( \frac{k_1}{T} \) and log \( \frac{k_2}{T} \) may be written:

\[
\begin{align*}
-\log \frac{k_1}{T} & = -\log \frac{k_{obs}}{T} + \log \left\{ \frac{[N_3^-]}{k_1} + \frac{k_2}{k_1} \right\} \tag{12} \\
-\log \frac{k_2}{T} & = -\log \frac{k_{obs}}{T} + \log \left\{ \frac{[N_3^-]}{k_2} + \frac{k_1}{k_2} \right\} + 1 \tag{13}
\end{align*}
\]

In Table 4.5 the values of \( \frac{k_2}{k_1} \) at 63.7°C and 73.1°C are given as (0.42±0.36)×10⁻² and (0.44±0.26)×10⁻², respectively. The extrapolated values for \( k_2 \) give rise to large uncertainties. The similarity in the values of \( \frac{k_2}{k_1} \) at the two different temperatures may be fortuitous but it
Figure 4.7. An Eyring plot for the temperature dependence of the reaction of $[\text{Mo(S}_2\text{CNET}_2\text{)}_2(\text{NO})_2]$ with sodium azide in dimethylsulphoxide.
tends to suggest that \( \frac{k_2}{k_1} \) is approximately constant over the range 52.8-73.1°C. That is, the two processes (1 and 2) have similar enthalpies of activation. In addition, as \( k_1 >> k_2 \) the quantity \( \log \left\{ [N_3^-] + \frac{k_2}{k_1} \right\} \) varies only slightly with moderate changes in \( \frac{k_2}{k_1} \) (see Table 4.8).

Table 4.8

The Variation in \( \log \left\{ [N_3^-] + \frac{k_2}{k_1} \right\} \) as a function of \( \frac{k_2}{k_1} \)

<table>
<thead>
<tr>
<th>( \frac{k_2}{k_1} )</th>
<th>( \log_{10} \left{ [NaN_3] + \frac{k_2}{k_1} \right} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-1.32</td>
</tr>
<tr>
<td>0.2\times10^{-2}</td>
<td>-1.30</td>
</tr>
<tr>
<td>0.44\times10^{-2}</td>
<td>-1.28</td>
</tr>
<tr>
<td>0.8\times10^{-2}</td>
<td>-1.25</td>
</tr>
<tr>
<td>10^{-2}</td>
<td>-1.23</td>
</tr>
</tbody>
</table>

Therefore, equation (12) may be written as

\[
-\log_{10} \frac{k_1}{T} = -\log_{10} k_{\text{obs}} - 1.28
\]

and the graph of \( -\log_{10} \frac{k_1}{T} \) will have a slope of 4739 and intercept of -8.81. Then using equations (4), (7) and (8), the thermodynamic parameters for the process associated with \( k_1 \) are: \( \Delta H_1^\# = 91\pm4 \text{ kj mole}^{-1} \) (21.7\pm1.0 kcal mole\(^{-1}\)), \( \Delta S_1^\# = -29\pm12 \text{ j deg}^{-1} \text{ mole}^{-1} \) (7\pm3 cal deg\(^{-1}\) mole\(^{-1}\)) and \( \Delta G_1^\# \) (63.7°C) = 101\pm8 kj mole\(^{-1} \) (24\pm2 kcal mole\(^{-1}\)).

It follows from equation (5) that,

\[
RT \ln \frac{k_1}{k_2} = \Delta G_2^\# - \Delta G_1^\# \]

(15)
and using the values of $\Delta G_1^\neq$ and $\frac{k_2}{k_1}$ ($= 0.42\pm0.26\times10^{-2}$) the value of $\Delta G_2^\neq$ calculated using (15) is $116\pm10$ kJ mole$^{-1}$ ($28\pm2.5$ kcal mole$^{-1}$).

The uncertainty in the value of $\frac{k_2}{k_1}$ precludes the use of equation (10) because the log term varies significantly with small changes in $\frac{k_2}{k_1}$.

4.8 Dithiocarbamate Substituent Effects on the Rate of Reaction

The azide dependence of the $[\text{Mo(S}_2\text{CNR}_2)_2(\text{NO})_2]-\text{NaN}_3$ reactions have been measured for $R = \text{Me, } \frac{1}{2}\text{Pyr, i-Pr, n-Bu}$ and Bz at 63.7°C. The rate data is presented in Table 4.9 and Figure 4.8 shows the $k_{\text{obs}}$ versus $[\text{N}_3^-]$ plots.

Least squares analyses of the data in Table 4.9 were used to evaluate the slopes ($k_1$) and intercepts ($k_2$) of the plots shown in Figure 4.8 and Table 4.10 summarises the results.

<table>
<thead>
<tr>
<th>$R$</th>
<th>$k_1\times10^3$ (mole$^{-1}$ litre sec$^{-1}$)</th>
<th>$k_2\times10^5$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>1.93$\pm$0.23</td>
<td>0.73$\pm$0.61</td>
</tr>
<tr>
<td>Et</td>
<td>1.86$\pm$0.22</td>
<td>0.78$\pm$0.59</td>
</tr>
<tr>
<td>$\frac{1}{2}\text{Pyr}$</td>
<td>1.27$\pm$0.15</td>
<td>0.42$\pm$0.39</td>
</tr>
<tr>
<td>i-Pr</td>
<td>1.18$\pm$0.14</td>
<td>0.63$\pm$0.39</td>
</tr>
<tr>
<td>n-Bu</td>
<td>1.71$\pm$0.20</td>
<td>0.60$\pm$0.55</td>
</tr>
<tr>
<td>Bz</td>
<td>10.4$\pm$1.3</td>
<td>3.13$\pm$3.12</td>
</tr>
<tr>
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<td>$[\text{NaN}_3] \times 10^2$</td>
<td>$10^4 \times [\text{Mo(S}_2\text{CNR}_2\text{)}_2(\text{NO})_2]$</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
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continued
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<tr>
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<th>$[[\text{Mo(S}_2\text{CNR}_2)_2(\text{NO})_2]] \times 10^4$</th>
<th>$[\text{NaN}_3] / [[\text{Mo(S}_2\text{CNR}_2)_2(\text{NO})_2]]$</th>
<th>$k_{\text{observed}} \times 10^5 \text{ (sec}^{-1}\text{)}$</th>
<th>$\tau_{\frac{1}{2}} \text{ (hrs)}$</th>
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Table 4.9 continued

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<td>$k_{\text{observed}} \times 10^5$ (sec$^{-1}$)</td>
<td>$\tau_{\frac{1}{2}}$ (hrs)</td>
</tr>
<tr>
<td>----</td>
<td>------------------</td>
<td>------------------</td>
<td>-----------------</td>
<td>------------------------</td>
<td>----------------</td>
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<td>25</td>
<td>15.1</td>
<td>1.28</td>
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</table>
4.10 The effects of added water and dioxygen on the reaction of $[\text{Mo(S}_2\text{CNPh}_2\text{)}_2\text{(NO)}_2]$ with sodium azide at 63.7°C in dimethyl sulphoxide.

Table 4.11 lists the reactions which were used to calculate the observed rate constants of the $[\text{Mo(S}_2\text{CNPh}_2\text{)}_2\text{(NO)}_2]$ reactions.

Figure 4.8. $k_{\text{obs}}$ vs. $[\text{N}_3^-]^{10^2}$ plots for the reactions of $[\text{Mo(S}_2\text{CNPh}_2\text{)}_2\text{(NO)}_2]$ with sodium azide at 63.7°C in dimethyl sulphoxide ($R = \text{Me}, \text{Et}, \frac{1}{2}\text{Pyr}, \text{n-Bu}, \text{i-Pr}, \text{Bz}$).
4.9 The Effect of Cations on the Rate of the [Mo(S₂CNEt₂)₂(NO)₂]⁻NaN₃ Reaction at 63.7°C.

Table 4.11 lists the cations which were used and the observed rates of the [Mo(S₂CNEt₂)₂(NO)₂]⁻NaN₃ reactions.

4.10 The Effects of Added Water and Dioxygen on the [Mo(S₂CNEt₂)₂(NO)₂]⁻NaN₃ Reaction Rate at 63.7°C.

Both water and oxygen were found to have retardatry effects upon the rate of reaction. Table 4.12 gives the observed rate data.

4.11 The Reactions of [Mo(S₂CNEt₂)₂(NO)₂] with KNCO and NaNCO in Dimethylsulphoxide at 63.7°C.

The preliminary kinetic studies on the reaction of [Mo(S₂CNEt₂)₂(NO)₂] with cyanate have shown that the reaction is mechanistically complex. The reaction was found to have a stable infinity value and the quantity \((a_T - a_\infty)/(a_0 - a_\infty)\) was taken to represent the fraction \([([Mo(S₂CNEt₂)₂(NO)₂)]_T)/([Mo(S₂CNEt₂)₂(NO)₂])_0\). Figures 4.9 and 4.10 show typical \((a_T - a_\infty)/(a_0 - a_\infty)\) versus time plots for reactions with NaNCO and KNCO, respectively, at different concentrations of [Mo(S₂CNEt₂)₂(NO)₂].

4.12 Errors

The errors in the slope and intercept values of the \(k_{obs}\) versus \([N₃⁻]\) plots were calculated assuming a ±5% error in \(k_{obs}\). For the Eyring Plot (Figure 4.7) the method
Table 4.11
Cation Effects on the \([\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2]\)-\(\text{NaN}_3\) Reaction at 63.7°C

<table>
<thead>
<tr>
<th>Salt</th>
<th>[Salt](\times10^2)</th>
<th>[(\text{NaN}_3)](\times10^2)</th>
<th>([\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2])](\times10^4)</th>
<th>([\text{NaN}_3]) (\frac{[\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2]]}{[\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2]})</th>
<th>(k_{\text{observed}})(\times10^5)</th>
<th>(\tau_{\frac{1}{2}}) (hr)</th>
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<tr>
<td>CsBr</td>
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<td>6.38</td>
<td>3.02</td>
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<td>7.16</td>
<td>44</td>
<td>-</td>
<td>-</td>
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<td>51</td>
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<td>3.50</td>
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</table>

* HgS precipitated.

Table 4.12
The Rates of the \([\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2]\)-\(\text{NaN}_3\) Reactions in the Presence of Water and Dioxygen

<table>
<thead>
<tr>
<th>Additive</th>
<th>[(\text{NaN}_3)](\times10^2)</th>
<th>([\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2])](\times10^4)</th>
<th>([\text{NaN}_3]) (\frac{[\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2]]}{[\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2]})</th>
<th>(k_{\text{observed}})(\times10^5)</th>
<th>(\tau_{\frac{1}{2}}) (hr)</th>
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<tr>
<td>([\text{H}_2\text{O}] = 0.57 \text{ M})</td>
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<td>7.39</td>
<td>42</td>
<td>5.18</td>
<td>3.71</td>
</tr>
<tr>
<td>saturated with (\text{O}_2)</td>
<td>3.11</td>
<td>6.82</td>
<td>46</td>
<td>3.0</td>
<td>6.4</td>
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</table>
Figure 4.9. Plots of \(\frac{A_t - A_\infty}{A_0 - A_\infty}\) for the reaction of [Mo(S₂CNEt₂)₂(NO)]̈ with sodium cyanate in dimethylsulphoxide at 63.7°C:

A: [NaNCO] = 3.81x10⁻²M, 
\([\text{[Mo(S₂CNEt₂)₂(NO)]}]\) = 4.9x10⁻⁴M

B: [NaNCO] = 3.82x10⁻²M,
\([\text{[Mo(S₂CNEt₂)₂(NO)]}}]\) = 7.5x10⁻⁴M
Figure 4.10. Plots of \( \frac{a_T - a_\infty}{a_0 - a_\infty} \) for the reaction of \([\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2]\) with potassium cyanide in dimethyl sulphoxide at 63.7°C.

A [KNCO] = 3.96×10^{-2} M, \([\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2]\) = 2.57×10^{-4} M
B [KNCO] = 3.96×10^{-2} M, \([\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2]\) = 4.5×10^{-4} M
C [KNCO] = 3.96×10^{-2} M, \([\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2]\) = 7.1×10^{-4} M.
described by Edwards, Monacelli and Ortaggi\textsuperscript{143} was used to calculate the errors in $\Delta H^\#$ and $\Delta S^\#$.

4.13 Discussion

The labelling studies described in chapter 3 for the reactions of \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{NO})_2]\) with azide and cyanate showed that one nitrosyl group per molecule reacts via an associative mechanism to give dinitrogen oxide. It was also pointed out that no reaction occurs in the absence of anion.

The kinetic studies on the \([\text{Mo}(\text{S}_2\text{CNR}_2)_2(\text{NO})_2]\)-\(\text{N}_3^-\) reactions have shown that the rate expression is:

\[
\frac{d}{dt} [\text{Mo}(\text{S}_2\text{CNR}_2)_2(\text{NO})_2)] = k_1[N_3^-] + k_2[\text{Mo}(\text{S}_2\text{CNR}_2)_2(\text{NO})_2]\]

That is, the reaction proceeds via two parallel reaction pathways; one shows a first order dependence on both the Mo complex and azide concentrations while the other is independent of azide and first order in Mo complex.

The azide dependent reaction is consistent with an associative mechanism involving \([\text{Mo}(\text{S}_2\text{CNR}_2)_2(\text{NO})_2]\) and azide in the rate determining step. A reaction scheme similar to that proposed in chapter 3 is given below:

\[
\begin{align*}
\text{[Mo}(\text{S}_2\text{CNR}_2)_2(\text{NO})_2] + \text{N}_3^- & \xrightarrow{k_1} \text{[MoN}_3(\text{S}_2\text{CNR}_2)_2(\text{NO})_2]^- \\
2\text{[MoN}_3(\text{S}_2\text{CNR}_2)_2\text{NO}]^- & \xrightarrow{\text{fast}} \text{[\{MoN}_3(\text{S}_2\text{CNR}_2)_2\text{NO}\}_2-\mu-N_2\text{O}_2]^{2^-}} \\
[\text{MoN}_3(\text{S}_2\text{CNR}_2)_2\text{NO}] + \text{N}_2\text{O} + (\text{CH}_3)_2\text{SO} & \xrightarrow{\text{fast}} [\text{mo}(\text{N}_3)_2(\text{S}_2\text{CNR}_2)_2\text{NO}]^- \\
\text{moN}_3(\text{S}_2\text{CNR}_2)_2\text{NO} + \text{N}_3^- & \xrightarrow{\text{fast}} \text{[mo}(\text{N}_3)_2(\text{S}_2\text{CNR}_2)_2\text{NO}]^- \\
\end{align*}
\]
The interpretation of the azide independent pathway is, however, more difficult. An insight into how this process may arise comes from the work of Johnson et al.\textsuperscript{144} dealing with a variable temperature \textsuperscript{1}H nmr study on [Mo(S₂CNMe₂)₂(NO)₂] in ethylene glycol. It was shown that, between 80-140°C, the NMe groups on the dithiocarbamate ligand were undergoing a rapid interconversion. Although the authors could not rule out a structural rearrangement they favoured a mechanism for the interconversion which involved a partly dissociated dithiocarbamate ligand. Such a dissociation under the reaction conditions could allow the coordination of an azide ion. Then the subsequent coordination of the free S of the dithiocarbamate would generate a similar intermediate to that generated in the associative mechanism. A possible reaction scheme for the azide independent pathway is:

\[
\begin{align*}
[\text{Mo}(S₂CNR₂)₂(NO)₂] & \xrightleftharpoons[k_{-2}]{k_2} [\text{Mo}(S₂CNR₂)(S-CNR₂)(NO)₂] \\
[S] & \text{fast} \Rightarrow \text{[MoN₃(S₂CNR₂)(S-CNR₂)]⁻} \blue{\text{(fast)}} \\
[\text{MoN₃(S₂CNR₂)(S-CNR₂)(NO)₂}]⁻ & \xrightarrow{\text{fast}} [\text{MoN₃(S₂CNR₂)₂(NO)₂}]⁻ \\
[S] & \text{fast} \Rightarrow \text{[MoN₃(S₂CNR₂)(S-CNR₂)]⁻} \blue{\text{(fast)}} \\
[\text{MoN₃(S₂CNR₂)₂(NO)₂}]⁻ & \xrightarrow{\text{fast}} [\text{MoN₃(S₂CNR₂)₂(NO)₂}]⁻
\end{align*}
\]

The reaction then follows the same course as the associative process. The rate expression for this scheme is:

\[
\frac{d}{dt}[\text{[Mo}(S₂CNR₂)₂(NO)₂]] = \frac{k₂k₃[N₃⁻]}{k_{-2} + k₃[N₃⁻]}[\text{[Mo}(S₂CNR₂)₂(NO)₂]]
\]

and for \(k₃[N₃⁻] >> k_{-2}\), this becomes

\[
\frac{d}{dt}[\text{[Mo}(S₂CNR₂)₂(NO)₂]] = k₂[\text{[Mo}(S₂CNR₂)(NO)₂]].
\]
The two rate processes that have been discussed are illustrated in Figure 4.11 and when combined they provide a satisfactory explanation for the observed reaction kinetics.

The temperature dependence studies on the [Mo(S₂CNMe₂)₂(NO)₂]-N₃⁻ reaction (section 4.7) established that the thermodynamic parameters for the associative process (k₁) were: ΔH₁‡ = 91±4 kJ mole⁻¹, ΔS₁‡ = -29±12 J deg⁻¹ mole⁻¹ and ΔG₁‡ (63.7°C) = 101±8 kJ mole. The limited thermodynamic data on reactions of this kind make any meaningful interpretation of the small negative entropy of activation difficult. The value of ΔS₁‡ must reflect the loss in translation degrees of freedom but other factors involving solvent interactions and changes in vibrational and rotational degrees of freedom could also be making a significant contribution to the entropy of activation.

The thermodynamic quantities obtained from the variable temperature 'H nmr studies on [Mo(S₂CNMe₂)₂(NO)₂] for the process which interconverts the NMe groups were ΔH₂‡ = 93±4 kJ mole, ΔS₂‡ = 17 J deg mole⁻¹ and ΔG₂‡ (128°C) = 86.2±0.4 kJ mole⁻¹. If it is assumed that this equilibration and the azide independent process (k₂) are due to partial dithiocarbamate dissociation then both should have similar enthalpies of activation. This implies that ΔH₁‡ and ΔH₂‡ have nearly the same value, consistent with the results of section 4.7. So, by letting ΔH₂‡ = 91±4 kJ mole⁻¹, the value calculated for ΔS₂‡ is -74±47 J deg⁻¹ mole⁻¹ (-18±11 cal deg⁻¹ mole). This entropy value is more negative than that obtained from the pmr experiment with [Mo(S₂CNMe₂)₂(NO)₂] and this may be due to the azide having
Figure 4.11. The proposed rate determining processes involved in the reactions of [Mo(S₂CNR₂)₂(NO)₂] with N₃⁻.
to compete with the free S of the dithiocarbamate for the sixth coordination site. The transition state for the azide independent pathway (k₂) could require the partially dissociated dithiocarbamate to be in a particular (unfavourable) configuration to facilitate the coordination of azide.

The effect of dithiocarbamate substituents upon the rates of the [Mo(S₂CNR₂)₂(NO)₂N₃]-NaN₃ reactions have been detailed in section 4.8. From the data presented it is clear that, with the exception of [Mo(S₂CNBz₂)₂(NO)₂], the substituent effect is small.

There are two obvious factors which should effect the rate of the associative process (k₁) and these are:

(a) Steric Effects

That is, the ease by which a seven coordinate complex is formed should be related to the steric bulk of the dithiocarbamate substituents.

Some experimental evidence for the existence of steric effects comes from a study by Colton and Scollary on the relative stabilities of the [Mo(S₂CNR₂)₂(CO)₃] complexes in the solid state. They found that the rate of loss of carbon monoxide to give [Mo(S₂CNR₂)₂(CO)₂] decreased in the order Bz₂ > Et₂ > Me₂ > Pyr in accord with the decreasing steric interactions. However, other factors such as crystal packing and the electronic nature of R could also be significant.

(b) Electronic Effects

It was shown in Chapter 2 that the greater the electron donating power of the dithiocarbamate ligand, the
larger was the energy gap, $\Delta$, between metal ($d_{xy}$, $d_{yz}$, $d_{z^2}$) orbitals and the $\pi^*_{b}$(NO) level. Upon coordination of azide to $[\text{Mo}(S_2\text{CNR}_2)_2(\text{NO})_2]$ an electron pair is transferred from the metal into the $\pi^*_{b}$(NO) orbital (Chapter 3) and consequently the magnitude of $\Delta$ should relate to the ease of azide ion coordination.

Interestingly, $[\text{Mo}(S_2\text{CNBz}_2)_2(\text{NO})_2]$ reacts far more rapidly than do the other dinitrosyl complexes having less bulky dithiocarbamate groups. This strongly suggests that electronic effects play the most significant role in determining the rates of reaction. The dibenzyldithiocarbamate ligand is the least electron donating of the dithiocarbamates studied$^{110}$ implying that $[\text{Mo}(S_2\text{CNBz}_2)_2(\text{NO})_2]$ has the smallest $\Delta$ value. The electron donor capacities of the dithiocarbamate ligands increase in the order $\text{Bz}_2 << \text{Me}_2 < \text{Pyr} < \text{Et}_2 ~ n\text{-Bu}_2 < \text{i-Pr}_2$ (see Chapter 2) while the observed rate constants decrease in the order $\text{Bz}_2 >> \text{Me}_2 > \text{Et}_2 > n\text{-Bu}_2 > \text{Pyr} ~ \text{i-Pr}_2$.

The rate of the $[\text{Mo}(S_2\text{CNC}_2\text{H}_4)_2(\text{NO})_2]$ reaction appears anomalous but more information on the $\Delta H^\neq$ values for each of the substituents is required before any definite conclusions can be made.

For the azide independent reaction pathway ($k_2$), any dithiocarbamate substituent effects are masked by the large errors involved with the values of $k_2$ and therefore will not be discussed in any detail.

It was seen in section 4.6 that the reactions of $[\text{Mo}(S_2\text{CNEt}_2)_2(\text{NO})_2]$ with KN$_3$ were always slightly faster than the corresponding reactions with NaN$_3$. The slopes of the $k_{obs}$ versus $[\text{N}_3^-]$ plots were the same but the intercepts
appeared to differ, \((1.15\pm0.62\times10^{-5}\text{ sec}^{-1}\) and \(0.78\pm0.59\times10^{-5}\text{ sec}^{-1}\) for KN\(_3\) and NaN\(_3\), respectively). Consideration of the errors involved shows that the two values are not significantly different. However, the systematic behaviour does suggest that the cation (Na\(^+\) or K\(^+\)) is effecting the rate of the azide independent pathway. Other cations (e.g., Ca\(^{2+}\), Ba\(^{2+}\), Cs\(^+\), Mg\(^{2+}\)) which were added to the \([\text{Mo(S}_2\text{CNEt}_2\text{)(NO)}_2]\) reaction solutions had relatively little effect on the observed rate constants.

Both water and dioxygen were found to retard the rate of reaction (section 4.7). A \([\text{Mo(S}_2\text{CNEt}_2\text{)(NO)}_2]\)-NaN\(_3\) reaction solution, 0.57 M in H\(_2\)O, had a rate constant 20\% lower than in the absence of water whereas for dioxygen a 50\% slower reaction was observed. The reduced reaction rate in the presence of water can be understood in terms of increased anion solvation by water molecules\(^{146}\) but the role dioxygen plays is not clear. Nitric oxide was also found to decrease the reaction rate (Chapter 3).

The kinetic studies on the reactions of \([\text{Mo(S}_2\text{CNEt}_2\text{)(NO)}_2]\) with potassium and sodium cyanate have shown that they are mechanistically complex. The reactions are far more rapid than those with azide and in addition a period of induction was observed. The length of the induction period depended on the concentration of \([\text{Mo(S}_2\text{CNEt}_2\text{)(NO)}_2]\) and also it differed between potassium and sodium cyanate (see Figures 4.9 and 4.10). Evidence for a specific cation effect between sodium and potassium ions has already been noted.

The observation of an induction period using spectro­
photometric techniques was first thought to suggest a series
type reaction in which one of the intermediates had a similar UV-visible spectrum to \([\text{Mo}(S_2\text{CNEt}_2)_2(\text{NO})_2]\). The reaction scheme considered was:

\[
\begin{align*}
\text{[Mo}(S_2\text{CNEt}_2)_2(\text{NO})_2] + \text{NCO}^- & \xrightarrow{k_1} \text{[MoNCO}(S_2\text{CNEt}_2)(S-\text{CNEt}_2)(\text{NO})_2]^- \\
\text{[MoNCO}(S_2\text{CNEt}_2)(S-\text{CNEt}_2)(\text{NO})_2]^- & \xrightarrow{k_2} \text{[MoNCO}(S_2\text{CNEt}_2)_2(\text{NO})_2]^- \\
2\text{[MoNCO}(S_2\text{CNEt}_2)_2(\text{NO})_2]^- & \text{fast} \rightarrow \text{N}_2\text{O} + \text{[MoNCO}(S_2\text{CNEt}_2)_2\text{NO}] + "\text{other Mo species}"
\end{align*}
\]

In this scheme \([\text{Mo}(S_2\text{CNEt}_2)_2(\text{NO})_2]\) and \([\text{MoNCO}(S_2\text{CNEt}_2)(S-\text{CNEt}_2)(\text{NO})_2]^-\) are suggested to have similar UV-visible spectra. As a large excess of cyanate was used in the reactions, the above mechanism simplifies to one of the type.

\[
\begin{align*}
A & \xrightarrow{k_1} B \\
B & \xrightarrow{k_2} C \\
2C & \text{fast} \rightarrow \text{products}
\end{align*}
\]

where

\[
\begin{align*}
k_1 &= k_1[\text{NCO}^-] \\
A &= [\text{Mo}(S_2\text{CNEt}_2)_2(\text{NO})_2] \\
B &= [\text{MoNCO}(S_2\text{CNEt}_2)(S-\text{CNEt}_2)(\text{NO})_2]^- \\
C &= [\text{MoNCO}(S_2\text{CNEt}_2)_2(\text{NO})_2]^- \\
\end{align*}
\]

This is a "pseudo-first order series reaction" and the analysis of such reactions has been treated by Frost and Pearson\(^{142}\). The concentration-time relationships are:

\[
\begin{align*}
A &= A_0 e^{-k_1 t} \\
B &= \frac{A_0 k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})
\end{align*}
\]

where \(A_0\) is the initial concentration of \(A\).
Let \( \alpha = A/A_0 \), \( \beta = B/A_0 \), \( \tau = k_1 t \) and \( K = k_2/k_1 \). If it is assumed that the quantity \( P = (a_t - a_\infty)/(a_0 - a_\infty) = \alpha + \beta = e^{-\tau} + \frac{1}{K-1} (e^{-\tau} - e^{-kT}) \) then a series of Powell plots may be constructed of \( P \) versus \( \log \tau \). Figure 4.12 shows the curves obtained for various values of \( K \). It is apparent that as \( K \) decreases the period of induction is increased. The curves have also been characterised by their time ratio values with \( P_1 = 0.85 \), \( P_2 = 0.65 \) and \( P_3 = 0.30 \) and the corresponding values of \( \tau_1, \tau_2, \tau_3, \frac{\tau_1}{\tau_2}, \frac{\tau_1}{\tau_3} \) and \( \frac{\tau_2}{\tau_3} \) have been listed for various \( K \) values in Table 4.13.

<table>
<thead>
<tr>
<th>K Value</th>
<th>( \tau_1 )</th>
<th>( \tau_2 )</th>
<th>( \tau_3 )</th>
<th>( \frac{\tau_1}{\tau_2} )</th>
<th>( \frac{\tau_1}{\tau_3} )</th>
<th>( \frac{\tau_2}{\tau_3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.259</td>
<td>0.536</td>
<td>1.310</td>
<td>0.483</td>
<td>0.198</td>
<td>0.409</td>
</tr>
<tr>
<td>5</td>
<td>0.331</td>
<td>0.639</td>
<td>1.427</td>
<td>0.518</td>
<td>0.232</td>
<td>0.448</td>
</tr>
<tr>
<td>2</td>
<td>0.490</td>
<td>0.856</td>
<td>1.812</td>
<td>0.547</td>
<td>0.270</td>
<td>0.495</td>
</tr>
<tr>
<td>1.1</td>
<td>0.652</td>
<td>1.179</td>
<td>2.328</td>
<td>0.553</td>
<td>0.280</td>
<td>0.506</td>
</tr>
<tr>
<td>0.5</td>
<td>0.980</td>
<td>1.792</td>
<td>3.624</td>
<td>0.547</td>
<td>0.270</td>
<td>0.495</td>
</tr>
<tr>
<td>0.333</td>
<td>1.228</td>
<td>2.284</td>
<td>4.791</td>
<td>0.538</td>
<td>0.256</td>
<td>0.477</td>
</tr>
<tr>
<td>0.25</td>
<td>1.449</td>
<td>2.745</td>
<td>5.956</td>
<td>0.528</td>
<td>0.243</td>
<td>0.461</td>
</tr>
</tbody>
</table>

The dashed line on Figure 4.11 corresponds to curve C of Figure 4.10 and clearly is not one of the family of curves for a pseudo-first order series reaction. This type of mechanism is also ruled out because the type of curve obtained in the \([\text{Mo}(S_2\text{CNET}_2)_2(\text{NO})_2]\)-NCO\(^-\) reactions is a
Figure 4.11. Powell plots for the first order series reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{2C \text{ fast}} \text{products}$$

in which the parameter used to follow the overall reaction is not changed by the first step in the reaction. The dashed line is curve C of Figure 4.10.
function of the concentration of \([\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]\).

The only reasonable explanation for the curves obtained in Figures 4.9 and 4.10 is that they represent an autocatalytic process which follows a rate expression of the type \[-\frac{d}{dt}[\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]] = (k_1 + k_2[B])[\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]^{-}; \]
where \([B]\) is the concentration of a catalyst produced during the reaction. However, the nature of the catalyst and the mechanism by which it catalyses the reaction are unknown.

A Summary

The kinetic studies on the \([\text{Mo}(\text{S}_2\text{CNR}_2)_2(\text{NO})_2]^{-}\text{N}_3^-\) reaction system have shown that two parallel reaction pathways exist. These are a dominant process involving both \([\text{Mo}(\text{S}_2\text{CNR}_2)_2(\text{NO})_2]\) and azide reacting in the rate determining step and a much slower reaction dependent only on the concentration of \([\text{Mo}(\text{S}_2\text{CNR}_2)_2(\text{NO})_2]\). It was suggested that this latter process involved partial dithiocarbamate dissociation. Both reaction pathways are thought to generate the same reaction intermediate as shown in Figure 4.11.

The labelling experiments described in Chapter 3 provided information on the nature of the nitrosyl reaction while the kinetic studies have dealt with the rate determining steps in the reaction. It is clear that the anion plays an essential activating role in the reaction and this is in accord with the discussion given in Chapter 1.

The reactions of \([\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{NO})_2]\) with cyanate have proven to be mechanistically complex. The same type of nitrosyl reaction is involved (labelling experiments of
Chapter 3) but the rate determining step involving cyanate appears to be catalysed by a product of the reaction. The reaction mechanism can, at present, be best described as being autocatalytic in nature.

It would have been desirable to use an alternative to the spectrophotometric method in following the kinetics but unfortunately no suitable alternatives were readily available. Vapour phase chromatography is one technique which could be used to monitor the dinitrogen oxide evolution but time did not permit its development.

Some reservations must therefore be held concerning the mechanisms suggested in this chapter.
5.1 Introduction

The chemistry of dinitrogen differs markedly from that of other related molecules (e.g., NO, CO, O$_2$, CuN$_2$) in that it is extremely unreactive. The relative inertness of the dinitrogen molecule may be understood in terms of the data compiled in Tables 5.1 and 5.2 (taken from reference 208).

Table 5.1

<table>
<thead>
<tr>
<th>Comparative physical properties of dinitrogen, diatomic, acetylene, carbon monoxide and nitric oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length ($\text{Å}$)</td>
</tr>
<tr>
<td>Ionisation energy (eV)</td>
</tr>
<tr>
<td>Dissociation energy (kcal)</td>
</tr>
<tr>
<td>Stretching frequency (cm$^{-1}$)</td>
</tr>
</tbody>
</table>

Aspects of Dinitrogen Fixation

The great strength of the nitrogen-nitrogen triple bond compared to the nitrogen-nitrogen double bond combined with the high ionisation potential and non-polarity of the molecule are significant factors contributing to the chemical inertness. Figure 5.1 shows the electronic structure of the dinitrogen molecule while in Figure 5.2 the dinitrogen energy levels are correlated with those in the other molecules listed in Table 5.1.

The N$_2^-$ ion has been identified in the mass spectrometer and also in crystalline samples of KN$_2$ and NaN$_2$ damaged by $\gamma$-irradiation$^{128}$, but no derivatives of the anion have
5.1 Introduction

The chemistry of dinitrogen differs markedly from that of other related molecules (e.g. NO, CO, O₂, C₂H₂) in that it is extremely unreactive. The relative inertness of the dinitrogen molecule may be understood in terms of the data compiled in Tables 5.1 and 5.2 (taken from reference 148).

Table 5.1

Comparative physical properties of dinitrogen, dioxygen, acetylene, carbon monoxide and nitric oxide

<table>
<thead>
<tr>
<th></th>
<th>N≡N</th>
<th>O=O</th>
<th>HC≡CH</th>
<th>CO</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length (Å)</td>
<td>1.098</td>
<td>1.207</td>
<td>1.208</td>
<td>1.128</td>
<td>1.150</td>
</tr>
<tr>
<td>Ionization energy (eV)</td>
<td>15.6</td>
<td>12.3</td>
<td>11.4</td>
<td>14.0</td>
<td>9.3</td>
</tr>
<tr>
<td>Dissociation energy (kcal)</td>
<td>225</td>
<td>118</td>
<td>200</td>
<td>235</td>
<td>150</td>
</tr>
<tr>
<td>Stretching frequency (cm⁻¹)</td>
<td>2331</td>
<td>1555</td>
<td>1974</td>
<td>2143</td>
<td>1876</td>
</tr>
</tbody>
</table>

The great strength of the nitrogen-nitrogen triple bond compared to the nitrogen-nitrogen double bond combined with the high ionisation potential and non-polarity of the molecule are significant factors contributing to the chemical inertness. Figure 5.1 shows the electronic structure of the dinitrogen molecule while in Figure 5.2 the dinitrogen energy levels are correlated with those in the other molecules listed in Table 5.1.

The N₂⁻ ion has been identified in the mass spectrometer and also in crystalline samples of KN₃ and NaN₃ damaged by γ-irradiation¹⁴⁸, but no derivatives of the anion have
Table 5.2
Comparison of single and multiple bond energies

<table>
<thead>
<tr>
<th></th>
<th>C-C</th>
<th>C-N</th>
<th>C-O</th>
<th>N-N</th>
<th>N-O</th>
<th>O-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triple bond</td>
<td>194</td>
<td>210</td>
<td>235</td>
<td>225</td>
<td>252</td>
<td></td>
</tr>
<tr>
<td>Ratio, triple:double</td>
<td>1.32</td>
<td>1.43</td>
<td>1.31</td>
<td>2.25</td>
<td>~3.0</td>
<td></td>
</tr>
<tr>
<td>Double bond</td>
<td>147</td>
<td>147</td>
<td>170</td>
<td>100</td>
<td>~80</td>
<td>96</td>
</tr>
<tr>
<td>Ratio, double:single</td>
<td>1.77</td>
<td>2.10</td>
<td>2.01</td>
<td>2.63</td>
<td>~2.0</td>
<td>2.91</td>
</tr>
<tr>
<td>Single bond</td>
<td>83</td>
<td>70</td>
<td>84</td>
<td>38</td>
<td>~40</td>
<td>33</td>
</tr>
</tbody>
</table>
ENERGY LEVELS IN THE NITROGEN MOLECULE

\[ \begin{align*}
\sigma_{g}^{2s} & : \text{strongly bonding} \\
\sigma_{u}^{2s} & : \text{weakly bonding}
\end{align*} \]

Figure 5.1

The reaction involving dinitrogen in the Haber-Schimmel process is 1.50 times as reactive as ammonia at 800°C in the presence of iron catalyst. The reaction is extremely slow at 20°C and reaches quantitative at 25°C (68°F). At 800°C, the rate of reaction is 1.50 x the rate at 25°C. The reaction occurs in the Haber-Schimmel process and the reaction conditions employed in the Haber-Schimmel process are a trade-off between reaction rate and the yield of ammonia.

For the purposes of this thesis, the term "dinitrogen fixation" will be taken to mean any reaction of the dinitrogen molecule. This rather broad definition also includes the reaction of dinitrogen with transition metals to yield dinitrogen complexes with covalent character. Interestingly, dinitrogen fixation is the only reaction of dinitrogen which occurs under standard conditions.

![Diagram of energy levels in the nitrogen molecule](image)

Figure 5.2
been isolated. $N_2^-$ should have an unpaired electron in its $\pi^*(N_2)$ level, making it isoelectronic with NO and $O_2^+$. Reactions involving dinitrogen generally require drastic conditions. For example, in the Haber-Bosch process, a mixture of dinitrogen and dihydrogen are reacted at temperatures of around 500°C and under several hundred atmospheres pressure, over an iron oxide catalyst, to yield ammonia in ∼35% yield.

The reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$ is virtually quantitative at 25°C ($\Delta G_f = -16.6 \text{ kJ mol}^{-1}$; $\Delta H_f = 46 \text{ kJ mol}^{-1}$; $\Delta S_f = 193 \text{ J deg}^{-1} \text{ mol}^{-1}$) but unfortunately the rate of reaction is extremely slow. At higher temperatures and pressures the equilibrium constant is far less favourable and the reaction conditions employed in the Haber-Bosch process are a trade-off between reaction rate and the yield of ammonia.

For the purposes of this thesis, the term "Dinitrogen fixation" will be taken to mean any reaction of the dinitrogen molecule. This rather broad definition also includes the reaction of dinitrogen with transition metals to yield dinitrogen complexes. Interestingly, this is the only reaction of dinitrogen which occurs under mild conditions. The possible modes of dinitrogen bonding to transition metal complexes are shown in Figure 5.1.
At present, only structures involving (a), (d) and (f) type bonding have been unequivocally established. The "end-on" bonding of dinitrogen shown in (a) is by far the most common but a number of bridging dinitrogen complexes (d) are known. However, only two examples of type (f) coordination have been structurally characterised to date\textsuperscript{151,152}.

The stimulus for the study of transition metal dinitrogen complexes has come from the fact that a variety of microorganisms are capable of fixing dinitrogen to ammonia under mild physiological conditions, i.e. at room temperature under one atmosphere pressure and in aqueous media\textsuperscript{153,154}. The enzyme responsible for the reduction of dinitrogen, known as nitrogenase, has been isolated from a number of microorganisms.

All of the nitrogenase enzymes appear to consist of two separate proteins, both of which are necessary for the fixation process. One component known as the "Mo-Fe-protein" has a molecular weight of around 200,000 and contains 1-2 molybdenum atoms, 20-40 iron atoms, 20-40 sulphide ions and more than 40 cysteiny1 residues. The other enzyme component, termed the "Fe-protein", is much smaller with a molecular weight between 40,000 and 50,000 and generally contains 4 iron atoms, 4 sulphide ions and 4 cysteiny1 units. Although
the structure of this protein has not been determined, it is a typical ferredoxin\textsuperscript{154} and therefore probably contains the iron in a quasicubic aggregate of the form \( \text{Fe}_4\text{S}_4(\text{S-protein})_4\).\textsuperscript{155,156}

When the two protein components, together with the monomagnesium salt of ATP and a suitable reducing agent (e.g. \( \text{Na}_2\text{S}_2\text{O}_4 \)) are present in neutral aqueous solution, dinitrogen is readily converted into ammonia under ambient conditions. In addition to dinitrogen, the enzyme is also capable of reducing a number of other molecules, e.g.

\[
\begin{align*}
\text{N}_3^- & \rightarrow \text{N}_2 + \text{NH}_3; \\
\text{N}_2\text{O} & \rightarrow \text{H}_2\text{O} + \text{N}_2; \\
\text{C}_2\text{H}_2 & \rightarrow \text{C}_2\text{H}_4; \\
\text{CN}^- & \rightarrow \text{CH}_4, \\
\text{NH}_3, \text{C}_2\text{H}_6, \text{C}_2\text{H}_4 \text{ and RNH}_2.
\end{align*}
\]

It now seems probable that the dinitrogen is reduced at a molybdenum atom on the Mo-Fe-protein and that the function of the Fe-protein is to facilitate the transfer of electrons to the active site. The fraternity of inorganic chemists interested in dinitrogen fixation have approached the problem from two different angles. A large number of chemists, exemplified by Chatt and co-workers in England, have chosen to study well characterised transition metal dinitrogen complexes\textsuperscript{157}. They and others have achieved considerable success in the fixation of dinitrogen bound to the metal under very mild conditions. Some of these reactions will be discussed in later sections.

The second approach has been to study "Inorganic soups" which generally consist of a mixture of transition metal complexes that are in most cases rather ill-defined, a reducing agent and a number of other ingredients which vary according to the experimenters tastes\textsuperscript{158}. The catalytic
activities of the soups towards reduction of dinitrogen or other nitrogenase substrates (usually $C_2H_2$) are then assessed.

By far the most significant contributions in this area have been made by G.N. Schrauzer and his co-workers$^{155}$. One phase of their work has centred on the oxo bridged Mo(V) cysteine complex, $Na_2[Mo_2O_2(Cys)_2]$ (1) which in aqueous alkaline solution, together with $NaBH_4$ or $Na_2S_2O_4$ reduces dinitrogen to ammonia. The dimer (1) is not the catalytically active species and it is thought to undergo partial dissociation in solution to give monomeric Mo(V) complexes. Schrauzer has suggested that these then undergo reduction to catalytically active Mo(IV) species which are responsible for the reduction of dinitrogen. This has been challenged by other workers who have shown that (1) may be reduced in a single 4 electron step at -1.2 to -1.3 V vs. SCE to Mo(III) species which reduce acetylene to ethylene$^{159}$. But whatever the exact nature of the catalyst, the fact remains that these solutions are capable of reducing dinitrogen under mild conditions. In addition high oxidation state complexes of molybdenum (either Mo(III) or Mo(IV)) are implicated. Schrauzer et al have also shown that the addition of ATP and/or the ferredoxin model compounds $[FeS_4(SR)_4]^{2-}$$^{160}$ significantly increase the rate of reduction$^{155}$. More recently, the cysteine complex (1) has been replaced by $[MoO(CN)_4(H_2O)]^{2-}$ and greater catalytic activity was observed$^{161}$. The importance of S donor ligands has also been demonstrated for the Mo-cysteamine and related ligand systems with the catalytic activity being $S > Se >> O$$^{162}$.

For the mechanism of reduction in these "soups" Schrauzer has postulated that the dinitrogen binds "side-on"
to the molybdenum as shown in Figure 5.3(b) and is then reduced in a two electron step to diazene. The presence of diazene in the reaction solutions was confirmed by adding fumarate; the reaction involved being: \( \text{N}_2\text{H}_2 + \text{O}_2\text{CCH} = \text{CHCO}_2^- \rightarrow \text{N}_2 + \text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2^- \). The diazene is then suggested to decompose and disproportionate according to the known reaction:

\[
3\text{N}_2\text{H}_2 \rightarrow 2\text{N}_2 + \text{H}_2 + \text{N}_2\text{H}_4
\]

The hydrazine then coordinates to the catalytically active molybdenum complex and is reduced to ammonia. An important feature of this postulated mechanism is that diazene is not reduced by the catalyst. Clearly, the choice of ingredients in Schrauzer's "soups" has been guided by the studies on the nitrogenase enzymes and the speculated nature of the active site. The success of these experiments must surely have strong implications as to the nature of the reduction in the enzymatic system. If the mechanism suggested by Schrauzer is applicable to nitrogenase, then the diazene disproportion reaction provides an explanation of why only 75% of the available electrons are utilised in the formation of ammonia and the remaining 25% goes into dihydrogen formation. The reaction scheme proposed by Schrauzer is shown in Figure 5.4.

![Schrauzer's reaction scheme for the enzymatic reduction of dinitrogen to ammonia.](image-url)
At present there are no known dinitrogen complexes in which the dinitrogen molecule binds side-on (Figure 5.3b). Since both dioxygen and acetylene can bond in this way, there is no obvious reason why dinitrogen should not. Presumably, the requirement for side-on bonding would be a similarity in the energies of the π*(N₂) and metal d orbitals in addition to a vacant coordination position.

For the well characterised terminal dinitrogen complexes it has been clearly established that in some cases the coordinated dinitrogen can be reduced to ammonia or intermediate nitrogen hydrides. However, the metals in these complexes are in low oxidation states and the ligands used (e.g. phosphines, cyclopentadiene) are far removed from the enzyme situation where molybdenum in its higher oxidation states bound by nitrogen, oxygen or sulphur donor atoms is implicated. But as Chatt has pointed out, no direct experimental evidence for the oxidation state of the molybdenum or the nature of the active site in nitrogenase has been obtained.

Many of the groups working in the area of low valent transition metal complexes appear far too anxious to proclaim to the world of the great biological significance of their work. After the dust has settled what remains is the fact that dinitrogen may be converted to ammonia via an intermediate low valent dinitrogen complex. However, Schrauzer has demonstrated that higher valent molybdenum complexes can also achieve this result and indeed, there may be several other facile ways of bringing about the conversion (e.g. nitrogenase(?)).
The remainder of this chapter will deal with some selected reactions of dinitrogen complexes with particular emphasis on the mode of activation of the dinitrogen towards reaction. In Chapter 1, Enemark and Feltham's concept of "Stereochemical Control of Valence"\textsuperscript{1} was used to rationalise observed nitrosyl reactivity. This is perhaps a rather grandiose title for something which is little more than an extension of the 16-18 electron rule\textsuperscript{88}, but it does tend to focus attention on the coordination sphere and valency of the metal. It will now be shown that similar principles may be applied to complexes of dinitrogen to give a unifying picture of their reactivity.

5.1 Protonation Reaction Involving $[\text{M(dppe)}_2(\text{N}_2)_2]$ and $[\text{M(PR}_3)_4(\text{N}_2)_2]$ ($\text{M} = \text{Mo or W}, \text{R} = \text{PMe_2O}$ or $\text{PMe}_2\text{O}$)

The reactions of the title compounds with various acids have been studied extensively by Chatt and co-workers. Some of the reported reactions are listed below:

\textit{trans-} $[\text{M(dppe)}_2(\text{N}_2)_2] + 2\text{HX}(>5 \text{ equivalents used}) \underset{0^\circ\text{C}}{\rightarrow} \text{THF}$

$\text{[MX}_2(\text{dppe})_2(\text{NH})_2] + \text{N}_2$ (1)$^{163}$

($\text{M} = \text{W, X=Cl}^-$ or $\text{Br}^-$; $\text{M} = \text{Mo, X=Br}^-$)

\textit{trans-} $[\text{Mo(dppe)}_2(\text{N}_2)_2] + 2\text{HCl}(\text{excess}) \underset{\text{RT}}{\rightarrow} \text{THF}$

$\text{[MoH}_n\text{Cl}_2(\text{dppe})_2] + 2\text{N}_2$ (2)$^{163}$

($n = 2 \text{ or } 4$)
trans-\([\text{W(dppe)}_2(\text{N}_2)_2]\) + 2\text{HCl} \ (2 \text{ equivalents}) \rightarrow \ \text{THF} \\
\text{RT} \ \\
[\text{WH(dppe)}_2(\text{N}_2)_2]\text{(HCl)}_2 \ \ (3)_{163}

cis-\([\text{W(PMe}_2\text{O)}_4(N)_2)_2]\) + 2\text{HCl} \ (>5 \text{ equivalents used}) \rightarrow \ \text{CH}_2\text{Cl}_2 \\
\text{0°C} \\
[\text{WC}(\text{PMe}_2\text{O})_4(\text{NNH}_2)_2]\text{Cl} + \text{N}_2 \ \ (4)_{163}

\text{cis-}[\text{M(PMe}_2\text{O)}_4(N)_2)_2] + 3\text{HCl} \ (\text{excess used}) \rightarrow \ \text{MeOH} \\
20°C \\
[\text{MX}_2(\text{PMe}_2\text{O})_3(\text{NNH}_2)_2] + \text{N}_2 + (\text{PHMe}_2\text{O})\text{Cl} \ \ (5)_{164} \\
(M=\text{Mo}, \text{X}=\text{Cl}^−; \text{M}=\text{W}, \text{X}=\text{Cl}^− \text{ or } \text{Br}^−)

trans-\([\text{W(PMe}_2\text{O)}_4(N)_2)_2]\) + 3\text{HCl} \ (\text{excess used}) \rightarrow \ \text{CH}_2\text{Cl}_2 \\

\text{MeOH} \\
\text{20°C} \\
\text{trans-}[\text{WC}_3(\text{PMe}_2\text{O})_2(\text{NNH}_2)_2] + \text{N}_2 + 2(\text{PHMe}_2\text{O})\text{Cl} \ \ (6)_{164}

trans-\([\text{W(PMe}_2\text{O)}_4(N)_2)_2]\) + \text{HCl} \ (\text{excess}) \rightarrow \ \text{MeOH} \\
\text{20°C} \\
1.9 \text{ mole NH}_3/\text{mole } \text{W} + 0.02 \text{ mole } \text{N}_2\text{H}_4/\text{mole } \text{W} + \text{N}_2 \ \ (7)_{164}

\text{cis-}[\text{M(PMe}_2\text{O)}_4(N)_2)_2] + \text{H}_2\text{SO}_4 \rightarrow \ 2\text{NH}_3 + \text{N}_2 \\
20°C + \text{other products} \ \ (8)_{165} \\
(M=\text{W}, \ 90\% \text{ yield and } M=\text{Mo}, \ 36\% \text{ yield based on the above stoichiometry})

trans-\([\text{M(PMe}_2\text{O)}_4(N)_2)_2]\) + \text{H}_2\text{SO}_4 \rightarrow \ 2\text{NH}_3 + \text{N}_2 \\
20°C + \text{other products} \ \ (9)_{165} \\
(M=\text{W}, \ 36\% \text{ yield and } M=\text{Mo}, \ 4\% \text{ yield based on the above stoichiometry})
MeOH
cis-[M(PMe₂O)₄(N₂)₂] + NH₃
Δ for 3-4h
or
hv for 30 h
(M=Mo or W; Yields: 1.7 mole NH₃/mole W and 0.08 mole NH₃/mole Mo)

Other reactions involving some of the products of the previous reactions are:

1. THF or MeOH

\[
[WH(dppe)_2(N₂)₂](HCl₂) \rightarrow [WH₂Cl₂(dppe)_2] + 2N₂
\]

2. CH₂Cl₂

\[
[WX₂(dppe)₂(NNH₂)] + NaA \rightarrow [WX(dppe)₂(NNH₂)]A + NaX
\]

(A = BØ₄⁻, ClO₄⁻ or PF₆⁻; can also use (Et₄N)BF₄ in CH₂Cl₂-MeOH)

3. NaCO₃ or Et₃N in MeOH

\[
[WX₂(dppe)₂(NHH₃)] \rightarrow [WX(dppe)₂(N₂H)]:
\]

(X = Cl⁻, Br⁻)

4. NaCO₃ or Et₃N in MeOH

\[
[WF(dppe)₂(NNH₂)](BF₄) \rightarrow [WF(dppe)₂(N₂H)]:
\]

5. THF

\[
[MoBr₂(dppe)₂(NHH₃)] + Et₃N \rightarrow [MoBr(dppe)₂(N₂H)]:
\]

6. THF

\[
[MoF₂(dppe)₂(NNH₂)](BF₄) + Et₃N \rightarrow [MoF₂(dppe)₂(N₂H)]:
\]

The nitrogen hydrides formed in reactions (1)-(16) are
named as follows.

- **diazene (diimide)** \(\text{HN} = \text{NH}\)
- **hydrazido-(2-) (aminoimido)** \(:\text{N} - \text{NH}_2\)
- **hydrazido-(1-)** \(:\text{NH} - \text{NH}_2\)
- **diazenido** \(\dot{\text{N}} = \text{NH}\)

The diazenido ligand is formally isoelectronic with NO and can be readily displaced from \([MX(dppe)_2(N_2H)]\) according to the equation

\[
[MX(dppe)_2(N_2H)] + 2\text{NO} \rightarrow N_2 + [MX(dppe)_2\text{NO}] + "\text{HNO}" \quad (17)
\]

For the purposes of this thesis the main point of interest lies in the initial activation of the dinitrogen molecule towards reaction. Enemark and Feltham have already pointed out that reaction (1) is "reminiscent" of the nitrosyl complex reaction in which \(\text{NO}^+\) is converted to \(\text{NO}^-\) by the coordination of a molecule to the metal.\(^1\)

However, the reaction appears to be a little more complicated than this. When \([W(dppe)_2(N_2)_2]\) was reacted with two equivalents of \(\text{HCl}\) at room temperature, the product isolated was \([WH(dppe)_2(N_2)_2](\text{HCl}_2)\) (reaction (3)). With greater than 5 equivalents of \(\text{HCl}\) at \(0^\circ\text{C}\), the diazene complex \([\text{WCl}_2(dppe)_2(\text{NHNH})]\) results, but interestingly, \([WH(dppe)_2(N_2)_2](\text{HCl}_2)\) and \(\text{HCl}\) react to give \([\text{WH}_2\text{Cl}_2(dppe)_2]\) (reactions (1) and (11), respectively). Clearly \([WH(dppe)_2(N_2)_2]^-\) is not an intermediate in the production of the diazene complex. The metal in \([WH(dppe)_2(N_2)_2](\text{HCl}_2)\) has a pentagonal bipyramidal coordination with the dinitrogen molecules occupying the axial positions.\(^{163}\)
No explanation has been offered for the difference in reactivity observed in reactions (1) and (3) and Chatt and co-workers have simply stated that the diazene complex results when excess acid is used. However, they seem to have ignored the fact that reactions (1) and (3) were carried out at 0°C and room temperature, respectively. Therefore the products obtained in (1) and (13) could be due to two different reactions with differing temperature dependencies. Figure 5.5 shows the types of mechanisms envisaged. At 0°C, it is suggested that $k_B >> k_A$ whereas at room temperature $k_A >> k_B$. The dinitrogen is thought to be activated towards reduction by the coordination of chloride to the tungsten. For reactions (4)-(10), similar types of mechanisms are proposed.

5.3 Alkylation and Acylation Reactions of $[M(dppe)\,_2(N_2)\,_2]_2$; $(M = \text{Mo or W})$

It has now been well established that one of the dinitrogen groups in $[M(dppe)\,_2(N_2)\,_2]$ can undergo a variety of alkylation and acylation reactions\textsuperscript{168-176}. In this section an attempt will be made to rationalise this reactivity along the same lines as for the protonation reactions. That is, a prior activation of one of the dinitrogen molecules brought about by the coordination of an alkyl or acyl halide to the metal.

The first acylation reaction reported was that of $[W(dppe)\,_2(N_2)\,_2]$ with acid chlorides, $RCOCl$ ($R = \text{Me, Et, Ph or } p-\text{MeOC}_6\text{H}_4$), to yield complexes formulated as $[WCl_2(dppe)\,_2(N_2HCOR)]$\textsuperscript{168}. The analogous reaction for the molybdenum complex has also been recently described\textsuperscript{169}.
Figure 5.5. The proposed mechanisms for the reactions of \( \text{trans-}[\text{W(dppe)}_2(N_2)] \) with HCl.
Figure 5.6 sets out a possible mechanism for the reaction.

Figure 5.6. A suggested mechanism for the reaction of

$\text{trans-}[\text{M(dppe)}_2(\text{N}_2)_2]$ ($\text{M} = \text{Mo or W}$) with $\text{RCOCl}$.

The paramagnetic Mo(1) species, $\text{[Mo(dppe)}_2(\text{N}_2)_2]^+$, isolated

in (19) and (21) are suggested to arise from a reaction
The reaction of alkyl halides with \( [M(dppe)_2(N_2)_2] \) are somewhat more difficult to achieve and require photochemical activation. In addition, complicated mixtures of products are obtained which include \([MX(dppe)_2(N_2R)], [MX(dppe)_2N_2], CH_4, CH_3CH_3 and H_2\). Some of the reported reactions are given below:

\[
\begin{align*}
\text{hv} & \quad \text{HBr} \\
[M(dppe)_2(N_2)_2] + RBr & \rightarrow N_2 + [MBr(dppe)_2(N_2R)] \quad \text{K}_2\text{CO}_3 \\
& \rightarrow [MBr_2(dppe)_2(N_2HR)] \quad (18)
\end{align*}
\]

\(M=\text{Mo}, R=\text{Me or Et}; M=\text{W}, R=\text{Me, Et or t-Bu}\)

\[
[W(dppe)_2(N_2)_2] + \text{CH}_3\text{Br} \text{ (excess)} \rightarrow [WBr_2(dppe)_2(NNMe_2)] \quad (19)
\]

\[
\begin{align*}
\text{hv} & \quad \text{h} \text{v} \\
[\text{Mo}(dppe)_2(N_2)_2] + \text{CH}_3\text{Cl} & \rightarrow [\text{MoCl}(dppe)_2N_2] + N_2 + \text{CH}_4 + \text{H}_2 \quad (20)
\end{align*}
\]

\[
\begin{align*}
\text{hv} & \quad \text{h} \text{v}
[\text{Mo}(dppe)_2(N_2)_2] + \text{CH}_3\text{Br} & \rightarrow [\text{MoBr}(dppe)_2N_2] + \\
& \rightarrow [\text{MoBr}(dppe)_2N_2] + \\
& \quad [\text{MoBr}(dppe)_2N_2\text{CH}_3] + \text{CH}_4 + \text{CH}_3\text{CH}_3 + \text{trace H}_2 \quad (21)
\end{align*}
\]

\[
\begin{align*}
\text{hv} & \quad \text{h} \text{v}
[W(dppe)_2(N_2)_2] + \text{CH}_2\text{Br}_2 & \rightarrow [WBr(dppe)_2(N_2\text{CH}_2)]\text{Br} + N_2 \quad (22)
\end{align*}
\]

\[
\begin{align*}
\text{hv} & \quad \text{HBr}
[M(dppe)_2(N_2)_2] + \text{CH}_3\text{Br} & \rightarrow [X] \rightarrow \\
& \rightarrow [\text{MBr}(dppe)_2(\text{NN}=\text{CH}((\text{CH}_2)_3\text{OH}))] + N_2 \quad (23)
\end{align*}
\]

The paramagnetic Mo(I) species, \([\text{MoX}(dppe)_2N_2]\), isolated in (20) and (21) are suggested to arise from a reaction.
involving free radicals, e.g. $\text{CH}_3\text{Br} \rightarrow \text{CH}_3^* + \text{Br}^*$

$$\text{Mo(dppe)}_2(\text{N}_2)_2 + \text{Br}^* \rightarrow \text{MoBr(dppe)}_2(\text{N}_2)_2 + \text{N}_2 \quad (24)$$

$$2\text{CH}_3^* \rightarrow \text{CH}_3\text{CH}_3$$

However, the formation of products of the type $[\text{MX(dppe)}_2(\text{N}_2 \text{R})]$ imply a similar mechanism to that for the acylation reactions. The role of the light may be to transfer a pair of electrons to a dinitrogen based MO and thereby facilitate the coordination of a molecule of alkyl halide. A mechanism which is consistent with these ideas is set out in Figure 5.7 for the reaction with $\text{CH}_2\text{Br}_2$.

Reaction (23) is particularly interesting in that the coordinated dinitrogen reacts with tetrahydrofuran to give an $\omega$-diazobutanol complex. The product from this reaction was originally thought to contain the tetrahydropyridazido molecule$^{173}$ but a later crystal structure revealed that the $\omega$-diazobutanol linkage, shown below, was actually present$^{174}$.

$$\begin{array}{c}
\text{W} = \text{N} \quad \text{N} \\
\text{CH} \quad \text{CH}_2 \quad \text{CH}_2 \\
\text{CH} \quad \text{CH}_2 \quad \text{OH}
\end{array}$$

By slightly modifying the mechanism of Figure 5.7 the formation of this product may be accounted for (Figure 5.8). The nucleophile and oxidant in Figure 5.8 have not been defined but THF could be involved in both functions.

5.3 The Reaction of $[\{\text{Zr(C}_5\text{Me}_5\text{N}_2\}_2-\mu-\text{N}_2\}]$ with HCl

Bercaw and co-workers$^{177,178}$ have reported that the title compound reacts with HCl, at $-80^\circ\text{C}$ in toluene, to yield
Figure 5.7. A possible mechanism for the photochemically activated reaction of \textit{trans-}[W(dppe)\textsubscript{2}(N\textsubscript{2})\textsubscript{2}] with CH\textsubscript{2}Br\textsubscript{2}.
Figure 5.8. A suggested mechanism for the photochemically activated reaction of trans-\([M(dppe)\text{2}_2(N_2)_2]\) (\(M = \text{Mo or W}\)) with \(\text{CH}_3\text{Br}\) in THF. The abbreviation ':nucl.' stands for some nucleophile present in the solution.
Hydrazine in 86% yield according to the equation:

\[ \{\text{Zr(C}_5\text{Me}_5\}_{2} \text{-} \mu_{-} \text{N}_2\} + 4\text{HCl} \to 2[\text{Zr(C}_5\text{Me}_5\}_{2} \text{Cl}_2] + \text{N}_2\text{H}_4 + 2\text{N}_2 \]

The crystal structure of the dinitrogen complex has been determined and it confirms that there are two terminal and one bridging dinitrogen ligand present.\(^{196}\)

Isotopic labelling studies employing \(^{15}\text{N}_2\) have shown that the dinitrogen reduced is not exclusively the bridging one and the following stoichiometry was observed:

\[
\{\text{Zr(C}_5\text{Me}_5\}_{2} \text{t} \} - \mu_{-} \text{N}_2\text{b} \} + 4\text{HCl} \to 2[\text{Zr(C}_5\text{Me}_5\}_{2} \text{Cl}_2] + \frac{3}{2}\text{N}_2\text{t} \\
+ \frac{1}{2}\text{N}_2\text{b} + \frac{1}{2}\text{N}_2\text{tH}_4 + \frac{1}{2}\text{N}_2\text{bH}_4 \tag{25} \]

\((t = \text{terminal}; \ b = \text{bridging})\)

These results may be explained on the basis of the ideas developed in the preceding sections. That is, a terminal dinitrogen complex may be activated towards reaction by the coordination of a molecule or anion to the metal. In Figure 5.9 a reaction scheme has been set out which rationalises the products obtained in equation (25). For the electron count it assumed that the pentamethylcyclopentadieny1 ligand is a six electron donor.
Figure 5.9. A mechanism for the reaction of \( \{\text{Zr(C}_5\text{Me}_5)_2\text{N}_2\} - \mu - \text{N}_2 \) with HCl which accounts for the products shown in equation (25).
6.1 Introduction

In 1967 Colton, Scollary and Tomlinson\(^{39}\) reported that [MoBr\(_3\)(CO)\(_x\)] reacted with NaS\(_2\)CNET\(_2\) (Me\(_2\)SO) to form a precipitate of [Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_x\)] which, on recrystallization in vacuo, lost one molecule of CO to give [Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_{x-1}\)]. It was also mentioned that the methanol.monotris-(S\(_2\)CNET\(_2\)) complex took up CO to reform the tricarbonyl compound. A later publication\(^{145}\) dealt with the volatility studies of the [Mo(S\(_2\)CNR\(_2\))\(_2\)(CO)\(_x\)] complexes as a function of the dithiocarbamate substituent R. The rates of loss of carbon monoxide on pumping under vacuum were found to be:

\[ \text{Bu}_2 > \text{Et}_2 > \text{Me} > \text{Pyr} = 0. \]

The di- and tricarbonyl complexes reacted with dioxygen to give Mo(V) complexes of the type [Mo\(_2\)O\(_3\)(S\(_2\)CNR\(_2\))\(_x\)].

Recently, some papers have appeared dealing with the reactivity of [Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_x\)]. The reported reactions are listed below:

\[ \text{(Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_x\))} + 2\text{NO} \rightarrow \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(NO)\(_x\)} + \text{CO (1)\(^{102}\)} \]

\[ \text{CH}_3\text{Cl}\_2 \]

\[ \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_x\)} + \text{CO} \rightarrow \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_{x-1}\)} \]

\[ \text{CH}_3\text{Cl}\_2 \]

\[ \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_x\) + \text{Et}_2\text{O} \rightarrow \text{CO (2)\(^{179}\)}} \]

\[ \text{CH}_3\text{Cl}\_2 \]

\[ \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_x\)} + \text{CO} \rightarrow \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_{x-1}\)} \]

\[ \text{CH}_3\text{Cl}\_2 \]

\[ \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_x\)} + \text{CO} \rightarrow \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_{x-1}\)} \]

\[ \text{CH}_3\text{Cl}\_2 \]

\[ \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_x\)} + \text{CO} \rightarrow \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_{x-1}\)} \]

\[ \text{CH}_3\text{Cl}\_2 \]

\[ \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_x\)} + \text{CO} \rightarrow \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_{x-1}\)} \]

\[ \text{CH}_3\text{Cl}\_2 \]

\[ \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_x\)} + \text{CO} \rightarrow \text{[Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_{x-1}\)} \]

\[ \text{CH}_3\text{Cl}\_2 \]

The Chemistry of [Mo(S\(_2\)CNET\(_2\))\(_2\)(CO)\(_2\)]
6.1 Introduction

In 1967 Colton, Scollary and Tomkins\(^98\) reported that \([\text{MoBr}_2(\text{CO})_4]\) reacted with \(\text{NaS}_2\text{CNEt}_2\cdot3\text{H}_2\text{O}\) in ethanol to yield a precipitate of \([\text{Mo(S}_2\text{CNEt}_2)_2(\text{CO})_3]\) which, on pumping under vacuum, lost one molecule of \text{CO} to give \([\text{Mo(S}_2\text{CNEt}_2)_2(\text{CO})_2]\). It was also mentioned that the methanol moistened dicarbonyl complex took up \text{CO} to reform the tricarbonyl complex. A later publication\(^{145}\) dealt with the relative stabilities of the \([\text{Mo(S}_2\text{CNR}_2)_2(\text{CO})_3]\) complexes as a function of the dithiocarbamate substituent \(\text{R}\). The rate of loss of carbon monoxide on pumping under vacuum was found to be \(\text{Bz}_2 > \text{Et}_2 > \text{Me}_2 > \text{Pyr} = 0\). The di- and tri-carbonyl complexes reacted with dioxygen to give \text{Mo(V)} complexes of the type \([\text{Mo}_2\text{O}_3(\text{S}_2\text{CNR}_2)_4]\).

Recently, some papers have appeared dealing with the reactivity of \([\text{Mo(S}_2\text{CNEt}_2)_2(\text{CO})_2]\). The reported reactions are listed below.

\[\text{[Mo(S}_2\text{CNEt}_2)_2(\text{CO})_2] + 2\text{NO} \rightarrow [\text{Mo(S}_2\text{CNEt}_2)_2(\text{NO})_2] + 2\text{CO} \ (1)^{97}\]

\[\text{[Mo(S}_2\text{CNEt}_2)_2(\text{CO})_2] + \text{CO} \xrightarrow{\text{CH}_2\text{Cl}_2} [\text{Mo(S}_2\text{CNEt}_2)_2(\text{CO})_3] \ (2)^{179}\]

\[\text{[Mo(S}_2\text{CNEt}_2)_2(\text{CO})_2] + 2\text{EtO}_2\text{CN}_2\text{CO}_2\text{Et} \xrightarrow{\text{CH}_2\text{Cl}_2} [\text{Mo(S}_2\text{CNEt}_2)_2(\text{EtO}_2\text{CN}_2\text{CO}_2\text{Et})_2] + 2\text{CO} \ (3)^{179}\]

\[\text{[Mo(S}_2\text{CNEt}_2)_2(\text{CO})_2] + 2\text{EtO}_2\text{CN}_2\text{CO}_2\text{Et} \xrightarrow{\text{CH}_2\text{Cl}_2} [\text{Mo(S}_2\text{CNEt}_2)_2(\text{EtO}_2\text{CN}_2\text{CO}_2\text{Et})_2] + 2\text{CO} \ (4)^{179}\]

\[\text{[Mo(S}_2\text{CNEt}_2)_2(\text{CO})_2] + \text{PO}_3 \xrightarrow{\text{CH}_2\text{Cl}_2} [\text{Mo(S}_2\text{CNEt}_2)_2(\text{CO})_2\text{PO}_3] \ (5)^{179}\]
\[
[\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{CO})_2] + \text{RC}_2\text{R}' \xrightarrow{\text{CH}_2\text{Cl}_2} [\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{CO})(\text{RC}_2\text{R}')] + \text{CO}
\]
(6)\textsuperscript{179}

\[(\text{R=}{\text{R}}'=\text{H}, \text{CO}_2\text{CH}_3 \text{ or } \emptyset; \text{R=H, R}'=\text{CH}_3, \emptyset \text{ or } \text{CO}_2\text{CH}_3; \text{R=CH}_3, \text{R}'=\emptyset)\]

\[
[\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{CO})_2] + 2\text{RC}_2\text{R}' \xrightarrow{\Delta} [\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{RC}_2\text{R}')]_2 + 2\text{CO}
\]
(7)\textsuperscript{179}

\[(\text{R=}{\text{R}}'=\text{H}, \text{CO}_2\text{CH}_3 \text{ or } \emptyset; \text{R=H, R}'=\text{CH}_3 \text{ or } \emptyset; \text{R}'=\text{CH}_3, \text{R}'=\emptyset)\]

\[
2[\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{CO})_2] + \text{N}_2\text{H}_4 \xrightarrow{\text{CH}_2\text{Cl}_2/\text{MeOH}} \text{N}_2\text{H}_4\text{H}\text{NEN}_{\text{CO}_2\text{Et}}
\]
(8)\textsuperscript{180}

Reactions (1), (5) and (8) were part of the work for this thesis.

The substituted diazene complexes obtained in reactions (3) and (4) were readily hydrolysed to give \([\text{MoO(S}_2\text{CNEt}_2\text{)}_2]\) and \([\text{MoO}_2(\text{S}_2\text{CNEt}_2\text{)}_2]\) respectively, in addition to \(\text{EtO}_2\text{CNEHCO}_2\text{Et}\).\textsuperscript{179} One other point worth noting is that the acetylenic protons in \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{CO})_2(\text{HC}_2\text{H})]\) occur at extremely low field in the pmr spectrum (δ12.3). This has been attributed to a 2π aromatic system of the type shown below:\textsuperscript{179}

Reactions (2), (5) and (8) involve the formation of seven coordinate \text{Mo(II)} complexes and reflects the tendency for \text{Mo(II)} to achieve an 18-electron system.\textsuperscript{129,163,181-190} This chapter considers a number of reactions of the 16-electron \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{CO})_2]\) which result in the formation
of seven coordinate complexes.

\[ \text{L} \equiv \text{monodentate N or P donor ligand} \]

or

\[ [\text{Mo(S}_2\text{CNEt}_2)_2(\text{CO})_2]_2 + \text{dppe} \rightarrow [\text{Mo(S}_2\text{CNEt}_2)_2(\text{CO})(\text{dppe})] + \text{CO} \]

Of particular interest to the field of nitrogen fixation are the reactions where \( \text{L} \) is a small N-donor ligand (e.g. \( \text{NH}_3, \text{N}_2\text{H}_4 \)). Complexes involving these ligands are implicated in the fixation of dinitrogen to yield ammonia by low valent molybdenum complexes (section 5.2) and also by nitrogenase. Therefore, a study of the nature of the Mo-N bond in the dicarbonyl complexes becomes relevant to the wider field of nitrogen fixation.

6.2 Complexes Prepared from \([\text{Mo(S}_2\text{CNEt}_2)_2(\text{CO})_2] \]

6.2.1 Experimental

All of the solvents and chemicals used were of AR grade quality. The preparations were carried out under dinitrogen employing both glove-box and Schlenk techniques and solvents were thoroughly deoxygenated prior to use.

6.2.2 Analyses

See section 2.2.2.

6.2.3 Preparation of Bis(N,N-diethylidithiocarbamato)dicarbonyl-molybdenum(II)

\([\text{Mo(CO)}_6] (1 \text{ g}, 3.78 \times 10^{-3} \text{ mole}) \text{ was suspended in} \]
dichloromethane (20 ml) and the solution was cooled to -78°C. Br₂ (0.61 g, 3.78×10⁻³ mole) in dichloromethane (2 ml) was then slowly added. On warming the solution to room temperature, CO was evolved and [MoBr₂(CO)₄] was formed. The dichloromethane was evaporated off in a dinitrogen stream and the residue was taken up in methanol (10 ml). NaS₂CNEt₂·3H₂O (1.70 g, 7.54×10⁻³ mole) in methanol (10 ml) was then added and orange [Mo(S₂CNEt₂)₂(CO)₃] was precipitated.

At this stage, the tricarbonyl complex was either:
(1) filtered off, washed with methanol and dried under vacuum to give [Mo(S₂CNEt₂)₂(CO)₂]. (2) Redissolved by adding dichloromethane (20 ml) and the resulting solution used in the preparation of [Mo(S₂CNEt₂)₂(CO)₂] derivatives.

6.2.4 µ-Hydrazinebis[bis(N,N-diethyl)dithiocarbamato]-dicarbonylmolybdenum(II)]

To the dicarbonyl solution prepared in situ (6.2.3) was slowly added hydrazine hydrate (0.15 g, 7.58×10⁻³ mole) in methanol (1 cc). The solution became dark red and a bright red crystalline product precipitated. The compound was filtered off and washed with methanol (3×10 ml). The precipitate was redissolved in dichloromethane (10 ml) and a drop of hydrazine hydrate added. The complex was obtained as small red needles on addition of methanol (50 ml). After filtering off and washing the product with methanol it was dried at 0°C under vacuum for 8 h. (Yield 0.98 g, 56%.) (Found: C, 30.94; H, 4.92; N, 9.13; S, 27.83. C₂₄H₄₄Mo₂N₆S₈O₄ requires C, 31.03; H, 4.78; N, 9.05; S, 27.61%).
6.2.5 μ-Methylhydrazinebis[bis(N,N-diethyldithiocarbamato)-
dicarbonylmolybdenum(II)]

Methylhydrazine (0.4 g, 8.68×10⁻³ mole) was added to the solution of [Mo(S₂CNEt₂)₂(CO)₂] prepared in situ (6.2.3) and the solution became dark red. Nitrogen was bubbled through the solution for a further half-hour and the dark red precipitate was then filtered off and washed with methanol. The product was taken up in dichloromethane (10 ml) and the solution was filtered. On addition of n-hexane small dark red needles were obtained and these were filtered off and washed with dichloromethane-hexane (1:10). The product was dried at 0°C, under vacuum, for 9 h. The yield was 0.93 g (52%). (Found: C, 31.50; H, 5.04; N, 8.88; S, 27.02. C₂₅H₄₆Mo₂N₆S₈O₄ requires: C, 31.84; H, 4.92; N, 8.91; S, 27.20%)

6.2.6 Bis(N,N-diethyldithiocarbamato)dicarbonyl(N,N-
dimethylhydrazine)molybdenum(II)

[Mo(S₂CNEt₂)₂(CO)₂] (0.52 g, 1.16×10⁻³ mole) was dissolved in dichloromethane (15 ml) and N,N-dimethylhydrazine (2 g, 3.3×10⁻² mole) added. The solution was filtered and n-hexane containing methylhydrazine (2 g NH₂NMe₂ per 150 ml of hexane) was slowly added to precipitate an orange crystalline product. The crystals were filtered off and washed with the methylhydrazine-hexane solution and dried under vacuum at 0°C for 22 h. (Found: C, 33.45; H, 5.87; N, 11.56; S, 24.35. C₁₄H₂₈MoN₄S₄O₂ requires C, 33.09; H, 5.55; N, 11.03; S, 25.24%)

Otherwise, the complexes listed above were obtained by a similar method.
6.2.7 Bis(N,N-diethyldithiocarbamato)dicarbonylamminemolybdenum(II)

Ammonia was bubbled through a solution of [Mo(S$_2$CNEt$_2$)$_2$(CO)$_2$] prepared in situ (6.2.3) and an orange precipitate formed. The precipitate was filtered off and washed with methanol. The complex was dissolved in ammonia saturated dichloromethane (10 ml) and the solution was filtered. The addition of methanol (50 ml) gave the product as orange needles. These were filtered off, washed with methanol and dried under vacuum at 0°C for 9 h. The yield was 0.98 g (56%). (Found: C, 30.74; H, 4.88; N, 9.11; S, 27.44. C$_{12}$H$_{23}$MoN$_3$S$_4$O$_2$ requires C, 30.96; H, 4.98; N, 9.03; S, 27.55%).

It was found necessary in the recrystallisation to saturate the dichloromethane solution with ammonia. Otherwise, the complex obtained lost ammonia to form [Mo(S$_2$CNEt$_2$)$_2$(CO)$_2$], on pumping under vacuum.

6.2.8 μ-Ethylenediaminebis[bis(N,N-diethyldithiocarbamato)dicarbonylmolybdenum(II)]

To a solution of [Mo(S$_2$CNEt$_2$)$_2$(CO)$_2$] (0.53 g, 1.18×10$^{-3}$ mole) in dichloromethane (20 ml), was slowly added ethylenediamine (0.04 g, 6.7×10$^{-4}$ mole) in dichloromethane (2 ml). After filtering the solution, methanol was added to deposit an orange crystalline product. This was filtered off, washed with methanol and dried at 0°C under vacuum for 10 h. (Found: C, 30.78; H, 4.79; N, 8.10; S, 24.70; Cl, 6.36. C$_{27}$H$_{50}$Mo$_2$N$_6$S$_8$O$_4$Cl$_2$ requires C, 31.12; H, 4.84; N, 8.07; S, 24.61; Cl, 6.80%). The analysis was calculated for one molecule of dichloromethane of crystallisation.
6.2.9 Bis(N,N-diethyldithiocarbamato)dicarbonylbenzoylhydrazinemolybdenum(II)

Benzoylhydrazine (0.51 g, $3.75 \times 10^{-3}$ mole) in dichloromethane (10 ml) was added to the $[\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{CO})_2]$ prepared in situ (6.2.3) and the solution became dark red. The solvent was evaporated off in a dinitrogen stream and the residue was taken up in dichloromethane (15 ml). n-Hexane was added to the filtered solution to deposit a red crystalline product which was filtered off and washed with dichloromethane-hexane (1:3). The compound was dried under vacuum at 0°C for 12 h to yield 1.3 g of product ($2.10 \times 10^{-3}$ mole, 53%). (Found: C, 37.82; H, 4.73; N, 9.37; S, 19.39; Cl, 4.66. C$_{19}$H$_{26}$MoN$_4$S$_4$O$_3$Cl$_{0.8}$ requires C, 37.66; H, 4.69; N, 9.06; S, 20.73; Cl, 4.58%). The analysis was calculated for 0.4 molecules of CH$_2$Cl$_2$ per molecule of complex.

6.2.10 Bis(N,N-diethyldithiocarbamato)dicarbonylpyridinemolybdenum(II)

$[\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{CO})_2]$ (0.42 g, $9.36 \times 10^{-4}$ mole) was dissolved in dichloromethane (10 ml) and pyridine (0.1 g, $1.26 \times 10^{-3}$ mole) in dichloromethane (2 ml) was added. The colour of the solution changed to a deep red and on addition of n-hexane, an orange crystalline product was obtained. This was filtered off, washed with dichloromethane-hexane (1:3) and dried at 0°C under vacuum for 10 h. (Found: C, 39.02; H, 4.95; Mo, 18.09; N, 7.94; S, 24.01. C$_{17}$H$_{25}$MoN$_3$S$_4$O$_2$ requires C, 38.70; H, 4.78; Mo, 18.19; N, 7.97; S, 24.31%).
6.2.11 \( \mu \)-Pyrazinebis[bis(N,N-diethyldithiocarbamato)dicarbonylmolybdenum(II)]

\[ \text{[Mo(S}_2\text{CNEt}_2)_2\text{(CO)}_2] \] (0.40 g, \( 8.92 \times 10^{-4} \) mole) was taken up in dichloromethane (15 ml) and pyrazine (0.04 g, \( 5 \times 10^{-4} \) mole) in dichloromethane (1 cc) slowly added. The solution became dark red. After filtering, n-hexane was added to precipitate a deep red crystalline material which was filtered off and washed with dichloromethane-hexane (1:3). The product was dried at 0°C under vacuum for 10 h. (Found: C, 34.54; H, 4.79; Mo, 19.46; N, 8.26; S, 26.16. \( \text{C}_{25}\text{H}_{44}\text{Mo}_2\text{N}_6\text{S}_8\text{O}_4 \) requires C, 34.42; H, 4.54; Mo, 19.65; N, 8.60; S, 26.25%).

6.2.12 Bis(N,N-diethylidithiocarbamato)dicarbonyltriphosphinemolybdenum(II)

Triphenylphosphine (0.99 g, \( 3.78 \times 10^{-3} \) mole) was added to the \([\text{Mo(S}_2\text{CNEt}_2)_2\text{(CO)}_2] \) prepared in situ (section 6.2.3) and the solution became dark red. The solvent was evaporated off in a dinitrogen stream and the residue taken up in dichloromethane (20 ml) and filtered. On addition of n-hexane a bright red crystalline product was obtained. The product was filtered off and washed with dichloromethane-hexane (1:5). The yield was 1.8 g.

A sample was recrystallised from dichloromethane-hexane and dried at 0°C under vacuum for 10 h. (Found: C, 52.73; H, 5.69; N, 3.85; S, 17.45; P, 3.99; Cl, 0.33. \( \text{C}_{33}\text{H}_{43}\text{MoN}_2\text{S}_4\text{O}_2\text{PCl}_{0.08} \) requires C, 52.75; H, 5.72; N, 3.66; S, 16.75; P, 4.04; Cl, 0.37%).

The above analysis has been calculated for 0.6 molecules of n-hexane and 0.04 molecules of dichloromethane of crystallisation. However, the pmr spectrum of the complex
initially precipitated suggested that approximately 0.25 molecules of dichloromethane was present. It therefore appears that the complex may crystallise with a variable amount of dichloromethane and n-hexane incorporated in the crystal lattice.

6.2.13 Bis(N,N-diethylthiocarbamato)carbonyl(1,2-bis(diphenylphosphino)ethane)molybdenum(II)

To the \([\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{CO})_2]\) prepared \textit{in situ} was added 1,2-bis(diphenylphosphino)ethane (1.51 g, \(3.78 \times 10^{-3}\) mole) in dichloromethane (10 ml). Gas evolution was evident and the solution became dark red. The solvent was evaporated off in a dinitrogen stream and the residue taken up in dichloromethane (10 ml). After filtering the solution, n-hexane was added to deposit a dark red crystalline compound. This was filtered off and washed with dichloromethane-hexane (1:3).

A sample was recrystallised from dichloromethane-hexane and dried at 0°C under vacuum for 10 h. (Found: C, 54.41; H, 5.75; N, 3.47; S, 15.12; P, 6.94. \(\text{C}_{37}\text{H}_{44}\text{MoN}_{2}\text{S}_{4}\text{P}_{2}0\) requires C, 54.29; H, 5.42; N, 3.42; S, 15.66; P, 7.56%).

The pnmr spectrum of the product initially precipitated indicated that about 0.15 molecules of dichloromethane of crystallisation was present. However, the analysis is consistent with no dichloromethane and again (see 6.2.12) it appears that a variable amount of dichloromethane may be occluded.
6.2.14 Other Reactions Attempted

Reactions of \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{CO})_2]\) were attempted with tetraethylammonium azide, 1,2-ethanedithiol, 2,2'-bipyridine and \(N,N,N',N'-\text{tetramethylethlenediamine}\) under similar conditions to those described previously. However, the starting material was recovered in each case.

6.3 Infrared Spectra

The instrumentation and techniques used have already been described in section 2.5.1. The infrared spectra of the complexes prepared in section 6.2 have been summarised in Table 6.1.

6.4 \(^1\text{H} \text{NMR Spectra}\)

The \(^1\text{H} \text{NMR} \) spectra were obtained in degassed deuterochloroform unless otherwise stated using the instrumentation described in 2.4. The spectra have been detailed in Table 6.2 and Figure 6.1 shows the spectrum of \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{CO})_2]_2-\mu-\text{N}_2\text{H}_4\).

6.5 Some Reactions Involving \([\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{CO})_2]\)-\(\mu-\text{N}_2\text{H}_4\)

6.5.1 Experimental

All of the reactions were carried out under dinitrogen employing glove-box and Schlenk techniques. Tetrahydrofuran was freshly distilled from lithium aluminium hydride under dinitrogen. All other solvents were AR grade and were deoxygenated by purging with dinitrogen.
### Table 6.1

Infrared Spectral Data (cm⁻¹)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu$(CO)</th>
<th>$\nu$(CN)</th>
<th>$\nu$(CS₂)</th>
<th>$\nu$(NC₂)</th>
<th>$\nu$(NH)</th>
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<tr>
<td>[Mo(S₂CNEt₂)₂(CO)₂]</td>
<td>2026w, 1935s, 1848s</td>
<td>1514s</td>
<td>1005w</td>
<td>1150m</td>
<td></td>
</tr>
<tr>
<td>[Mo(S₂CNEt₂)₂(CO)₂]₂-(\mu)-N₂H₆</td>
<td>2022w, 1927s 1843s</td>
<td>1503s</td>
<td>1003w</td>
<td>1148m</td>
<td>3264w, 3211w, 3126vw</td>
</tr>
<tr>
<td>[Mo(S₂CNEt₂)₂(CO)₂]₂-(\mu)-N₂H₃CH₃</td>
<td>2022w, 1930s, 1844s</td>
<td>1502s</td>
<td>1003w</td>
<td>1148m</td>
<td></td>
</tr>
<tr>
<td>[Mo(S₂CNEt₂)(CO)₂{NH₂N(CH₃)₂}]</td>
<td>2020m, 1927s, 1839s</td>
<td>1502s</td>
<td>1004w</td>
<td>1148m</td>
<td>3265w</td>
</tr>
<tr>
<td>[Mo(S₂CNEt₂)₂(CO)₂NH₃]</td>
<td>2024w, 1930sh, 1910s</td>
<td>1835s</td>
<td>1503s</td>
<td>1002w</td>
<td>1151m</td>
</tr>
<tr>
<td>[Mo(S₂CNEt₂)₂(CO)₂]₂-(\mu)-en</td>
<td>2024w, 1925s, 1847s</td>
<td>1495s</td>
<td>1009w</td>
<td>1146m</td>
<td>3313m, 3249w</td>
</tr>
<tr>
<td>[Mo(S₂CNEt₂)(CO)₂(NH₂NHCΟO)]</td>
<td>2024m, 1934s, 1840s</td>
<td>1667 (of NH₂NHCΟO)</td>
<td>1503s</td>
<td>1008w</td>
<td>1151m</td>
</tr>
<tr>
<td>[Mo(S₂CNEt₂)₂(CO)₂(Py)]</td>
<td>2024m, 1918s, 1838s</td>
<td>1498s</td>
<td>1005w</td>
<td>1147m</td>
<td></td>
</tr>
<tr>
<td>[Mo(S₂CNEt₂)₂(CO)₂]₂-(\mu)-Pyz</td>
<td>2024s, 1929vs, 1851s</td>
<td>1505s, 1509s</td>
<td>1004w</td>
<td>1150m</td>
<td></td>
</tr>
<tr>
<td>[Mo(S₂CNEt₂)₂(CO)₂P0₃]</td>
<td>1934s, 1851s</td>
<td>1518s</td>
<td>1001w</td>
<td>1149m</td>
<td></td>
</tr>
<tr>
<td>[Mo(S₂CNEt₂)₂CO(dppe)]</td>
<td>1816s, 1797sh</td>
<td>1487s</td>
<td>1008w</td>
<td>1145m</td>
<td></td>
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**a** hexachlorobutadiene mull

**b** of dithiocarbamate
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift ($\delta \pm 0.02$ ppm)</th>
<th>Assignment</th>
</tr>
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<tbody>
<tr>
<td>[Mo(S$_2$CNEt$_2$)$_2$(CO)$_2$]</td>
<td>t 1.28, q 3.77</td>
<td>CH$_3$ of dtc, CH$_2$ of dtc</td>
</tr>
<tr>
<td>[Mo(S$_2$CNEt$_2$)$_2$(CO)$_2$]$_2$-µ-N$_2$H$_4$</td>
<td>t 1.26, q 3.70, s 5.07</td>
<td>CH$_3$ of dtc, CH$_2$ of dtc, N$_2$H$_4$</td>
</tr>
<tr>
<td>[Mo(S$_2$CNEt$_2$)$_2$(CO)$_2$]$_2$-µ-N$_2$H$_3$CH$_3$</td>
<td>t 1.25, s 2.81, q 3.74, s 4.64</td>
<td>CH$_3$ of dtc, CH$_3$ of N$_2$H$_3$CH$_3$, CH$_2$ of dtc, NH of N$_2$H$_3$CH$_3$</td>
</tr>
<tr>
<td>[Mo(S$_2$CNEt$_2$)$_2$(CO)$_2$NH$_2$N(CH$_3$)$_2$]</td>
<td>t 1.28, s 2.50, s 3.21, q 3.77</td>
<td>CH$_3$ of dtc, CH$_3$ of NH$_2$N(CH$_3$)$_2$, NH$_2$ of NH$_2$N(CH$_3$)$_2$, CH$_2$ of dtc</td>
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<tr>
<td>[Mo(S$_2$CNEt$_2$)$_2$(CO)$_2$NH$_3$]</td>
<td>t 1.25, s 2.42, q 3.72</td>
<td>CH$_3$ of dtc, NH$_3$, CH$_2$ of dtc</td>
</tr>
<tr>
<td>[Mo(S$_2$CNEt$_2$)$_2$(CO)$_2$]$_2$-µ-en.CH$_2$Cl$_2$</td>
<td>t 1.16, m 2.64, s,br 3.20, q 3.66, s 5.75</td>
<td>CH$_3$ of dtc, CH$_2$ of en overlapping with residual proton peak of (CD$_3$)$_2$SO, NH$_2$ of en, CH$_2$ of dtc, CH$_2$Cl$_2$</td>
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<tr>
<th>Compound</th>
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<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo(S₂CNEt₂)₂(CO)₂(N₂H₃CH₃)]</td>
<td>t 1.26</td>
<td>CH₃ of dtc</td>
</tr>
<tr>
<td></td>
<td>s 2.72</td>
<td>CH₃ of N₂H₃CH₃</td>
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<tr>
<td></td>
<td>q 3.74</td>
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<tr>
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<td>s 4.08</td>
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<tr>
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<tr>
<td></td>
<td>q 3.64</td>
<td>CH₂ of dtc</td>
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<tr>
<td></td>
<td>ps 5.28</td>
<td>overlapping CH₂Cl₂ and NH₂</td>
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<tr>
<td></td>
<td>m 7.4-7.84</td>
<td>aromatic protons</td>
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<tr>
<td></td>
<td>s 8.38</td>
<td>NH</td>
</tr>
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<td>[Mo(S₂CNEt₂)₂(CO)₂Py]</td>
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<td>CH₂ of dtc</td>
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<tr>
<td></td>
<td>m 7.34</td>
<td>3,5 protons of pyridine</td>
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<tr>
<td></td>
<td>m 7.72</td>
<td>4 proton of pyridine</td>
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<td></td>
<td>m 9.00</td>
<td>2,6 protons of pyridine</td>
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<tr>
<td></td>
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<td>CH₂ of dtc</td>
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<tr>
<td></td>
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<td>Pyz</td>
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<tr>
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<tr>
<td></td>
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<tr>
<td></td>
<td>q 3.69</td>
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<tr>
<td></td>
<td>s 5.28</td>
<td>CH₂Cl₂</td>
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<td>PØ₃</td>
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continued
Table 6.2 (continued)

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<tbody>
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<tr>
<td></td>
<td>c 3.53</td>
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<td></td>
<td>s 5.28</td>
<td>CH₂Cl₂</td>
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<tr>
<td></td>
<td>7.1-7.8</td>
<td>aromatic protons</td>
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</tbody>
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- See Table 2.2 for abbreviations; All solvents were predried over 4A molecular sieve.
- In (CD₃)₂SO
Figure 6.1. The 'H nmr spectrum of $[\text{Mo}(S_2\text{CNEt}_2)_2(\text{CO})_2] - \mu-\text{N}_2\text{H}_4$ in deoxygenated deuterochloroform.
6.5.2 Oxidation Reactions

(a) With HgO

A solution of \([\text{Mo(S}_2\text{CNEt}_2\text{)(CO)}_2]_2-\mu-\text{N}_2\text{H}_4\) (0.23 g, 2.48×10\(^{-4}\) mole) in dichloromethane (10 ml) was stirred with yellow mercuric oxide (0.06 g, 2.77×10\(^{-4}\) mole) for 24 hours. A mercury mirror formed on the vessel wall during this time. The solution was filtered and n-hexane added to precipitate a red-purple powder.

An infrared spectrum of the product showed three strong carbonyl bands and the expected dithiocarbamate structure. The pmr spectrum of the product suggested that it was a mixture of \([\text{Mo(S}_2\text{CNEt}_2\text{)(CO)}_2]_2\) and \([\text{Mo(S}_2\text{CNEt}_2\text{)(CO)}_2]_2-\mu-\text{N}_2\text{H}_4\).

(b) With \(\text{H}_2\text{O}_2/\text{Cu}^{2+}\) at 0°C

\([\text{Mo(S}_2\text{CNEt}_2\text{)(CO)}_2]_2-\mu-\text{N}_2\text{H}_4\) (0.98 g, 1.05×10\(^{-3}\) mole) was dissolved in tetrahydrofuran (30 ml) and anhydrous sodium sulphate (4 g) added. The solution was cooled to -78°C and in a brisque nitrogen stream \(\text{H}_2\text{O}_2\) (0.12 ml of a 30% w/v solution; 1.06×10\(^{-3}\) mole) and \(\text{CuSO}_4\) (0.05 ml of a 0.05 M aqueous solution) were added with vigorous stirring. The solution was allowed to warm to 0°C and during this process gas was evolved and the colour changed from red to purple and then to red-brown after a further hour. The tetrahydrofuran was pumped off at -20°C and the residue dried at room temperature under high vacuum. The residue was extracted with tetrahydrofuran (10 ml) and the solution filtered. On cooling the solution to -78°C no product was precipitated and so n-hexane was added to yield a brown powder.

The infrared spectrum of the powder showed only weak
carbonyl bands at 1927 cm\(^{-1}\) and 1847 cm\(^{-1}\) in addition to the dithiocarbamate structure. Peaks at 936 and 963 cm\(^{-1}\) of medium intensity suggested the presence of Mo=O species. The pmr spectrum showed complicated diethyldithiocarbamate resonances but no other absorptions were observed in the \(\delta 15\) to \(\delta 10\) region.

\((c)\) With \(\text{H}_2\text{O}_2/\text{Cu}^{2+}\) at \(-20^\circ\text{C}\)

\([\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{CO})_2]_2-\mu-\text{N}_2\text{H}_4\) (0.49 g, \(5.27\times10^{-4}\) mole) was dissolved in tetrahydrofuran (5 ml) and anhydrous sodium sulphate (4 g) added. The slurry was cooled to \(-78^\circ\text{C}\) and in a brisque nitrogen stream, with vigorous stirring, \(\text{H}_2\text{O}_2\) (0.06 ml of a 30% w/v solution, \(5.29\times10^{-4}\) mole) and \(\text{CuSO}_4\) (0.05 ml of a 0.05 M aqueous solution) were added. On warming to \(-20^\circ\text{C}\) the solution became purple and gas was evolved. After 15 minutes the tetrahydrofuran was pumped off and the residue dried at room temperature under high vacuum. The residue was extracted with dichloromethane (10 ml) and the solution was filtered and n-hexane added to deposit a red-purple product.

The products infrared spectrum showed two strong carbonyl bands and the dithiocarbamate structure. The pmr spectrum indicated that a mixture of diethyldithiocarbamate containing products was present in addition to a small amount of unreacted starting material. No resonances attributable to diazene species were detected.

6.5.3 The Attempted Reduction of \([\text{Mo(S}_2\text{CNEt}_2\text{)}_2(\text{CO})_2]_2-\mu-\text{N}_2\text{H}_4\) using \(\text{Pt/H}_2\)

Hydrogen was bubbled over a platinum black electrode.
in a dichloromethane solution of \([\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{CO})_2]_2\mu-\text{N}_2\text{H}_4\) for 1 hour. The product obtained on addition of methanol was found to be the starting material.

6.5.4 Cyclic Voltametry on \([\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{CO})_2]_2\mu-\text{N}_2\text{H}_4\)

The cyclic voltamogram of \([\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{CO})_2]_2\mu-\text{N}_2\text{H}_4\) obtained in dichloromethane saturated in \(\text{Et}_4\text{NClO}_4\) is shown in Figure 6.2 (see section 2.7.1 for a description of the apparatus used).

6.6 The Molecular Structure of \([\text{Mo}(\text{S}_2\text{CNET}_2)_2(\text{CO})_2]_2\mu-\text{N}_2\text{H}_4\) (2)

The structure on the dichloromethane solvate of (2) was determined separately at the University of Arizona, U.S.A., in collaboration with J.H. Enemark, R.D. Feltham, J.I. Gelder, P.L. Johnson and J.A. Broomhead. A preliminary communication on the structural determination has been published\(^{180}\). The main conclusions are included here for completeness.

Figure 6.3 shows the numbering scheme and perspective view of (2) which includes both positions of the disordered \(\text{N}_2\text{H}_4\) unit. Tables 6.3, 6.4 and 6.5 summarise the crystal data and selected bond distances and bond angles, respectively.

Each Mo atom of the dimer is seven coordinate with the coordination sphere consisting of two \(cis\) carbonyl groups, four S atoms from two dithiocarbamates and one nitrogen from the bridging hydrazine ligand. The four S atoms about each Mo are coplanar but the interligand S-Mo-S angles are grossly dissimilar as shown in figure 6.4.
Figure 6.2. The cyclic voltamogram of \( [\text{Mo(S}_2\text{CNET}_2)_2(\text{CO})_2]^-\mu-\text{N}_2\text{H}_4 \) in \( \text{CH}_2\text{Cl}_2/\text{sat. Et}_4\text{NClO}_4 \).
Figure 6.3. The perspective view of $[\text{Mo}(\text{S}_2\text{CNEt}_2)_2(\text{CO})_2]_2\mu-\text{N}_2\text{H}_4$ showing the two disordered positions of the bridging hydrazine ligand. The ethyl groups of the dithiocarbamate ligands have been omitted for clarity.
### Table 6.3

Crystal Data for [Mo(CO)$_2$(S$_2$CNEt)$_2$]$_2$N$_2$H$_4$.CH$_2$Cl$_2$

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<thead>
<tr>
<th></th>
<th>Distance (Å)</th>
<th></th>
<th>Distance (Å)</th>
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</thead>
<tbody>
<tr>
<td>a</td>
<td>13.872(7) Å</td>
<td>b</td>
<td>14.145(13) Å</td>
</tr>
<tr>
<td>c</td>
<td>13.695(9) Å</td>
<td>α</td>
<td>118.50(5)°</td>
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<tr>
<td>β</td>
<td>103.28(3)°</td>
<td>γ</td>
<td>65.76(4)°</td>
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<tr>
<td>Space Group</td>
<td>PT</td>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>$d_{\text{obs}}$</td>
<td>1.56(1) g cm$^{-3}$</td>
<td>$d_{\text{calcd}}$</td>
<td>1.57 g cm$^{-3}$</td>
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### Table 6.4

Selected Bond Distances in [Mo(CO)$_2$(S$_2$CN(C$_2$H$_5$)$_2$]$_2$N$_2$H$_4$.CH$_2$Cl$_2$

<table>
<thead>
<tr>
<th>A-B</th>
<th>Distance (Å)</th>
<th>A-B</th>
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<td>Mo2-S5</td>
<td>2.524(2)</td>
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<td>Mo1-S2</td>
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<td>Mo2-S6</td>
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<td>Mo2-S8</td>
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Table 6.5

Selected Bond Angles in \([\text{Mo(CO)}_2(\text{S}_2\text{CN(C}_2\text{H}_5)_2)]_2\text{N}_2\text{H}_4\cdot\text{CH}_2\text{Cl}_2\)

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<td>S6-Mo2-C24</td>
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</tr>
<tr>
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<td>Mo2-S7-C18</td>
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<tr>
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Figure 6.5. Diagram of the two disordered stereochemistries of the inner coordination sphere about Mo1. The Mo1(CO)$_2$N plane is in the place of the paper and the S1-S4 plane is normal to the plane of the paper.
Figure 6.4. The arrangement of dithiocarbamate ligands about the Mo.

Each Mo atom is displaced ~0.4 Å from its trapezoidal plane of S atoms towards the carbonyl groups and the Mo(CO)₂ unit forms a plane nearly perpendicular to the corresponding plane of S atoms. Figures 6.5(a) and 6.5(b) present a view of the Mo(CO)₂ fragment for Mo₁ in the two possible coordination geometries, with respect to the plane of S atoms. Geometries 6.5(a) and 6.5(b) occur in the ratio 65:35 for Mo₁ because of the disorder while for Mo₂ the geometries 6.5(a) and 6.5(b) are in the ratio 35:65. Thus each molecule of (2) contains one Mo atom with coordination geometry 6.5(a) and one Mo atom with geometry 6.5(b). The data crystal contained the geometries 6.6(a) and 6.6(b) in the ratio 65:35.

Figure 6.6
Each coordination geometry gives rise to two distinctly different Mo-N bond lengths. Both kinds of Mo-N distances are substantially longer than the Mo-N bond length of 2.26 Å observed for the Mo(II) complex \([\eta^1-C_5H_5]Mo(CO)_2(COCH_2CH_2NH_2)\) and suggests that the hydrazine may be weakly bound. This could account for the fact that the other atoms in the coordination sphere do not appear to be detectably different for the two modes of attachment of the bridging hydrazine ligand.

The conformation about the N-N bond of the bridging hydrazine is gauche with the torsional angles of the Mo1-N5-N6-Mo2 and Mo1-N5'-N6'-Mo2 being 60° and 43°, respectively. The N-N bond distance of 1.44(2) Å was similar to the 1.46 Å found in \([N_2H_5][N_3]\).

6.7 Discussion

[Mo(S₂CNEt₂)₂(CO)₂] (1) was found to react with a variety of small molecules to form seven coordinate complexes of the type [Mo(S₂CNEt₂)₂(CO)₂Y] (Y = NH₃, N₂H₃CH₃, N₂H₃COØ, Py, NH₂N(CH₃)₂, PØ₃, CO), [Mo(S₂CNEt₂)₂(CO)₂]-µ-Z (Z = N₂H₄, N₂H₃CH₃, en, Pyz) and [Mo(S₂CNEt₂)₂(CO)(dppe)]. The seven coordinate complexes tend to be moderately air stable in the solid state but are oxidised readily in solution. Solid samples deteriorate over a period of several hours. All of the above complexes were characterised by analyses and IR and 'H nmr spectroscopy.

When (1) was reacted with hydrazine in dichloromethane-methanol a bright red crystalline product was deposited, viz. [Mo(S₂CNEt₂)₂(CO)₂]-µ-N₂H₄ (2). The crystal structure
determination on the dichloromethane solvate of (2) was carried out at the University of Arizona and the results were described in section 6.6. The molecule of dichloromethane is only incorporated when the crystals are grown slowly from dichloromethane-methanol. The relatively long Mo-N bond lengths observed in the structure of (2) suggests that the hydrazine molecule is weakly bound and this also appears to be the case for the other N-donor ligands. For example, when the hydrazine, methylhydrazine and ammonia complexes of (1) were dried at room temperature under vacuum the analyses were always low in nitrogen implying that the molecules were slowly being pumped off. Consequently, all complexes were routinely dried at 0°C. Other evidence for the weakness of the Mo-N bond will be seen in the following discussion.

The introduction of methyl substituents on the hydrazine produces a number of effects. When excess methylhydrazine was added to a dichloromethane-methanol solution of (1) the methylhydrazine bridged complex, \([\text{Mo}(S_2\text{CNEt}_2)_2(\text{CO})_2]_2-\mu-\text{N}_2\text{H}_3\text{CH}_3\), precipitated. However, in dichloromethane, the product obtained on addition of n-hexane was \([\text{Mo}(S_2\text{CNEt}_2)_2(\text{CO})_2-(\text{N}_2\text{H}_3\text{CH}_3)]\).

With \(\text{N, N-dimethylhydrazine in dichloromethane, (1) gives the extremely labile complex [Mo(S}_2\text{CNEt}_2)_2(\text{CO})_2-\{\text{NH}_2\text{N}(\text{CH}_3)_2\}]\). A very large excess of \(\text{N, N-dimethylhydrazine has to be present during the isolation of the compound to avoid precipitating (1).}\)

\(\text{N, N-Dimethylhydrazine presumably coordinates to the molybdenum through the NH}_2\ group as N, N, N', N'-tetramethyl-ethylenediamine does not form a complex with (1). Since benzoylhydrazine and (1) give the relatively non-labile
[Mo(S₂CNEt₂)₂(CO)₂(NH₂NHCOO)], it would appear that electron donating substituents on the hydrazine increase the lability in the Mo-N bond.

When ammonia was bubbled through a dichloromethane-methanol solution of (1) a bright orange precipitate of [Mo(S₂CNEt₂)₂(CO)₂NH₃] was obtained. Interestingly this compound does *not* lose ammonia on pumping at 0°C under vacuum but the product recrystallised from dichloromethane-methanol does. Apparently the presence, in solution, of an excess of ammonia is required for the formation of a stable crystalline form. These results clearly show that the ammonia molecule, like hydrazine, is weakly bound to the molybdenum.

Pyridine and pyrazine are molecules which contain "aromatic" nitrogen atoms and they react with (1) in dichloromethane to give the orange [Mo(S₂CNEt₂)₂(CO)₂Py] and intense red-purple [Mo(S₂CNEt₂)₂(CO)₂]₂-µ-Pyz complexes, respectively. The compounds do not appear to be labile.

(1) was found to react with triphenylphosphine to give the red complex [Mo(S₂CNEt₂)₂(CO)₂PØ₃]. This reaction has also been recently reported by McDonald and co-workers. With 1,2-bis(diphenylphosphino)ethane one molecule of carbon monoxide was displaced to give [Mo(S₂CNEt₂)₂(CO)(dppe)]. The complexes formed with phosphorus donor ligands seem more stable and this probably reflects the greater affinity of Mo(II) for phosphorus rather than nitrogen. This is strikingly illustrated by the reaction of ethylenediamine with (1) to give the unusual bridged complex [Mo(S₂CNEt₂)₂(CO)₂]-µ-en rather than chelating as does 1,2-bis(diphenylphosphino)ethane.
Figure 6.7 summarises the reactions of (1) which have been described above. Also, a number of other reactions of (1) were attempted (with $\text{N}_3^-$, 2,2'-bipy, $\text{Me}_4\text{en}$ and $\text{SHCH}_2\text{CH}_2\text{SH}$) but in each case the starting material was recovered. The fact that 2,2'-bipyridine does not coordinate and pyridine does, presumably reflects the greater steric bulk of the former combined with the weakness of the Mo-N bond. The specificity of the seventh coordination site is also born out by the non reactivity of (1) with azide and 1,2-ethanedithiol and the marked changes in the nature of the Mo-N bond observed with the methyl substituted hydrazines.

**Infrared Spectra**

The infrared spectra of the complexes prepared have been summarised in Table 6.1. It is interesting to note that, for all but one of the dicarbonyl complexes, three carbonyl absorptions are observed at ~2025, ~1930 and ~1840 cm$^{-1}$. The first mentioned band varies in intensity from complex to complex and can even differ in different preparations of the one complex. The remaining bands are always strong in intensity. The dichloromethane solution spectrum of (2) also exhibits three carbonyl absorptions so that solid state effects are not responsible.

The crystal structure of the dichloromethane solvate of (2) shows that the carbonyl groups are *cis* and consequently only two carbonyl absorptions are expected. This is indeed found to be the case for crystalline samples of (2) grown slowly from dichloromethane-methanol$^{127}$. However, material deposited more rapidly from solution exhibits three carbonyl bands in its infrared spectrum.
Figure 6.7. Some Reactions of $[\text{Mo(S}_2\text{CNET}_2\text{)}_2(\text{CO})_2]$
The above evidence is consistent with the dicarbonyl complexes being present as a mixture of isomers. Two possible isomeric forms are illustrated in Figure 6.8.

Both cis and trans isomers have been shown to exist in the related complexes \([\text{Mo(dppe)}_2(\text{CO})_2]^n\) and \([\text{Mo(dppm)}_2(\text{CO})_2]^n\) \((n = 0, +1, +2)\). So the additional carbonyl band at \(\sim 2025 \text{ cm}^{-1}\) may tentatively be attributed to isomer II of Figure 6.8. One way of establishing the presence of isomeric complexes would be to obtain the \(^{13}\text{C}\) spectra of the compounds.

The characteristic diethylidithiocarbamate absorption bonds are all present (see chapter 2) and for the complexes containing NH bonds the \(v(\text{NH})\) stretching frequencies are observed between 3380 and 3120 cm\(^{-1}\). These peaks are fairly sharp implying the absence of hydrogen bonding.

\('^1\text{H NMR Spectra}\n
The '\(^1\text{H}\) nmr spectra detailed in Table 6.2 appear relatively straightforward in their interpretation with the diethylidithiocarbamate and the other resonances present
being assigned on the basis of their proton count and chemical shifts.

In the preceding discussion it was suggested that the dicarbonyl complexes may exist as a mixture of isomers, but no multiplicity was observed for the diethyldithiocarbonate resonances ($A_3X_2$ pattern). If a mixture of isomers is present, then this could imply that the ethyl groups are all chemically equivalent.

The positions of the NH resonance is, as expected, a function of the type of substituents present and varies between $\delta 8.38$ ([Mo($S_2CNEt_2$)$_2$(CO)$_2$NH$_2$NHCOCO]) and $\delta 2.42$ ([Mo($S_2CNEt_2$)$_2$(CO)$_2$NH$_3$]). The nmr solvents were all dried over 4A molecular sieve prior to use as in some cases the NH resonances were not observed in undried solvents. This behaviour is indicative of rapid proton exchange occurring between the NH protons and the water molecules present in the solution.

The Reactivity of $[Mo(S_2CNEt_2)_2(CO)_2]_2-u-N_2H_4$ (2)

Oxidation reactions were carried out on (2) using solid yellow mercuric oxide in dichloromethane at room temperature and with one equivalent of hydrogen peroxide-Cu(II) catalyst in tetrahydrofuran at both 0°C and -20°C. In all cases the hydrazine bridge appears to have been oxidised but no diazene complexes could be detected in the pmr spectra of the products. A mercury mirror was formed in the first mentioned reaction and the product was identified as (1) from its ir and nmr spectra. (1) is also the product from the other two reactions but at 0°C it appears to decompose to uncharacterised molybdenum oxo species after about 1 hour.
The cyclic voltamogram of (2) (Figure 6.2) shows that the complex may be oxidised at ~0.6-0.9 V to a species which rapidly decomposes to a third product that can be reduced between -0.2 and -1.0 V.

\[ \text{(2)} \xrightarrow{-e^{-} \text{ fast }} \text{B} \xrightarrow{+e^{-}} \text{C} + \text{D} \]

i.e.

If B is a µ-diazene complex then its rapid conversion to C most probably involves the dissociation and spontaneous disproportionation and decomposition of diazene (see chapter 5).

An attempt was made to reduce (2) at a H₂/Pt (black) electrode to the ammonia complex, \([\text{Mo(S₂CNEt}_2]_2(\text{CO})_2\text{NH}_3]\), but no reaction was observed.
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