A THESIS

entitled

COMPLEXES OF MOLYBDENUM AND
TUNGSTEN WITH SULPHUR-DONOR LIGANDS

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CHARLES GRAHAM YOUNG

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The work described in this thesis is the candidate's own except as otherwise stated.

Charles Graham Young
Chemistry Department
Faculty of Science
Australian National University
Canberra, A.C.T.
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The following publications have been derived from the work described in this thesis.


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ABSTRACT

The investigation of sulphur-donor ligand complexes of molybdenum and tungsten is an area of active research due to the relevance of such compounds to the active site structure and reactivity of molybdoenzymes. This Thesis describes the preparation and study of new sulphur-donor ligand complexes of molybdenum and tungsten and, where appropriate, their relevance to molybdoenzyme systems.

Chapter One briefly describes, with emphasis on their molybdenum sites, the structure and reactivity of the enzymes, xanthine oxidase, sulphite oxidase and nitrogenase. This literature survey presents an overview of the current state of molybdoenzyme and related model studies and presents a background to the work described in this Thesis. This background is further developed in the introductory sections of each chapter.

Chapter Two deals with the preparation, characterization and reactivity of the seven-coordinate monooxo-Mo(VI) complexes, \([\text{MoO}(\text{S}_2\text{CNR})_3]^+\) (R = Me, Et, Pr, Bu), isolated from the reaction \(\sigma\beta\text{-MoO}_2(\text{S}_2\text{CNR})_2\text{HX} (X = \text{BF}_4^-, \text{PF}_6^-, \text{ClO}_4^-)\) as simple \(X^-\) salts. Using a variety of physical and spectroscopic techniques, a mononuclear rigid pentagonal bipyramidal structure has been established for these orange complexes. The catalytic oxidation of PPh₃ to OPPh₃ by the \([\text{MoO}(\text{S}_2\text{CNEt})_3]^+\) complex represents the first catalytic oxygen atom transfer reaction involving a monooxo-Mo(VI) complex and provides evidence for the participation of such centres, possibly present in xanthine oxidase, in oxygen atom transfer reactions. Other reactions of this complex are also presented.
The preparation of the dinuclear mixed oxidation state (Mo(IV,V)) complexes, \([\text{Mo}_2\text{O}(\text{S}_2\text{CNR}_2)_6]^+\) (R = Me, Et), is described in Chapter Three. These complexes are the first stable, readily prepared oxo- and sulphur-donor ligand complexes of molybdenum which contain mixed, biologically relevant oxidation states. The compound, \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{BF}_4\), has been studied in detail and its structure has been established by a single crystal x-ray structure determination. The complex cation is composed of two pentagonal bipyramidal molybdenum moieties bridged by an axial \(\mu\)-oxo-ligand. The molybdenum atom environments are crystallographically identical and the \(\mu\)-oxo-ligand is near linear. Investigation of the near infrared spectra of the complex suggests that the unpaired electron in the complex is completely delocalised over both molybdenum atoms. The existence of this compound provides support for proposed mixed oxidation state centres in certain molybdoenzymes.

Chapter Four describes the preparation and characterization of the versatile tungsten carbonyl complexes, \(\text{cis-}[\text{W}(\text{S}_2\text{CNR}_2)_2(\text{CO})_2 \rightleftharpoons \text{W}(\text{S}_2\text{CNR}_2)_2(\text{CO})_3]\) (R = Me, Et). The studies reported suggest that the unsaturated 16-electron dicarbonyl complexes participate in a monomer-dimer equilibrium in solution and that, in the solid state, the methyl and ethyl derivatives exist as monomers and dimers, respectively. The tricarbonyl complexes possess monomeric seven-coordinate facial tricarbonyl structures. The reaction of these carbonyl complexes with various N- and P-donor ligands and acetylene results in the formation of the mononuclear complexes, \(\text{W}(\text{S}_2\text{CNR}_2)_2(\text{CO})_2\text{L}\) (L = CO, \(\text{N}_2\text{H}_3\text{Me}\), \(\text{N}_2\text{H}_2\text{Me}_2\), \(\text{NH}_3\), \(\text{NH}_2\text{NHCOPh}\), \(\text{C}_5\text{H}_4\text{N}\), \(\text{NH}_2\text{NHSO}_2\text{PhMe}\), \(\text{PPh}_3\)) and \(\text{W}(\text{S}_2\text{CNET}_2)_2(\text{CO})(\text{C}_2\text{H}_2)\), and the bridged complexes \([\text{W}(\text{S}_2\text{CNR}_2)_2(\text{CO})_2]_2-\mu-B\) (B = \(\text{N}_2\text{H}_4\), \(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\)). The physical and spectroscopic properties of these complexes are presented. The chemical oxidation of the new \(\mu\)-hydrazine complex, \([\text{W}(\text{S}_2\text{CNET}_2)_2(\text{CO})_2]_2-\mu-\text{N}_2\text{H}_4\), did not produce isolable \(\mu\)-diimine complexes.
The chemistry of several potentially tetradeutate sulphur-donor ligands is described in Chapter Five. In the complexes formed upon the reaction of $\text{M(CO)}_6$ ($\text{M} = \text{Mo}, \text{W}$) and 1,4,8,11-tetrathiaycloctetradecane ($L^1$) and 3,6,10,13-tetrathiabicyclo[13.4.0]nona-1,16,18-triene ($L^2$), the macrocyclic tetrathiaether ligands are only partially coordinated to $\text{fac-Mo(CO)}_3$ and $\text{W(CO)}_4$ moieties. The ligand coordination modes of the complexes $\text{fac-Mo(CO)}_3L^1, L^2$ and $\text{cis-W(CO)}_4L^2$ represent unprecedented coordination modes for the $L^1$ and $L^2$ ligands. Further binding of the ligands or the binding of atmospheric dinitrogen does not occur upon removal of carbonyl ligands. Some chemistry of 1,4,8,11-tetrathiaundecane is also presented in Chapter Five.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>acac</td>
<td>acetylacetonato-</td>
</tr>
<tr>
<td>Ar</td>
<td>aryl</td>
</tr>
<tr>
<td>bipy</td>
<td>2,2'-bipyridine</td>
</tr>
<tr>
<td>Bu^n</td>
<td>n-butyl, -CH₂CH₂CH₂CH₃</td>
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<tr>
<td>CO</td>
<td>capped octahedron</td>
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<tr>
<td>CTP</td>
<td>capped trigonal prism(atic)</td>
</tr>
<tr>
<td>cyst-OMe</td>
<td>cysteinato-methyl ester</td>
</tr>
<tr>
<td>dipic</td>
<td>pyridine-2,6-dicarboxylato-</td>
</tr>
<tr>
<td>dmf</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>dppe</td>
<td>1,2-bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>dppm</td>
<td>bis(diphenylphosphino)methane</td>
</tr>
<tr>
<td>en</td>
<td>ethylenediamine</td>
</tr>
<tr>
<td>e.s.r.</td>
<td>electron spin resonance</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl, -CH₂CH₃</td>
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<tr>
<td>e.x.a.f.s.</td>
<td>extended x-ray absorption fine structure</td>
</tr>
<tr>
<td>HMDE</td>
<td>hanging mercury drop electrode</td>
</tr>
<tr>
<td>Infrared</td>
<td>br, broad; m, medium; s, strong; sh, shoulder; vs, very strong; w, weak.</td>
</tr>
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<td>L¹</td>
<td>1,4,8,11-tetrathiacyclotetradecane</td>
</tr>
<tr>
<td>L²</td>
<td>3,6,10,13-tetrathiabicyclo[13.4.0]nona-1,16,18-triene</td>
</tr>
<tr>
<td>L³</td>
<td>1,4,8,11-tetrathiaundecane</td>
</tr>
<tr>
<td>Me</td>
<td>methyl, -CH₃</td>
</tr>
<tr>
<td>Mo-O&lt;sub&gt;t&lt;/sub&gt;</td>
<td>terminal oxo- ligand</td>
</tr>
<tr>
<td>Mo-S&lt;sub&gt;t&lt;/sub&gt;</td>
<td>terminal sulphido- ligand</td>
</tr>
<tr>
<td>n.m.r.</td>
<td>nuclear magnetic resonance. d, doublet; m, multiplet; s, singlet; q, quartet; t, triplet.</td>
</tr>
<tr>
<td>ox</td>
<td>8-hydroxyquinolinato-</td>
</tr>
<tr>
<td>PB</td>
<td>pentagonal bipyramid(al)</td>
</tr>
<tr>
<td>phen</td>
<td>1,10-phenanthroline</td>
</tr>
<tr>
<td>Pr&lt;sup&gt;i&lt;/sup&gt;</td>
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<td>pyridine</td>
</tr>
<tr>
<td>pyz</td>
<td>pyrazine</td>
</tr>
<tr>
<td>S&lt;sub&gt;ax&lt;/sub&gt;</td>
<td>axial sulphur atom</td>
</tr>
<tr>
<td>S&lt;sub&gt;eq&lt;/sub&gt;</td>
<td>equatorial sulphur atom</td>
</tr>
<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td>thf</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>tetramethylsilane</td>
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<td>tox</td>
<td>8-mercaptoquinolinato-</td>
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<tr>
<td>x.a.s.</td>
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CHAPTER ONE

MOLYBDENUM AND MODEL STUDIES

1.1 INTRODUCTION

The importance and challenge of molybdenum bioinorganic and biomimetic chemistry is reflected in Orme-Johnson's description of nitrogenase related research as-

"... a scientific area, so complex in fundamentals and details, and so consequential in practical global import and effect ..."

W.H. Orme-Johnson, 1981

Molybdenum is known to be crucial to the biological activity of six enzymes; nitrogenase, xanthine oxidase, sulphite oxidase, aldehyde oxidase, xanthine dehydrogenase and nitrate reductase. Nevertheless, the coordination environment and role of molybdenum in these enzymes is not well understood. Their high molecular weight and structural complexity have hindered isolation and complete biochemical characterization, while a lack of suitable crystallinity has prevented single crystal x-ray diffraction studies. Also, prior to recent work employing x-ray absorption spectroscopy, the direct spectroscopic characterization of the molybdenum centres in several molybdoenzymes had been severely limited.

Extensive model studies have been invaluable aids towards the elucidation of the environment and function of enzymatic molybdenum. The early recognition of a sulphur containing molybdenum coordination sphere in some enzymes prompted the investigation of molybdenum complexes with sulphur-donor ligands, a field which continues to be of major importance.
This Thesis describes the preparation and study of new sulphur-donor ligand complexes of molybdenum and tungsten. These complexes exhibit structural and chemical features of some relevance to various molybdoenzymes, and where appropriate these relationships are discussed. In this chapter, a brief description of these enzymes and associated model studies is presented.

1.2 XANTHINE OXIDASE AND SULPHITE OXIDASE

1.2.1 Xanthine Oxidase

In mammals, xanthine oxidase catalyses the oxidation of hypoxanthine (6-oxypurine) to xanthine (2,6-dioxypurine, I) and of xanthine to uric acid (2,6,8-trioxypurine, II, Equation 1),\(^{11,12}\) these reactions being the pre-excretory steps in purine catabolism.\(^{13}\)

\[
\begin{align*}
\text{(I)} & \quad + \text{H}_2\text{O} & \rightarrow & \quad \text{(II)} \\
\end{align*}
\]

\[\text{H}_2\text{O} \rightarrow \text{O}^+ + 2\text{H}^+ + 2\text{e}^- \quad (1)\]

In the following, the enzymes' function will be discussed in terms of Equation (1) only, i.e. xanthine as substrate.

Bovine milk xanthine oxidase\(^{11,14}\) is dimeric (molecular weight ca. 280,000) with each subunit containing one molybdenum atom, two \(\text{Fe}_2\text{S}_2(\text{SR})_4\) type clusters and a Flavin Adenine Dinucleotide (FAD) molecule. The extensive biochemical studies of xanthine oxidase have been reviewed.\(^{11,12}\)
While it is certain that substrate reduction occurs at the molybdenum site, the structure of the site and the mechanism involved are not completely understood. At the various stages of the catalytic cycle, the presence of Mo(VI), Mo(V) and Mo(IV) metal centres is generally accepted. The similar redox potentials (ca. 355 mV) of the Mo(VI)/Mo(V) and Mo(V)/Mo(IV) couples make a simple two electron transfer from xanthine to Mo(VI) a likely initial step in catalysis. Such two electron transfers are intimately involved in the oxygen atom transfer reactions of oxomolybdenum complexes. Also, it can be noted that xanthine oxidase effects the nett transfer of an oxygen atom to xanthine, paralleling model oxygen atom transfer reactions.

The spatial relationship between the two molybdenum atoms in xanthine oxidase is presently unknown although models involving both mononuclear and dinuclear active sites have been proposed. Support for the mononuclear active site comes primarily from inhibitor binding studies using alloxanthine, a substrate which upon reduction of the Mo(VI) enzyme, binds strongly to the resulting Mo(IV) centres. Equally strong binding of one alloxanthine molecule to each molybdenum atom is observed, suggesting alloxanthine binding to two independent metal centres. Wentworth, however, contends that alloxanthine binding does not preclude the presence of dinuclear species in the reduced form of the enzyme-substrate complex.

Oxidised xanthine oxidase undergoes a desulphurization reaction with CN⁻, producing an inactive 'desulpho' form of the enzyme and SCN⁻. The 'desulpho' enzyme results from the loss of either a sulphido-, persulphido-, or cysteine sulphur atom. Whether the sulphur atom is a ligand or not is uncertain, although recent studies suggest that the atom involved is a terminal sulphido-ligand (Mo-S₄).
Electron spin resonance (e.s.r.) techniques have been applied extensively to the study of xanthine oxidase,\textsuperscript{11,29} and have allowed intimate examination of the catalytic processes occurring on or near the molybdenum atoms.\textsuperscript{11,29} The initial two electron reduction of the Mo(VI) atom to Mo(IV) by xanthine is followed by a redistribution of the electrons within the redox centres of the enzyme, producing e.s.r. active Mo(V)\textsuperscript{11,17} (in the cycling enzyme \(\approx 30\%\) of the molybdenum is present as Mo(V)\textsuperscript{17}). The observed Mo(V) e.s.r. signals vary in complexity depending upon the reducing conditions and the presence of various ions\textsuperscript{11,29,30} indicative of an available metal binding site.

Under certain conditions, the e.s.r. spectra of xanthine oxidase exhibit hyperfine interactions due to two protons close to the Mo(V) centre. These interactions persist at high pH; the pK\(_a\) of proton dissociation for the strongly coupled proton being \(\approx 8\) and \(\approx 10.1\) in the functional and 'desulpho' enzymes respectively.\textsuperscript{11} The abstraction of protons from the C-8 position of the purine to the strongly coupled site near the molybdenum has been demonstrated by deuteration studies. Evidence suggests that only the strongly coupled proton is transferred from the substrate to the enzyme in this process.\textsuperscript{30} This behaviour strongly supports an enzyme mechanism involving coupled proton and electron transfer\textsuperscript{30,33,34} (see later).

The proton binding sites are believed to be metal-adjacent ligand atoms\textsuperscript{25} although some controversy exists as to the types of atoms involved. Hyperfine splittings due to \(^{17}\)O and \(^{33}\)S have been observed recently in e.s.r. studies,\textsuperscript{37-39} indicating the presence of oxygen and sulphur in the molybdenum coordination sphere and thus their possible participation as proton binding sites. Indeed, it has been suggested\textsuperscript{25} that the oxidised enzyme contains a Mo-S\(_t\) group which upon reduction becomes protonated to Mo-SH, this sulphur atom being the one removed from the
oxidised enzyme by CN\(^-\). In a manner analogous to model chemistry, the following reaction is envisaged (Equation 2):

\[
\text{Enzyme-Mo-S}_t^+ + \text{CN}^- + \text{H}_2\text{O} \rightarrow \text{Enzyme-Mo-O}_t^- + \text{SCN}^- + 2\text{H}^+ + 2\text{e}^- \tag{2}
\]

The pK\(_a\) of the strongly coupled proton in the functional (ca. 8) and 'desulpho' (ca. 10.1) enzymes can be explained if the proton site in these two forms is assumed to be a Mo-S\(_t\) and Mo-O\(_t\) ligand, respectively, the acidity of protons bound to sulphur being generally greater than those bound to oxygen. To date, \(^{14}\)N hyperfine splitting of the enzyme e.s.r. signals has not been observed but model complexes containing Mo-NH moieties show \(^{14}\)N couplings sufficiently small to be unresolved in enzyme e.s.r. studies. Recent x-ray absorption spectroscopy (x.a.s.) and extended x-ray absorption fine structure (e.x.a.f.s.) studies of xanthine oxidase have indicated an oxo- and sulphur-donor ligand environment at the molybdenum site, and have provided evidence for a sulphur atom at 2.25 Å from the molybdenum. In accord with the postulates of Gutteridge et al., this Mo-S\(_t\) group appears to be replaced by a Mo-O\(_t\) group in the 'desulpho' enzyme. Recent e.x.a.f.s. studies of the related cyanolysable molybdoenzyme, xanthine dehydrogenase, support a similar mechanism for desulphurization of this enzyme. Coordinated nitrogen has not been detected by e.x.a.f.s. studies of xanthine oxidase.

Coupled proton and electron transfer mechanisms for xanthine oxidase have been proposed by Stiefel et al., Olson et al. and Bray et al. The recent model of Bray et al., shown in Figure 1.1, assumes Mo-S\(_t\) to be the proton binding site. The Michaelis complex (I) is formed by binding the substrate to molybdenum via the N-9 atom, whereupon an unidentified nucleophile, X (persulphide according to Olson et al.), attacks the C-8 position. A coupled electron (via N-9) and proton (to Mo-S\(_t\)) transfer, and the reaction of the C-8 carbonium ion with X leads
Proposed mechanism for xanthine oxidase activity (Bray et al.\textsuperscript{18}). Bold face type denotes atoms of, or derived from, the 7-, 8- and 9- positions of xanthine.

to intermediate (II). Subsequent pH dependent hydrolysis leads to the formation of products with or without prior -SH proton exchange.

Mechanisms involving oxygen atom transfer have also been proposed for xanthine oxidase on the basis of the nett transfer of an oxygen atom to xanthine during enzyme catalysis (Equation 1).\textsuperscript{19-22,34} In support of this mechanism, Murray et al.\textsuperscript{50} claim that a small but significant transfer of $^{18}$O from $^{18}$O$_2$ to uric acid occurs during xanthine oxidase turnover at pH 8.7. This transfer presumably occurs through the intermediate formation of an $^{18}$oxomolybdenum species.

1.2.2 Sulphite Oxidase

The molybdenum and haem containing enzyme, sulphite oxidase,
catalyses the oxidation of sulphite to sulphate according to Equation (3).

\[
\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^- 
\]

(3)

The importance of sulphite oxidase in animals is its ability to transform the toxins \(\text{SO}_3^{2-}\) and \(\text{SO}_2\) gas (products of the oxidative degradation of sulphur containing amino acids) into the relatively innocuous \(\text{SO}_4^{2-}\)-ion.\(^{51}\)

Sulphite oxidase exists as a dimer (molecular weight \(\approx 110,000\)) and besides one atom of molybdenum, each subunit contains a b-type cytochrome centre. Enzymatic sulphite oxidation uses water as the source of oxygen and cytochrome c as the ultimate physiological electron acceptor.\(^{52}\) The sulphite is oxidised at the molybdenum centre, which is in turn re-oxidised by the \(b_5\)-like haem.\(^{53}\) The proposed molybdenum and iron atom oxidation states involved in the catalytic cycle are shown in Figure 1.2.\(^{48}\) As isolated, the enzyme contains Mo(VI) and low spin Fe(III)-haem (Soret band 413 nm). Reduction by sulphite results in a low spin Fe(II)-haem (Soret band 423 nm) and an e.s.r. active (\(g = 1.97\)) Mo(V) centre. Addition of dithionite results in loss of the e.s.r. signal due to the formation of Mo(IV). Although the number of electrons transferred to the metal by the substrate is unknown, a two

![Figure 1.2. A proposed catalytic cycle for sulphite oxidase.\(^{48}\)](image)
electron reduction of a Mo(VI) centre to Mo(IV) is favoured, along with subsequent one electron processes to re-form Mo(VI) via a Mo(V) intermediate. The molybdenum and haem centres of the enzyme have been studied extensively by e.s.r. and spectrophotometric techniques, respectively. Electron spin resonance studies of the enzyme show the presence of only one (cf. two in the case of xanthine oxidase) strongly coupled proton (pKₐ ~ 8) at the molybdenum active site. As with xanthine oxidase this proton is not a metal hydride but is located instead on an atom (N, S or O) adjacent to the metal.

Recently, trypsin cleavage of rat liver sulphite oxidase has allowed the separation, isolation and partial characterization of the b₅-cytochrome fragment (molecular weight ~ 9,500) and molybdenum fragment (molecular weight ~ 47,000). In the molybdenum fragment, the visible absorption spectrum is similar, although of lower intensity, to that of Fe₂S₂ type species, suggesting sulphur coordination about the molybdenum atom.

Molybdenum x.a.s. and e.x.a.f.s. studies of sulphite oxidase and its various reduced forms indicate the presence of one or two Mo-Oₐ groups and a sulphur-containing molybdenum coordination sphere. The molybdenum sites shown in Figure 1.3 have been proposed for sulphite oxidase on the basis of combined e.s.r. and e.x.a.f.s. results.

![Figure 1.3. Proposed molybdenum site in sulphite oxidase, based on e.x.a.f.s. and e.s.r. studies.](image-url)
Although the metal oxidation states involved in sulphite oxidase activity are reasonably well established, the intimate mechanism of sulphite oxidation at the molybdenum centre is uncertain; processes involving coupled proton-electron transfer \(^{33,34}\) and oxygen atom transfer have been proposed.\(^{19-22,34}\) Also, the presence of two molybdenum atoms per enzyme molecule makes the participation of dinuclear molybdenum centres in the catalytic cycle a possibility;\(^{19}\) the e.s.r. properties of sulphite oxidase suggest the presence of mixed oxidation state centres should this be the case.

1.2.3 Model Studies

The enzymes, xanthine oxidase, sulphite oxidase and nitrate reductase appear to be related by a common molybdenum cofactor (Mo-co) which can be extracted from and exchanged between the enzymes.\(^5^4\) Thus, model studies directed at an individual enzyme from this group may be applicable to the other enzymes.

The comparison of enzyme e.s.r. spectra\(^{11,29}\) with those of structurally defined Mo(V) model complexes has been a primary approach to the elucidation of enzymatic molybdenum site structures. The propensity of Mo(V) to form dinuclear species\(^9\) and the possible participation of these species in enzyme systems\(^9,19\) has prompted the extensive study of dinuclear \(\mu\)-oxo and \(\mu\)-sulphido-Mo(V) complexes. The structural characterization of \(\text{Mo}_2\text{O}_3,\,\text{Mo}_2\text{O}_4,\,\text{Mo}_2\text{O}_2(\mu-\text{O})(\mu-\text{S}),\,\text{Mo}_2\text{O}_2(\mu-\text{S})_2,\,\text{Mo}_2\text{S}_4,\,\text{Mo}_2\text{S}_4\) and O- and S-containing triply-bridged \(^{85-91}\) units, many with sulphur-donor co-ligands, has been reported. Unfortunately, these complexes are generally poor models for the e.s.r. active Mo(V) enzyme sites since they are, in most cases, diamagnetic (due to strong electron coupling of the Mo(V) centres). Nevertheless, some measurements in solution have been interpreted in terms of dinuclear paramagnetic solution species.\(^92-94\)
Also, several µ-oxo- and µ-sulphido-Mo(V) complexes undergo a one electron reduction in solution to give transiently stable e.s.r. active species, believed to be dinuclear mixed oxidation state Mo(IV,V) complexes. 95-104 A di-µ-oxo- mixed oxidation state complex, (pyH)[Mo₂O₄(ox)₂] has also been postulated to form upon the chemical reduction of [Mo₂O₄(ox)₂py₂]. 108 None of the above complexes have been isolated from solution. The increased stability of these complexes upon increasing sulphur content 95-99 (stability order µ-oxo < triple-bridge < di-µ-sulphido-) is consistent with the possible presence of a mixed oxidation state species in the sulphur rich enzyme active sites. The localization of the unpaired electron in such complexes to a single molybdenum atom could produce an e.s.r. spectrum resembling that of xanthine oxidase or sulphite oxidase, both in integrated intensity and in the pattern of hyperfine splitting. Recently, the first mixed oxidation state sulphur-donor ligand complex of molybdenum, [Mo₂O₃(S₂CNEt₂)₄]⁻, was isolated in the compound (H₂O₂)[Mo₂O₃(S₂CNEt₂)₄]₃⁺. 61 The e.s.r. properties of this compound are consistent with the interaction of the unpaired electron with only one molybdenum atom, suggesting that e.s.r. signals typical of mononuclear Mo(V) may be produced by mixed oxidation state enzyme centres.

New synthetic methods have provided an increasing number of monomeric Mo(V) complexes amenable to crystallographic and detailed e.s.r. studies. The complexes [MoOCl₅]²⁻ and [MoOCl₄]⁻ and many of their derivatives have been studied, 109-119 including complexes of the formula MoOCl₃L, MoOClL₂ and MoOClL (where L is a bi-, tri- or tetradeutate O-, N- or S-donor ligand). 115-119 The complex cis-MoOCl(tox)₂ (tox = 8-mercaptoquinoline) has been structurally characterised 118 and has been cited as a possible model for xanthine oxidase. 11 This complex is similar to those reported by Marov et al. 119
which exhibit e.s.r. parameters similar to the xanthine oxidase very rapid signal. The preparation of mononuclear oxo-Mo(V) complexes of biologically relevant thiolato-ligands has been difficult due to the tendency of these ligands to form bridged complexes. Nevertheless, a series of complexes of the formula \([\text{MoO}(\text{XR})_4]^\cdot (X = \text{S}, \text{Se}; R = \text{Et}, \text{Ph}, \text{p-toly1}, \text{CH}_2\text{Ph})\) have been prepared (or stabilised at -60°C) and studied by x-ray crystallography and electrochemical and e.s.r. methods. 102-107

Electron spin resonance studies of \(\text{Mo}(\text{S}_2\text{CNEt}_2)(\text{SC}_6\text{H}_4\text{NH})_2, \quad \text{Mo}(\text{S}_2\text{CNEt}_2)(\text{SC}_6\text{H}_4\text{S})_2, \quad \text{Mo}(\text{S}_2\text{PPr}_2)(\text{SC}_6\text{H}_4\text{NH})_2\) and \([\text{Mo}(\text{SC}_6\text{H}_4\text{NH})_3]^\cdot\) indicate that \(^{14}\text{N}\) coupling to Mo(V) may be sufficiently small to be unobserved in enzyme e.s.r. spectra. 34, 41-45 The recently prepared \([\text{MoOL}]^\cdot (L = \text{tetradentate aminothiol})\) complexes shown in Figure 1.4, are notable model complexes for molybdoenzyme oxidase/reductases. 45 These complexes possess an oxo- and sulphur-donor coordination sphere, exhibit

\[
\begin{array}{c}
\text{S} \\
\text{O} \\
\text{S} \\
\text{Mo} \\
\text{N} \\
\text{R} \\
\text{R}
\end{array}
\]

Figure 1.4. Monomeric oxo-molybdenum complexes with tetradentate aromatic aminothiols (Spence et al. 45 R = H, CH₃).

coupled proton-electron transfer reactions, and display \(^1\text{H}\) and \(^{14}\text{N}\) hyperfine coupling to Mo(V) in their e.s.r. spectra.

Oxygen atom transfer reactions are frequently observed in oxomolybdenum model chemistry. 9, 19-22 The reaction of \(\text{cis-MoO}_2(\text{S}_2\text{CNEt}_2)_2\) with \(\text{PPh}_3\) 19-20, 121-125 and of polymer supported
oxomolybdenum complexes with various 'substrates'\textsuperscript{126} are most relevant to enzymatic processes. The reaction of $\text{cis-MoO}_2(S_2\text{CNEt}_2)_2$ and PPh$_3$ in air results in the catalytic aerial oxidation of PPh$_3$ to OPPh$_3$,\textsuperscript{121} shown in Figure 1.5. This type of reaction is related to the oxygen atom transfer mechanisms proposed for xanthine and sulphite oxidases and nitrate reductase.\textsuperscript{9,19-22,24} A similar reaction has been reported for $\text{cis-MoO}_2(\text{tox})_2$.\textsuperscript{120} In a study involving the oxygen atom transfer reactions of various $\text{cis}$-dioxomolybdenum(VI) complexes, an enhancement of the complexes' oxidising ability was observed with increasing coordination sphere sulphur content.\textsuperscript{120} This supports the possible participation of oxygen atom transfer reactions in the sulphur rich molybdoenzyme active sites.

1.3 NITROGENASE

1.3.1 Structure and Function of Nitrogenase

The complex and important process of biological nitrogen fixation has been the subject of extensive scientific investigation,\textsuperscript{127-129} yet the structure and mechanism of the processes' essential enzyme component,
Nitrogenase, remains unclear.

Nitrogenase is composed of two metalloproteins. The larger protein is a tetramer of molecular weight \( 220,000 \) which contains molybdenum and iron in the ratio 2:24-34. The smaller iron protein contains four iron atoms and has a molecular weight of \( 67,000 \). The iron in both proteins is associated with an equal number of acid labile sulphur atoms and both proteins are necessary for dinitrogen reduction. The necessary presence of molybdenum for nitrogenase activity has been demonstrated and although it is believed to be the site of dinitrogen reduction, there is as yet no firm evidence for this. Hydrogen evolution from nitrogenase during dinitrogen reduction and the experiments of Shrauzer and of Nikonova and Shilov suggest the following reaction for nitrogenase catalysis.

\[
\text{N}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow 2\text{NH}_3 + \text{H}_2
\]

(4)

Nitrogenase is significantly different from the other molybdoenzymes, possessing a more complex structure, a unique iron containing cofactor (FeMo-co, see later) and a mechanism which does not involve oxygen atom transfer to or from substrates.

The study of the molybdenum centre of nitrogenase has been severely hampered by a lack of informative spectroscopic techniques. However, significant advances over the past five years have remoulded the conception of the nitrogenase molybdenum site and have redirected model studies. Firstly, an extremely air sensitive Fe-Mo-cofactor (FeMo-co) has been isolated from the Fe-Mo-protein of several nitrogenases. The FeMo-co from \( A.\ vinelandii \), \( C.\ pasteurianum \), \( K.\ pneumoniae \) and other microorganisms are capable of activating the nitrogenase extract from the mutant \( A.\ vinelandii\ UW45 \), which is itself incapable of dinitrogen reduction. FeMo-co contains iron, molybdenum
and acid labile sulphur in the ratio 8:1:6 and Mössbauer, e.s.r. and e.x.a.f.s. studies indicate its structural similarity to the molybdenum site in the Fe-Mo proteins. Secondly, e.x.a.f.s. studies of the Fe-Mo-proteins of the nitrogenases from C. pasteurianum and A. vinelandii suggest the following molybdenum site structural features: (i) the closest shell of atoms consists of 3-4 sulphur atoms at 2.35 Å, with 1-2 iron atoms at 2.72 Å, and (ii) the absence of Mo-Ot, Mo-St and Mo-Mo moieties. The molybdenum site structures consistent with e.x.a.f.s. results are shown in Figure 1.6. E.x.a.f.s. studies of nitrogenase in the presence of dinitrogen show no evidence for dinitrogen binding to molybdenum, possibly due to the strong e.x.a.f.s. produced by the iron and molybdenum scatterers.

The large number of proposed mechanisms for dinitrogen reduction by nitrogenase reflects the extreme complexity of this process. A common feature of most mechanisms is the postulated formation of enzyme-bound intermediates during dinitrogen reduction, although the nature of such intermediates is debatable. The trapping of an enzyme-bound intermediate and the interpretation of HD production during dinitrogen reduction supports the involvement of diimine intermediates in this process. Also, hydrazine is a substrate of nitrogenase, thus establishing the potential of a hydrazine bound
intermediate during nitrogen reduction. Schrauzer\textsuperscript{135} has proposed that the enzyme functions via the formation of a $\eta^2$-dinitrogen complex which is initially reduced to $\eta^2$-diimine. Subsequent disproportionation of the diimine intermediate yields a hydrazine intermediate and traces of dinitrogen and dihydrogen. Reduction of the hydrazine intermediate then produces ammonia. Enemark\textsuperscript{143} has also proposed a mechanistic scheme based on the intermediate formation of $\eta^2$-diimine from an initial side-on bound $\eta^2$-dinitrogen complex. While the involvement of diimine and hydrazine in dinitrogen reduction is propounded by many workers and is the basis of many model studies, other mechanisms, some of which exclude diimine and hydrazine formation, have also been proposed.\textsuperscript{32,34,144-147}

1.3.2 Model Studies

Nitrogenase model studies have involved 1) the determination of the chemical requirements for the binding and subsequent reduction of dinitrogen at metal centres, and 2) the modelling of the structure of the nitrogenase active site by metal complexes or systems.\textsuperscript{149}

Studies related to the binding and activation of dinitrogen by metal complexes have been extensively reviewed\textsuperscript{9,127-129,149-155} and have provided much insight into the possible mechanism of nitrogenase activity. The isolation of a wide variety of transition metal complexes containing dinitrogen, hydrazine, diimine and related N-donor ligands\textsuperscript{9,153,155} attests to the binding of dinitrogen to a metal site in nitrogenase and to its reduction via metal bound intermediates. The dinitrogen complexes of iron have not attracted the attention given to those of molybdenum and tungsten but their existence\textsuperscript{153,155} suggests that the binding and reduction of dinitrogen at an iron centre in nitrogenase should not be excluded as a possible enzyme mechanism. Model studies to date have concentrated on the chemistry of dinitrogen on tertiary phosphine-Mo(0) or W(0) centres\textsuperscript{32,153,155} and these have
provided evidence for various possible enzyme mechanisms. The investigation of hydrazine and diimine complexes of molybdenum and tungsten has also attracted attention in view of the possible presence of such intermediates in dinitrogen fixation. Complexes of this type warrant further investigation.

Although a primary feature of the molybdenum site in nitrogenase, model sulphur-donor ligand complexes which bind and reduce dinitrogen have rarely been realized. Only one sulphur-donor ligand complex of dinitrogen has been reported;\textsuperscript{156} the unstable $\sigma^2\delta$-Mo(N$_2$)$_2$(PMe$_2$Ph)$_2$(PhSCH$_2$CH$_2$SPh).

Also, the greater stability of tungsten complexes compared to their molybdenum analogues is frequently useful in probing the chemistry of dinitrogen and related N-donor ligand complexes.

Since the e.x.a.f.s. studies of nitrogenase, there has been intense activity directed towards the preparation and characterization of heterometallic complexes of iron, molybdenum and sulphur which display structural features similar to those in Figure 1.6. Various complexes, representative of these efforts, are shown in Figure 1.7.

The self-assembly of iron-molybdenum cluster compounds from solutions containing FeCl$_3$/[MS$_4$]$^{2-}$/RS$^-$ (M = Mo, W; R = (variously) Et, CH$_2$Ph, Ph) has yielded the double cubane complexes $[\text{M}_2\text{Fe}_6\text{S}_9(\text{SR})_9]^{3-}$, $[\text{Mo}_2\text{Fe}_6\text{S}_9(\text{SR})_9]^{3-}$, and $[\text{M}_2\text{Fe}_7\text{S}_8(\text{SR})_{12}]^{3-}$.\textsuperscript{157,158} These tetranuclear clusters have been studied by electronic, e.s.r. and Mössbauer spectroscopy and x-ray crystallography.\textsuperscript{149} The complexes exhibit e.x.a.f.s. similar to that of FeMo-co and nitrogenase Fe-Mo proteins, suggesting that these Type I complexes are good preliminary models for the molybdenum site in nitrogenase.\textsuperscript{149} The complexes
Figure 1.7. Examples of structurally characterised nitrogenase model complexes. a) $[\text{Mo}_2\text{Fe}_7\text{S}_8(\text{SeEt})_{12}]^{3-}$; b) $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SeEt})_3]^{3-}$; c) $[(\text{SCH}_2\text{CH}_2\text{S})\text{MoS}_3]_2\text{Fe}]^{3-}$; d) $[(\text{MoS}_4)_2\text{Fe}]^{3-}$.

$[\text{W}_2\text{Fe}_6\text{S}_8(\text{SR})_6(\text{OMe})_3]^{3-}$, $[\text{Fe}_4\text{S}_4(\text{MS}_4)_4]^{6-}$ and the water soluble $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SCH}_2\text{CH}_2\text{OH})_3]^{3-}$ are also known. Despite the observation of substrate reduction ($\text{H}_2$ evolution from protic solutions) using $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SR})_9]^{5-}$, the coordination saturation of the molybdenum atoms in these double cubane complexes may prevent their binding and activation of nitrogenase substrates. The preparation of cubane complexes containing coordinatively unsaturated molybdenum atoms is thus a topic of current interest.$^{169,170}$

Models of the Type II active site have been prepared by the reaction of the potentially bidentate ligands $[\text{MS}_4]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$) with suitable iron centres.$^{171,172}$ The many examples of this class of complex contain near linear arrays of tetrahedrally coordinated iron and molybdenum atoms linked via di-µ-sulphido-bridges.$^{173-183}$ With the exception of
\[ \{\{SCH_2CH_2S\}MoS_3\}_2Fe \] (Figure 1.7), iron-molybdenum complexes containing multidentate thiolato-ligands have not been reported. However, a growing interest in such complexes is developing.

Although several examples of the "string bag" Type III site have been reported, none have been structurally characterised.

Recently, the two major aims of nitrogenase model studies have been combined in the preparation and study of molybdenum and iron complexes which contain biologically relevant N-donor ligands. 

![Diagram](image-url)
CHAPTER TWO

THE PREPARATION, CHARACTERIZATION AND REACTIVITY
OF THE OXOMOLYBDENUM(VI) COMPLEXES, \([\text{MoO(S}_2\text{CNR}_2)_3]^+\)

2.1 INTRODUCTION

For the molybdenum centres in the enzymes xanthine oxidase and sulphite oxidase, current evidence suggests a sulphur environment about high oxidation state molybdenum and the presence of at least one oxo-ligand.\(^{11,28,29,47}\) Also, mechanisms involving oxygen atom transfer have been proposed for these and related molybdoenzymes.\(^{19-22,34}\) These mechanisms involve the transfer of an oxygen atom, formally bound to the metal as an oxo-ligand (O\(^2^-\)), to or from the metal centre. Thus, in the mechanism proposed for sulphite oxidase\(^{22,34}\) (Figure 2.1), the

\[
\begin{align*}
\text{Mo=O} & \quad \text{Mo=O} & \quad \text{Mo=O} \\
\text{O} & \quad \text{O} & \quad \text{O} \\
\text{S} & \quad \text{S} & \quad \text{S} \\
\text{O} & \quad \text{O} & \quad \text{O} \\
\end{align*}
\]

Figure 2.1. An oxygen atom transfer mechanism for enzymatic sulphite oxidation.\(^{22}\)

transfer of an oxygen atom to sulphite results in the reduction of the original oxo-Mo(VI) centre to Mo(IV) and concomitant formation of
sulphate. Conversely, for nitrate reductase\textsuperscript{22,34} (Figure 2.2), an

\begin{center}
\begin{align*}
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{IV} & \quad \text{Mo} = \text{O} \\
\end{align*}
\end{center}

Figure 2.2. An oxygen atom transfer mechanism for enzymatic nitrate reduction.\textsuperscript{22}

oxygen atom from nitrate is transferred to a Mo(IV) centre resulting in the formation of an oxo-Mo(VI) centre and nitrite. Enzymatic oxygen atom transfer mechanisms involving dinuclear molybdenum sites have also been proposed.\textsuperscript{19}

The postulation of enzymatic oxygen atom transfer is primarily based on the oxygen atom transfer reactions of oxomolybdenum model complexes. Thus, the further investigation of mixed oxo- and sulphur-donor ligand complexes and their oxygen atom transfer chemistry is relevant to the active site structure and reactivity of molybdoenzymes.

**Oxygen Atom Transfer to Tertiary Phosphines**

The reaction of \(\sigma\sigma\)-MoO\(_2\)L\(_2\) complexes and tertiary phosphines, PR\(_3\),\textsuperscript{20,120-125} proceeds via oxygen atom transfer to yield the initial products, MoOL\(_2\) and OPR\(_3\). The final molybdenum product is, however, dictated by the equilibrium given in Equation (5)

\[
\sigma\sigma\text{-MoO}_2L_2 + MoOL_2 \rightleftharpoons L_2Mo\text{-}O\text{-MoL}_2
\]
When L is $S_2CNR_2^-$, $S_2PPPh_2^-$ or tox, this equilibrium allows the isolation of both $MoOL_2$ and $Mo_2O_3L_4$ complexes, depending upon the amount of PR$_3$ employed in the reaction.\textsuperscript{121-125} In the cases where L is ox, acac or cyst-OMe, Equation (5) is not an equilibrium but instead lies completely to the right, resulting in the isolation of $Mo_2O_3L_4$ complexes only.\textsuperscript{125}

The observed catalytic oxidation of triphenylphosphine (PPh$_3$) by the complex, $cis$-$MoO_2(S_2CNEt_2)_2$ (Figure 1.5), prompted considerable investigation of this and related reactions.\textsuperscript{121-125} This reaction is a good model for the type of oxygen atom transfer process envisaged to occur at the molybdenum site in enzymes, but clearly is not a model for the enzyme processes themselves. The oxidation of PPh$_3$ by polymer supported Mo(VI)-tripeptide complexes has also been reported.\textsuperscript{126}

**Oxygen Atom Transfer to Molybdenum and Tungsten Complexes**

Oxygen atom transfer from $cis$-$MoO_2(S_2CNEt_2)_2$ to another molybdenum complex has been observed\textsuperscript{187} (Equation 6) and intercomplex oxygen atom transfer has been employed to obtain otherwise difficult to prepare tungsten complexes\textsuperscript{187,188} (Equations 7 and 8; $R = Me, Et$, $R' = H, Ph$)

\[
\begin{align*}
&cis-MoO_2(S_2CNEt_2)_2 + Mo(S_2CNEt_2)_2(CO)_2 \rightarrow 2MoO(S_2CNEt_2)_2 + 2CO & (6)\textsuperscript{187} \\
&WO(S_2CNR_2)_2(HC_2R') + MoO_2(S_2P(OEt)_2)_4 \rightarrow \text{WO}(S_2CNR_2)_2(HC_2R') + 2MoO(S_2P(OEt)_2)_2 + CO & (7)\textsuperscript{188} \\
&W(S_2CNR_2)_2(CO)_2PPh_3 + 2MoO_2(S_2P(OEt)_2)_4 \rightarrow ciss-WO_2(S_2CNR_2)_2 + 4MoO(S_2P(OEt)_2)_2 + 2CO + PPh_3 & (8)\textsuperscript{187}
\end{align*}
\]

**Oxygen Atom Transfer Reactions Involving Monooxomolybdenum Complexes**

Oxygen atom transfer from various substances (e.g. $(CH_3)_2SO$, pyO, O$_2$) to $MoO(S_2CNEt_2)_2$ has been reported;\textsuperscript{189} these reactions result in the formation of $cis$-$MoO_2(S_2CNEt_2)_2$ by a reaction of the type shown in Figure 2.2. Several of these reported reactions have been subsequently
disproved. Also, during the course of the present work, the first oxygen atom transfer reactions of monooxo-Mo(VI) complexes were reported (Equations 9 and 10, \( X = \text{Cl}^- \) or \( \text{Br}^- \)) but catalytic oxidation reactions have not been accomplished using such complexes.

\[
\text{MoOX}_2(S_2CNET}_2)_2 + 2\text{PPh}_2\text{Et} \rightarrow \text{MoX}_2(S_2CNET}_2)_2(\text{PPh}_2\text{Et}) + \text{OPPh}_2\text{Et} \tag{9}
\]

\[
\text{MoOCl}_2(S_2CNET}_2)_2 + \text{PhNCO} \rightarrow \text{Mo}(\text{NPh})\text{Cl}_2(S_2CNET}_2)_2 + \text{CO}_2 \tag{10}
\]

A feature of the oxygen atom transfer reactions described above is the frequent appearance of \( N,N \)-dialkyldithiocarbamato-ligands. While the predominance of dithiocarbamato-complexes in the oxygen atom transfer reactions of molybdenum may be somewhat accidental, it also reflects the ability of dithiocarbamato-ligands to stabilise high oxidation state metal ions. Although ligands of this type are unlikely in enzyme systems, much insight into the nature of enzymatic molybdenum centres has been gained from the extensive investigation of (dithiocarbamato)molybdenum complexes. Certainly, the above reactions indicate the propensity of oxygen atom transfer reactions in high oxidation state oxomolybdenum chemistry and thus their possible participation in enzyme centres of this type. Calorimetric studies have also shown that the oxidation of sulphite ion and acetaldehyde and (possibly) the reduction of nitrate by oxo(dithiocarbamato)molybdenum complexes is thermodynamically favourable.

This chapter describes the preparation, characterization and reactions of the oxomolybdenum(VI) compounds \([\text{MoO(S}_2\text{CNR}_2)_3]\)X (hereafter \( R = \text{Me}, \text{Et}, \text{Pr}^i, \text{Bu}^n; X = \text{BF}_4^-, \text{PF}_6^-, \text{ClO}_4^-, \) unless specified). The cations \([\text{MoO(S}_2\text{CNR}_2)_3]\)\(^+\) (\( R = \text{Et}, \text{Pr}^n \)) have been reported, but in the absence of simple synthetic procedures and detailed spectroscopic properties.
2.2 EXPERIMENTAL SECTION

2.2.1 General

The experimental details common to the whole of this thesis are described below. Those peculiar to the various areas of study are described in the appropriate chapters.

Chemicals and solvents were LR grade or higher and unless specified were used without further purification. Microanalyses were carried out by the Australian National University Microanalytical Service. Carbon, hydrogen, nitrogen, sulphur and oxygen analyses were performed using 185B and CE1106 Automatic Analysers, other elements being determined by conventional microanalytical methods. Molecular weights were determined by vapour pressure osmometry.

Unless specified all solid state infrared spectra employed the cesium iodide disc technique and were recorded on a Perkin Elmer 683 infrared spectrophotometer calibrated with polystyrene. Solution infrared spectra were recorded in sodium chloride cells. Electronic spectra were recorded on a Cary 219 spectrophotometer using matched quartz cells.

$^1$H nuclear magnetic resonance ($^1$H n.m.r.) spectra were recorded on Jeolco Minimar ($B = 23.49 \text{T} , 100 \text{ MHz for } ^1\text{H}$), Pulse Fourier Transform Varian CFT-20 ($B = 18.70 \text{T} , 79.6 \text{ MHz for } ^1\text{H}$) and Bruker HFX-270 ($B = 63.42 \text{T} , 270 \text{ MHz for } ^1\text{H}$, employing a Nicolet 1180 72K memory computer) spectrometers. Noise decoupled $^{13}$C nuclear magnetic resonance ($^{13}$C-$^1$H n.m.r.) spectra were recorded on the Varian CFT-20 (19.9 MHz for $^{13}$C) and Bruker HFX-270 (67.89 MHz for $^{13}$C) instruments. $^{31}$P-$^1$H n.m.r. were recorded on a JEOL HX-90Q ($B = 22.0 \text{T} , 37.9 \text{ MHz for } ^{31}\text{P}$) spectrometer. On the
Varian CFT-20 spectrometer, the experimental temperature was recorded by a Comark Electronic Thermometer (to ± 0.5°).

Conductivity measurements employed a Philips P.R. 9500 direct reading conductivity bridge and sample concentrations of \(10^{-3}\) M. X-ray powder patterns were recorded using an Automatic Philips P.W. 1049 Counter Diffractometer (Philips P.W. 1010 generator) using Ni-filtered Cu-\(K_\alpha\) (\(\lambda = 1.5418\) Å).

Techniques for Air Sensitive Chemistry

The air sensitivity of many compounds necessitated their preparation and manipulation under anaerobic conditions.

Apparatus: Standard Schlenk and glovebox techniques were used. A Schlenk line apparatus, described in Appendix I, was designed and constructed to facilitate rapid manipulations under anaerobic conditions.

Solvents and reagents: Following initial purification, solvents were refluxed over a suitable drying agent under an atmosphere of high purity nitrogen. The drying agents used for various solvents were: 

- \(\text{CH}_3\text{CN}, \text{CaH}_2; \text{C}_6\text{H}_6, \text{Na/K}; \text{CH}_2\text{Cl}_2, \text{P}_2\text{O}_5; \text{CH}_3\text{CH}_2\text{OH}, \text{Mg(OCH}_3\text{CH}_3)_2; \text{n-hexane}, \text{Na/K}; \text{CH}_3\text{OH}, \text{Mg(OCH}_3)_2; \text{thf, Na/K}.\) The solvents were then distilled into collecting vessels under a flow of dinitrogen. The transfer of solvents to reaction vessels employed gas-tight syringes or stainless steel tubing. In some instances solvents were deoxygenated by saturation with dinitrogen for 30 minutes. Air sensitive starting materials and products were stored in sealed vessels under dinitrogen.

2.2.2 Preparation of the Compounds \([\text{MoO(S}_2\text{CNR}_2)_3]X\)

2.2.2.1 Materials

The compounds \(\text{NaS}_2\text{CNMe}_2.2\text{H}_2\text{O}\) (Aldrich Chemicals, Milwaukee) and \(\text{NaS}_2\text{CNET}_2.3\text{H}_2\text{O}\) (Eastman Chemicals, Rochester) were used without further purification. The compounds \(\text{NaS}_2\text{CNR}_2\) (\(R = \text{Pr}^i, \text{Bu}^n\)) were prepared.
according to Equation (11).  

\[
\text{CS}_2 + \text{NHR}_2 + \text{NaOH} \rightarrow \text{NaS}_2\text{CNR}_2 + \text{H}_2\text{O}
\]  

The method of Moore and Larson\textsuperscript{216} was found most convenient and reliable for the preparation of cis-MoO\textsubscript{2}(S\textsubscript{2}CNR\textsubscript{2})\textsubscript{2} complexes. The complexes Mo(N\textsubscript{2}COPh)(S\textsubscript{2}CNET\textsubscript{2})\textsubscript{3}\textsuperscript{217} (Et\textsubscript{4}N)\textsubscript{2}[MoS\textsubscript{4}]\textsuperscript{218,16} and (Et\textsubscript{4}N)\textsubscript{2}[WS\textsubscript{4}]\textsuperscript{219,16} were prepared by literature methods. The following were prepared as described.

\textbf{cis-Dioxobis(N,N-diisopropyldithiocarbamato)molybdenum(VI)}

A solution of NaS\textsubscript{2}CNPr\textsubscript{2} (2.0 g, 10.0 mmol) and Na\textsubscript{2}MoO\textsubscript{4}.2H\textsubscript{2}O (1.67 g, 6.90 mmol) in water (42 mL) was treated (dropwise) with 0.4 M HNO\textsubscript{3} (35 mL). The orange solid obtained was filtered, dried under vacuum and recrystallised twice from benzene/petroleum spirits (40-70° B.P.).

\textbf{Anal. } Calcd. for C\textsubscript{14}H\textsubscript{30}MoN\textsubscript{2}O\textsubscript{2}S\textsubscript{4}: C, 34.9; H, 5.9; N, 5.9.

Found: C, 35.4; H, 5.9; N, 5.7%.

Infrared spectrum: ν(Mo-O\textsubscript{t}) at 912 and 881 cm\textsuperscript{-1}.

\textbf{\textsuperscript{1}H n.m.r. spectrum, 100 MHz (CDC\textsubscript{13}):} δ1.49 (24H, d, J = 7.4 Hz, 8 x CH\textsubscript{3}), 4.8-4.5 (4H, br m, 4 x CH).

\textbf{Chlorotris(N,N-diethylidithiocarbamato)molybdenum(IV)}

The compound was prepared by modification of the method of Bishop et al.\textsuperscript{217} A stirred suspension of Mo(N\textsubscript{2}COPh)(S\textsubscript{2}CNET\textsubscript{2})\textsubscript{3} (1.0 g, 1.48 mmol) in deoxygenated methanol (15 mL) under dinitrogen was treated with HCl gas for 5 min to produce a deep green solution which was allowed to stand (in the dark) overnight. The crystalline solid which formed was filtered, washed with methanol and dried under vacuum. The yield was 0.66 g (78%).

\textbf{Anal. } Calcd. for C\textsubscript{15}H\textsubscript{30}ClMoN\textsubscript{3}S\textsubscript{6}: C, 31.3; H, 5.2; Mo, 16.7; N, 7.3; S, 33.4. Found: C, 31.5; H, 5.3; Mo, 16.5; N, 7.2; S, 33.4 %.
All starting materials were characterised by elemental analysis and infrared and n.m.r. spectroscopy.

2.2.2.2 Preparation of [MoO(S₂CNR₂)₃]ₓ

**Oxotris(N,N-dimethyl dithiocarbamato)molybdenum(VI) Tetrafluoroborate**

A suspension of cis-MoO₂(S₂CNMe₂)₂ (0.82 g, 2.2 mmol) in acetone (100 mL) was treated with 31% aqueous HBF₄ (1 mL) and stirred in the dark for 4 hrs. Following filtration of the reaction mixture, ether (160 mL) was added to the filtrate to yield a yellow green solid (0.7 g). The solid was extracted with dichloromethane (170 mL) and after filtration, ether was added to the orange filtrate to yield a yellow solid. The compound was recrystallised from dichloromethane/ether.

The yield was 0.45 g (55%, all yields based on S₂CNR₂⁻).

**Anal.** Calcd. for C₉H₁₈BF₄MoN₃O₅S₅: C, 19.3; H, 3.2; Mo, 17.2; N, 7.5; S, 34.4. Found: C, 19.5; H, 3.8; Mo, 17.5; N, 7.4; S, 34.4 %.

**Oxotris(N,N-dimethyl dithiocarbamato)molybdenum(VI) Hexafluorophosphate**

The preparation, which follows that given above, employed a solution of cis-MoO₂(S₂CNMe₂)₂ (2.0 g, 5.43 mmol) in acetone (150 mL) and 1 mL of 65% aqueous HPF₆. Recrystallization from methanol/ether yielded 1.0 g (45%) of yellow crystals.

**Anal.** Calcd. for C₁₀.₅H₂₄F₆MoN₃O₂₃PS₅: C, 19.4; H, 3.7; N, 6.5; P, 4.8; S, 29.6. Found: C, 19.4; H, 3.5; N, 6.2; P, 4.7; S, 29.6 %.

The analysis indicates 1.5 molecules of methanol of crystallization.

**Oxotris(N,N-dimethyl dithiocarbamato)molybdenum(VI) Perchlorate**

The preparation, which follows that given for [MoO(S₂CNMe₂)₃]BF₄, employed a solution of cis-MoO₂(S₂CNMe₂)₂ (2.0 g, 5.43 mmol) in acetone (150 mL) and 2 mL of 68% aqueous HClO₄. The yield of yellow crystals was 0.85 g (42%).

**Anal.** Calcd. for C₉H₁₈ClMoN₃O₄S₅: C, 18.9; H, 3.2; Cl, 6.2; N, 7.4;
Oxotris(N,N-diethylthiocarbamato)molybdenum(VI) Tetrafluoroborate

A suspension of cis-MoO$_2$(S$_2$CNEt$_2$)$_2$ (10.0 g, 23 mmol) in acetone (20 mL) was treated with 31% aqueous HBF$_4$ (10 mL) and stirred in the dark for 3 hrs. The suspension was reduced in volume to ca. 25 mL and following the addition of methanol (25 mL), was filtered to remove an insoluble brown-green solid (F1). The filtrate was treated with dichloromethane (25 mL) then ether to precipitate the orange product. The solid was recrystallised from methanol/ether and dried at 100°C under vacuum for 1 hr. The yield was 6.7 g (68%).

Anal. Calcd. for C$_{15}$H$_3$O$_8$Mo$_3$N$_3$S$_4$: C, 28.0; H, 4.7; Mo, 14.9; N, 6.5; S, 29.8. Found: C, 28.1; H, 5.0; Mo, 14.7; N, 6.5; S, 29.5 %.

The green brown solid (F1) was recrystallised twice from dichloromethane/ether to yield orange crystals of [MoO(S$_2$CNEt$_2$)$_3$][Mo$_6$O$_{19}$]. The yield was 1.2 g (21% based on molybdenum).

Anal. Calcd. for C$_{30}$H$_5$O$_8$Mo$_8$N$_6$S$_{12}$: C, 18.1; H, 3.0; Mo, 38.5; N, 4.0; O, 16.9; S, 19.3. Found: C, 18.2; H, 3.1; Mo, 38.5; N, 4.4; O, 16.8; S, 19.3 %.

Infrared spectrum: 2980w, 2930w, 2870w, 1545s, 1515s, 1460s, 1440s, 1380m, 1355m, 1280s, 1200s, 1155m, 1100m, 1075m, 955s, 935s, 910m, 800vs, 605w, 570w, 440w, 375w, 355w cm$^{-1}$.

$^1$H n.m.r. spectrum, 80 MHz (CDCl$_3$): δ1.20 (3H, t, J = 7.2 Hz, CH$_3$); 1.44-1.47 (15H, 3 overlapping t, J = 7.0 Hz, 5 x CH$_3$); 3.66 (2H, q, J = 7.0 Hz); 3.8-4.2 (10H, 3 overlapping q, 5 x CH$_2$).

Conductivity: $\Lambda_0 = 155 \Omega^{-1}\text{cm}^2\text{mole}^{-1}$ (for 2:1 electrolytes $\Lambda_0 \sim 115-200 \Omega^{-1}\text{cm}^2\text{mole}^{-1}$).
dark for 4 hrs. The solution was reduced in volume to 15 mL and then filtered. Methanol (15 mL) was added to the filtrate, followed by ether to precipitate the orange product. Recrystallization was effected from methanol/ether. The yield was 1.1 g (51%).

Oxotris(N,N-diethyldithiocarbamato)molybdenum(VI) Perchlorate

A suspension of cis-MoO₂(S₂CNEt₂)₂ (2.0 g, 4.6 mmol) in acetone (50 mL) was treated with 68% aqueous HClO₄ (1 mL) and stirred in the dark for 4 hrs. Subsequent treatment followed that of the previous preparation. The yield was 1.4 g (70%).

Oxotris(N,N-diethyldithiocarbamato)molybdenum(VI) Tetrafluoroborate

A suspension of MoCl(S₂CNEt₂)₃ (0.4 g, 0.69 mmol) in deoxygenated dichloromethane (15 mL) under dinitrogen was treated with 98% doubly labelled ¹⁸O₂ gas (20 mL, ~0.9 mmol) and the mixture stirred for 4 hrs to yield an orange solution. NaBF₄ (0.2 g) in methanol (30 mL) was added and the solution reduced to dryness. The residue was recrystallised from dichloromethane/ether. The yield of orange crystals, containing a mixture of [Mo¹⁶O(S₂CNEt₂)₃]BF₄ and [Mo¹⁸O(S₂CNEt₂)₃]BF₄, was 0.17 g (38%).

Oxotris(N,N-diisopropyldithiocarbamato)molybdenum(VI) Tetrafluoroborate

A solution of cis-MoO₂(S₂CNPr₂)₂ (0.35 g, 0.73 mmol) in acetone (30 mL) was treated with 31% aqueous HBF₄ (0.7 mL). The solution was stirred in the dark for 16 hrs whereupon a yellow solid precipitated. The compound was isolated by filtration and recrystallised from dichloromethane/ether. The yield was 0.18 g (50%).
**Oxotris(N,N-di-n-butylidithiocarbamato)molybdenum(VI) Tetrafluoroborate**

A solution of cis-MoO₂(S₂CNBu₂)₂ (0.35 g, 0.65 mmol) in acetone (15 mL) was treated with 31% aqueous HBF₄ (0.5 mL). The solution was reduced to 7 mL and filtered. Ether was added and slow cooling produced orange crystals of product. The yield was 0.14 g (40%).

**2.2.3 Characterization of the Compounds [MoO(S₂CNR₂)₃]X**

**2.2.3.1 Conductivity Measurements**

The molar conductivities of the compounds are given in Table 2.1.

**Table 2.1**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\Lambda_0$ (Ω⁻¹cm²mole⁻¹)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MoO(S₂CNMe₂)₃]BF₄</td>
<td>CH₃NO₂</td>
<td>83</td>
</tr>
<tr>
<td>[MoO(S₂CNMe₂)₃]BF₄</td>
<td>CH₃CN</td>
<td>141</td>
</tr>
<tr>
<td>[MoO(S₂CNMe₂)₃]PF₆</td>
<td>CH₃NO₂</td>
<td>80</td>
</tr>
<tr>
<td>[MoO(S₂CNMe₂)₃]ClO₄</td>
<td>CH₃NO₂</td>
<td>79</td>
</tr>
<tr>
<td>[MoO(S₂CNET₂)₃]BF₄</td>
<td>CH₃NO₂</td>
<td>84</td>
</tr>
<tr>
<td>[MoO(S₂CNET₂)₃]BF₄</td>
<td>CH₃CN</td>
<td>127</td>
</tr>
<tr>
<td>[MoO(S₂CNET₂)₃]BF₄</td>
<td>CH₃OH</td>
<td>85</td>
</tr>
<tr>
<td>[MoO(S₂CNET₂)₃]PF₆</td>
<td>CH₃NO₂</td>
<td>78</td>
</tr>
<tr>
<td>[MoO(S₂CNET₂)₃]ClO₄</td>
<td>CH₃NO₂</td>
<td>80</td>
</tr>
<tr>
<td>[MoO(S₂CNPr₂)₃]BF₄</td>
<td>CH₃NO₂</td>
<td>83</td>
</tr>
<tr>
<td>[MoO(S₂CNBu₂)₃]BF₄</td>
<td>CH₃NO₂</td>
<td>83</td>
</tr>
</tbody>
</table>

(a) the typical $\Lambda_0$ ranges for 1:1 electrolytes in the solvents are²²⁰: CH₃NO₂ 60-115, CH₃CN 120-160 and CH₃OH 80-115 Ω⁻¹cm²mole⁻¹.
Table 2.2
Infrared Spectra of $[\text{MoO}(S_2\text{CNR}_2)_3]^+$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(CN)</th>
<th>$\nu$(NC$_2$)</th>
<th>$\nu$(C=S)</th>
<th>$\nu$(Mo-O$_t$)</th>
<th>$\nu$(Mo-S)</th>
<th>Anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{MoO}(S_2\text{CNMe}_2)_3]\text{BF}_4$</td>
<td>1573s, 1570s</td>
<td>1243m</td>
<td>b</td>
<td>935s</td>
<td>380sh, 370m</td>
<td>1100s, br 530w, 520w</td>
</tr>
<tr>
<td></td>
<td>1547s, 1535s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{MoO}(S_2\text{CNMe}_2)_3]\text{PF}_6$</td>
<td>1575s, 1570s</td>
<td>1240m</td>
<td>1050w</td>
<td>935s</td>
<td>380sh, 370m</td>
<td>838s, 555s</td>
</tr>
<tr>
<td></td>
<td>1547s, 1540s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{MoO}(S_2\text{CNMe}_2)_3]\text{ClO}_4$</td>
<td>1575s, 1570s</td>
<td>1240m</td>
<td>b</td>
<td>935s</td>
<td>380sh, 370m</td>
<td>1100s, 627s, 620s, 570w</td>
</tr>
<tr>
<td></td>
<td>1545s, 1535s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{MoO}(S_2\text{CNET}_2)_3]\text{BF}_4$</td>
<td>1550s, 1520s</td>
<td>1155s</td>
<td>1005m</td>
<td>935s</td>
<td>380sh, 370m</td>
<td>1095s, br 530w, 520w</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{MoO}(S_2\text{CNET}_2)_3]\text{PF}_6$</td>
<td>1550s, 1540sh</td>
<td>1155s</td>
<td>1003w</td>
<td>935s</td>
<td>380sh, 370m</td>
<td>850s, 565s</td>
</tr>
<tr>
<td></td>
<td>1520s, 1515sh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{MoO}(S_2\text{CNET}_2)_3]\text{ClO}_4$</td>
<td>1550s, 1540s</td>
<td>1150s</td>
<td>1000w</td>
<td>935s</td>
<td>380sh, 370m</td>
<td>1100s, 627s, 620s, 570w</td>
</tr>
<tr>
<td></td>
<td>1527s, 1522s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{MoO}(S_2\text{CNPr}_2)_3]\text{BF}_4$</td>
<td>1532s, 1520s</td>
<td>1150s</td>
<td>950sh</td>
<td>935s</td>
<td>380w, 370w</td>
<td>1067s, br 530w, 520w</td>
</tr>
<tr>
<td></td>
<td>1498s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{MoO}(S_2\text{CNU}_2)_3]\text{BF}_4$</td>
<td>1553s, 1535sh</td>
<td>1110m</td>
<td>958m</td>
<td>933s</td>
<td>380w, 370w</td>
<td>1095s, br</td>
</tr>
<tr>
<td></td>
<td>1520s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) In CsI. s, strong; m, medium; w, weak; br, broad; sh, shoulder. Dithiocarbamato-ligand assignments follow Reference 222.

b) Bands obscured by BF$_4^-$ or ClO$_4^-$ bands.
2.2.3.2 Infrared Spectra

The infrared spectra of the compounds are summarised in Table 2.2. The infrared spectra of \([\text{MoO(S}_2\text{CNET}_2)_3]X\) \((X = \text{BF}_4^-, \text{PF}_6^-)\) are presented for discussion in Figure 2.5.

The infrared spectrum of a sample of mixed \(^{16}\text{O}\) and \(^{18}\text{O}\) labelled \([\text{MoO(S}_2\text{CNET}_2)_3]\text{BF}_4\) (from Section 2.2.2) in the \(v(\text{Mo-O}_t)\) region is compared to the spectrum of pure \([\text{Mo}^{16}\text{O(S}_2\text{CNET}_2)_3]\text{BF}_4\) in Table 2.3 and Figure 2.7 (Section 2.3). The calculated absorption bands for \([\text{Mo}^{18}\text{O(S}_2\text{CNET}_2)_3]\text{BF}_4\) were obtained from consideration of a simple diatomic Mo-O oscillator.\(^{221}\)

<table>
<thead>
<tr>
<th>Oxygen Isotope Present</th>
<th>Observed</th>
<th>Calculated for (v(\text{Mo}^{18}\text{O}_t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{16}\text{O})</td>
<td>935</td>
<td>--</td>
</tr>
<tr>
<td>(^{16}\text{O}) and (^{18}\text{O})</td>
<td>935, 889</td>
<td>889</td>
</tr>
</tbody>
</table>

2.2.3.3 \(^1\text{H N.M.R. Spectra}\)

The \(^1\text{H n.m.r. spectra of the compounds [MoO(S}_2\text{CNR}_2)_3]\text{BF}_4\) are given in Table 2.4. The \(^1\text{H n.m.r. spectra of [MoO(S}_2\text{CNR}_2)_3]\text{BF}_4\) \((R = \text{Me, Et})\) are presented for discussion in Figures 2.9 and 2.11, respectively.

Solvent Dependence of \(^1\text{H N.M.R. Spectra}\)

\([\text{MoO(S}_2\text{CNMe}_2)_3]\text{BF}_4\): The \(^1\text{H n.m.r. spectra of [MoO(S}_2\text{CNMe}_2)_3]\text{BF}_4\) in various solvents are summarised in Table 2.5.

\([\text{MoO(S}_2\text{CNET}_2)_3]\text{BF}_4\): The \(^1\text{H n.m.r. spectra of [MoO(S}_2\text{CNET}_2)_3]\text{BF}_4\) in various solvents are summarised in Table 2.6.
### Table 2.4

<table>
<thead>
<tr>
<th>Compound</th>
<th>Resonance Parameters</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MoO(S₂CNMe₂)₃]BF₄</td>
<td>3.15, 3H, s</td>
<td>CH₃ - c</td>
</tr>
<tr>
<td></td>
<td>3.40, 6H, s</td>
<td>CH₃ - a or a'</td>
</tr>
<tr>
<td></td>
<td>3.45, 3H, s</td>
<td>CH₃ - b</td>
</tr>
<tr>
<td></td>
<td>3.49, 6H, s</td>
<td>CH₃ - a or a'</td>
</tr>
<tr>
<td>[MoO(S₂CNEt₂)₃]BF₄</td>
<td>1.20, 3H, t, J&lt;sub&gt;CH₃-CH&lt;/sub&gt; = 7.2 Hz</td>
<td>CH₃ - c</td>
</tr>
<tr>
<td></td>
<td>1.44, 6H, t, J&lt;sub&gt;CH₃-CH&lt;/sub&gt; = 7.0 Hz</td>
<td>CH₃ - a or a'</td>
</tr>
<tr>
<td></td>
<td>1.45, 3H, t, J&lt;sub&gt;CH₃-CH&lt;/sub&gt; = 7.0 Hz</td>
<td>CH₃ - b</td>
</tr>
<tr>
<td></td>
<td>1.47, 6H, 6, J&lt;sub&gt;CH₃-CH&lt;/sub&gt; = 7.0 Hz</td>
<td>CH₃ - a or a'</td>
</tr>
<tr>
<td></td>
<td>3.66, 2H, q, J&lt;sub&gt;CH₂-CH&lt;/sub&gt; = 7.0 Hz</td>
<td>CH₂ - c</td>
</tr>
<tr>
<td></td>
<td>3.8-4.2, 10H, 3 overlapping q</td>
<td>CH₂ - a, a', b</td>
</tr>
<tr>
<td>[MoO(S₂CNPr₂)₃]BF₄</td>
<td>1.39, 6H, d, J&lt;sub&gt;CH₃-CH&lt;/sub&gt; = 6.0 Hz</td>
<td>CH₃ - c</td>
</tr>
<tr>
<td></td>
<td>1.62, 30H, dd, J&lt;sub&gt;CH₃-CH&lt;/sub&gt; = 6.0 Hz</td>
<td>CH₃ - a, a', b</td>
</tr>
<tr>
<td></td>
<td>4.5-5.0, 6H, m</td>
<td>CH - a, a', b, c</td>
</tr>
<tr>
<td>[MoO(S₂CNBu₂n)₃]BF₄</td>
<td>1.34, 3H, t, J&lt;sub&gt;CH₃-CH&lt;/sub&gt; = 5.4 Hz</td>
<td>CH₃ - c</td>
</tr>
<tr>
<td></td>
<td>1.74, 15H, t, J&lt;sub&gt;CH₃-CH&lt;/sub&gt; = 5.4 Hz</td>
<td>CH₃ - a, a', b</td>
</tr>
<tr>
<td></td>
<td>3.50-3.85, 36H, m</td>
<td>CH₂ - a, a', b, c</td>
</tr>
</tbody>
</table>

a) In CDCl₃/TMS, except [MoO(S₂CNMe₂)₃]BF₄ in CD₃CN.

b) s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

c) See Figure 2.8 for substituent labelling scheme.
Table 2.5

$^1$H N.M.R. (80 MHz) of [MoO(S$_2$CNMe$_2$)$_3$]BF$_4$ in Various Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta$, ppm (N$^2$ of protons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD$_3$CN</td>
<td>3.49(6) 3.45(3) 3.40(6) 3.15(3)</td>
</tr>
<tr>
<td>CD$_3$NO$_2$</td>
<td>3.64(6) 3.57(3) 3.54(6) 3.25(3)</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>3.56(6) 3.50(3) 3.48(6) 3.21(3)</td>
</tr>
<tr>
<td>(CD$_3$)$_2$CO</td>
<td>3.70(6) 3.60(9) - 3.28(3)</td>
</tr>
<tr>
<td>(CD$_3$)$_2$SO</td>
<td>3.55(-) 3.46(-)</td>
</tr>
</tbody>
</table>

Table 2.6

$^1$H N.M.R. (80 MHz) of [MoO(S$_2$CNEt$_2$)$_3$]BF$_4$ in Various Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta$ (ppm), N$^2$ of protons, multiplicity$^a$, J</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD$_3$CN, CDCl$_3$, (CD$_3$)$_2$CO</td>
<td>As in Table 2.4</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>1.16,3H,t,$J_{CH_3-CH} = 7.2$ Hz</td>
</tr>
<tr>
<td></td>
<td>1.18,3H,t,$J_{CH_3-CH} = 7.0$ Hz</td>
</tr>
<tr>
<td></td>
<td>1.43,12H,t,$J_{CH_3-CH} = 6.8$ Hz</td>
</tr>
<tr>
<td></td>
<td>3.40-3.67,4H,m</td>
</tr>
<tr>
<td></td>
<td>3.81,8H,q,$J_{CH_2-CH} = 7.0$ Hz</td>
</tr>
<tr>
<td>(CD$_3$)$_2$SO</td>
<td>1.30,-,t,$J_{CH_3-CH} = 7.0$ Hz</td>
</tr>
<tr>
<td></td>
<td>3.79-4.05,-,m.</td>
</tr>
</tbody>
</table>

$^a$ t = triplet, q = quartet, s = singlet, m = multiplet.
Table 2.7

$^{13}$C-{$^1$H} - N.M.R. Spectra of $[\text{MoO}(\text{S}_2\text{CNR}_2)_3]\text{BF}_4^a$ and Mo($\text{S}_2\text{CNET}_2)_3\text{NO}$

<table>
<thead>
<tr>
<th>Compound (Solvent)</th>
<th>δ, ppm (Relative Peak Height, %)</th>
<th>Assignment$^{b,c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]\text{BF}_4$ (CDCl$_3$/CD$_3$NO$_2$)</td>
<td>36.95(100), 38.52(98)</td>
<td>CH$_3$ - a, a'</td>
</tr>
<tr>
<td>$[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]\text{BF}_4$ (CD$_3$NO$_2$, 30°C)</td>
<td>40.88(50), 41.27(50)</td>
<td>CH$_3$ - b, c</td>
</tr>
<tr>
<td></td>
<td>194.72(18), 197.47(10)</td>
<td>S$_2$CN.I,II respectively</td>
</tr>
<tr>
<td>$[\text{MoO}(\text{S}_2\text{CNET}_2)_3]\text{BF}_4$ (CD$_3$NO$_2$, 65°C)</td>
<td>12.07(25), 12.64(100), 12.99(68)</td>
<td>CH$_3$ - a, a', b, c</td>
</tr>
<tr>
<td></td>
<td>45.54(50), 47.07(48)</td>
<td>CH$_2$ - a, a'</td>
</tr>
<tr>
<td></td>
<td>48.26(23), 48.86(25)</td>
<td>CH$_2$ - b, c</td>
</tr>
<tr>
<td></td>
<td>195.06(25), 197.63(16)</td>
<td>S$_2$CN.I,II respectively</td>
</tr>
<tr>
<td>$[\text{MoO}(\text{S}_2\text{CNET}_2)_3]\text{BF}_4$ (CD$_3$NO$_2$, 95°C)</td>
<td>12.59(100)</td>
<td>CH$_3$</td>
</tr>
<tr>
<td></td>
<td>47.14(42)</td>
<td>CH$_2$</td>
</tr>
<tr>
<td></td>
<td>196.40(3)</td>
<td>S$_2$CN</td>
</tr>
<tr>
<td>Mo($\text{S}_2\text{CNET}_2)_3\text{NO}$ (CDCl$_3$)</td>
<td>12.21(46), 12.45(100), 12.64(46)</td>
<td>CH$_3$ - a, a', b, c</td>
</tr>
<tr>
<td></td>
<td>42.97(65), 43.77(68)</td>
<td>CH$_2$ - a, a'</td>
</tr>
<tr>
<td></td>
<td>45.16(43), 45.73(40)</td>
<td>CH$_2$ - b, c</td>
</tr>
<tr>
<td></td>
<td>195.0(5), unobs.</td>
<td>S$_2$CN</td>
</tr>
<tr>
<td>$[\text{MoO}(\text{S}_2\text{CNPr}_2)_3]\text{BF}_4$ (CDCl$_3$)</td>
<td>19.48(33), 19.66(33), 19.83(20), 20.25(100)</td>
<td>CH$_3$ - a, a', b, c</td>
</tr>
<tr>
<td></td>
<td>52.70(31), 53.76(41)</td>
<td>CH - a, a', b, c</td>
</tr>
<tr>
<td></td>
<td>194.59(12), 196.42(8)</td>
<td>S$_2$CN.I,II respectively</td>
</tr>
</tbody>
</table>

a) Routine pulse delay of 2 s used to observe S$_2$CN resonances.
b) See Figure 2.8 for substituent labelling scheme.
c) Mo($\text{S}_2\text{CNET}_2)_3\text{NO}$ isostructural to $[\text{MoO}(\text{S}_2\text{CNR}_2)_3]^+$ (Figure 2.8).
2.2.3.4 Noise Decoupled $^{13}$C N.M.R. Spectra

The $^{13}$C-$^1$H n.m.r. spectra of $[\text{MoO}(S_2\text{CNR}_2)_3]\text{BF}_4$ ($R = \text{Me, Et, Pr}^1$) are given in Table 2.7 along with the spectrum of $\text{Mo}(S_2\text{CNET}_2)_3\text{NO}$ for comparison. The $^{13}$C-$^1$H n.m.r. spectra of $[\text{MoO}(S_2\text{CNR}_2)_3]\text{BF}_4$ ($R = \text{Me, Et}$) are shown in Figure 2.12.

2.2.3.5 Electronic Spectra

The electronic spectra of $[\text{MoO}(S_2\text{CNR}_2)_3]\text{BF}_4$ ($R = \text{Me, Et, Pr}^1$) are given in Table 2.8. The electronic spectrum of $[\text{MoO}(S_2\text{CNET}_2)_3]\text{BF}_4$, representative of the series, is shown in Figure 2.3, along with Beer's Law plots for the complexes over the concentration range $10^{-3}$ M to $10^{-4}$ M.

### Table 2.8

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ nm ($\varepsilon$, $1\text{cm}^{-1}\text{mole}^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{MoO}(S_2\text{CNMe}_2)_3]\text{BF}_4$</td>
<td>$\text{CH}_3\text{NO}_2$</td>
<td>404 (4060)</td>
<td>$L \rightarrow M$ CT</td>
</tr>
<tr>
<td>$[\text{MoO}(S_2\text{CNET}_2)_3]\text{BF}_4$</td>
<td>$\text{CH}_3\text{NO}_2$</td>
<td>405 (4270)</td>
<td>$L \rightarrow M$ CT</td>
</tr>
<tr>
<td>$[\text{MoO}(S_2\text{CNET}_2)_3]\text{BF}_4$</td>
<td>$\text{CH}_3\text{OH}$</td>
<td>405 (4200)</td>
<td>$L \rightarrow M$ CT</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250 (56000)</td>
<td>$\pi \rightarrow \pi^*$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>212 (27500)</td>
<td>$\pi \rightarrow \pi^*$</td>
</tr>
<tr>
<td>$[\text{MoO}(S_2\text{CNPr}_2)_3]^+\text{BF}_4$</td>
<td>$\text{CH}_3\text{NO}_2$</td>
<td>405 (4120)</td>
<td>$L \rightarrow M$ CT</td>
</tr>
</tbody>
</table>

2.2.4 The Reactions of $[\text{MoO}(S_2\text{CNET}_2)_3]\text{BF}_4$

2.2.4.1 Oxygen Atom Transfer Reactions

(a) Reaction with Triphenylphosphine

Addition of PPh$_3$ to solutions of $[\text{MoO}(S_2\text{CNET}_2)_3]\text{BF}_4$ in dichloromethane, methanol or nitromethane results in the immediate formation of a red-brown solution. Upon standing in air, the solutions
Figure 2.3. I: The electronic spectrum of [MoO(S\textsubscript{2}C\textsubscript{2}N\textsubscript{2}Et\textsubscript{2})\textsubscript{3}]BF\textsubscript{4} in a) nitromethane, right abscissa; b) methanol, left abscissa.

II: Absorbance vs. concentration plots for [MoO(S\textsubscript{2}CNMe\textsubscript{2})\textsubscript{3}]BF\textsubscript{4} (▲▲) [MoO(S\textsubscript{2}C\textsubscript{2}N\textsubscript{2}Et\textsubscript{2})\textsubscript{3}]BF\textsubscript{4} (▼▼) and [MoO(S\textsubscript{2}CNPr\textsubscript{2})\textsubscript{3}]BF\textsubscript{4} (●●) in nitromethane.
slowly revert to the original orange colour. The cycle can be repeated by further addition of PPh₃. The final products of the cyclic reaction were shown to be [MoO(S₂CNEt₂)₃]BF₄ and OPPh₃ by the following experiments.

**Isolation of [MoO(S₂CNEt₂)₃]BF₄ from Reaction Mixture**

A solution of [MoO(S₂CNEt₂)₃]BF₄ (0.2 g, 0.31 mmol) in dichloromethane (10 mL) was treated with PPh₃ (0.12 g, 0.45 mmol) and stirred until the original orange coloration had re-formed (ca. 6 hrs). Methanol (20 mL) was added to the solution, followed by ether whereupon orange crystals precipitated. After drying at 100°C for 1 hr, the yield of re-formed [MoO(S₂CNEt₂)₃]BF₄ was 1.69 g (85%). The identity of the substance was confirmed by x-ray powder diffractometry. For [MoO(S₂CNEt₂)₃]BF₄, 2θ (Cu-Kα radiation): 6.55s, 11.60w, 12.05w, 12.20w, 13.05w, 13.80w, 14.80w, 18.10w, 18.70m.

**¹H N.M.R. Spectrum of Reaction Mixture**

A solution of [MoO(S₂CNEt₂)₃]BF₄ (0.10 g, 0.16 mmol) in dichloromethane (5 mL) was treated with PPh₃ (0.083 g, 0.31 mmol). After the solution colour had returned to orange, a further 0.16 mmol of PPh₃ was added and stirring continued until orange [MoO(S₂CNEt₂)₃]⁺ had re-formed. Up to five equivalents (~0.5 mmol) of PPh₃ were added in a similar manner. The ¹H n.m.r. spectrum of the products (after reduction of the reaction mixture to dryness and dissolution of the residue in CDCl₃) showed [MoO(S₂CNEt₂)₃]BF₄ and OPPh₃ to be the final products. A similar experiment in methanol indicated that slow conversion of [MoO(S₂CNEt₂)₃]⁺ to cis-MoO₂(S₂CNEt₂)₂ occurs in this solvent.

**³¹P-¹H N.M.R. Spectrum of Reaction Mixture**

A solution of [MoO(S₂CNEt₂)₃]BF₄ (0.1 g, 0.16 mmol) in methanol (5 mL) was treated with PPh₃ (0.041 g, 0.16 mmol) and
stirred until the original orange coloration re-formed. The $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. spectrum of this solution is shown in Figure 2.4, along with the spectra of $\text{PPh}_3$ and $\text{OPPh}_3$ in methanol. Triphenylphosphine is not converted to $\text{OPPh}_3$ in methanol in the absence of $[\text{MoO(S}_2\text{CNET}_2)_3]\text{BF}_4$.

![Figure 2.4](image)

**Figure 2.4.** $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. study of the reaction of $[\text{MoO(S}_2\text{CNET}_2)_3]\text{BF}_4$ and $\text{PPh}_3$ in methanol. The spectra of a) the reaction mixture, $\delta$ 30.7 ppm; b) $\text{PPh}_3$, $\delta$ -7.6 ppm and $\text{OPPh}_3$, $\delta$ 30.7 ppm ($\delta$ relative to trimethylphosphate).

b) **Reaction with Phenylisocyanate**

A suspension of $[\text{MoO(S}_2\text{CNET}_2)_3]\text{BF}_4$ (0.10 g, 0.16 mmol) in deoxygenated toluene (10 mL) under dinitrogen was treated with PhNCO (0.084 mL, 0.77 mmol) and the mixture refluxed for 4.5 hrs. The toluene was decanted leaving a red oil which was triturated with ether (ca. 15 mL)
in air to yield a yellow solid. Recrystallization from dichloromethane/
η-hexane yielded yellow crystals of [Mo(NPh)(S₂CNEt₂)₃]BF₄ (0.089 g, 80%).
The compounds' spectroscopic properties are similar to those of the
previously reported PF₆⁻ salt.¹⁹⁸

Analyzed. Calcd. for C_{21}H_{35}BF₄MoN₄S₅: C, 35.1; H, 4.9; N, 7.8. Found:
C, 34.9; H, 4.9; N, 7.7%.

Infrared spectrum: 2980w, 2940w, 2770w, 1535s, 1510s, 1460s, 1440s,
1380m, 1360m, 1280s, 1205m, 1150m, 1060 br, s. 915w, 850w, 760m, 675w,
560w, 520w, 470w cm⁻¹.

No ν(Mo-Oₜ) bands are present.

¹H n.m.r. spectrum, 80 MHz (CDCl₃): Overlapping triplets at δ1.25,
1.36, 1.39 (J ~ 7.2 Hz, 18H, 6 x CH₃); 3.7-4.0 (m, 12H, 6 x CH₂); 7.26
(s, 1H, p-CH of NPh); 7.40 (s, 4H, o-, m- CH of NPh).

2.2.4.2 Dithiocarbamato-Ligand Displacement Reactions

a) Reaction with Hydrochloric Acid

A stirred solution of [MoO(S₂CNEt₂)₃]BF₄ (0.10 g, 0.16 mmol) in
acetone (1 mL) was treated with concentrated hydrochloric acid (1 mL).
Water (10 mL) was added after 1 hr and the mixture was cooled. The
yellow crystalline solid formed was filtered, washed with water and
dried in vacuo. The yield was 0.07 g (90%). The product was identified
as MoOCl₂(S₂CNEt₂)₂ by infrared spectroscopy.²¹⁴

Infrared spectrum: 2990s, 2950m, 2880w, 1530s, 1460s, 1440s, 1385s,
1360m, 1295m, 1280s, 1205m, 1150m, 1100m, 1075m, 1000w, ν(Mo-Oₜ) at
950s, 935s, 920m, 850m, 780m, 580w, 415w, 375m, 360m, 295m cm⁻¹.

b) Reaction with Sodium Sulphide

A solution of [MoO(S₂CNEt₂)₃]BF₄ (0.22 g, 0.34 mmol) in acetone/
benzene (1:1, 24 mL) was treated with a solution of Na₂S.9H₂O (0.082 g,
0.34 mmol) in water (25 mL) and after stirring for 6 hrs the solution
was reduced to dryness. The residue was dissolved in dichloromethane
(10 mL) and extracted with water (3 x 20 mL). The dichloromethane phase was dried over 4A molecular sieve. Addition of cyclohexane to the solution followed by slow evaporation led to blue crystals of MoO(S_2)(S_2CNEt_2)_2^{78}, which were filtered and washed with cyclohexane.

Infrared spectrum: 2980w, 2950w, 2870w, 1530s, 1495s, 1460s, 1455s, 1380m, 1355m, 1300m, 1275s, 1205s, 1150m, 1095m, 1070m, 1000w, ν(Mo-O_t) at 920s and 910s, 845w, 780w, ν(S-S) 555m, 475w cm⁻¹.

¹H n.m.r. spectrum, 80 MHz (CDCl₃): δ1.20 (3H, t, J = 7.2 Hz, CH₃); 1.43 (6H, superimposed t, J = 7.2 Hz, 2 x CH₃); 1.46 (3H, t, J = 7.2 Hz, CH₃); 3.65 (2H, q, J = 7.2 Hz); 3.91 (2H, q, J = 7.2 Hz); 3.95 (2H, q, J = 7.2 Hz); 4.00 (2H, q, J = 7.2 Hz, all CH₂ resonances)

2.2.4.3 Reduction Reactions

a) Reaction with Zinc or Sodium Dithionite

A mixture of [MoO(S₂CNEt₂)₃]BF₄ (0.20 g, 0.31 mmol) and zinc metal (0.10 g) under dinitrogen was treated with dichloromethane (25 mL) and the mixture stirred for 1 hr. After filtration, the filtrate was reduced to dryness under vacuum and then trititated under dinitrogen with deoxygenated ethanol (40 mL). The red solid formed was filtered, washed with ethanol and vacuum dried. The yield of MoO(S₂CNEt₂)₂ was 0.12 g (92%).

Infrared spectrum: 2980w, 2940w, 2870w, 1523s, 1460s, 1440s, 1380m, 1355m, 1280s, 1200s, 1150m, 1095m, 1075w, 1065w, 1000w, ν(Mo-O) 960s, 905w, 840m, 775w, 560w, 470s cm⁻¹.

¹H n.m.r. spectrum, 80 MHz (CDCl₃): δ1.29 (12H, t, J = 7.2 Hz, 4 x CH₃); 3.94 (8H, q, J = 7.2 Hz, 4 x CH₂).

The reaction of [MoO(S₂CNEt₂)₃]BF₄ and Na₂S₂O₄ in dichloromethane/water (1:1) also yields MoO(S₂CNEt₂)₂.
b) Reaction with Tetraethylammonium Tetrathiomolybdate(VI)

A solution of \((\text{Et}_4 \text{N})_2[\text{MoS}_4]\) (0.048 g, 0.1 mmol) in acetonitrile (2 mL) was slowly added to a stirred solution of \([\text{MoO(S}_2\text{CNEt}_2)_3]\text{BF}_4\) (0.063 g, 0.1 mmol) in acetonitrile (2 mL) resulting in an immediate red-brown coloration. After 1.5 hrs, the solution was filtered to yield yellow crystals of \(\text{Mo}_2\text{O}_2\text{S}_2(\text{S}_2\text{CNEt}_2)_2\) which were recrystallised from dichloromethane/ether. The yield was 0.04 g (35%).

**Anal.** Calcd. for C\(_{10}\)H\(_{20}\)Mo\(_2\)N\(_2\)O\(_2\)S\(_2\): C, 20.6; H, 3.5; N, 4.8; S, 32.9. Found: C, 20.4; H, 3.5; N, 4.2; S, 32.7 %.

Infrared spectrum: 2980w, 2940w, 2870w, 1535s, 1460m, 1440m, 1380w, 1360m, 1280m, 1200m, 1150m, 1100w, 1070w, 1000w, \(\nu(\text{Mo-O}_\text{t})\) 964 and 935m, 910w, 845w, \(\nu(\text{MoS}_2\text{Mo})\) 477w, 340w, 470w cm\(^{-1}\).

Addition of ether to the filtrate precipitated a blue and yellow solid mixture. The blue compound was identified as \(\text{MoO(S}_2\text{)}(\text{S}_2\text{CNEt}_2)_2\) from its infrared spectrum.

c) Reaction with Tetraethylammonium Tetrathiotungstate

A solution of \((\text{Et}_4 \text{N})_2[\text{WS}_4]\) (0.22 g, 0.38 mmol) in dichloromethane/acetonitrile (1:2, 6 mL) was added dropwise to a solution of \([\text{MoO(S}_2\text{CNEt}_2)_3]\text{BF}_4\) (0.24 g, 0.37 mmol) in dichloromethane (2 mL) and the mixture slowly stirred for 2.5 hrs. The mixture was loaded onto the top of a silica gel column (Kieselgel 60, 35-70 mesh) and eluted as follows:

1. with toluene to remove a green band (F1);
2. with acetonitrile to remove a brown band (F2);
3. with dichloromethane to remove a yellow band (F3).

Evaporation of F1 and recrystallisation of the solid from methanol yielded \(\text{MoO(S}_2\text{)}(\text{S}_2\text{CNEt}_2)_2\). A pure compound could not be isolated from F2. Evaporation of F3 yielded 0.10 g of orange crystals of \(\text{MoWO}_2\text{S}_2(\text{S}_2\text{CNEt}_2)_2\).
Anal. Calcd. for C₁₀H₂₀MoN₂O₂S₅W: C, 17.8; H, 3.0; Mo, 14.2; N, 4.1; S, 28.5; W, 27.5. Found: C, 18.0; H, 3.0; Mo, 11.3; N, 4.0; S, 29.9; W, 33.4%.

Infrared spectrum: 2980w, 2940w, 2870w, 1540s, 1460m, 1440w, 1380w, 1360m, 1280m, 1200m, 1155m, 1095w, 1070w, v(M-O₄) 968s and 960s, 910w, 840w, 780w, 530m, 477m, 375w, 340w cm⁻¹.

d) Reaction with Sodium Sulphite and Tetraphenylphosphonium Sulphite

The reaction of [MoO(S₂CNEt₂)₃]BF₄ containing solutions with one equivalent of Na₂SO₃ or (PPh₄)₂SO₃ resulted in the formation of Mo₂O₃(S₂CNET)₄ (identified by its infrared spectrum). Various reaction conditions are given below.

<table>
<thead>
<tr>
<th>SO₃²⁻ source</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₃</td>
<td>CH₃CN</td>
<td>25</td>
<td>Mo₂O₃(S₂CNET)₄</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>CH₂Cl₂/H₂O</td>
<td>25</td>
<td>&quot;</td>
</tr>
<tr>
<td>(PPh₄)₂SO₃</td>
<td>CH₃OH</td>
<td>25</td>
<td>&quot;</td>
</tr>
<tr>
<td>(PPh₄)₂SO₃</td>
<td>CH₃CN</td>
<td>25</td>
<td>&quot;</td>
</tr>
<tr>
<td>(PPh₄)₂SO₃</td>
<td>CH₃CN</td>
<td>48</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

e) Reaction with Xanthine and Salicylaldehyde

Addition of xanthine or salicylaldehyde to [MoO(S₂CNEt₂)₃]BF₄ containing solutions resulted in no observed reaction.

2.3 DISCUSSION

2.3.1 Preparation and Characterization of Compounds

The orange compounds [MoO(S₂CNR₂)₃]X are readily prepared by the reaction of cis-MoO₂(S₂CNR₂)₂ and HX in acetone. Analytical, physical and spectroscopic characterization of the compounds is consistent with their formulation as simple salts of the monomeric seven coordinate cations, [MoO(S₂CNR₂)₃]⁺. Accordingly, the compounds exhibit
conductivities typical of 1:1 electrolytes$^{220}$ and a diamagnetism (by n.m.r.) consistent with the presence of Mo(VI).

The infrared spectra of the compounds $[\text{MoO}(\text{S}_2\text{CNEt}_2)_3]X$ ($X = \text{BF}_4^-, \text{PF}_6^-$), shown in Figure 2.5, exemplify the spectral features of the compounds. Diagnostic dithiocarbamato-ligand bands appear in three regions of the infrared spectra.$^{191,192}$

1600-1500 cm$^{-1}$: This region is associated with the $\nu(\text{CN})$ mode of the ligand, which, being intermediate between the $\nu(\text{CN})$ frequencies of single and double CN bonds ($\approx 1240$ and 1600 cm$^{-1}$ respectively), indicates appreciable interaction of the nitrogen lone pair with the $\pi$-system of the CS$_2$ moiety.$^{191,192}$ For $[\text{MoO}(\text{S}_2\text{CNR}_2)_3]X$, considerable

Figure 2.5. The infrared spectra of $[\text{MoO}(\text{S}_2\text{CNEt}_2)_3]X$. $X = \text{BF}_4^-$, $-$; $X = \text{PF}_6^-$, $-$- in CsI
variation in the ligand environments, both within the complex and the
crystal lattice, is indicated by the presence of several strong $\nu$(CN)
bands in this region. The observed sequence of $\nu$(CN) is

$$
\nu_{Me}$(CN) > $\nu_{Et}$(CN) > $\nu_{Pr}$(CN) < $\nu_{Bu}$(CN)
$$

Although not strictly indicative of the CN bond force constants\textsuperscript{223}
(due to the difference in "effective mass" of the various -NR\textsubscript{2} groups),
the $\nu$(CN) order closely parallels the CN-bond force constant order
determined for these ligands in other complexes,\textsuperscript{222} \textit{viz.}

$$
K_{Me}$(CN) > $K_{Et}$(CN) > $K_{Pr}$(CN) ~ $K_{Bu}$(CN)
$$

1050-950 cm\textsuperscript{-1}: In this region, the infrared spectra of dithiocarbamato-
complexes are reliably diagnostic of the bonding mode of the ligand,\textsuperscript{191,192}
examples of which are shown in Figure 2.6. The $\nu$(C=S) bands in this

Figure 2.6. Examples of structurally characterised dithiocarbamato-
ligand bonding modes; a) Co(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{3}\textsuperscript{226}; b) [Zn(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{3}]\textsuperscript{-}, Et\textsubscript{4}N\textsuperscript{+}
salt\textsuperscript{227}; c) Ru(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{3}NO.\textsuperscript{228} The ethyl groups have been omitted
for clarity.

region show the following features upon ligand coordination:

a) For symmetrical bidentate coordination (\textit{e.g.} Co(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{3}\textsuperscript{226}) the
equivalence of the CS bonds results in the observation of a single
\( \nu(C=S) \) band.

b) For unsymmetrical bidentate coordination (e.g. \((\text{Et}_4\text{N})[\text{Zn}(\text{S}_2\text{CNMe}_2)\text{}_3]\)\(^{227}\) where the \(\text{Zn-S} \) bond lengths are appreciably different) a splitting of the \(\nu(C=S)\) mode into two bands is observed. Splittings of less than 20 cm\(^{-1}\) generally imply unsymmetrical bidentate coordination.

c) Monodentate coordination (e.g. \(\text{Ru}(\text{S}_2\text{CNEt}_2)_3\text{NO}\)\(^{228}\)) results in two \(\nu(C=S)\) bands attributable to the free and coordinated CS groups. The original criterion for monodentate coordination proposed by Bonati and Ugo\(^{229}\) has been modified\(^{222,230}\) such that monodentate bonding should be concluded only if the splitting exceeds 20 cm\(^{-1}\).

Symmetrical bidentate binding of the dithiocarbamato-ligands in \([\text{MoO}(\text{S}_2\text{CNET}_2)_3]^+\) is supported by the observation of a single \(\nu(C=S)\) band in the infrared spectra of the compounds. The slight asymmetrical binding of the unique axial-equatorial ligand in these complexes (crystallographically determined in the case of \([\text{MoO}(\text{S}_2\text{CNET}_2)_3]^+\)\(^{199}\)) is not revealed in the infrared spectra.

400-350 cm\(^{-1}\): Relatively few far-infrared studies of dithiocarbamato-complexes have been reported. However, several normal coordinate analyses\(^{222-224}\) support the previous assignment of bands in this region to \(\nu(M-S)\) modes. The \([\text{MoO}(\text{S}_2\text{CNR}_2)_3]X\) compounds exhibit bands at 380(sh) and 370 cm\(^{-1}\) assignable to \(\nu(\text{Mo-S})\).

Recent investigations employing \(^{18}\text{O}\) and \(^{18}\text{O}/^{17}\text{O}\) enriched oxomolybdenum complexes\(^{231}\) have shown that \(\nu(\text{Mo}-^{16}\text{O}_\ell)\) vibration modes occur between 970 and 800 cm\(^{-1}\). The bands at 935 cm\(^{-1}\) in the compounds \([\text{MoO}(\text{S}_2\text{CNR}_2)_3]X\) were thus assigned to \(\nu(\text{Mo-O}_\ell)\) and this was confirmed for \([\text{MoO}(\text{S}_2\text{CNET}_2)_3]\text{BF}_4\) by \(^{18}\text{O}\) labelling experiments. The mixed isotope complex \([\text{Mo}^{18,16}\text{O}(\text{S}_2\text{CNET}_2)_3]^+\) was prepared via the reaction\(^{197}\) of \(\text{MoCl}(\text{S}_2\text{CNET}_2)_3\) and 98% \(^{18}\text{O}_2\), the \(^{16}\text{O}\) content of the isolated compound
being due to exchange of the $^{18}O$ label with air and/or solvent in the latter stages of workup. The spectrum of $^{18}O$ enriched $[\text{MoO}(\text{S}_2\text{CNEt}_2)_3]\text{BF}_4$ (Figure 2.7) shows bands at 935 and 889 cm$^{-1}$ due to $\nu(\text{Mo-}^{16}O_t)$ and $\nu(\text{Mo-}^{18}O_t)$ respectively. A simple harmonic oscillator treatment$^{221}$ of the Mo-$^{16,18}O$ bonds predicts the presence of $\nu(\text{Mo-}^{18}O_t)$ at 889 cm$^{-1}$ (assuming $\nu(\text{Mo-}^{16}O_t) = 935$ cm$^{-1}$), in excellent agreement with that observed. Thus the infrared band at 935 cm$^{-1}$ in the complexes $[\text{MoO}(\text{S}_2\text{CNR}_2)_3]^+$ can be unambiguously assigned to $\nu(\text{Mo-O}_t)$.

Figure 2.7. The infrared spectra of a) $[\text{Mo}^{16}O(\text{S}_2\text{CNEt}_2)_3]\text{BF}_4$; b) a mixture of $[\text{Mo}^{16}O(\text{S}_2\text{CNEt}_2)_3]\text{BF}_4$ and $[\text{Mo}^{18}O(\text{S}_2\text{CNEt}_2)_3]\text{BF}_4$. 
Other infrared bands result from the dithiocarbamato-ligands and the counterions, $X^-$ (Table 2.2).

The n.m.r. spectra of the complexes indicate a stereochemically rigid pentagonal bipyramidal (PB) solution structure. The proposed structure, shown in Figure 2.8, has approximate $C_{5h}$ symmetry and corresponds to the geometry predicted by energy minimization studies.$^{232}$

In this structure the molybdenum and oxygen atoms and dithiocarbamato-ligand II lie on the quasi-mirror plane of the molecule; while the dithiocarbamato-ligands I are symmetrically disposed across the quasi-mirror plane. The rigid double bond character of the CN bond leads to four inequivalent alkyl substituents, $a$, $a'$, $b$ and $c$ in such a structure. The $^1$H n.m.r. spectrum of [MoO(S$_2$CNMe$_2$)$_3$]BF$_4$, shown in Figure 2.9, shows four resonances of relative intensity 2:1:2:1. While such a spectrum readily identifies the PB structure of the complex, the assignment of the resonances to specific substituents (viz. $a$, $a'$, $b$ or $c$) is more difficult.

Figure 2.8. The solution structure of the [MoO(S$_2$CNMe$_2$)$_3$]$^+$ complexes.
Figure 2.9. The $^1$H n.m.r. spectrum of $[\text{MoO(S}_2\text{CNMe}_2)_3]\text{BF}_4$ in CDCl$_3$/CD$_3$CN (80 MHz).

The short bond lengths (1.68 Å for R = Et$^{199}$) and high $\nu$(Mo-O$_t$) frequencies of the Mo-O$_t$ bonds in the $[\text{MoO(S}_2\text{CNR}_2)_3]^+$ complexes indicate significant $\pi$-bonding within the Mo-O$_t$ groups. Indeed, a $\pi$-bond order of greater than 1.5 for these bonds is not unreasonable in view of the $\pi$-bond order of 1.5 established for the similar Mo-O$_t$ bonds of cis-mer-MoOX$_2$(S$_2$CNEt$_2$)$_2$ (X = Cl$^-$, Br$^-$).$^{235}$ The electrophilic nature of the oxo-ligand, reflected in reactivity studies, also indicates extensive involvement of the oxygen valence electrons in the Mo-O$_t$ bond (see later). Overlap of the oxygen(2-) $p_x$, $p_y$ and $p_z$ orbitals ($x$ defined along the Mo-O$_t$ bond) with metal orbitals would result in one $\sigma$- and two $\pi$-bonds and a bonding description qualitatively similar to the well known triple bond of acetylene. The electron distribution
along the Mo-Oₜ bond will be assumed constant in lieu of an exact model.

The field effects of the anisotropic Mo-Oₜ bond will strongly influence substituent chemical shifts. To describe the field effects of the (assumed) cylindrically symmetric Mo-Oₜ bond, two susceptibilities, $\chi_{||}$ and $\chi_{\perp}$ (parallel and perpendicular to the bond axis respectively) are necessary. The anisotropic shift of a resonating $^1$H nucleus, $\Delta \sigma$, is given by Equation (12),

$$\Delta \sigma = \delta_{\text{no anisot.}} - \delta_{\text{anisot.}} = \frac{(\chi_{||} - \chi_{\perp})(1-3\cos^2\theta)}{12\pi r^3}$$

where $r$ is the length of the vector between the centre of the Mo-Oₜ bond and the $^1$H nucleus and $\theta$ is the angle between this vector and the principal symmetry axis of the Mo-Oₜ bond. For the Mo-Oₜ bond, $\chi_{||}$ will be large and negative in relation to $\chi_{\perp}$, due to the high $\pi$-electron diamagnetic susceptibility parallel to the Mo-Oₜ bond axis. The resulting (de)shielding zones associated with the Mo-Oₜ bond in [MoO(S₂CNMe₂)₃]⁺ are shown in Figure 2.10.

In the [MoO(S₂CNMe₂)₃]⁺ complex, all methyl groups with the exception of CH₃-C lie within the deshielding zone of Mo-Oₜ. Hence, with confidence, the high field resonance at 63.15 ppm can be assigned to the shielded CH₃-C group. It follows from the spectral integration, that the 63.45 ppm resonance is due to CH₃-B. This group along with methyl groups a and a' lie within the deshielding zone and hence resonate at relatively low field. The similar chemical shifts of the CH₃-a and CH₃-a' groups prevent an unambiguous assignment of these resonances. Further chemical shift influences, e.g. the $\pi$-bond anisotropy of the CN bonds are 'second order' to the influence of the Mo-Oₜ bond but still contribute significantly to the final chemical shifts.
Figure 2.10. The conical shielding ($\Delta\sigma^{+ve}$) zone associated with the Mo-O$_t$ bond in $[\text{MoO(S}_2\text{CNEt}_2)_3]$$. The portions of the structure having solid bond lines lie outside the shielding zone (viz. in the deshielding zone).

The most reasonable assignment of the $^1\text{H n.m.r.}$ spectrum of $[\text{MoO(S}_2\text{CNEt}_2)_3]\text{BF}_4$ is: $\delta$ 3.15 ppm, CH$_3$-c; $\delta$ 3.45 ppm, CH$_3$-b; $\delta$ 3.40 ppm and $\delta$ 3.49 ppm, CH$_3$-a and CH$_3$-a'.

The $^1\text{H n.m.r.}$ spectrum of $[\text{MoO(S}_2\text{CNMe}_2)_3]\text{BF}_4$, shown in Figure 2.11, exhibits a similar pattern of resonances. The high field $\delta$1.20 ppm triplet can be assigned to the methyl protons of substituent c; the remaining methyl resonances appear at $\delta$ $\alpha$. 1.45 ppm. The triplet resonance of substituent b is just visible amid the larger a, a' resonances. The predicted structure of the methylene proton resonances is also clearly shown in this spectrum. The $^1\text{H n.m.r.}$ spectra of the remaining compounds have been similarly interpreted (Table 2.4).
Figure 2.11. The $^1$H n.m.r. spectrum of $[\text{MoO}(\text{S}_2\text{CNET}_2)_3]\text{BF}_4$ in CDCl$_3$ (270 MHz).

No significant solvent dependent structural changes$^{239}$ are revealed in the $^1$H n.m.r. spectra of $[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]\text{BF}_4$ in various solvents. A general pattern of resonances attributable to substituents a, a', b and c in the PB structure is observed although resonance overlap occurs in some cases. In (CD$_3$)$_2$SO, two equal intensity resonances are observed. However, the ligand properties of (CD$_3$)$_2$SO and the reaction of $[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]\text{BF}_4$ with (CH$_3$)$_2$SO at ca. 40°C suggest that solvolysis rather than a change in coordination geometry leads to the spectrum observed here.

The $^1$H n.m.r. spectra of $[\text{MoO}(\text{S}_2\text{CNET}_2)_3]\text{BF}_4$ also show little
change in most solvents. In $\text{d}^2$-dichloromethane, however, the spectrum exhibits an upfield doublet of triplets, indicating 1) near accidental equivalence of the $b$, $c$ substituents in the PB structure due to electric field or anisotropy effects of the solvent, or 2) a distorted capped trigonal prismatic structure in solution. Again, in $(\text{CD}_3)_2\text{SO}$, solvolysis of the complex is reflected in the simplified spectrum.

The $^{13}\text{C}-\{^1\text{H}\}$ n.m.r. spectra of the compounds are consistent with a rigid PB structure for $[\text{MoO}(\text{S}_2\text{CNR}_2)_3]^+$ complexes in solution. For

![Chemical Shift, $\delta$ (ppm)](image)

Figure 2.12. The $^{13}\text{C}-\{^1\text{H}\}$ n.m.r. spectra of a) $[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]\text{BF}_4$ in CH$_3$CN/CH$_3$NO$_2$; b) $[\text{MoO}(\text{S}_2\text{CNEt}_2)_3]\text{BF}_4$ in CHCl$_3$.

$[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]\text{BF}_4$, four resonances from substituents $a$, $a'$, $b$ and $c$ are observed as shown in Figure 2.12a. Also, two $\text{S}_2\text{CN}$ resonances due to the inequivalent dithiocarbamato-ligands I and II are present at low field. The $^{13}\text{C}-\{^1\text{H}\}$ n.m.r. spectrum of $[\text{MoO}(\text{S}_2\text{CNEt}_2)_3]\text{BF}_4$ (Figure 2.12b)
can be similarly interpreted and is virtually identical to the spectrum of \( \text{Mo(S}_2\text{CNET}_2)_3\text{NO} \), a complex believed to possess a PB structure in solution.\(^{244,245}\) Again, two \( S_2\text{CN} \) resonances are observed at low field. The chemical shifts of the \( S_2\text{CN} \)-carbon atoms in the \( [\text{MoO(S}_2\text{CNR}_2)_3]^+ \) complexes are relatively low compared with other dithiocarbamato-complexes, a reflection of the complexes' high fractional oxidation number (0.86).\(^{237}\)

Variable temperature \(^{13}\text{C}-\{^1\text{H}\} \) n.m.r. spectroscopy indicates that \([\text{MoO(S}_2\text{CNET}_2)_3]^+\) becomes stereochemically non-rigid at \( \alpha \cdot 65^\circ \text{C} \) and is fully fluxional at \( 95^\circ \text{C} \). Stereochemical rigidity has been observed in several other complexes of the form \([\text{MX(S}_2\text{CNR}_2)_3]\) (where \( X \) is a mono- or quasi-monodentate ligand) and appears to be enhanced by multiply bonded axial ligands, \( X.\(^{208,238-246}\)

A PB solution structure for the complexes is further supported by the observed seven coordinate PB structure of the cation in \([\text{MoO(S}_2\text{CNET}_2)_3][\text{Mo}_2\text{O}_4\text{F}_6]\).\(^{199}\) In \([\text{MoO(S}_2\text{CNET}_2)_3]^+\), the axial sites are occupied by the oxo-ligand and a sulphur atom from the spanning equatorial-axial dithiocarbamato-ligand while the remaining dithiocarbamato-ligands occupy equatorial positions. Indeed, this stereochemistry is displayed by all structurally characterised complexes of the type \([\text{MX(S}_2\text{CNR}_2)_3].\(^{199-213}\) The capped trigonal prismatic structure of \( \text{Hf(\eta^5-C}_5\text{H}_5)(S}_2\text{CNPr}_2)_3 \) suggested by solution studies\(^{246}\) is yet to be crystallographically confirmed in the solid state. In \([\text{MoO(S}_2\text{CNET}_2)_3]^+\), the Mo-S bond \( \text{trans-} \) to the oxo-ligand is considerably longer than the average equatorial Mo-S bond distance indicative of the strong \( \text{trans-} \) influence of the terminal oxo-ligand.\(^9,200,214\)

The electronic spectra (Figure 2.3, Table 2.8) of the compounds are characterised by strong absorptions at \( \alpha \cdot 405 \text{ nm (e \sim 4200 1cm}^{-1}\text{mole}^{-1})\)
For $R = \text{Me}, \text{Et}$ and $\text{Pr}^1$ this absorption band follows Beer's Law over the concentration range $10^{-3}$ to $10^{-4}$ M (Figure 2.3), indicating the presence of discrete stable monomeric species in CH$_3$NO$_2$ solutions. Assignment of this band to a charge transfer (CT) transition is based on the high molar extinction coefficient, the absence of d-d transitions in these d$^0$ Mo(VI) complexes and the absence of this band in the spectrum of the free ligand. The absorption spectrum of $[\text{MoO}(S_2\text{CNEt}_2)_3]^+$ is in good agreement with the spectrum reported for a solution species assigned the same formula ($\lambda_{\text{max}}$ 370-400 nm, $\varepsilon$ 4200 lcm$^{-1}$ mole$^{-1}$).$^{196}$

Below 400 nm, the electronic spectrum of $[\text{MoO}(S_2\text{CNEt}_2)_3]BF_4$ in CH$_3$OH is characterised by transitions located on the $S_2\text{CNEt}_2^-$ ligand. Sodium diethyldithiocarbamate exhibits bands at 255 (12600), 288 (10000) and 357 (65) nm in ethanol,$^{281}$ these being assigned to $\pi \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ ligand transitions.$^{247-250}$ The bands at 255 nm have been assigned to $\pi \rightarrow \pi^*$ transitions.$^{251}$ $[\text{MoO}(S_2\text{CNEt}_2)_3]^+$ exhibits very intense absorptions at 250 (56000) and 212 (27500) nm assigned to $\pi \rightarrow \pi^*$ transitions.

In contrast to the previously reported$^{197-199}$ preparations of $[\text{MoO}(S_2\text{CNR}_2)_3]^+$ ($R = \text{Et}, \text{Pr}^n$), the preparations given here for $[\text{MoO}(S_2\text{CNR}_2)_3]X$ are simple, employ readily available starting materials and produce a good yield of pure crystalline product. Originally$^{199}$ $[\text{MoO}(S_2\text{CNR}_2)_3]^+$ ($R = \text{Et}, \text{Pr}^n$) were isolated in the compounds $[\text{MoO}(S_2\text{CNR}_2)_3]_2[\text{Mo}_2\text{O}_4\text{F}_6]$, formed by the decomposition of unstable MoOF$_2$(S$_2$CNR$_2$)$_2$. Subsequently, the preparation of $[\text{MoO}(S_2\text{CNEt}_2)_3]\text{Cl}$ by the aerial oxidation of MoCl(S$_2$CNEt$_2$)$_3$ in methanol was reported.$^{197}$ While the last reaction proceeds readily and has a desirable counterion, both reactions employ starting materials which require multistage preparations.$^{199,217,214}$

Following completion of the present work, the preparation of
MoO(S₂CNET₂)₃BF₄ by the reaction of σ²-MoO₂(S₂CNET₂)₂ and HBF₄
was reported by Maatta and Wentworth. The formation of [MoO(S₂CNR₂)₃]⁺
by this reaction necessarily proceeds with the formation of other
molybdenum containing products due to the stoichiometric excess of
molybdenum in the starting material. Other products were not mentioned
by Maatta and Wentworth; however, the formation of up to two by­
products accompanies this reaction. The major byproduct in the
preparation of [MoO(S₂CNET₂)₃]BF₄ is orange [MoO(S₂CNET₂)₃]₂[Mo₆O₁₉].
This compound was characterised by elemental analysis, conductivity and
spectroscopic studies (see Section 2.2.3). Its isolation suggests that
the excess molybdenum appears primarily in the form of [Mo₆O₁₉]²⁻.
Although their formation is probable, the analogous products
[MoO(S₂CNR₂)₃]₂[Mo₆O₁₉] (R = Me, Pr, Bu) are not isolated during
preparative procedures. The formation of polymolybdate species at low
pH in the absence of other ligands has been observed elsewhere.²⁵²,²⁵³
A green insoluble non-crystalline product is also frequently formed in
small amounts but remains uncharacterised due to its insolubility. Due
to the variable and non-quantitative preparative isolation of the
reaction products, the exact stoichiometry of the reaction remains
unknown.

The protonation reactions of oxymolybdenum(VI) complexes have been
studied extensively and may be rationalised by the application of the
electroneutrality principle²⁵⁴ to the Mo(VI) centre. For example, the
strong σ- and π- donor capacity of the oxo-ligands of [MoO₄]²⁻
effectively neutralises the high charge of the Mo(VI) ion in this complex.
Upon protonation and eventual loss of the oxo-ligands at low pH, an
increase in coordination number from 4 to 6 is necessary to maintain
Mo(VI) electroneutrality.²⁵⁵

The oxo-ligands of σ²-dioxo-Mo(VI) complexes undergo two types of
reaction: 1) attack of the oxo-ligand on electrophiles, e.g. \( H^+ \); and
2) attack of the oxo-ligand by nucleophiles, e.g. \( PPh_3 \). In the
reaction of cis-MoO\(_2\)(S\(_2\)CNR\(_2\))\(_2\) and HX (\( X = BF_4^- \), PF\(_6^- \) and ClO\(_4^- \)), the
dominant reaction is oxo-ligand protonation since the conjugate bases,
\( X^- \), are poor nucleophiles. A reduction of the electron donor capacity
of the oxo-ligand(s) occurs upon protonation, and ultimate loss of an
oxo-ligand (as \( OH^- \) or \( H_2O \)) produces a highly reactive species. In order
to re-establish the electroneutrality of the Mo(VI) centre, this species
abstracts a dithiocarbamato-ligand from a neighbouring molecule to
produce the stable \([\text{MoO}(S_2CNR_2)_3]^+\) complexes.

2.3.2 Reactivity of \([\text{MoO}(S_2CNEt_2)_3]\)BF\(_4\)

The reactions of \([\text{MoO}(S_2CNEt_2)_3]\)BF\(_4\) can be classified into
three general types:
1. Oxygen atom transfer reactions involving the oxo-ligand.
2. Displacement of a dithiocarbamato-ligand without metal reduction.
3. Reduction of the metal and concomitant modification of the
coordination sphere.

Oxygen Atom Transfer Reactions

The reaction of \([\text{MoO}(S_2CNEt_2)_3]\)BF\(_4\) and \( PPh_3 \) in dichloromethane
in the presence of oxygen results in the nett catalytic oxidation of
\( PPh_3 \) to OPPh\(_3\). The catalytic reaction was initially suggested by the
re-formation of the original orange coloration of \([\text{MoO}(S_2CNEt_2)_3]\)BF\(_4\)
solutions upon standing, following their almost immediate colour change
to red-brown upon addition of \( PPh_3 \). Subsequent investigation showed
that up to five equivalents of \( PPh_3 \) could be converted into OPPh\(_3\) by
\([\text{MoO}(S_2CNEt_2)_3]^+\) (with accompanying aerial oxidation of the Mo(IV)-
species formed by the reaction). The presence of \([\text{MoO}(S_2CNEt_2)_3]^+\) upon
completion of the catalytic cycle has been established by both chemical
and spectroscopic methods. Also, the \(^{31}\text{P}-\{^1\text{H}\} \) n.m.r. spectrum of a
methanolic reaction mixture, upon completion of the catalytic cycle, exhibits only one resonance attributable to OPPh$_3$ ($\delta$30.7 ppm) and the absence of the original PPh$_3$ resonance ($\delta$-7.6 ppm). $^{31}$P-$^1$H n.m.r. also indicates that under the reaction conditions, PPh$_3$ is not converted to OPPh$_3$ in the absence of [MoO(S$_2$CNEt$_2$)$_3$]$^+$. These experiments firmly establish the catalytic aerial oxidation of PPh$_3$ to OPPh$_3$ by [MoO(S$_2$CNEt$_2$)$_3$]$^+$. The catalysis proceeds with $\approx$ 100% efficiency in dichloromethane but in methanol slow decomposition of [MoO(S$_2$CNEt$_2$)$_3$]$^+$ prevents a truly catalytic reaction over long periods. The reaction, shown schematically in Figure 2.13, proceeds via an efficient oxygen atom transfer reaction involving initial nucleophilic attack on the electron-deficient oxo-ligand by PPh$_3$. The initially formed Mo(IV)-species (presumably [Mo(S$_2$CNEt$_2$)$_3$]$^+$) has not been isolated. An identical reaction under anaerobic conditions results in the formation of the $\mu$-oxo- mixed oxidation state complex [Mo$_2$O(S$_2$CNEt$_2$)$_6$]BF$_4$, discussed in Chapter Three.

The catalytic oxidation of PPh$_3$ by cis-dioxomolybdenum(VI) complexes has been cited as a relevant model reaction for the proposed
oxygen atom transfer mechanisms of xanthine oxidase, sulphite oxidase and related molybdoenzymes. While it appears likely that a cis-dioxo-moiety is present in sulphite oxidase this would not appear to be the case for xanthine oxidase. Studies suggest that a monooxomolybdenum(VI) centre is present in functional xanthine oxidase, along with a sulphur coordination sphere containing a Mo-S group. An oxygen atom transfer mechanism for this enzyme must therefore involve oxygen atom transfer from the monooxomolybdenum(VI) centre to substrate. However, in contrast to cis-dioxomolybdenum(VI) complexes, catalytic oxidation reactions have not been reported for monooxomolybdenum(VI) centres such as that in xanthine oxidase. The catalytic oxidation of PPh₃ by [MoO(S₂CNEt₂)₃]⁺ demonstrates for the first time the ability of monooxomolybdenum(VI) complexes to participate in catalytic oxidation reactions. The complex is, however, incapable of catalytically oxidising the biological substrates xanthine and sulphite and salicylaldehyde. Cis-dioxomolybdenum(VI) complexes also fail to oxidise these substances. Modification of the coordination sphere of [MoO(S₂CNEt₂)₃]⁺ and investigation of the oxygen atom transfer properties of the resulting complexes would be an interesting pursuit. The previously reported reaction of MoOCl₂(S₂CNEt₂)₂ and PPh₂Et resulted in the reaction shown in Equation (9). The reaction products, MoX₂(S₂CNEt₂)₂(PPh₂Et) (X = Cl⁻, Br⁻), were not reported to re-form in air; here the X⁻ and PPh₂Et ligands may provide stabilization to the Mo(IV) species. The presence of sulphur-donor ligands may on the other hand be crucial to the catalytic oxidation of PPh₃ by [MoO(S₂CNEt₂)₃]⁺.

The reaction of [MoO(S₂CNEt₂)₃]BF₄ and PhNCO proceeds according to equation (13)

\[ [\text{MoO}(S_2\text{CNEt}_2)_3]BF_4 + \text{PhNCO} \rightarrow [\text{Mo}(\text{NPh})(S_2\text{CNEt}_2)_3]BF_4 + \text{CO}_2 \] (13)
and follows similar reactions described for \( \text{MoOCl}_2(S_2\text{CNEt}_2)_2 \) and oxorhenium complexes; \(^{256}\) \([\text{Mo}(\text{NPh})(S_2\text{CNEt}_2)_3]PF_6\) has been previously reported. \(^{198}\)

The replacement of a dithiocarbamato-ligand is observed in several reactions of \([\text{MoO}(S_2\text{CNEt}_2)_3]BF_4\). The reaction of \([\text{MoO}(S_2\text{CNEt}_2)_3]BF_4\) and aqueous hydrochloric acid results in the formation of the known \(\text{cis-mer-MoOCl}_2(S_2\text{CNEt}_2)_2\), possibly via the intermediate formation of \(\text{cis-MoO}_2(S_2\text{CNEt}_2)_2\) under the hydrolysing conditions of the reaction.

The reaction of \([\text{MoO}(S_2\text{CNEt}_2)_3]BF_4\) and \(\text{Na}_2\text{S}\) was attempted in an effort to prepare the fully sulphur-ligated complex \([\text{MoS}(S_2\text{CNEt}_2)_3]^+\) or an oxo-sulphido-complex. The reaction, however, leads to the formation of the known \(\text{MoO}(S_2)(S_2\text{CNEt}_2)_2\) as do similar reactions with other reagents employed to introduce Mo-S\(_t\) into oxomolybdenum complexes, e.g. \(\text{P}_4\text{S}_10\) and \(\text{H}_2\text{S}\).

Reduction of the Mo(VI) centre in \([\text{MoO}(S_2\text{CNEt}_2)_3]BF_4\) results in the modification of the ligand set and the formation of the previously reported complexes \(\text{MoO}(S_2\text{CNEt}_2)_2\), \(^{225}\) \(\text{Mo}_2\text{O}_2\text{S}_2(S_2\text{CNEt}_2)_2\) \(^9\) and \(\text{Mo}_2\text{O}_3(S_2\text{CNEt}_2)_4\). \(^9\) The two electron reduction of the complex with zinc metal or \(\text{Na}_2\text{S}_2\text{O}_4\) results in the facile loss of dithiocarbamate from the resulting Mo(IV) centre and the formation of \(\text{MoO}(S_2\text{CNEt}_2)_2\). The reaction of \([\text{MoO}(S_2\text{CNEt}_2)_3]BF_4\) with the tetrathiometallate ions \([\text{MS}_4]^{2-}\) (\(\text{M}=\text{Mo, W}\)) leads to the formation of di-\(\mu\)-sulphido-complexes of the type \(\text{MO}_2\text{S}_2(S_2\text{CNEt}_2)_2\) (\(\text{M}=\text{Mo, W}\) respectively). The mechanism of the reaction is unknown, however, the formation of a mixed metal complex in the \([\text{WS}_4]^{2-}\) reaction suggests that the bidentate binding of \([\text{MS}_4]^{2-}\) to \([\text{MoO}(S_2\text{CNEt}_2)_3]^+\), or a reduced fragment thereof, is crucial to the formation of the di-\(\mu\)-sulphido bridge. The reaction of \([\text{MoO}(S_2\text{CNEt}_2)_3]BF_4\) and \([\text{WS}_4]^{2-}\) provides a convenient route to the mixed metal complex.
MoWO$_2$S$_2$(S$_2$CNET$_2$)$_2$ which may prove to be a useful starting material for other mixed metal complexes.
3.1 INTRODUCTION

The study of mixed oxidation state compounds has a long and intriguing history.\textsuperscript{257,258} For more than two centuries after the discovery of the first mixed oxidation state compound, Prussian Blue,\textsuperscript{262,263} mixed oxidation state chemistry remained a rather arcane science. However, over the last 20 years mixed oxidation state chemistry has developed into an important field of chemical research. This development follows the initial rationalization\textsuperscript{258-260} and subsequent refinement\textsuperscript{257} of the preparative\textsuperscript{264} and theoretical\textsuperscript{261} principles involved in such chemistry.

The participation of polymetallic mixed oxidation state centres in enzymes is widespread.\textsuperscript{265} The postulation of dinuclear molybdenum centres in the molybdoenzymes, xanthine oxidase, sulphite oxidase and nitrate reductase\textsuperscript{19} also implicates the possible participation of such centres in the catalytic cycles of these enzymes. In a dinuclear active site model, the mononuclear Mo(V) characteristics of the enzymatic e.s.r. signals\textsuperscript{11,29} are most reasonably accounted for by a mixed oxidation state formulation, \textit{e.g.} Mo(IV,V) or Mo(V,VI), in which the unpaired electron is localised on only one molybdenum atom. A prerequisite for the evaluation of such centres in enzyme systems is the preparation and structural and e.s.r. characterization of pertinent model complexes,
mixed oxidation state oxo- and sulphur-donor ligand complexes of molybdenum.

The majority of mixed oxidation state compounds of molybdenum are of the oxyanion type. The blue Mo(IV,VI) complex, $K_6[Mo_{2}^{IV}Mo_{1}^{VI}(CN)_8O_6].2H_2O$, has been reported but remains tentatively characterised. The tetranuclear complex, $Mo_4Cl_4O_6(OPr^+)_6$, has been characterised crystallographically and contains distinct seven coordinate Mo(V) and Mo(VI) centres (two of each). Also, the crystal structure and magnetic and e.s.r. properties of the Mo(II,III) compound, $K_3[Mo_2(SO_4)_4].3.5H_2O$, have been reported by Cotton et al. Here, e.s.r. studies indicate that the unpaired electron is evenly distributed over two magnetically equivalent molybdenum atoms. The Mo(II,III) complexes, $[Mo_2X_8]^{3-}$ (X = Cl$$^-$, Br$$^-$), originally characterised by x-ray crystallography, have been re-formulated as $[Mo_2X_8H]^3-$ on the basis of their diamagnetism. These studies highlight the need to confirm mixed oxidation state formulations by careful magnetic susceptibility measurements. Recently, mixed oxidation state complexes of the form $[Mo(\eta^5-C_5H_4R)(\mu-X)MoX_2)_2$ (R = H, Me, Bu$$^-$; X = O, S) were reported.

Mixed oxidation state molybdenum complexes containing biologically relevant ligands, in particular sulphur-donor ligands, are extremely rare. Transient Mo(IV,V) complexes have been proposed to exist in solution upon the electrochemical and chemical reduction of dinuclear Mo(V) complexes but their instability has prevented isolation and characterization. However, the Mo(IV,V) complex, $[Mo_2O_3(S_2CNEt_2)_4]^-$, has recently been stabilised in a mixed crystal of composition $(H_3O_2)[Mo_2O_3(S_2CNEt_2)_4]_3$. This anion exhibits e.s.r. spectra consistent with the localization of the unpaired electron on one molybdenum atom, a situation similar to that likely in e.s.r. active dinuclear molybdoenzyme active sites.
This chapter describes the synthesis and properties of the new oxo-bridged mixed oxidation state complexes \([\text{Mo}_2\text{O}(S_2\text{CNR}_2)_6]^+\) \((R = \text{Me}, \text{Et})\) and the x-ray crystal structure of \([\text{Mo}_2\text{O}(S_2\text{CNEt}_2)_6]\text{BF}_4\).

3.2 EXPERIMENTAL SECTION

3.2.1 Materials and Methods

The compounds \([\text{MoO}(S_2\text{CNR}_2)_3]\text{X}\) \((R = \text{Me}, \text{Et}; X = \text{BF}_4^-, \text{PF}_6^-, \text{ClO}_4^-)\) and \(\text{MoCl}(S_2\text{CNEt}_2)_3\) were prepared as described in Section 2.2.2. Unless specified, all preparations and solution studies of the \([\text{Mo}_2\text{O}(S_2\text{CNR}_2)_6]\text{X}\) compounds were performed under a dinitrogen atmosphere using deoxygenated solvents.

Solid state magnetic susceptibilities were measured by the Gouy method using a magnet-tube combination calibrated with mercuric tetrathiacyanatocobaltate(II).\(^{273,274}\) Mass susceptibilities were calculated using the formula,

\[
\chi_g = \frac{2wgI}{WH^2}
\]  

where \(W\) = weight of sample, \(w\) = change in weight of sample in magnetic field, \(g = 981\ \text{cm/sec}^2\), \(l = \text{length of sample in tube}\) and \(H^2 = 44.7 \times 10^6\ \text{oersted}^2\). Solution magnetic susceptibilities were measured by the Evans n.m.r. method\(^ {275,276}\) employing a Jeolco Minimar 100 MHz spectrometer. Mass susceptibilities were calculated using Equation (15)

\[
\chi_g = \frac{3\Delta f}{2\pi fm} + \chi_0
\]  

where \(m = \text{concentration of paramagnetic substance (g/mL)}\), \(\Delta f = \text{separation of the resonance positions for two identical protons in the two solutions (Hz)}\), \(f = \text{frequency of spectrometer operation (10}^8\ \text{Hz})\) and \(\chi_0 = \text{mass susceptibility of the solvent}. \text{Molar susceptibilities} (\chi_m = \chi_g \times \text{molecular weight}) \text{were corrected for diamagnetic contributions using Pascal's constants.}^{277,278}\) The effective magnetic moment,
\( \mu_{\text{eff}} \) was calculated using Equation (16)

\[
\mu_{\text{eff}} = 2.83\sqrt{\chi_m} \times T \quad \text{Bohr Magnetons (16)}
\]

where \( T \) = absolute temperature of measurement.

Electrochemical experiments used \( \alpha \cdot 10^{-3} \) M solutions of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNMe}_2)_6]\text{BF}_4\) in 0.1 M \( \text{Et}_4\text{NCIO}_4/\text{CH}_3\text{CN} \) (20°C). Cyclic voltammograms at a HMDE (PAR Model 303 SMDE) were recorded on a PAR Model 170 Electrochemistry System, using a \( \text{Ag/AgNO}_3(\text{CH}_3\text{CN}) \) reference electrode (+ 0.337 V vs. SCE) and a platinum wire auxiliary electrode. Cyclic voltammograms at a platinum work electrode were recorded on a PAR Electrochemistry System employing the following units: PAR Model 175 Universal Programmer, PAR Model 172 Potentiostat/Galvanostat and PAR Model 179 Digital Coulometer. The experiment used an \( \text{Ag/AgCl} \) reference electrode (+ 0.19 V vs. SCE) and a platinum wire auxiliary electrode.

Coulometry was performed using the following units: AMEL Model 551 Potentiostat and Model 731 Digital Integrator and PAR Model 377 Coulometry System. A mercury pool work electrode, a platinum gauze auxiliary electrode and a \( \text{Ag/AgNO}_3(\text{CH}_3\text{CN}) \) reference electrode were used. Transfer of the electrolysed solutions to optical cells was effected via gas-tight syringes.

Near-infrared spectra were recorded using a Cary-14 spectrophotometer operating in the infrared mode.

3.2.2. Preparation of the Compounds \([\text{Mo}_2\text{O}(\text{S}_2\text{CNMe}_2)_6]\text{X}\) 
\( \mu-\text{Oxo-hexakis(}N,N\text{-diethyl}dithiocarbamato)\text{dimolybdenum(IV, V)} \) 
Tetrafluoroborate

A mixture of \([\text{MoO}(\text{S}_2\text{CNMe}_2)_3]\text{BF}_4\) (0.3 g, 0.47 mmol) and triphenylphosphine (0.12 g, 0.46 mmol) was dissolved in methanol (25 mL) and the resulting solution was stirred for 3 hrs. After cooling at 2°C
for 1 hr, the mixture was filtered in air and the green-black crystals obtained were washed with methanol/ether (1:10) and dried under vacuum. The yield was 0.18 g (65%).

**Anal.** Calcd. for C₃₀H₅₀BF₄Mo₂N₅₀S₁₂: C, 30.4; H, 5.1; Mo, 16.2; N, 7.1; P, nil; S, 32.5.

Found: C, 30.4; H, 5.1; Mo, 16.0; N, 7.0; P, nil; S, 32.7 %.

**µ-Oxo-hexakis(N,N-diethylidithiocarbamato)dimolybdenum(IV,V) Hexafluorophosphate**

A mixture of [MoO(S₂CNEt₂)₃]PF₆ (0.27 g, 0.38 mmol) and triphenylphosphine (0.10 g, 0.38 mmol) was dissolved in methanol (15 mL) and the resulting solution was stirred for 2 hrs. The green-black crystalline solid isolated by filtration was washed with methanol/ether (1:10) and dried under vacuum. The yield was 0.16 g (67%).

**Anal.** Calcd. for C₃₀H₅₀F₆Mo₂N₅₀PS₁₂: C, 29.5; H, 5.0; Mo, 15.7; N, 6.9; P, 2.5; S, 31.5.

Found: C, 29.3; H, 5.0; Mo, 15.8; P, 2.4; S, 31.5 %.

**µ-Oxo-hexakis(N,N-diethylidithiocarbamato)dimolybdenum(IV,V) Perchlorate**

A mixture of [MoO(S₂CNEt₂)₃]ClO₄ (0.3 g, 0.46 mmol) and triphenylphosphine (0.12 g, 0.46 mmol) was dissolved in methanol (25 mL) and the solution was stirred for 3 hrs. The green-black crystalline solid isolated by filtration was washed and dried as described above. The yield was 0.14 g (50%).

**Anal.** Calcd. for C₃₀H₅₀ClMo₂N₅₀S₁₂: C, 30.1; H, 5.0; Cl, 3.0; Mo, 16.0; N, 7.0; O, 6.7; S, 32.1.

Found: C, 30.1; H, 5.0; Cl, 3.0; Mo, 15.8; N, 7.0; O, 7.0; S, 32.2 %.

**µ-Oxo-hexakis(N,N-diethylidithiocarbamato)dimolybdenum(IV,V) Chloride**

A suspension of MoCl(S₂CNEt₂)₃ (1.37 g, 2.38 mmol) in methanol (50 mL) was stirred in air for 4 hrs and then filtered to yield a clear orange solution of [MoO(S₂CNEt₂)₃]Cl. The solution was deoxygenated.
and added to triphenylphosphine (0.63 g, 2.40 mmol) under dinitrogen. After stirring for 4 hrs the solution was reduced under vacuum to a volume of ca. 15-20 mL. Ether (350 mL) was added and the solution cooled at 2°C for 2 hrs. The green-black crystalline solid was isolated, washed and dried as above. The yield was 0.73 g (52%).

**Anal.** Calcd. for C$_{30}$H$_{60}$ClMo$_2$N$_6$OS$_{12}$: C, 31.8; H, 5.3; Cl, 3.1; Mo, 16.9; N, 7.4; S, 33.9.

Found: C, 31.9; H, 5.5; Cl, 2.9; Mo, 16.9; N, 7.4; S, 33.8 %.

The N,N-dimethylthiocarbamato-analogues were also prepared by the method above (reaction time 24 hrs). The compounds are highly insoluble and are generally obtained in slightly impure (by analysis) form. The use of homogeneous reaction conditions did not improve the product yield or purity.

### 3.2.3 Characterization of the Compounds \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]\)X

#### 3.2.3.1 Conductivity Measurements

The molar conductivities of the soluble compounds are given in Table 3.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>(\Lambda_0) ((\Omega^{-1})cm²mole⁻¹)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6])\text{BF}_4</td>
<td>CH$_3$OH</td>
<td>82</td>
</tr>
<tr>
<td>([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6])\text{BF}_4</td>
<td>CH$_3$CN</td>
<td>85</td>
</tr>
<tr>
<td>([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6])\text{PF}_6</td>
<td>CH$_3$OH</td>
<td>76</td>
</tr>
<tr>
<td>([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6])\text{ClO}_4</td>
<td>CH$_3$OH</td>
<td>81</td>
</tr>
<tr>
<td>([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6])\text{Cl}</td>
<td>CH$_3$OH</td>
<td>76</td>
</tr>
</tbody>
</table>

\(^a\) The typical \(\Lambda_0\) range for 1:1 electrolytes in the solvents are\(^{220}\): CH$_3$OH, 80-115 and CH$_3$CN, 60-115 \(\Omega^{-1}\)cm²mole⁻¹.
### Table 3.2

Infrared Spectra of $[\text{Mo}_2\text{O}(\text{S}_2\text{CNR}_2)_6]^x$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(CN)</th>
<th>$\nu$(NC$_2$)</th>
<th>$\nu$(C=S)</th>
<th>$\nu$(CSS)</th>
<th>$\nu_{as}$(MoOMo)</th>
<th>$\nu$(Mo-S)</th>
<th>Anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Mo}_2\text{O}(\text{S}_2\text{CNMe}_2)_6]\text{BF}_4$</td>
<td>1545s</td>
<td>1250m</td>
<td>b</td>
<td>935w, 905w</td>
<td>675w, br</td>
<td>365w</td>
<td>1070s, 530w, 520w</td>
</tr>
<tr>
<td>$[\text{Mo}_2\text{O}(\text{S}_2\text{CNMe}_2)_6]\text{PF}_6$</td>
<td>1545s</td>
<td>1250m</td>
<td>1050w</td>
<td>935w, 905w</td>
<td>675w, br</td>
<td>365w</td>
<td>840vs, 560s</td>
</tr>
<tr>
<td>$[\text{Mo}_2\text{O}(\text{S}_2\text{CNMe}_2)_6]\text{ClO}_4$</td>
<td>1545s</td>
<td>1250m</td>
<td>b</td>
<td>935w, 905w</td>
<td>680w, br</td>
<td>370w</td>
<td>1090s, 830w</td>
</tr>
<tr>
<td>$[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{BF}_4$</td>
<td>1510s</td>
<td>1150m</td>
<td>1000w</td>
<td>935, 910, 905w$^c$</td>
<td>665br, w</td>
<td>365w</td>
<td>1070s, 530w, 520w</td>
</tr>
<tr>
<td>$[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{PF}_6$</td>
<td>1510s</td>
<td>1150m</td>
<td>1000w</td>
<td>935, 910, 900w$^c$</td>
<td>670w</td>
<td>360w</td>
<td>840vs, 560s</td>
</tr>
<tr>
<td>$[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{ClO}_4$</td>
<td>1510s</td>
<td>1150m</td>
<td>1000w</td>
<td>935, 910, 903w$^c$</td>
<td>660w</td>
<td>360w</td>
<td>1090s, 830w</td>
</tr>
<tr>
<td>$[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{Cl}$</td>
<td>1510s</td>
<td>1150m</td>
<td>1000w</td>
<td>933, 910, 903w$^c$</td>
<td>675w</td>
<td>365w</td>
<td>-</td>
</tr>
</tbody>
</table>

a) In CsI. s, strong; m, medium; w, weak; br, broad. Dithiocarbamato-ligand assignments follow Reference 222.

b) Bands obscured by BF$_4^-$ or ClO$_4^-$ bands. c) All bands are weak.
3.2.3.2 Infrared Spectra

The infrared spectra of the compounds are summarised in Table 3.2. Those of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]X (X = \text{BF}_4^-, \text{Cl}^-)\) are presented for discussion in Figure 3.2.

3.2.3.3 Magnetic Susceptibility Measurements

The results of solid state and solution magnetic susceptibility measurements on \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]X (X = \text{BF}_4^-, \text{Cl}^-)\) are given in Table 3.3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Physical Form</th>
<th>(\mu_{\text{eff}}) (B.M.)</th>
<th>Temp. (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{BF}_4)</td>
<td>solid</td>
<td>2.17</td>
<td>296.4</td>
</tr>
<tr>
<td>([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{BF}_4)</td>
<td>\text{CHCl}_3/TMS solution</td>
<td>2.10</td>
<td>301.0</td>
</tr>
<tr>
<td>([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{Cl})</td>
<td>solid</td>
<td>2.01</td>
<td>294.5</td>
</tr>
</tbody>
</table>

3.2.3.4 Electrochemistry

The cyclic voltammogram of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{BF}_4\) at a HMD electrode is presented for discussion in Figure 3.3. The parameters for the reduction of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{BF}_4\) at HMD and platinum electrodes are summarised in Table 3.4.

<table>
<thead>
<tr>
<th>Work/Reference Electrodes</th>
<th>(E_0) (V)(^a)</th>
<th>Scan Rate (mVs(^{-1}))</th>
<th>(\Delta E_p) (mV)</th>
<th>(i_{\text{ox}}/i_{\text{red}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMDE/(Ag/0.1 M AgNO(_3), CH(_3)CN)</td>
<td>-0.77((-0.44))</td>
<td>100</td>
<td>75</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>78</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>78</td>
<td>1.00</td>
</tr>
<tr>
<td>Pt/(Ag/AgCl)(^b)</td>
<td>-0.43((-0.24))</td>
<td>100</td>
<td>70</td>
<td>0.98</td>
</tr>
</tbody>
</table>

\(^a\) Figures in parentheses are vs. SCE; \(^b\) At Pt, irreversible oxidation waves occur at 0.12, 0.45 and 0.99 V and are accompanied by an irreversible reduction wave at -0.29 V.
Electrolysis (at -1.2 V)/coulometry of a \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{BF}_4\) (1.033 x 10^{-8} moles) solution in 0.1 M Et_4NCIO_4/CH_3CN (pre-electrolysed at -1.2 V to no current uptake) showed that 1.198 coulombs were required for complete electrolytic reduction of the complex. This corresponds to a transfer of 1.24 electrons/molecule during the reduction process.

3.2.3.5 Electronic Spectral Data

1800-800 nm Region: The near-infrared spectrum of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{BF}_4\) in acetonitrile is presented for discussion in Figure 3.14, along with the spectra of \(\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6\) (from Section 3.2.3.4) and an air-oxidised solution of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{BF}_4\) (containing \([\text{MoO}(\text{S}_2\text{CNEt}_2)_3]\text{BF}_4\) and \(\sigma_2\sigma\)-\(\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2\)). The spectra of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{BF}_4\) in a variety of solvents are summarised in Table 3.5.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>((1/D_{op} - 1/D_{op})^{279})</th>
<th>(\lambda_{max} (\nu_{max})) nm (cm(^{-1}))</th>
<th>(\varepsilon) (1cm(^{-1}) mole(^{-1}))</th>
<th>(\Delta\nu_2) a (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH_3CN^b</td>
<td>0.526</td>
<td>1310 (7630) 890 (11230)</td>
<td>1100 220</td>
<td>1380</td>
</tr>
<tr>
<td>C_6H_6O_3^c</td>
<td>0.481</td>
<td>1310 (7630) 890 (11230)</td>
<td>1090 220</td>
<td>1400</td>
</tr>
<tr>
<td>(CH_3)_2SO</td>
<td>0.438</td>
<td>1310 (7630) 890 (11230)</td>
<td>1140 230</td>
<td>1390</td>
</tr>
<tr>
<td>C_6H_6NO_2</td>
<td>0.384</td>
<td>1310 (7630) 890 (11230)</td>
<td>1160 250</td>
<td>1400</td>
</tr>
<tr>
<td>d-CHCl_3</td>
<td>-</td>
<td>1310 (7630) 890 (11230)</td>
<td>1100 220</td>
<td>1380</td>
</tr>
</tbody>
</table>

a) Bandwidth at half height; the 890 nm band is a shoulder.
b) In this solvent, the bands follow Beer's Law over the concentration range 2.5 x 10^{-4} to 3.4 x 10^{-3} M. c) Propylene carbonate.
800-300 nm Region: The electronic spectrum of $[\text{Mo}_2\text{O(S}_2\text{CNET}_2)_6]\text{BF}_4$ in methanol is shown in Figure 3.1 and summarised in Table 3.6. As shown in Figure 3.1, the absorption bands follow Beer's Law over the concentration range, $1.5 \times 10^{-4}$ to $2.1 \times 10^{-5}$ M. The electronic spectrum of $\text{Mo}_2\text{O(S}_2\text{CNET}_2)_6$ (from Section 3.2.3.4) is also given in Table 3.6.

### Table 3.6

<table>
<thead>
<tr>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (1 cm$^{-1}$ mole$^{-1}$)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (1 cm$^{-1}$ mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>677</td>
<td>2440</td>
<td>668</td>
<td>570</td>
</tr>
<tr>
<td>497</td>
<td>19200</td>
<td>494</td>
<td>7180</td>
</tr>
<tr>
<td>440</td>
<td>14400</td>
<td>441</td>
<td>6510</td>
</tr>
<tr>
<td>410</td>
<td>13400</td>
<td>400</td>
<td>6400</td>
</tr>
</tbody>
</table>

3.2.4 The X-Ray Crystal Structure of $\mu$-Oxo-hexakis($N,N$-diethyl-dithiocarbamato)dimolybdenum(IV,V) Tetrafluoroborate, $[\text{Mo}_2\text{O(S}_2\text{CNET}_2)_6]\text{BF}_4$.

**Crystallography:** Crystals of $[\text{Mo}_2\text{O(S}_2\text{CNET}_2)_6]\text{BF}_4$ were obtained by slow evaporation of a methanol solution of the compound under anaerobic conditions. Preliminary photographs were obtained using Weissenberg (Nonius) and precession (Charles Supper) cameras with Ni-filtered Cu-$K_\alpha$ radiation. The observed lattice symmetry and reflection conditions ($hkl$ for $h + k = 2n$ and $h0l$ for $l = 2n$) indicated that the crystals were monoclinic with possible space groups $C2/c$ ($C_{2h}^6$, No. 15283) or $C2$ ($C_2$, No. 9285). The lattice constants determined by preliminary photographs were $a = 13.24$ Å, $b = 30.95$ Å, $c = 12.44$ Å and $\beta = 97.6^\circ$.

The density calculated on the basis of four molecules of $[\text{Mo}_2\text{O(S}_2\text{CNET}_2)_6]\text{BF}_4$ per unit cell is 1.561 g cm$^{-3}$. This compares favourably with the observed value of 1.563(5) g cm$^{-3}$, determined by
Figure 3.1. I: The electronic spectrum of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]\text{BF}_4\) in methanol. II: Absorbance vs. concentration plots for the absorption bands in I; 677 nm (▼), 497 nm (◆), 440 nm (△) and 410 nm (▲).
flotation in carbon tetrachloride at 37.5°C.\textsuperscript{281}

A plate-like crystal bounded by \{101\} and \{010\} faces, with approximate dimensions of 0.04 x 0.13 x 0.50 mm, was selected for the collection of intensity data, and mounted on a quartz fibre with Araldite adhesive. The intensity data were collected on a Philips PW1100/20 automatic four circle diffractometer using graphite monochromated Mo-$\lambda_\alpha$ radiation. Intensities were measured using the $\theta$ - $2\theta$ scan technique with a scan rate of 2.4 °min\textsuperscript{-1} and scan width of $(1.6 + 0.68\tan\theta)^\circ$. The counting chain in the PW1100/20 diffractometer has a linear response up to 100,000 cps and as there were no data approaching this intensity, attenuators were not used. Stationary crystal-stationary counter background measurements of 10 s duration were recorded at each extreme of the scan width and were assumed to vary linearly between these extremes. The intensities of three standard reflections (600, 1,12,0 and 006) monitored at hourly intervals, showed no overall trend with time although frequent recentring of the crystal on these reflections was required. A new set of lattice constants was calculated upon each recentring. In order to accurately define the lattice constants an average was taken of the values calculated upon each crystal recentring. The maximum deviation of the individual parameters from their mean value was taken as a realistic error for the lattice constants. The lattice constants thus determined were $a = 13.24(1)$ Å, $b = 30.86(4)$ Å, $c = 12.42(1)$ Å and $\beta = 97.89(4)^\circ$. Data within the range $4 < 2\theta$ (Mo-$\lambda_\alpha$) < $50^\circ$ and spanning one unique quadrant of reciprocal space $(\pm h,k,l)$ were collected. The total of 4235 symmetry permitted reflections were converted to structure amplitudes by the usual method on the PDP-11 computer in the Research School of Chemistry, A.N.U. The integrated intensity, $I$, of a given reflection and its estimated standard deviation, $\Delta I$, were calculated from the following expressions:
\[ I = [\sigma p - (t_p/t_b) (B1 + B2)] \]  

(17)

\[ \Delta I = [\sigma p + (t_p/t_b)^2 (B1 + B2)]^{1/2} \]  

(18)

where \( \sigma p \) is the scan count, \( B1 \) and \( B2 \) are the background counts at the limits of the scan range and \( t_p \) and \( t_b \) are the scan time and total background counting time respectively. Any reflection with \( I \leq 0 \) was considered unobserved and reflections for which the two background measurements differed significantly (i.e. \(|B1 - B2|/(B1 + B2)^{1/2} \geq 2.0\) were also discarded. The Lorentz-polarization factor, \( LP \), is given by the equation below

\[ LP = (\cos^2 \theta + \cos^2 \theta_m)/[\sin 2\theta (1 + \cos^2 \theta_m)] \]  

(19)

where \( \theta \) and \( \theta_m \) are the Bragg angles for the reflection concerned and the monochromator respectively. The observed structure factor amplitudes, \( F_0 \), and their standard deviations, \( \sigma_1 \), were calculated according to Equations (20) and (21) respectively.

\[ F_0 = [I/LP]^{1/2} \]  

(20)

\[ \sigma_1 = \frac{\Delta I}{2F_0 LP} \]  

(21)

Since the linear absorption coefficient of \([\text{Mo}_2\text{O(S}_2\text{CNET}_2)_6]\text{BF}_4\) for Mo-\( K_\alpha \) radiation is 10.10 cm\(^{-1}\) and the estimated maximum error resulting from neglect of absorption corrections was \( \alpha \approx 8\% \), absorption corrections were not applied.

The data were sorted into the desired order for efficient operation of subsequent programs by the program SORTER. Two reflection data files, used in subsequent operations, were generated by SORTER. The first file, required as input to the MULTAN series of direct methods programs,
contained all 4235 symmetry permitted reflections. The second file, used for all calculations except the initial direct methods solution of the structure, contained unique reflections for which $I > 2\sigma(I)$ (3131 in number). The statistical discrepancy factor for the data set, defined as $\sum \sigma | F_o |$, was 0.039. The crystal data and an experimental summary are given in Table 3.7.

### Table 3.7

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>$C_{30}H_{60}BF_4Mo_2N_6OS_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>1183.30 amu</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$C2/c$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>(at 21 ± 1°C)</td>
<td>$a = 13.24(1)$ Å</td>
</tr>
<tr>
<td></td>
<td>$b = 30.86(4)$ Å</td>
</tr>
<tr>
<td></td>
<td>$c = 12.42(1)$ Å</td>
</tr>
<tr>
<td></td>
<td>$\beta = 97.89(4)^\circ$</td>
</tr>
<tr>
<td>Unit cell volume</td>
<td>$U = 5027$ Å</td>
</tr>
<tr>
<td>Density, measured</td>
<td>1.563(5) g cm$^{-3}$ (by flotation in CCl$_4$ at 37.5°C)</td>
</tr>
<tr>
<td>Formula units per cell</td>
<td>$Z = 4$</td>
</tr>
<tr>
<td>Density, calculated</td>
<td>1.561 g cm$^{-3}$</td>
</tr>
<tr>
<td>Radiation used for data collection</td>
<td>$\text{Mo-K}_\alpha$, graphite crystal monochromated ($\lambda = 0.7107$ Å)</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.04 x 0.13 x 0.50 mm</td>
</tr>
<tr>
<td>Reflection forms recorded</td>
<td>(± $h,k,l$)</td>
</tr>
<tr>
<td>Angular range</td>
<td>$4^\circ &lt; 2\theta(\text{Mo-K}_\alpha) &lt; 50^\circ$</td>
</tr>
<tr>
<td>Type of scan</td>
<td>$\theta &lt; 2\theta$</td>
</tr>
<tr>
<td>Scan width</td>
<td>$(1.6 + 0.68\tan \theta)^\circ$</td>
</tr>
<tr>
<td>Total observed reflections</td>
<td>4235</td>
</tr>
<tr>
<td>Number of unique reflections</td>
<td>3131</td>
</tr>
<tr>
<td>with $I &gt; 2\sigma(I)$</td>
<td></td>
</tr>
<tr>
<td>Statistical discrepancy factor</td>
<td>0.039</td>
</tr>
</tbody>
</table>

**Structure Solution and Refinement:** The structure was solved by direct methods in the space group $C2/c$. The complete set of symmetry allowed reflections was used as input to program NORMAL, which converts $F_o$ values...
into normalised structure factors, $E_o$, according to Equation (22).

$$E_{hkl}^2 = \frac{|F_{hkl}|^2}{\sum_{j=1}^{n} f_j^2}$$  \hspace{1cm} (22)

where $\varepsilon$ is 2 for general reflections and 4 for $0k0$ and $h0l$ reflections. The distribution of $|E|$ values, and of functions of average $E$, agreed well with the theoretical distributions calculated for centrosymmetric structures. The centric space group, $C2/c$, was therefore assumed in subsequent calculations.

The 400 reflections having the largest $|E_{hkl}|$ values were phased by iterative use of the weighted tangent formula (by the MULTAN series of direct methods programs). The molybdenum, oxygen and sulphur atoms were revealed in the resulting $E$ map. All subsequent calculations were based on the set of 3131 unique reflections with $I > 2\sigma(I)$. Structure factor calculations using a scattering model composed of the molybdenum and sulphur atoms (all with temperature factors of 2.6 Å$^2$, as calculated by NORMAL) produced a reliability index $R = \Sigma F_o/F' - 2$ of 0.286 where $\Delta F = |F_o| - |F'_o|$ and $F_o$ are calculated structure factor amplitudes. A subsequent difference Fourier located all nitrogen and carbon atoms except the methyl group carbon atoms and reaffirmed the presence of oxygen in a special position (on the $C_2$ axis, as indicated in the initial $E$ map).

Refinement of the structure was commenced using isotropic temperature factors and unit weights. The function minimised in least-squares refinements was $\Sigma\omega(|F'_o| - |F_o|)^2$ where $\omega$ is the weight assigned to the $F_o$ values. Also, as required by symmetry restrictions, the $x$, $z$, $\beta_{12}$ and $\beta_{23}$ parameters of the oxygen and (later) boron atoms were kept fixed at 0.25$\alpha$, 0.0$\alpha$, 0.0 and 0.0 respectively. Atoms N(1) to C(9)
were incorporated into the scattering model with initial isotropic temperature factors of 2.6 \AA^2. Subsequent block-diagonal least-squares refinement to $R = 0.08$ and concomitant difference syntheses located all non-hydrogen atoms with the exception of F(1B) and F(2B). A parallel refinement in the acentric space group, $C\alpha$, produced atomic positions not significantly different to those of the refined centric structure. Refinement was thus continued in space group $C2/\alpha$.

Subsequent full-matrix least-squares refinement employing anisotropic temperature factors converged with $R = 0.038$. Concomitant difference syntheses located atoms F(1B) and F(2B) of the disordered BF$_4^-$ ion as well as the dithiocarbamato-ligand hydrogen atoms. Although in the sterically favoured staggered positions, the experimental hydrogens produced somewhat distorted methyl group geometries. Hence, calculated hydrogen atoms were included in the scattering model (at $R = 0.051$). The hydrogen atom positions were calculated assuming fully staggered conformations using a C-H bond length of 0.95 \AA and tetrahedral carbon atom geometries. Hydrogen atoms were assigned isotropic thermal parameters 10% greater than those of the carbon atoms to which they are bonded. The hydrogen atom parameters were included in subsequent least-squares calculations but were not refined.

Subsequent refinement cycles used the weighting scheme, $w = 1/\sigma^2$ where $\sigma$ was $\sigma_2$, calculated from Equation (23) using an experimental uncertainty factor of $\rho = 0.045$.\textsuperscript{285,286}

$$\sigma_2 = [\sigma_1^2 + \frac{1}{4}(\rho F_o)^2]^{1/2} \quad (23)$$

In an attempt to further define the disorder of the BF$_4^-$ ion, the boron and fluorine atoms were removed from the scattering model and their positional coordinates re-established by refinement and difference syntheses based on a scattering model composed of all other atoms. This procedure indicated a BF$_4^-$ disorder consisting of two distorted
tetrahedral forms of the ion having equal site occupancies. The new positional coordinates of the B, F(1), F(2), F(1B) and F(2B) atoms were returned to the scattering model. Subsequent refinement of the site occupancy parameters of F(1) to F(2B) produced occupancy factors differing by less than 6% from the 50% occupancy initially input for each atom. Calculations with occupancy values of 60:40 and 70:30 (for F(1):F(1B) and F(2):F(2B)) increased the $R$ value.

Final cycles of full-matrix least-squares refinement, employing a damping factor of 0.5 to facilitate convergence of the oscillating BF$_4^-$ parameters, converged with $R = 0.035$ and

$$R^1 = \left[ \frac{\sum |F_o| - |F_e|}{\sum |F_o|^2} \right]^{1/2} = 0.041$$

In the last cycle, the maximum parameter shift of the non-BF$_4^-$ atoms was 0.1 $\sigma$, the maximum parameter shift for the BF$_4^-$ atoms being 0.3 $\sigma$. A final difference Fourier map was featureless, with a maximum residual electron-density peak of 0.4 eÅ$^{-3}$. The atomic scattering factors used in the calculations were taken from Doyle and Turner$^{287}$ and Stewart et al.$^{288}$ (for hydrogens) and the anomalous dispersion factors were taken from Cromer and Liberman.$^{289}$ A summary of the structure solution and refinement is given in Table 3.8.

The structure solution and refinement, performed using a UNIVAC 1100/42 computer at the Australian National University Computing Centre, employed the following programs from the ANUCRYS Crystallographic Program Library.$^{290,291}$

**ANUFOR**
For three-dimensional Fourier syntheses (based on structure factors). A modification of the University of Canterbury Fourier program by R.J. Dellaca.

**HYDGEN**
A program for the calculation of hydrogen atom positions.
Table 3.8

\[ \text{[Mo}_2\text{O(S}_2\text{CNET}_2)_6\text{]}\text{BF}_4: \] Structure Solution and Refinement

| Space group indicated by intensity statistics | C2/c |
| Method of structure solution | MULTAN direct methods package |
| Least-squares refinement | Block-Diagonal and Full-Matrix |
| Function minimized | \( \sum \omega |F_o| - |F_a|^2 \) |
| Source of atomic scattering factors | Mo, S, F, O, N, C, B (Doyle and Turner, Ref. 287) H (Stewart et al. Ref. 288) |
| Anomalous dispersion | Mo \( \Delta f' = -1.825, \Delta f'' = 0.688 \) (e) S \( \Delta f' = 0.110, \Delta f'' = 0.124 \) (e) (e) = electrons, Ref. 289 |
| Final weights for refinement | \( w = 1/\sigma^2 \) |
| \( R = \frac{\sum \omega |F_o| - |F_a|^2}{\sum |F_o|^2} \) | 0.035 |
| \( R_1 = \left[ \frac{\sum \omega |F_o| - |F_a|^2}{\sum \omega |F_o|^2} \right]^{1/2} \) | 0.041 |
| \( \left[ \frac{\sum \omega |F_o| - |F_a|^2}{(m-n)} \right]^{1/2} \) | 1.054 |

LISTER

For tables of final atomic parameters with standard deviations.

MEANPL

For least-squares planes calculations, by D.M. Taylor, based on NRC#22 by M.E. Pippy.

MULTAN 77

A system of computer programs for the automatic solution of crystal structures by direct methods techniques, by P. Main, L. Lessinger, M.M. Woolfson, G. Germain and J-P. De Clercq, incorporating NORMAL, for normalised structure factors and statistics and MULTAN, for multiple solutions by the tangent formula.

ORTEP

A Fortran thermal ellipsoid plot program for crystal structure illustrations by C.K. Johnson.

ORFFEL

A function and error program for geometrical calculations from full-matrix refined parameters.
Results: Final atomic coordinates and thermal parameters for the non-hydrogen atoms of the asymmetric unit of $[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{BF}_4$ are presented in Table 3.9. The hydrogen atom parameters for the asymmetric unit are given in Table 3.10. Appendix II contains a table of observed and calculated structure factor amplitudes. Bond lengths, polyhedral edge lengths and bond angles within the coordination groups of $[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+$ are given in Table 3.11. The bond lengths, bond angles and important interatomic distances pertaining to the dithiocarbamato-ligands are given in Table 3.12. Selected mean plane calculations and interplane dihedral angles are presented in Tables 3.13 and 3.14 respectively. Selected structural parameters for the disordered tetrafluoroborate ion are given in Table 3.15.
Table 3.9.
Atomic Coordinates and Anisotropic Thermal Parameters (Å²)
of the Non-Hydrogen Atoms in the Asymmetric Unit of [Mo₂O(S₂CNET₂)₆]BF₄

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>u₁₁</th>
<th>u₂₂</th>
<th>u₃₃</th>
<th>u₁₂</th>
<th>u₁₃</th>
<th>u₂₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)</td>
<td>-0.166(3)</td>
<td>0.4317(3)</td>
<td>0.5919(3)</td>
<td>0.060(2)</td>
<td>0.050(2)</td>
<td>0.034(2)</td>
<td>0.015(2)</td>
<td>0.013(2)</td>
<td>-0.003(2)</td>
</tr>
<tr>
<td>N(2)</td>
<td>0.3186(3)</td>
<td>0.3788(3)</td>
<td>0.4527(3)</td>
<td>0.036(2)</td>
<td>0.056(3)</td>
<td>0.042(2)</td>
<td>-0.004(2)</td>
<td>0.004(2)</td>
<td>0.002(2)</td>
</tr>
<tr>
<td>N(3)</td>
<td>-0.2144(3)</td>
<td>0.2377(3)</td>
<td>0.3615(3)</td>
<td>0.044(2)</td>
<td>0.045(2)</td>
<td>0.044(2)</td>
<td>-0.006(2)</td>
<td>0.009(2)</td>
<td>-0.003(2)</td>
</tr>
<tr>
<td>C(1)</td>
<td>-0.1105(3)</td>
<td>0.4071(1)</td>
<td>0.5367(3)</td>
<td>0.036(2)</td>
<td>0.035(2)</td>
<td>0.026(2)</td>
<td>-0.003(2)</td>
<td>0.007(2)</td>
<td>-0.002(2)</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.2197(3)</td>
<td>0.3702(1)</td>
<td>0.4413(3)</td>
<td>0.038(2)</td>
<td>0.045(2)</td>
<td>0.048(1)</td>
<td>0.001(1)</td>
<td>0.004(1)</td>
<td>0.011(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>-0.1525(3)</td>
<td>0.2712(1)</td>
<td>0.3756(3)</td>
<td>0.040(3)</td>
<td>0.046(3)</td>
<td>0.028(2)</td>
<td>0.006(2)</td>
<td>0.112(2)</td>
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<tr>
<td>C(4)</td>
<td>-0.1707(4)</td>
<td>0.4233(2)</td>
<td>0.7068(4)</td>
<td>0.088(4)</td>
<td>0.076(4)</td>
<td>0.037(3)</td>
<td>0.023(3)</td>
<td>0.025(3)</td>
<td>-0.004(3)</td>
</tr>
<tr>
<td>C(5)</td>
<td>-0.2313(4)</td>
<td>0.4657(2)</td>
<td>0.5371(4)</td>
<td>0.094(4)</td>
<td>0.068(4)</td>
<td>0.053(3)</td>
<td>0.046(3)</td>
<td>0.022(3)</td>
<td>0.001(3)</td>
</tr>
<tr>
<td>C(6)</td>
<td>0.3528(4)</td>
<td>0.4235(2)</td>
<td>0.4411(3)</td>
<td>0.042(2)</td>
<td>0.059(3)</td>
<td>0.072(4)</td>
<td>0.000(2)</td>
<td>0.004(3)</td>
<td>-0.005(3)</td>
</tr>
<tr>
<td>C(7)</td>
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<td>0.3451(2)</td>
<td>0.4778(4)</td>
<td>0.033(2)</td>
<td>0.074(2)</td>
<td>0.054(3)</td>
<td>0.000(2)</td>
<td>0.011(3)</td>
<td>-0.003(3)</td>
</tr>
<tr>
<td>C(8)</td>
<td>-0.1765(4)</td>
<td>0.1931(2)</td>
<td>0.3698(5)</td>
<td>0.054(3)</td>
<td>0.055(3)</td>
<td>0.079(4)</td>
<td>-0.014(3)</td>
<td>-0.003(3)</td>
<td>0.003(3)</td>
</tr>
<tr>
<td>C(9)</td>
<td>-0.3247(3)</td>
<td>0.2434(2)</td>
<td>0.3315(4)</td>
<td>0.045(3)</td>
<td>0.063(3)</td>
<td>0.089(4)</td>
<td>-0.013(2)</td>
<td>0.017(2)</td>
<td>-0.012(3)</td>
</tr>
<tr>
<td>C(10)</td>
<td>-0.1524(6)</td>
<td>0.4592(3)</td>
<td>0.7804(5)</td>
<td>0.167(7)</td>
<td>0.121(6)</td>
<td>0.148(3)</td>
<td>0.114(2)</td>
<td>0.006(4)</td>
<td>0.004(5)</td>
</tr>
<tr>
<td>C(11)</td>
<td>-0.3334(4)</td>
<td>0.4494(2)</td>
<td>0.6857(5)</td>
<td>0.065(4)</td>
<td>0.156(7)</td>
<td>0.083(5)</td>
<td>0.041(4)</td>
<td>0.011(4)</td>
<td>0.012(4)</td>
</tr>
<tr>
<td>C(12)</td>
<td>0.3562(4)</td>
<td>0.4368(2)</td>
<td>0.3257(5)</td>
<td>0.074(2)</td>
<td>0.065(4)</td>
<td>0.086(4)</td>
<td>-0.006(3)</td>
<td>0.026(3)</td>
<td>0.021(3)</td>
</tr>
<tr>
<td>C(13)</td>
<td>0.4595(4)</td>
<td>0.3380(2)</td>
<td>0.3885(5)</td>
<td>0.070(4)</td>
<td>0.090(4)</td>
<td>0.077(4)</td>
<td>0.094(3)</td>
<td>0.023(3)</td>
<td>0.003(3)</td>
</tr>
<tr>
<td>C(14)</td>
<td>-0.1426(5)</td>
<td>0.1774(2)</td>
<td>0.2661(5)</td>
<td>0.088(4)</td>
<td>0.063(4)</td>
<td>0.127(6)</td>
<td>0.014(3)</td>
<td>0.037(4)</td>
<td>-0.015(4)</td>
</tr>
<tr>
<td>C(15)</td>
<td>-0.3604(2)</td>
<td>0.2335(2)</td>
<td>0.2149(5)</td>
<td>0.118(5)</td>
<td>0.118(5)</td>
<td>0.064(4)</td>
<td>0.009(3)</td>
<td>-0.007(3)</td>
<td>-0.010(4)</td>
</tr>
<tr>
<td>B</td>
<td>0.0</td>
<td>0.0570(5)</td>
<td>0.25</td>
<td>0.081(9)</td>
<td>0.096(10)</td>
<td>0.070(7)</td>
<td>0.0</td>
<td>0.032(7)</td>
<td>0.0</td>
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<tr>
<td>F(1)</td>
<td>-0.0003(14)</td>
<td>0.0733(8)</td>
<td>0.1797(16)</td>
<td>0.180(15)</td>
<td>0.424(35)</td>
<td>0.167(17)</td>
<td>-0.133(18)</td>
<td>0.130(14)</td>
<td>-0.015(18)</td>
</tr>
<tr>
<td>F(2)</td>
<td>-0.0975(7)</td>
<td>0.2169(10)</td>
<td>0.092(7)</td>
<td>0.029(7)</td>
<td>0.336(9)</td>
<td>0.040(7)</td>
<td>0.027(6)</td>
<td>0.032(6)</td>
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a. The anisotropic temperature factor is of the form $T = \exp[-2\pi^2(h^2a^2u_{11} + k^2b^2u_{22} + l^2c^2u_{33} + 2hka^b*u_{12} + 2hka^c*u_{13} + 2kbc^*u_{23})]$; estimated standard deviations are given in parentheses.
### Table 3.10

Atomic Coordinates and Isotropic Thermal Parameters ($\bar{R}^2$) of the Hydrogen Atoms in the Asymmetric Unit of $[\text{Mo}_2\text{O(S}_2\text{CNET}_2)_6]\text{BF}_4$.

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<th>z/c</th>
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a) The hydrogen atoms are numbered with reference to the carbon atoms to which they are attached.
Table 3.11
Selected Bond Lengths, Bond Angles and Interatomic Distances for the Coordination Group of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\)BF_4\(^a\)

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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S(5) · ·S(6)</td>
<td>2.815(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Estimated standard deviations are given in parentheses.

b) These atoms pertain to the portion of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\)BF_4 related to the asymmetric unit by the \(C_2\) axis.
Table 3.12
Bond Lengths and Bond Angles of the \(N,N\)-Diethyldithiocarbamato-Ligands

<table>
<thead>
<tr>
<th>Ligand I</th>
<th>Ligand II</th>
<th>Ligand III</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond Lengths ((\text{A}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S(1)··S(2)</td>
<td>2.893(1)</td>
<td>S(3)··S(4)</td>
<td>2.815(2)</td>
</tr>
<tr>
<td>S(1)-C(1)</td>
<td>1.716(4)</td>
<td>S(3)-C(2)</td>
<td>1.697(4)</td>
</tr>
<tr>
<td>S(2)-C(1)</td>
<td>1.738(4)</td>
<td>S(4)-C(2)</td>
<td>1.724(5)</td>
</tr>
<tr>
<td>C(1)-N(1)</td>
<td>1.316(5)</td>
<td>C(2)-N(2)</td>
<td>1.324(5)</td>
</tr>
<tr>
<td>N(1)-C(4)</td>
<td>1.476(5)</td>
<td>N(2)-C(6)</td>
<td>1.465(6)</td>
</tr>
<tr>
<td>N(1)-C(5)</td>
<td>1.464(6)</td>
<td>N(2)-C(7)</td>
<td>1.469(6)</td>
</tr>
<tr>
<td>C(4)-C(10)</td>
<td>1.471(8)</td>
<td>C(6)-C(12)</td>
<td>1.498(7)</td>
</tr>
<tr>
<td>C(5)-C(11)</td>
<td>1.500(8)</td>
<td>C(7)-C(13)</td>
<td>1.490(7)</td>
</tr>
<tr>
<td>Bond Angles (degrees)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-S(1)-C(1)</td>
<td>87.2(1)</td>
<td>Mo-S(3)-C(2)</td>
<td>90.4(1)</td>
</tr>
<tr>
<td>Mo-S(2)-C(1)</td>
<td>88.1(1)</td>
<td>Mo-S(4)-C(2)</td>
<td>90.0(1)</td>
</tr>
<tr>
<td>S(1)-C(1)-S(2)</td>
<td>113.8(2)</td>
<td>S(3)-C(2)-S(4)</td>
<td>110.7(2)</td>
</tr>
<tr>
<td>S(1)-C(1)-N(1)</td>
<td>124.8(3)</td>
<td>S(3)-C(2)-N(2)</td>
<td>125.4(3)</td>
</tr>
<tr>
<td>S(2)-C(1)-N(1)</td>
<td>121.4(3)</td>
<td>S(4)-C(2)-N(2)</td>
<td>123.9(3)</td>
</tr>
<tr>
<td>C(1)-N(1)-C(4)</td>
<td>122.5(4)</td>
<td>C(2)-N(2)-C(6)</td>
<td>119.5(4)</td>
</tr>
<tr>
<td>C(1)-N(1)-C(5)</td>
<td>120.5(4)</td>
<td>C(2)-N(2)-C(7)</td>
<td>122.6(4)</td>
</tr>
<tr>
<td>N(1)-C(4)-C(10)</td>
<td>114.2(5)</td>
<td>N(2)-C(6)-C(12)</td>
<td>113.8(4)</td>
</tr>
<tr>
<td>N(1)-C(5)-C(11)</td>
<td>113.5(5)</td>
<td>N(2)-C(7)-C(13)</td>
<td>113.2(4)</td>
</tr>
</tbody>
</table>

Interatomic Distances: C(12)··C(13), 3.388(8); C(14)··C(15), 3.349(8); C(11)··C(12), 3.857(8); C(13)··C(15), 3.650(9); C(14)··C(14), 3.850(12).

a) Estimated standard deviations are given in parentheses.
b) These atoms pertain to the portion of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]\text{BF}_4\) related to the asymmetric unit by the \(C_2\) axis.
### Table 3.13

\([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]\text{BF}_4^{:}\) Least-Squares Planes and Atomic Deviations (Å) Therefrom.\(^a\)

<table>
<thead>
<tr>
<th>Plane</th>
<th>Mo–O–Mo</th>
<th>Equatorial Planes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane 1:</td>
<td>(-0.9847x + 0.0y - 0.1743z + 0.1163 = 0)</td>
<td>Mo* -0.0000(3) Mo*b 0.0000(3)</td>
</tr>
<tr>
<td>S(1)</td>
<td>0.0000(3)</td>
<td>0* 0.0000(0) S(3)* (-1.705(1))</td>
</tr>
<tr>
<td>S(4)</td>
<td>(-2.312(1))</td>
<td>S(5) (0.226(1)) S(6) (2.408(1))</td>
</tr>
<tr>
<td>Plane 2:</td>
<td>(0.2340x - 0.1183y - 0.9650z + 6.1694 = 0)</td>
<td>Mo* 0.0008(3) S(3)* (0.021(1))</td>
</tr>
<tr>
<td>S(5)*</td>
<td>0.036(1)</td>
<td>S(6)* (-0.027(1)) S(1) (-2.510(1))</td>
</tr>
<tr>
<td>S(2)</td>
<td>(-0.576(1))</td>
<td>0 1.839(1)</td>
</tr>
<tr>
<td>Plane 3b:</td>
<td>(0.2340x + 0.1183y - 0.9650z - 0.0339 = 0)</td>
<td>Displacements as in Plane 2 but of opposite sign.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Plane</th>
<th>Mo–S(1)–S(2) Planes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane 4:</td>
<td>(-0.8338x - 0.5285y - 0.1594z + 5.8293 = 0)</td>
</tr>
<tr>
<td>S(2)*</td>
<td>(-0.003(1))</td>
</tr>
<tr>
<td>S(2)</td>
<td>(1.505(1))</td>
</tr>
<tr>
<td>C(2)</td>
<td>(-2.872(4))</td>
</tr>
<tr>
<td>Plane 5b:</td>
<td>(-0.8338x + 0.5285y - 0.1594z - 5.5595 = 0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Plane</th>
<th>Ligands I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane 6:</td>
<td>(-0.7479x - 0.6163y - 0.2466z + 7.5666 = 0)</td>
</tr>
<tr>
<td>S(1)</td>
<td>(0.301(0))</td>
</tr>
<tr>
<td>C(11)</td>
<td>(1.466(7))</td>
</tr>
<tr>
<td>Plane 7b:</td>
<td>(-0.7479x + 0.6163y - 0.2466z - 6.6869 = 0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Plane</th>
<th>Ligands II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane 8:</td>
<td>(0.1430x - 0.1605y - 0.9766z + 6.8245 = 0)</td>
</tr>
<tr>
<td>S(3)</td>
<td>(0.000(4))</td>
</tr>
<tr>
<td>Mo</td>
<td>(0.214(4))</td>
</tr>
<tr>
<td>C(13)</td>
<td>(1.257(6))</td>
</tr>
<tr>
<td>Plane 9b:</td>
<td>(0.1430x + 0.1605y - 0.9766z - 0.6952 = 0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Plane</th>
<th>Ligands III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane 10:</td>
<td>(0.2715x - 0.0324y - 0.9619z + 5.4430 = 0)</td>
</tr>
<tr>
<td>S(3)</td>
<td>(0.005(4))</td>
</tr>
<tr>
<td>Mo</td>
<td>(0.184(3))</td>
</tr>
<tr>
<td>C(15)</td>
<td>(1.272(6))</td>
</tr>
<tr>
<td>Plane 11b:</td>
<td>(0.2715x + 0.0324y - 0.9619z + 0.7052 = 0)</td>
</tr>
</tbody>
</table>

\(^a\) Atoms marked with an asterisk were used in calculating the planes; equations are in Cartesian (Å) coordinates.

\(^b\) The plane or atom displacements pertain to the portion of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]\text{BF}_4^{:}\) related to the asymmetric unit by the \(c_2\) axis.
Table 3.14
Dihedral Angles Between Planes

<table>
<thead>
<tr>
<th>Planes</th>
<th>Angle</th>
<th>Planes</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 2(3)</td>
<td>93.57</td>
<td>2(3) 9(8)</td>
<td>16.88</td>
</tr>
<tr>
<td>1 4(5)</td>
<td>31.91</td>
<td>2(3) 10(11)</td>
<td>5.38</td>
</tr>
<tr>
<td>1 6(7)</td>
<td>38.79</td>
<td>2(3) 11(12)</td>
<td>8.91</td>
</tr>
<tr>
<td>1 8(9)</td>
<td>88.31</td>
<td>4 5</td>
<td>63.81</td>
</tr>
<tr>
<td>1 10(11)</td>
<td>95.72</td>
<td>4(5) 6(7)</td>
<td>8.64</td>
</tr>
<tr>
<td>2 3</td>
<td>13.59</td>
<td>4(5) 8(9)</td>
<td>83.03</td>
</tr>
<tr>
<td>2(3) 4(5)</td>
<td>88.78</td>
<td>4(5) 10(11)</td>
<td>93.21</td>
</tr>
<tr>
<td>2(3) 5(4)</td>
<td>95.96</td>
<td>6(7) 8(9)</td>
<td>76.53</td>
</tr>
<tr>
<td>2(3) 6(7)</td>
<td>82.19</td>
<td>6(7) 10(11)</td>
<td>86.90</td>
</tr>
<tr>
<td>2(3) 7(6)</td>
<td>90.57</td>
<td>8(9) 10(11)</td>
<td>10.45</td>
</tr>
<tr>
<td>2(3) 8(9)</td>
<td>5.79</td>
<td>8(9) 11(10)</td>
<td>13.34</td>
</tr>
</tbody>
</table>

a) For the planes given in Table 3.13; equivalent plane combinations are given in parentheses and all angles are in degrees.

Table 3.15
Bond Lengths and Bond Angles for the Tetrafluoroborate Ion

<table>
<thead>
<tr>
<th>Ion A</th>
<th>Ion B</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-F(1)</td>
<td>1.19(2) Å</td>
</tr>
<tr>
<td>B-F(2)</td>
<td>1.36(1) Å</td>
</tr>
<tr>
<td>F(1)-B-F(2)</td>
<td>113.3(10)°</td>
</tr>
<tr>
<td>F(1)-B-F(1)b</td>
<td>130.3(30)°</td>
</tr>
<tr>
<td>F(1)-B-F(2)b</td>
<td>80.7(12)°</td>
</tr>
<tr>
<td>F(2)-B-F(2)b</td>
<td>147.1(18)°</td>
</tr>
<tr>
<td>Others</td>
<td></td>
</tr>
<tr>
<td>F(1)-B-F(1B)</td>
<td>81.6(11)°</td>
</tr>
<tr>
<td>F(1)-B-F(1B)b</td>
<td>140.3(19)°</td>
</tr>
</tbody>
</table>

a) Estimated standard deviations are given in parentheses.
b) Atoms are those related to the asymmetric unit by the C2 axis.
3.3 DISCUSSION

3.3.1 Preparation and Characterization of Compounds

The reaction of $[\text{MoO}(S_2\text{CNET}_2)_3]\text{BF}_4$ and triphenylphosphine in the presence of oxygen results in the catalytic oxidation of triphenylphosphine to triphenylphosphine oxide, according to Figure 2.13. In an attempt to isolate and characterise the Mo(IV) intermediate formed in the cycle's initial stage, the reaction was performed (in methanol) under anaerobic conditions. Under these conditions, the reaction yields green-black dichroic crystals of the mixed oxidation state compound, $[\text{Mo}_2\text{O}(S_2\text{CNET}_2)_6]\text{BF}_4$. The compounds $\left[\text{Mo}_2\text{O}(S_2\text{CNR}_2)_6\right]X$ ($R = \text{Me, Et}; X = \text{BF}_4^-, \text{PF}_6^-, \text{ClO}_4^-$, $R = \text{Et}; X = \text{Cl}^-$) are readily prepared by analogous reactions.

The mechanism involved in the formation of these complexes is uncertain. However, a likely mechanism involves the following sequence of reactions: 1) the formation of the reactive $[\text{Mo}(S_2\text{CNR}_2)_3]^+$ complex via an oxygen atom transfer reaction between $[\text{MoO}(S_2\text{CNR}_2)_3]^+$ and $\text{PPh}_3$; 2) the reaction of $[\text{Mo}(S_2\text{CNR}_2)_3]^+$ and unreacted $[\text{MoO}(S_2\text{CNR}_2)_3]^+$ to form intermediate $\mu$-oxo-bridged Mo(IV,VI) or Mo(V,V) complexes (the Mo(V,V) complex may be formed by electron transfer within the Mo(IV,VI) complex), and 3) the reduction of these dinuclear complexes by reductants such as methanol or free dithiocarbamate (from the decomposition of $[\text{Mo}(S_2\text{CNR}_2)_3]^+$, for example) to yield the mixed oxidation state compounds under discussion. Other mechanisms involving the reaction of mononuclear Mo(IV) and Mo(V) species may also be envisaged. In any case, the high stability of the compounds and their relative insolubility in methanol leads to good yields of high purity product.

The new compounds, which are air stable in the solid state but rapidly oxidised in solution, are formulated on the basis of elemental analysis and conductivity studies. In methanol, the molar
conductivities of the compounds, \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]\)X, \((\alpha = 80 \ \Omega^{-1} \ \text{cm}^2 \ \text{mole}^{-1})\) are typical of 1:1 electrolytes.\(^{220}\)

The infrared spectra of the compounds are summarised in Table 3.2, and for \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]\)X \((X = \text{BF}_4^-, \text{Cl}^-)\), are displayed in Figure 3.2.

![Infrared spectra of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]\)X](#)

**Figure 3.2.** a) Infrared spectrum of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]\)BF\(_4\), with a concentration enhanced spectrum in the 800-250 cm\(^{-1}\) region; b) Infrared spectrum of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]\)Cl in the 1150-1000 cm\(^{-1}\) region. This spectrum is otherwise identical to spectrum a).

The infrared spectra show the presence of bands due to bidentate dithiocarbamato-ligands \(v(\text{CN})\) at 1545 \((R = \text{Me})\) and 1510 cm\(^{-1}\) \((R = \text{Et})\); a single \(v(\text{CS})\) band at 1050 \((R = \text{Me})\) and 1000 cm\(^{-1}\) \((R = \text{Et})\)\(^{191,192}\). Bands attributable to the counterions, \(X^-\), are also present.

The absence of a strong band in the \(v(\text{Mo-O})\) region of the spectra (970-800 cm\(^{-1}\)) firmly establishes the absence of terminal oxo-ligation in these compounds. Only weak \(v(\text{CSS})\) ligand modes are observed in this region. The weak band at \(\approx 655 \ \text{cm}^{-1}\) in all compounds is tentatively assigned to the \(v_{\text{as}}(\text{MoOMo})\) vibration. The nature of this band is shown
in the spectrum of $[\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]BF_4$ (Figure 3.2). Its position does not correlate well with the $\nu_{\text{as}}(\text{MoOMo})$ range determined for dinuclear Mo(V) complexes (785-730 cm$^{-1}$) due to the considerable structural difference between these compounds and the $[\text{Mo}_2\text{O}(\text{S}_2\text{CNR}_2)_6]^+$ complexes. A band in the 690-670 cm$^{-1}$ region has been assigned to the $\mu$-oxo-bridged vibrations in dinuclear Mo(III) complexes. The infrared spectra of $\mu$-oxo-molybdenum complexes which do not contain terminal oxo-ligands have not been reported previously. The weakness of the $\nu_{\text{as}}(\text{MoOMo})$ band and an inability to prepare highly enriched $[\text{Mo}_2^{18}\text{O}(\text{S}_2\text{CNET}_2)_6]^+$ has prevented unambiguous band assignment. The other weak bands in the vicinity of the $\nu_{\text{as}}(\text{MoOMo})$ band can be attributed to the dithiocarbamato-ligands or $X^-$. The mixed oxidation state formulation, implicit in the chemical formulae of the compounds, is supported by the magnetic, electrochemical and spectral properties of $[\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]BF_4$. The magnetic moment of this complex (and the Cl$^-$ salt, Table 3.3) indicates the presence of one unpaired electron per dinuclear complex, consistent with the Mo(IV,V) formulation. It is probable that the unpaired electron, a legacy of the d$^1$ Mo(V) ion, is delocalised between the two molybdenum sites (see later). A further contribution to the magnetic moment is also evident from the increased value of $\mu_{\text{eff}}$ over the spin-only value for one unpaired electron, i.e. 1.73 B.M.

The cyclic voltammogram of $[\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]BF_4$ in acetonitrile at a HMD electrode is shown in Figure 3.3 and exhibits a quasi-reversible ($\Delta E_p = 77$ mV) cathodic process at $E_0 = -0.77$ V (process 1,1'). The ratio $\frac{i_{\text{ox}}}{i_{\text{red}}}$ for this process is close to 1.0 even at slow scan rates, indicative of the formation of a stable reduction product. The number of electrons transferred to each molecule of complex during process 1 was determined to be 1.2 by controlled potential (-1.2 V) electrolysis/
Figure 3.3. The cyclic voltammogram of [Mo$_2$O(S$_2$CNEt$_2$)$_6$]BF$_4$ in 0.1 M Et$_4$NCIO$_4$/CH$_3$CN at a HMD electrode, scan rate 100 mVs$^{-1}$.

coulometry in acetonitrile. The value of 1.2 supports the one electron reduction of [Mo$_2$O(S$_2$CNEt$_2$)$_6$]$^+$ during process 1, the somewhat high value being explained by the extreme air sensitivity of the complex in solution. All the above data are consistent with the chemically reversible process shown in Equation (24).

$$\text{[Mo}_2\text{IV,V}_0\text{(S}_2\text{CNEt}_2)_6]^{+} \xrightarrow{1} \text{Mo}_2\text{IV,IV}_0\text{(S}_2\text{CNEt}_2)_6}$$

Cyclic voltammetry at a platinum electrode over the potential range 0.0 to -1.5 V also exhibits a quasi-reversible (Δ$E_p = 70$ mV) process analogous to 1,1'. At a platinum electrode, anodic scanning to +1.2 V results in three irreversible oxidation peaks at +0.12, +0.45 and +0.99 V. Subsequent cathodic scans show a new irreversible reduction peak at -0.29 V in addition to process 1,1'. This irreversible reduction peak is
associated with an unidentified oxidation product. Thus, electrochemical oxidation of the complex (and possibly the dithiocarbamato-ligands) results in irreversible µ-oxo-bridge cleavage, also a feature of the aerial oxidation of the complex.

The electronic spectrum of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\)BF_4 is discussed in Section 3.3.3.

On the basis of the foregoing results, a dinuclear structure composed of two seven-coordinate PB molybdenum moieties linked via an axial µ-oxo-ligand was proposed for \([\text{Mo}_2\text{O}(\text{S}_2\text{CNR}_2)_6]^+\); this structure was confirmed by the x-ray crystal structure determination of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\)BF_4.

3.3.2 The X-Ray Crystal Structure of µ-Oxo-hexakis(\(N, N\)-diethyl-dithiocarbamato)dimolybdenum(IV, V) Tetrafluoroborate

In the crystalline state, \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\)BF_4 consists of discrete \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\) and BF_4⁻ ions. In the cation, each molybdenum atom has a distorted pentagonal bipyramidal (PB) coordination geometry, the PB moieties being linked through a shared axial oxygen atom, the µ-oxo-ligand. The tetrafluoroborate ion is disordered and has been adequately modelled by two distorted tetrahedral forms of equal site occupancy. Both ions have a \(C_2\) symmetry imposed by the space group.

The \(C_2\) axis through oxygen in \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\) dictates the equivalence of both molybdenum containing moieties in the complex. It is thus convenient to discuss the molybdenum coordination sphere and the dithiocarbamato-ligand geometries of the complex in terms of its asymmetric unit. The asymmetric unit of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\) is shown in Figure 3.4, along with the atom and ligand labelling schemes.

The molybdenum coordination sphere displays a distorted pentagonal bipyramidal geometry with the bridging oxygen atom occupying an axial
Figure 3.4. Perspective view of the asymmetric unit of $[\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+$ showing the atom and ligand labelling schemes. Non-hydrogen atoms are shown as ellipsoids of 50% probability and hydrogen atoms as spheres of convenient (arbitrary) size. In this unit the oxygen atom has a one half occupancy.

position; dithiocarbamato-ligand I spans the other axial position and one equatorial position, while the remaining equatorial sites accommodate dithiocarbamato-ligands II and III. The maximum symmetry for this type of PB structure is $C_{2h}$, with the metal atom, the monodentate ligand and the unique bidentate spanning ligand in the mirror plane. With the exception of the dithiocarbamato- methyl groups, $C_{2h}$ symmetry is closely
Several procedures for the quantitative description of seven-coordinate polyhedral geometries have been developed.\textsuperscript{233,234} One such method\textsuperscript{293} describes the coordination polyhedron by a set of $\delta$ angles which, for $\left[\text{Mo}_2\text{O(S}_2\text{CNEt}_2\right)_6]^+$, correspond to the dihedral angles between the polyhedral faces which intersect along the edges $S(1)\cdots S(3)$, $S(1)\cdots S(6)$ and the internal "edge" $S(3)\cdots S(6)$. Using equalised metal ligand bond lengths of 1.0 Å, the calculated $\delta$ parameters for $\left[\text{Mo}_2\text{O(S}_2\text{CNEt}_2\right)_6]^+$ are 46.3°, 49.6° and -80.9°, respectively. A similar set of $\delta$ parameters for the corresponding edges on the opposite side of the equatorial plane, i.e. $O\cdots S(3)$, $O\cdots S(6)$ and $S(3)\cdots S(6)$, are 63.5°, 61.6° and -63.0°. These normalised $\delta$ parameters are in good agreement with those calculated for an idealised $D_{5h}$ PB geometry (54.4°, 54.4°, -72.8°\textsuperscript{293}). The major deviation of the last parameter in both $\delta$ sets reflects the primary distortion of the spanning dithiocarbamato-ligand (see later). The $\delta$ parameters differ substantially from those calculated for the $C_{2v}$ monocapped trigonal prism (41.5, 0.0, 0.0) and the $C_{3v}$ monocapped octahedron (16.2, 16.2, 16.2).\textsuperscript{293} The bond angles subtended at the molybdenum atom also corroborate the PB geometry.\textsuperscript{233} These angles, given in Table 3.11, closely match those which define a PB geometry, i.e. idealised angles of $0\text{-Mo-S}_\text{ax} = 180^\circ$, $0\text{-Mo-S}_\text{eq}$ and $S_\text{ax}\text{-Mo-S}_\text{eq} = 90^\circ$ and $S_\text{eq}\text{-Mo-S}_\text{eq} = 72^\circ$ (where ax = axial and eq = equatorial).

The principal distortions of the coordination group from an idealised PB geometry is shown in Figure 3.5; a view of the MoO$_5$S$_6$ group from an aspect perpendicular to the quasi-mirror plane defined by atoms Mo, O, S(1) and S(2) (mean displacement of the atoms defining the plane = 0.018 Å). The equatorial plane is defined by the atoms Mo, S(3), S(4), S(5) and S(6), these atoms having a mean displacement from the plane of
Figure 3.5. The principal distortions of the MoOS₆ coordination groups of [Mo₂O(S₂CNEt₂)₆]⁺. The quasi-mirror plane lies in the plane of the paper.

0.026 Å. The dihedral angle between the equatorial and quasi-mirror planes closely approximates the ideal PB value of 90° (88.8°). In the following, the term 'equatorial girdle' is used to describe the five equatorial sulphur atoms, S(2) to S(6), whereas 'equatorial' plane refers to the coplanar Mo and S(3) to S(6) atoms. Both O and S(1) atoms are displaced from the quasi-five-fold axis through the molybdenum centre and perpendicular to the equatorial plane (0.187 Å, 5.8° and 0.268 Å, 6.1° respectively). Sulphur atom S(2) is 0.576 Å (13.4°) below the equatorial plane, due to the inability of the dithiocarbamato-ligand to span a full 90° angle.

Important interatomic distances within the molybdenum coordination sphere are shown in Figure 3.6. Equal Mo-S bond lengths are observed
Figure 3.6. Interatomic distances within the MoOS₆ coordination groups of [Mo₂O(S₂CNEt₂)₆]⁺ (see also Table 3.11).

Within each equatorial ligand but the Mo-S bonds of ligand II (2.498 Å) are slightly shorter than those of ligand III (2.518 Å). The dinuclear structure of [Mo₂O(S₂CNEt₂)₆]⁺ and crystal packing effects are likely to be the major influence here. In the unique ligand I, two significantly different (6σ) Mo-S bond lengths are observed. The equatorial donor atom of this ligand exhibits the shortest Mo-S bond (2.484 Å) in the complex, possibly due to its displacement from the steric confines of the equatorial plane. The Mo-S bond trans- to the oxo-ligand is the longest Mo-S bond in the complex (2.528 Å, see later).

The distances between adjacent sulphur atoms in the equatorial girdle range from 2.815 Å to 3.054 Å all of which are much shorter than the sum of the van der Waals radii for sulphur (3.54 Å²). The average interligand S···S distance within the equatorial girdle is a short 3.035 Å. In other 1,1- and 1,2-dithiochelate complexes, similar interligand S···S distances have been interpreted in terms of stabilizing interdonor bonding.
forces. The contribution of such interactions to the stabilization of the equatorial girdle in PB tris(dithiocarbamato)-complexes is, however, debatable. Interligand distances between the equatorial and axial sulphur atoms are of the order of the van der Waals contact distance (av. 3.60 Å). Only minor 'puckering' of the atoms in the equatorial plane is observed.

It is interesting to compare the coordination geometries of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\) and the mononuclear complex, \([\text{MoO}(\text{S}_2\text{CNEt}_2)_3]^+\). Although qualitatively similar, noticeable differences in the two coordination geometries result from the disparate electronic nature of the oxo-ligands. Firstly, the equatorial planes of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\) are considerably less distorted than that of \([\text{MoO}(\text{S}_2\text{CNEt}_2)_3]^+\). In \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\), the molybdenum atoms are coplanar (displacement = 0.003 Å) with the equatorial planes, as reflected in the dihedral angle between the MoS_2 planes of equatorial ligands II and III, a mere 2.6°. The associated O-Mo-S eq angles range from 88.6° to 97.6° with an average value (92.8°) close to the idealised value of 90°. In contrast, the molybdenum atom in \([\text{MoO}(\text{S}_2\text{CNEt}_2)_3]^+\) is significantly above (0.26 Å) the corresponding equatorial plane due to a movement of the Mo-S bonds away from the Mo-O_t group (O-Mo-S eq angles range from 91.4° to 106.9°, av. 97.7°). This distortion leads to a dihedral angle of 14.5° between the MoS_2 planes of the equatorial ligands. In both complexes, the average O⋯S eq interatomic distance is 3.18 Å; this suggests that the major cause of the \([\text{MoO}(\text{S}_2\text{CNEt}_2)_3]^+\) distortion is the short bond distance (1.684 Å) of the multiply bonded terminal oxo-ligand. The longer (1.848 Å) single bonded µ-oxo-ligand is both sterically and electronically incapable of distorting the equatorial plane in \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\), despite any steric relief this may offer. The Mo-S eq bonds of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\) are slightly longer (0.016 Å av.) than those of \([\text{MoO}(\text{S}_2\text{CNEt}_2)_3]^+\), possibly due to the containment of the molybdenum atom within the equatorial sulphur plane.
and the lower oxidation state of the metal in the dinuclear complex.

Secondly, the Mo-S bonds trans- to the μ-oxo-ligand in [Mo₂O(S₂CNEt₂)₆]⁺ are considerably shorter than the corresponding bond of [MoO(S₂CNEt₂)₃]⁺ (2.526 Å and 2.630 Å respectively). The similar average $S_{eq} \cdots S_{ax}$ interatomic distances in both complexes suggest that the considerable displacement of the equatorial girdle away from the Mo-Oₜ group in [MoO(S₂CNEt₂)₃]⁺ makes a steric contribution to the lengthening of the Mo-S$_{ax}$ bond in this case. The strong electronic trans- influence of the multiply bonded Mo-Oₜ group$^9$,199,200,214 also contributes to the lengthening of the Mo-S$_{ax}$ bond in [MoO(S₂CNEt₂)₃]⁺. The shorter Mo-S$_{ax}$ bond length in [Mo₂O(S₂CNEt₂)₆]⁺ is due to both the absence of the steric influence present in [MoO(S₂CNEt₂)₃]⁺, and a significant reduction of the trans- influence of the oxo-ligand when complexed in the bridging mode.

The PB coordination geometry of [Mo₂O(S₂CNEt₂)₆]⁺ is now a familiar structural feature of seven coordinate complexes of the type MXL₃ (where X and L are mono- and bidentate ligands respectively). This coordination geometry is exclusively adopted by the complexes MX(S₂CNR₂)₃, the PB plane being stabilised by the small bite (normalised value ca. 1.13$^{232}$) of the dithiocarbamato-ligands.$^{199-213}$ As in [Mo₂O(S₂CNEt₂)₆]⁺, major distortions in these complexes result from the inability of the unique axial-equatorial ligand to span a full 90° angle. Stereochemical aspects of PB coordination have been discussed by Kepert.$^{232}$

Bond lengths and angles within the dithiocarbamato-ligands (Table 3.12) are consistent with the values found for other related dithiocarbamato-complexes.$^{199-212}$ The bite characteristics of the equatorial ligands II and III are similar (bite (S⋯S) av. 2.815 Å, bite angle (S-Mo-S) av. 68.3°, Mo-S-C av. 90.4°). The unique spanning
ligand I, however, exhibits an increased bite and bite angle (2.893 Å and 70.5° respectively) and a correspondingly smaller Mo-Š-C angle (av. 87.7°). Similar structural features have been observed in related complexes and are due in part to the compression of the bite of ligands II and III in the crowded equatorial plane. The large bite of the spanning ligand also reflects its efforts to locate its sulphur atoms as close to the ideal axial and equatorial sites as the rigid dithiocarbamato-ligand will allow.

A slight inequality in the S-C bond lengths of the dithiocarbamato-ligands is also observed. For each equatorial ligand, the S-C bond closest to the spanning ligand I is shortened (1.70 Å versus 1.72 Å). A similar difference is noted for the S-C bonds of ligand I. These differences may reflect a compromise by which slight distortion of the S-C bonds enables a favourable equatorial atom packing and a minimum of interligand contact. Inequalities of up to 0.05 Å have been reported for the S-C bond lengths of dithiocarbamato-complexes. The C-N (av. 1.319 Å) and C-S (av. 1.716 Å) bond distances are intermediate between respective single and double bond distances (C-N 1.47 Å, C=N 1.27 Å, C-S 1.81 Å, C=S 1.61 Å) indicative of delocalised π-bonding in the S₂CN portion of the ligands.

The six atoms defining the stereochemically rigid S₂C₃ structure of the dithiocarbamato-ligands are nearly co-planar for each ligand. The maximum displacement of these atoms from their respective mean planes is 0.068 Å, with the average displacement of the 18 atoms of the three ligands being 0.017 Å (Table 3.13). The twisting of the ligands about the C-N bonds is responsible for the deviations from planarity, and in ligands I, II, III respectively, dihedral angles of 2.73°, 0.51° and 2.65° are observed between the S₂CN and CNC₂ mean planes. The chelate rings of the dithiocarbamato-ligands are also folded along the S···S bite edge. The
Figure 3.7. A perspective view of the [Mo₂O(S₂CNEt₂)₆]⁺ ion. Atoms are shown as ellipsoids of 50% probability and atom numbers are unbracketed for clarity. Hydrogen atoms have been omitted.
dihedral angles between the $S_2CNC_2$ ligand plane and the corresponding $MoS_2$ plane are 10.0°, 5.9° and 5.8° for ligands I, II and III respectively. The folding of the chelate rings is also reflected in the displacement of the molybdenum atom from the dithiocarbamato-ligand planes; 0.30 Å, 0.21 Å and 0.18 Å for ligands I, II and III, respectively. The cause of these features lies in the dinuclear structure of $[Mo_2O(S_2CNEt_2)_6]^+$ and the crystal packing of the solid described later. The ethyl substituents of ligands II and III are syn-, whereas those of ligand I are anti-. The syn- conformation is dictated by crystal packing forces and is rarely observed in dithiocarbamato-complexes, being present in only two previously reported seven-coordinate tris(dithiocarbamato) complexes, $TaS(S_2CNET_2)_3$\cite{205} and $Te(S_2CNET_2)_3$Ph.\cite{213}

The $[Mo_2O(S_2CNEt_2)_6]^+$ complex, shown in Figures 3.7 and 3.8, is composed of two PB asymmetric units linked via a common axial oxygen atom: the near linear ($Mo-O-Mo$ 175.6°) bridging oxo-ligand. The bridging oxygen atom lies on the molecular $C_2$ axis and, necessarily, this axis is contained in the $Mo_2O$ plane. The bond length (1.848 Å) and angle of the

![Figure 3.8. Stereoscopic view of $[Mo_2O(S_2CNEt_2)_6]^+$ along the $C_2$ axis. Non-hydrogen atoms are shown as ellipsoids of 50% probability. Hydrogen atoms are spheres of convenient arbitrary size.](image)
µ-oxo-ligand are typical of similar features in previously reported structures, the bond length and angle ranges for µ-oxo-molybdenum complexes being 1.851-1.936 Å and 136.1-180° respectively.\(^9,56-74\) The µ-oxo-bridges are more nearly linear than indicated by the above bond angle range, as the low 136.1° bridge angle is present in the uncommon equatorially bridged PB structure of \([\{\text{MoO(O}_2\text{)}_2(\text{H}_2\text{O})\}_2\text{O}\}]^{2-}\).\(^58,59\)

Where the other ligands are dithiocarbamato-ligands only, the respective bond length and angle ranges are 1.854-1.875 Å and 172.2-180°.\(^61-63\) The Mo-O bond length is consistent with a Mo-O bond order of one in \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\)\(^8\).\(^30\) The Mo··Mo interatomic distance (3.693 Å) indicates the absence of direct metal-metal bonding within the Mo₂O triangle.

The equatorial planes of the PB moieties are nearly perpendicular to the Mo₂O plane, the dihedral angles being 93.6°. Also, as shown in Figure 3.9, the sulphur atoms of the two equatorial girdles occupy nearly eclipsed positions. When viewed along the Mo··Mo vector, sulphur atoms S(4) and S(6) are only ca. 2° from a fully eclipsed position, while pairs S(2),S(3) and S(5),S(5) are less eclipsed (by ca. 9° and 8° respectively). The interatomic distances pertaining to the pairs of 'eclipsed' sulphur atoms are also indicated in Figure 3.9.

The equatorial planes within \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\)\(^8\) are not parallel but are tilted by 13.6° with respect to each other. This feature is clear in the stereodiagram shown in Figure 3.8. Both equatorial girdles tilt so as to bring the S(2) atoms closer to the S(3) atoms of the other equatorial girdle, as reflected in the closer approach of the intergirdle S(2),S(3) pairs (3.85 Å) compared to the S(4),S(6) and S(5),S(5) pairs (3.96 Å and 4.21 Å respectively). The region of the spanning ligands, the least sterically crowded in the complex, can readily accommodate the closer approach of the S(2),S(3) atom pairs,
Figure 3.9. Top: A view of the [Mo₂O(S₂CNEt₂)₆]⁺ ion along the Mo···Mo vector. Atoms with and without asterisks refer to those of different asymmetric units (atom numbers are unbracketed for clarity).

Bottom: A schematic representation of the above; the dithiocarbamato-ligands of the two asymmetric units are shown as solid and dashed lines.
thereby reducing steric interactions between the equatorial ligands.

The equatorial ligands of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]^+\) are 'staggered' with respect to one another as indicated in Figure 3.9. This allows the ethyl substituents of these ligands to occupy (relatively) sterically uncrowded positions between the equatorial planes. The \textit{syn-} conformation of the equatorial ligand substituents is dictated by intermolecular forces, and represents an effective reduction in intermolecular steric interaction with minimal intramolecular interaction (see Figure 3.13). Nevertheless, the \textit{syn-} conformation of the equatorial ligands results in several non-bonded contacts which are significantly shorter than the van der Waals contact distance\(^{298}\) (4.0 Å for methyl-methyl contacts). These contacts are between atoms \(\text{C}(12)\cdots\text{C}(13), 3.39(1)\) Å; \(\text{C}(14)\cdots\text{C}(15), 3.35(1)\) Å; \(\text{C}(11)\cdots\text{C}(12)^* , 3.86(1)\) Å; \(\text{C}(13)\cdots\text{C}(15)^*, 3.65(1)\) Å; \(\text{C}(14)\cdots\text{C}(14)^* 3.85(1)\) Å (* = atom of adjoining asymmetric unit).

The structure of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]^+\) is unique in \(\mu\)-oxo(dithiocarbamato)molybdenum chemistry, it being the first dimeric seven coordinate complex of this type and the first dithiocarbamato-molybdenum complex to exhibit \(\mu\)-oxo-bridging in the absence of terminal oxo-ligation. Previously,\(^{61-63}\) all \(\mu\)-oxo(dithiocarbamato)molybdenum complexes have exhibited terminal oxo-ligation and coordination numbers of six or less. Indeed, all \(\mu\)-oxo-complexes of molybdenum, with the exception of \([\text{Mo}\{\text{HB}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}\{\text{NO}\}_2\text{O}].\(^{55}\) contain terminal oxo-ligation.\(^{56-74}\) In these complexes the \(\text{Mo}_2\text{O}_2(\mu-O)\) unit predominates,\(^{58-74}\) the terminal oxo-groups being \(\sigma^2\)- or \(\tau\)- (with respect to the \(\mu\)-oxo bridge) depending on the other ligands involved.

One atom bridged PB complexes are restricted to the structural types shown in Figure 3.10, where bridge formation ensures that the metal coordination geometry remains relatively undisturbed.\(^{58,59,299-306}\)
The complex $[\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]^+$ is the first $\mu$-oxo-bridged molybdenum complex of structural Type A. Previously, only one seven-coordinate $\mu$-oxo-complex of molybdenum, the peroxo-complex $[[\text{MoO}(\text{O}_2)]_2(\text{H}_2\text{O})}_2\text{O}]^{2-}$, had been structurally characterised.\textsuperscript{58,59} In this case, the $\mu$-oxo-ligand is a shared equatorial atom (Type B structure); the Mo-O bond length is 1.93 Å and the Mo-\(\mu\)-Mo angle is severely bent (148.6° for pyH\textsuperscript{+} salt,\textsuperscript{58} 136.1° for K\textsuperscript{+} salt\textsuperscript{59}). The $\mu$-oxo- complexes of other seven-coordinate transition metal complexes do, however, exhibit Type A geometry. These complexes,\textsuperscript{299-305} the majority of which contain titanium,\textsuperscript{301-302} display a near linear (> 167.6°) $\mu$-oxo-bridge and eclipsed pentagonal girdle atoms. Axially bridged PB complexes of molybdenum are preceded, as the Type A fluoro-bridged $[[\text{MoO}(\text{O}_2)(\text{dipic})]_2\text{F}]^{304}$ and sulphido-bridged $[[\text{Mo}(\text{CN})_6]_2\text{S}]^{6+305}$ complexes have been structurally characterised.

The tetrafluoroborate ion in $[\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]\text{BF}_4$ is disordered and has been modelled by two equally contributing superimposed molecular geometries. The geometries of these contributing forms are severely distorted from ideal tetrahedral geometries, a result of the disorder.
and the high degree of thermal motion within the BF$_4^-$ molecular ion (Table 3.15). Figure 3.11 displays one of the contributing BF$_4^-$ structures along with the complete model of the disorder.

![Figure 3.11. a) Perspective view of one contributing form of the BF$_4^-$ disorder; b) complete model of the BF$_4^-$ ion in [Mo$_2$O(S$_2$CNEt$_2$)$_6$]BF$_4$. Ellipsoids represent 50% probability.](image)

The packing of the ions within the unit cell can be seen in Figure 3.12. A stereoscopic view of the unit cell contents is given in Figure 3.13. The influence of the crystal packing on the dithiocarbamato-ligand substituent conformations is readily appreciated upon inspection of Figure 3.13. Only one intermolecular contact is significantly shorter than the van der Waals contact distance of 3.4 Å, i.e. C(11)···F(1), 3.20 Å. Other close contacts involving the BF$_4^-$ ion are: C(7)···F(2B), 3.35 Å; C(4)···F(2), 3.40 Å; C(10)···F(2), 3.40 Å; C(14)···F(2B), 3.41 Å; C(12)···F(1B), 3.45 Å.
Figure 3.12. Packing diagram for the monoclinic \( C2/c \) unit cell of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]\text{BF}_4\). The hydrogen atoms have been omitted.
3.3.3 On the Electronic Structure and Biological Relevance of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\text{BF}_4\).

The degree of oxidation state delocalization is an important feature of mixed oxidation state compounds and has a strong influence on their physical properties. Robin and Day\textsuperscript{258} have also used it as a criterion for the classification of such compounds. Modifications to this scheme have been recently proposed by Piepho, Krausz and Schatz,\textsuperscript{261} who have incorporated vibronic coupling into the theoretical treatment of mixed oxidation state compounds. One modification notes that compounds containing crystallographically equivalent metal centres are not necessarily delocalised but may vary from completely delocalised to completely localised depending upon the magnitude of vibronic coupling. The modified Robin and Day scheme recognises the following classes of dinuclear compounds.
Class I, $\alpha = 0^+$. The oxidation states are strongly localised on crystallographically distinct metal sites and the properties of the compounds are essentially a superposition of those of the constituent metal centres. The intervalence transfer (IT = $[a,b] \rightarrow [b,a]^+$) bands are of high energy ($> 27000 \text{cm}^{-1}$) reflecting the gross structural or electronic difference of the constituent metal centres.

Class II $0 < \alpha < 0.707$. The metal ions are in crystallographically similar or identical coordination environments and possess distinguishable although slightly delocalised oxidation states. The compounds exhibit IT bands in the visible region and spectroscopic properties which exhibit some characteristics of the constituent ions.

Class III-A, $\alpha = 0.707$. The metal ions are crystallographically indistinguishable and oxidation state delocalization is complete. The compounds exhibit low energy absorption bands associated with the mixed oxidation state formulation and other properties which are distinctly different from those of the constituent ions.

Classes II and III correspond to the localised weak interaction and delocalised strong interaction classes proposed by Allen and Hush.\(^{259}\)

The properties of $[\text{Mo}_2 \text{O(S}_2\text{CNEt}_2)_6] \text{BF}_4$ support its classification as a Class III-A compound in which the molybdenum atoms possess an average oxidation state of 4.5. In the crystal structure of the compound, the equivalence of the molybdenum sites is consistent with, but not conclusive

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\(^{+}\) The oxidation state delocalization parameter, $\alpha$, is a measure of the orbital overlap in the ground state of the complex $\psi_g = (1 - \alpha^2)^{1/2} \phi_a + \alpha \phi_b$, where $\psi_g$ is the ground state wave function and $\phi_a$, $\phi_b$ are the wave functions for the mixed oxidation state components of the molecular orbital system. $\alpha$ is thus a measure of the mixing of the metal oxidation states.

\(^{\dagger}\) In the $[a,b]$ state the metal ions in coordination sites A and B have oxidation states of a and b respectively. In the $[b,a]$ state these sites contain metal ions of oxidation states b and a respectively.
evidence for, a Class III-A classification of the complex; a Class I complex can be clearly discounted. The thermal motion of the atoms within the coordination sphere is sufficiently large (root-mean-square amplitude range, 0.15-0.24 Å) to conceal the presence of a Class II molybdenum site inequivalence. Since the metal-ligand bond lengths associated with localised PB Mo(IV) and Mo(V) sites are likely to differ by less than 0.1 Å, the smearing amplitude of the coordination sphere atoms in a Class II system undergoing rapid IT would also be less than 0.1 Å. This value is much smaller than the overall root-mean-square amplitudes of these atoms and hence this Class II formulation is also consistent with the crystallographic result. Nevertheless, several features of the structure favour the strict metal equivalence of a Class III-A formulation. Firstly, the PB coordination geometry of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]^+\) and the lack of structurally characterised PB Mo(V) complexes suggests that the coordination spheres of localised Mo(IV) and Mo(V) ions would show a greater structural disparity than is consistent with the thermal parameters of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]^+\). Secondly, the thermal parameters of the complex are very similar to those reported for mononuclear dithiocarbamatomolybdenum complexes in which unusual dynamic motion is absent, i.e. the thermal motion of the complex may be readily accounted for by the 'natural' vibration of the constituent atoms alone. In particular, the thermal parameters of the molybdenum and oxygen atoms show no unusual features. The symmetrical packing of the BF\(_4^-\) counterions with respect to the molybdenum centres in \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]^+\) suggests equivalent metal charge densities, in further support of a Class III-A formulation.

A low energy absorption band is a conspicuous feature of the electronic spectra of Class II and Class III-A compounds; \([\text{Mo}_2\text{O}(\text{S}_2\text{CNET}_2)_6]\text{BF}_4\) is no exception and exhibits a well defined absorption band at 1310 nm (7630 cm\(^{-1}\)). This band, shown in Figure 3.14, may be
Figure 3.14. The near-infrared spectra of a) \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\)\(\text{BF}_4\) in acetonitrile; b) \(\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6\) in 0.1 M \(\text{Et}_4\text{NCIO}_4\)/acetonitrile (from Section 3.2.3.4) and c) solution a) following aerial oxidation.

assigned to an electronic transition uniquely associated with the mixed oxidation state complex, as it is absent from the spectra of the one electron reduction product, presumably \(\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6\), and air oxidized solutions of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\)\(\text{BF}_4\).

Since the origin of the 1310 nm band is determined by the ground and excited electronic states of the complex, its properties provide valuable information on the degree of oxidation state delocalization. In a Class II system, the band would represent the intervalence transfer (IT) transition, shown in Equation (25).
Here the optical transition occurs instantaneously on the vibrational timescale resulting in Mo(IV) and Mo(V) ions in the equilibrium coordination spheres of the other oxidation state. Thus the energy between the ground and excited mixed oxidation states, $E_{op}$, is determined by the excess vibrational energy content of the excited state over the ground state. A theoretical treatment of Class II IT bands has been developed by Hush and has been verified by many studies of localised Class II Ru(II,III) complexes. For a Class III-A system, the band would represent an electronic transition between the ground and excited state molecular orbitals of a completely delocalised $[4\frac{1}{2},4\frac{1}{2}]$ complex. Hush's theory is inappropriate to the description of bands of this origin.

The properties of the 1310 nm band deviate considerably from those predicted by Hush for Class II systems, clearly supporting the alternative Class III-A formulation. According to Hush, the lower limit for the bandwidth of a Class II IT band (at 300°K) is given by Equation (26), where $v_{\text{max}}$ is the energy of the IT band and $\Delta v_{\frac{1}{2}}$ is the bandwidth at half height.

$$v_{\text{max}} = (\Delta v_{\frac{1}{2}})^2/2310$$

Since $v_{\text{max}}$ is 7630 cm$^{-1}$, the calculated value for $\Delta v_{\frac{1}{2}}$ is 4200 cm$^{-1}$, very much larger than the observed value of 1390 cm$^{-1}$. Also, the energy of the IT band in Class II complexes is predicted to be solvent dependent as both inner sphere ($\lambda_i$) and outer sphere (solvent) vibrational modes ($\lambda_o$) contribute to the excess vibrational energy of the IT excited state. For a symmetric (A = B) dinuclear complex, $E_{op}$, is given by Equation (27), where $m$ is the extent

$$E_{op} = \lambda_i + \lambda_o = \lambda_i + (me)^2\left(\frac{a_1}{2} + \frac{a_2}{2} - \frac{1}{d}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)$$
of charge transfer in the IT process, e is the unit electron charge, 
a_1 and a_2 are the nuclear radii of the electron donor and acceptor sites, 
d is the internuclear site separation and D_{opt} and D_s are the optical and 
static dielectric constants of the medium. Equation (27) predicts a 
linear variation of E_{opt} with changing solvent dielectric properties 
\left(\frac{1}{D_{opt}} - \frac{1}{D_s}\right). However, this solvent dependence may break down if the IT 
band is sufficiently small (< \alpha. 3.4 kcal/mole). In such a case, 
the relaxation time associated with solvent reorganization is slower than 
the rate of electron transfer (\alpha. 10^{10} \text{ s}^{-1} at room temperature) and the 
solvent molecules occupy an equilibrium solvent sphere around the 
complex. At these levels, a localised vs. delocalised description 
becomes a matter of definition, the usual criterion for delocalization 
being that the lifetime of a particular mixed oxidation state is shorter 
than the vibrational timescale (\alpha. 10^{-13} \text{ s}). In the near-infrared 
spectra of [Mo_2O(S_2CNEt_2)_6]BF_4, summarised in Table 3.5, the insensitivity 
of \nu_{max} to the dielectric properties of the medium strongly suggests that 
the charge distribution is symmetrical and essentially the same in the 
ground and excited states, as expected for a Class III-A system. 
Certainly, the rate of electron transfer between sites exceeds \alpha. 10^{10} \text{ s}^{-1}.

The electronic spectrum of the compound in the visible region also 
supports a Class III-A formulation, as the intense absorption bands at 
677(2440), 497(19200), 440(14400) and 410 nm (13400 1cm^{-1}mole^{-1}) cannot 
be attributed to discrete Mo(IV) and Mo(V) centres. The similarity of 
the spectra of [Mo_2O(S_2CNEt_2)_6]^+ and Mo_2O(S_2CNEt_2)_6 suggest the 
presence of a molecular orbital system which is almost identical for 
both complexes.

A Class III-A formulation is also favoured by the very nature of 
[Mo_2O(S_2CNEt_2)_6]^+. The short metal-metal distance and the participation 
of the oxygen p-orbitals in Mo-O-Mo \pi-bonding would facilitate strong
metal interactions similar to those observed in other second and third row transition metal μ-oxo-complexes, e.g. in the μ-oxo-Ru(III) complexes \([L_2XRuORuXL_2]^{n+}\) (where \(L = \text{bipy, phen}; \ X = \text{Cl}^-, \text{NO}_2^-, \text{H}_2\text{O}\)) and the mixed oxidation state complex \([\text{bipy}_2\text{ClRuORuClbipy}_2]^3+\).\(^{315}\)

The crystallographic and electronic spectral properties of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\) are strikingly similar to those of the well known Creutz-Taube (C-T) complex, \([\text{(NH}_3)_5\text{RupyzRu(NH}_3)_5]^5+.\(^{316-320}\) Both these complexes possess crystallographically equivalent metal centres and exhibit near-infrared spectra which are atypical of Class II systems. Their visible spectra are also distinctly different from those of their constituent ions. The C-T complex has been extensively studied but its degree of oxidation state delocalization is still an issue of some controversy; recent investigations tend to favour a Class III-A formulation.\(^{317-320}\) In view of the difficulty experienced in the formulation of the C-T complex and the (to date) limited studies of the similar \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\) complex, the Class III-A formulation of the molybdenum complex must be considered tentative. Further investigations of the mixed oxidation state aspect of \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\) by single crystal e.s.r. and resonance Raman\(^{320}\) techniques are in progress. The Mo(IV,IV) complex \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]\) also warrants further investigation and should be readily isolable from solution upon its bulk electrolytic preparation from \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\). Since it is likely to be diamagnetic, n.m.r. investigations as well as interesting comparative studies with \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\) should be possible.

The \([\text{Mo}_2\text{O}(\text{S}_2\text{CNEt}_2)_6]^+\) complex is a rare mixed oxidation state oxo- and sulphur-donor ligand complex of molybdenum, the related complex \([\text{Mo}_2\text{O}_3(\text{S}_2\text{CNEt}_2)_4]^-\) being the only previously reported\(^6\) example of this type. The \([\text{Mo}_2\text{O}_3(\text{S}_2\text{CNEt}_2)_4]^-\) complex was isolated in a mixed crystal of \((\text{H}_2\text{O})[\text{Mo}_2\text{O}_3(\text{S}_2\text{CNEt}_2)_4]\) and was characterised by x-ray crystallography
and single crystal e.s.r. The e.s.r. spectra of the compound displays molybdenum hyperfine splitting consistent with the presence of localised Mo(V) centres in the anion (also suggested by the unsymmetrical packing of the H₂O₂⁺ ions with respect to [Mo₂O₃(S₂CNEt₂)₄]⁻). This result provides unprecedented evidence for the exhibition of 'mononuclear' Mo(V) e.s.r. signals by dinuclear centres such as those proposed for certain molybdoenzymes.¹⁹ However, electrochemical studies suggest that this anion is only transiently stable⁹⁵⁻¹⁰¹ and hence (H₂O₂)[Mo₂O₃(S₂CNEt₂)₄] represents a fortuitous isolation and stabilization of the anion in a host lattice. Also, further study of this anion has been inhibited by preparative difficulties.³²¹

In contrast, [Mo₂O(S₂CNEt₂)₆]BF₄ is a pure, stable and preparatively reproducible mixed oxidation state oxo- and sulphur-donor ligand compound of molybdenum. The stability of the complex may be explained in part by the high sulphur content of the coordination sphere as the stability of transient electrochemically produced Mo(IV,V) complexes has been observed to increase with increasing sulphur coordination.⁹⁵⁻⁹⁹ The high sulphur content of molybdoenzyme active sites may thus favour the formation of mixed oxidation state centres during catalysis; the isolation of [Mo₂O₃(S₂CNEt₂)₄]⁻ and [Mo₂O(S₂CNEt₂)₆]⁺ shows that such centres are certainly capable of existence should the molybdenum atoms in molybdoenzymes be closely associated. It may also be noted that [Mo₂O(S₂CNEt₂)₆]⁺ is formed from, and is oxidised to, two mononuclear metal centres, similar to Wentworth's¹⁹ proposed formation and oxidation of dinuclear enzyme centres.

The [Mo₂O(S₂CNEt₂)₆]⁺ complex appears to be oxidation state delocalised and if so the interaction of the unpaired electron with both molybdenum atoms may be observed in the single crystal e.s.r. spectra. While such spectra would be inconsistent with those of the molybdoenzymes, they would represent the first single crystal e.s.r. measurements of such a delocalised Mo(IV,V) system.
CHAPTER FOUR

TUNGSTEN CARBONYL COMPLEXES WITH SULPHUR-, NITROGEN- AND PHOSPHORUS-DONOR COLIGANDS

4.1 INTRODUCTION

The formation of enzyme-bound intermediates is a postulate of many proposed nitrogenase mechanisms.\(^{31-34,144-147}\) Although the nature of these intermediates is largely unknown there is good evidence to support the involvement of diimine and hydrazine intermediates in biological dinitrogen fixation.\(^{34-36}\) A hydrazine intermediate is further supported by the identification of hydrazine as a substrate of nitrogenase.\(^{34,35}\) The investigation of diimine, hydrazine and related N-donor ligand complexes of molybdenum and tungsten is thus of considerable interest.

Although possessing a similar descriptive chemistry, analogous complexes of molybdenum and tungsten may differ markedly in stability, with those of tungsten being generally more stable (both thermodynamically and kinetically).\(^{32,155}\) This stability difference is reflected in the properties of individual complexes\(^{322}\) as well as in the reactivity of these metals in biological and model systems. The reactivity difference of molybdenum and tungsten centres is highlighted by a comparison of the molybdoenzymes and their tungsten-substituted analogues.\(^{323-326}\) The catalytic activity of the molybdoenzymes suggests that molybdenum centres, through the limited stabilization of substrate intermediates, possess a lability which is essential for catalysis.
On the other hand, the inactivity of the 'tungstenzymes' suggests that tungsten centres form robust metal complexes possibly at intermediate stages of catalysis. In model systems also, tungsten is observed to stabilise highly reactive reduced dinitrogen intermediates, a property which makes the study of tungsten chemistry a valuable adjunct to nitrogenase model studies.

This chapter describes the preparation and characterization of the tungsten complexes \( W(S_2CNR_2)_2(CO)_3 \) and \( \sigma \delta-W(S_2CNR_2)_2(CO)_2 \) (hereafter \( R = Me, Et, \) unless specified) and their reactions with a variety of \( N- \) and \( P- \) donor ligands and acetylene. The redox reactions of the complex \([W(S_2CNEt_2)_2(CO)_2]_2-\mu-N_2H_4\) was also investigated in an attempt to isolate stabilised reaction products. During the course of this work the preparations of \( W(S_2CNR_2)_2(CO)_3 \) and \( W(S_2CNMe_2)_2(CO)_2 \) were independently reported. 

The Chemistry of \( \sigma \delta-Mo(S_2CNEt_2)_2(CO)_2 \).

A variety of complexes of relevance to nitrogenase catalysis have been prepared from the coordinatively unsaturated 16-electron complex \( \sigma \delta-Mo(S_2CNEt_2)_2(CO)_2 \). The reported reactions of this complex are summarised below.

\[
\begin{align*}
\text{Mo}(S_2CNEt_2)_2(CO)_2 + L & \rightarrow \text{Mo}(S_2CNEt_2)_2(CO)_2L \\
L &= CO, PPh_3, NH_2NMe_2, NH_3, NH_2NHCOPh, py, NH_2HSO_2PhMe
\end{align*}
\]

\[
\begin{align*}
2\text{Mo}(S_2CNEt_2)_2(CO)_2 + B & \rightarrow [\text{Mo}(S_2CNEt_2)_2(CO)_2]_2-\mu-B \\
B &= N_2H_4, \text{en, NH}_2\text{NHMe, pyrazine}
\end{align*}
\]

\[
\begin{align*}
\text{Mo}(S_2CNEt_2)_2(CO)_2 + L & \rightarrow \text{Mo}(S_2CNEt_2)_2(CO)L + CO \\
L &= RC_2R' \ (R = R' = H, \text{CO}_2\text{CH}_3 \text{ or Ph}; \ R = H, R' = \text{CH}_3, \text{Ph or CO}_2\text{CH}_3; \ R = \text{CH}_3, R' = \text{Ph}) \text{ or dppe}
\end{align*}
\]
\[
Mo(S_2CNEt_2)_2(CO)_2 + 2L \rightarrow Mo(S_2CNEt_2)_2L_2 + 2CO
\]  
(31)

\[
L = NO,^3^3^3 ONPh,^3^3^4 EtO_2CN_2CO_2Et, RC_2R' (R, R' as in Equation (30)) and L_2 = EtO_2CN_2CO_2Et^1^4^6
\]

\[
Mo(S_2CNEt_2)_2(CO)_2 + 2ArN_3 \rightarrow Mo(NAV)_2(S_2CNEt_2)_2 + 2CO + 2N_2
\]  
(32)  

\[
Mo(S_2CNEt_2)_2(CO)_2 + S_8 \rightarrow [Mo(S_2CNEt_2)_2(S_2O)]_2 + \text{others}
\]  
(33)  

\[
Mo(S_2CNEt_2)_2(CO)_2 + MoO_2(S_2CNEt_2)_2 \rightarrow 2MoO(S_2CNEt_2)_2 + 2CO
\]  
(34)  

\[
Mo(S_2CNEt_2)_2(CO)_2 + O_2NPh \rightarrow MoO(ONPh)(S_2CNEt_2)_2 + 2CO
\]  
(35)

The reaction of \(cis\)-\(Mo(S_2CNEt_2)_2(CO)_2\) with various N-donor ligands (Equations 28 and 29) results in the formation of a series of mononuclear and dinuclear complexes,\(^3^3^1\) including the interesting \(\mu\)-hydrazine complex \([\text{Mo}(S_2CNEt_2)_2]_2-\mu-N_2H_4\).\(^3^3^1,^3^3^2\) The attempted oxidation of the hydrazine ligand in this complex resulted in decomposition, possibly due to the high instability of the diimine complex initially formed.\(^3^3^1\) The oxidation of other chromium, molybdenum and tungsten hydrazine complexes has been reported to yield diimine complexes, however, the molybdenum species are very reactive (stability order \(W>Cr>>Mo\)).\(^3^3^5-^3^3^8\) The reaction of \(cis\)-\(Mo(S_2CNEt_2)_2(CO)_2\) with acetylene and its substituted analogues (Equations 30 and 31) gives products of two types,\(^1^4^6\) \(Mo(S_2CNEt_2)_2(CO)(RCR')\) and \(Mo(S_2CNEt_2)_2(RCR')_2\). Spectral data suggests that RCR' acts as a four electron donor in the former complexes and as a three electron donor in the latter complexes. Also, \(cis\)-\(Mo(S_2CNEt_2)_2(CO)_2\) readily binds the diimine ligand \(EtO_2CN_2CO_2Et\) to yield the complexes \(Mo(S_2CNEt_2)_2(EtO_2CN_2CO_2Et)_n\) \((n = 1,2;\) Equation 31); upon hydrolysis these compounds yield the hydrazine, \(EtO_2CNHNHCO_2Et\), and \(MoO(S_2CNEt_2)_2\) and \(cis\)-\(MoO_2(S_2CNEt_2)_2\), respectively.\(^1^4^6\)
4.2 EXPERIMENTAL SECTION

4.2.1 Materials and Methods

W(CO)₆ (Fluka Chemicals, Switzerland), Na₅S₂CNMe₂·2H₂O (Aldrich Chemicals, Milwaukee) and Na₅S₂CNEt₂·3H₂O (Eastman Chemicals, Rochester) were used without further purification. The method of Friedman et al. was used to prepare p-toluenesulphonylhydrazine. All manipulations were performed under an atmosphere of dinitrogen using dried deoxygenated solvents. ¹H and ¹³C-{¹H} n.m.r. spectra were recorded in dry deoxygenated solvents under dinitrogen. Tris(acetylacetonato)chromium(III) (30 mg/mL) was added to ¹³C-{¹H} n.m.r. samples as a shiftless paramagnetic relaxation reagent. Carbonyl resonances remained unobserved with pulse delays of up to 20 s in the absence of this reagent. Electronic spectra were recorded under the following anaerobic conditions: cis-W(S₂CNR₂)₂(CO)₂ in dichloromethane and tetrahydrofuran; W(S₂CNR₂)₂(CO)₃ in dichloromethane (deoxygenated and saturated with CO).

4.2.2 Preparation of Complexes

Tricarbonyl(1,1-dimethylthiocarbamato)tungsten(II)

W(CO)₆ (1.5 g, 4.3 mmol) was suspended in dichloromethane (25 mL) at -78°C (acetone/solid CO₂). Dibromine (0.22 mL, 4.3 mmol) was added by injection and the mixture stirred magnetically. Upon slight warming a vigorous gas evolution occurred and a red-brown solution was formed. This was evaporated (at room temperature) to dryness on a vacuum line and the residue (WBr₂(CO)₄) dissolved in methanol (15 mL). Gas evolution took place and a red solution was obtained. This was filtered directly into a stirred solution of Na₅S₂CNMe₂·2H₂O (1.6 g, 8.9 mmol) in methanol (15 mL). The crude brown solid was filtered off, washed with methanol (2x15 mL) and dried. Orange crystals were obtained.
upon recrystallisation from dichloromethane/methanol. The yield was 1.2 g (55%).

**Anal.** Calcd. for C_{9}H_{12}N_{2}O_{3}S_{4}W: C, 21.3; H, 2.4; N, 5.5; S, 25.2.
Found: C, 21.5; H, 2.6; N, 5.3; S, 25.3%.

cis-Dicarbonylbis(N,N-dimethyldithiocarbamato)tungsten(II)

W(S_{2}CNMe_{2})_{2}(CO)_{3} (0.15 g, 0.3 mmol) in methanol (15 mL) was refluxed and stirred for 45 min. On cooling a dark green crystalline solid was obtained which was filtered off, washed with methanol and dried under vacuum. The yield was 0.13 g (90%).

**Anal.** Calcd. for C_{9}H_{12}N_{2}O_{3}S_{4}W: C, 20.0; H, 2.5; N, 5.8; S, 26.7.
Found: C, 19.5; H, 2.8; N, 5.7; S, 26.6%.

Tricarbonylbis(N,N-diethyldithiocarbamato)tungsten(II)

W(CO)_{6} (4 g, 11 mmol) in dichloromethane (60 mL) at -78°C was treated with dibromine (0.58 mL, 11 mmol) and a procedure identical to that given for the dimethyldithiocarbamato-analogue was followed. The WBr_{2}(CO)_{4} was dissolved in methanol (30 mL) and treated with a solution of NaS_{2}CNEt_{2}.3H_{2}O (5.17 g, 23 mmol) in methanol (30 mL). The yield of orange crystalline product was 4.5 g (73%).

**Anal.** Calcd. for C_{13}H_{20}N_{2}O_{3}S_{4}W: C, 27.7; H, 3.6; N, 5.0; S, 22.7.
Found: C, 27.7; H, 3.8; N, 4.9; S, 22.5%.

cis-Dicarbonylbis(N,N-diethyldithiocarbamato)tungsten(II)

W(S_{2}CNEt_{2})_{2}(CO)_{3} (0.80 g, 1.4 mmol) was refluxed and stirred in methanol (15 mL) for 1 hr. On cooling a purple crystalline solid was obtained and was isolated as for the dimethyldithiocarbamato-analogue. The yield was 0.71 g (94%).

**Anal.** Calcd. for C_{12}H_{20}N_{2}O_{3}S_{4}W: C, 26.9; H, 3.8; N, 5.2; S, 23.9.
Found: C, 26.7; H, 3.9; N, 5.3; S, 24.1%.
µ-Hydrazine-bis [dicarbonylbis(N,N-dimethyldithiocarbamato)tungsten(II)]

W(S₂CNMe₂)₂(CO)₃ (0.1 g, 0.2 mmol) in dichloromethane (10 mL) was treated with hydrazine hydrate (0.05 g, 1 mmol) in 1:1 dichloromethane/methanol (15 mL). The orange solution was allowed to stand for 4 hr whereupon the product precipitated. The compound was filtered off, washed with methanol and dried overnight. More solid could be obtained from the filtrate by the addition of methanol. The yield was 0.082 g (85%).

Anal. Calcd. for C₁₅H₂₉N₅O₄S₃W₂: C, 19.4; H, 2.8; N, 8.4; S, 25.8.
Found: C, 19.2; H, 2.8; N, 8.3; S, 25.8%.

µ-Hydrazine-bis [dicarbonylbis(N,N-diethyldithiocarbamato)tungsten(II)]

This complex was prepared by a procedure identical to that given for the dimethyldithiocarbamato-analogue, and was precipitated by the addition of methanol as deep-red crystals. The yield was 79%.

Anal. Calcd. for C₂₁H₄₄N₆O₄S₃W₂: C, 26.1; H, 4.0; N, 7.6; S, 23.2.
Found: C, 25.9; H, 4.1; N, 7.5; S, 23.3%.

µ-Ethylenediamine-bis [dicarbonylbis(N,N-dimethyldithiocarbamato)tungsten(II)]

A suspension of W(S₂CNMe₂)₂(CO)₂ (0.10 g, 0.21 mmol) in dichloromethane (2 mL) was treated dropwise with ethylenediamine (0.024 g, 0.4 mmol) to precipitate a yellow solid. Recrystallisation of this solid from dichloromethane/methanol yielded the orange complex, which was filtered, washed with methanol and dried under vacuum. The yield was 0.09 (80%).

Anal. Calcd. for C₁₅H₃₂N₅O₄S₃W₂: C, 21.2; H, 3.2; N, 8.2; S, 25.1.
Found: C, 21.1; H, 3.2; N, 8.1; S, 25.4%.

µ-Ethylenediamine-bis [dicarbonylbis(N,N-diethyldithiocarbamato)tungsten(II)]

A suspension of W(S₂CNEt₂)₂(CO)₂ (0.12 g, 0.22 mmol) in dichloromethane (3.5 mL) was treated dropwise with neat ethylenediamine (0.024 g, 0.4 mmol) to give a clear red solution. This was filtered and methanol (8 mL) was added slowly to give the red product which was washed with methanol and vacuum dried. The yield was 0.08 g (63%).
Anal. Calcd. for C_{27.5}H_{13}N_{6}O_{4}S_{8}W_{2}: C, 26.2; H, 4.1; N, 6.7; S, 20.4. Found: C, 25.9; H, 4.4; N, 6.7; S, 20.1%. The analysis indicates 1.5 molecules of dichloromethane of crystallisation.

Dicarbonylbis(N,N-dimethyldithiocarbamato)methylhydrazinetungsten(II)

W(S_{2}CNMe_{2})_{2}(CO)_{3} (0.10 g, 0.2 mmol) was dissolved in dichloromethane (3 mL) and treated with methylhydrazine (0.05 g, 1 mmol). After occasional swirling for 30 minutes, ether (5 mL) was added to precipitate the product. After recrystallisation from dichloromethane/ether (containing a few drops of methylhydrazine), the orange solid was filtered off, washed with ether (containing a few drops of NH_{2}NHMe) and dried under vacuum for 1 hr. The yield was 0.084 g (80%).

Anal. Calcd. for C_{9.2}H_{10.5}Cl_{0.5}N_{4}O_{2}S_{4}W: C, 20.2; H, 3.4; N, 10.2; S, 23.4. Found: C, 19.8; H, 3.3; N, 10.2; S, 23.0%. The analysis indicates 0.25 molecules of dichloromethane of crystallisation.

Dicarbonylbis(N,N-diethyldithiocarbamato)methylhydrazinetungsten(II)

A solution of W(S_{2}CNEt_{2})_{2}(CO)_{3} (0.12 g, 0.22 mmol) in dichloromethane (1.5 mL) was treated with methylhydrazine (0.06 mL, 1.3 mmol) and the solution allowed to stand 1 hr. Addition of ether (8 mL) precipitated the red-orange product. This was recrystallised from dichloromethane/ether containing a few drops of methylhydrazine. The product was washed with ether. The yield was 0.1 g (80%).

Anal. Calcd. for C_{13}H_{26}N_{4}O_{2}S_{4}W: C, 26.8; H, 4.5; N, 9.6; S, 22.0. Found: C, 26.9; H, 4.6; N, 9.5; S, 21.9%.

Dicarbonylbis(N,N-dimethyldithiocarbamato)(N,N-dimethylhydrazinetungsten(II)

A suspension of W(S_{2}CNMe_{2})_{2}(CO)_{2} (0.10 g, 0.21 mmol) in dichloromethane (3 mL) was treated dropwise with NH_{2}NMe_{2} (0.08 g, 1 mmol) to form a red solution. Addition of n-hexane precipitated the orange solid which
was filtered and washed with n-hexane. Relatively rapid decomposition of the product prevented elemental analysis.

**Dicarbonylbis(N,N-diethylldithiocarbamato)(N,N-dimethyldimethyldihydrazine)tungsten(II)**

This complex was prepared by a procedure identical to that given for the dimethyldithiocarbamato-analogue. Decomposition again prevented elemental analysis.

**Benzoylhydrazinedicarbonylbis(N,N-dimethyldithiocarbamato)tungsten(II)**

A suspension of \(W(S_2CNMe_2)_2(CO)_2\) (0.10 g, 0.21 mmol) in dichloromethane (2 mL) was treated with benzoylhydrazine (0.044 g, 0.3 mmol) in dichloromethane (2 mL) to give an orange solution. After filtration, n-hexane was added to yield the orange complex. The yield was 0.093 g (72%).

**Anal.** Calcd. for \(C_{15.5}H_{21}ClN_4O_3S_4W\): C, 28.0; H, 3.2; N, 8.4; S, 19.3.

Found: C, 27.9; H, 3.2; N, 8.3; S, 19.5%. The analysis indicates 0.5 molecules of dichloromethane of crystallisation.

**Benzoylhydrazinedicarbonylbis(N,N-diethyldithiocarbamato)tungsten(II)**

This complex was prepared by a procedure identical to that given for the dimethyldithiocarbamato-analogue. The yield was 80%.

**Anal.** Calcd. for \(C_{19.5}H_{29}ClN_4O_3S_4W\): C, 32.5; H, 4.1; N, 7.8; S, 17.8.

Found: C, 33.3; H, 4.1; N, 7.8; S, 17.9%. The analysis indicates 0.5 molecules of dichloromethane of crystallisation.

**Dicarbonylbis(N,N-dimethyldithiocarbamato)(p-toluenesulphonyldihydrazine)tungsten(II)**

This complex was prepared by a procedure identical to that given for the diethyldithiocarbamato-analogue below. The yield was 78%.

**Anal.** Calcd. for \(C_{15}H_{22}N_4O_4S_5W\): C, 26.4; H, 3.2; N, 8.2; S, 24.1.

Found: C, 26.6; H, 3.3; N, 8.1; S, 23.8%.
Dicarbonylbis(N,N-diethyldithiocarbamato)(p-toluenesulphonylhydrazine)tungsten(II)

A solution of \( W(S_2CNEt_2)_2(CO)_3 \) (0.10 g, 0.2 mmol) in dichloromethane (3 mL) was treated with NH\(_2\)NHSO\(_2\)PhMe (0.06 g, 0.3 mmol) in dichloromethane (2 mL). n-Hexane was added to precipitate the complex, which after filtration was washed with n-hexane and dried. The yield was 0.106 g (80%).

**Anal.** Calcd. for C\(_{19}\)H\(_{30}\)N\(_1\)O\(_i\)S\(_5\)W: C, 31.5; H, 4.2; N, 7.7; S, 22.1. Found: C, 31.5; H, 4.0; N, 7.3; S, 21.5%.

Amminedicarbonylbis(N,N-dimethyldithiocarbamato)tungsten(II)

Ammonia was passed through a solution of \( W(S_2CNMe_2)_2(CO)_3 \) (0.1 g, 0.2 mmol) in dichloromethane (4 mL) for a period of 10 min. The resulting orange crystalline solid was washed with methanol and dried under vacuum. The yield was 0.068 g (70%).

**Anal.** Calcd. for C\(_{8.2}\)H\(_{15}\)sCl\(_0\).sN\(_3\)O\(_2\)S\(_4\)W: C, 19.1; H, 3.0; Cl, 3.1; N, 8.1; S, 24.7. Found: C, 19.1; H, 3.0; Cl, 3.4; N, 8.1; S, 25.1%. The analysis indicates 0.25 molecules of dichloromethane of crystallisation.

Amminedicarbonylbis(N,N-diethyldithiocarbamato)tungsten(II)

This complex was prepared by a method analogous to that given for the dimethyldithiocarbamato- complex. The yield was 73%.

**Anal.** Calcd. for C\(_{12.2}\)H\(_{23.5}\)sCl\(_9\).sN\(_3\)O\(_2\)S\(_4\)W: C, 25.6; H, 4.1; N, 7.3; S, 22.3. Found: C, 25.7; H, 3.9; N, 7.3; S, 22.3%. The analysis indicates 0.25 molecules of dichloromethane of crystallisation.

Dicarbonylbis(N,N-dimethyldithiocarbamato)pyridinetungsten(II)

A solution of \( W(S_2CNMe_2)_2(CO)_3 \) (0.01 g, 0.2 mmol) in dichloromethane (5 mL) was treated with pyridine (0.05 g, 0.6 mmol) to yield an
orange solution from which the complex was precipitated with n-hexane. The orange compound was filtered off, washed with n-hexane (pyridine saturated) and dried under nitrogen. The yield was 0.085 g (78%).

**Anal.** Calcd. for C_{13}H_{17}N_{3}O_{2}S_{4}W: C, 27.9; H, 3.1; N, 7.5; S, 22.9. Found: C, 27.9; H, 3.1; N, 7.4; S, 22.8.

**Dicarbonylbis(N,N-diethyldithiocarbamato)pyridinetungsten(II)**

A suspension of W(S_{2}CNEt_{2})_{2}(CO)_{2} (0.12 g, 0.21 mmol) in dichloromethane (3 mL) was treated with pyridine (0.05 g, 0.6 mmol) to give an orange solution. This was filtered and the product precipitated by the addition of n-hexane. It was washed with dichloromethane/hexane (1:3 v/v) and vacuum dried. The yield was 0.11 g (80%).

**Anal.** Calcd. for C_{17}H_{25}N_{3}O_{2}S_{4}W: C, 33.2; H, 4.1; N, 6.8; S, 20.8. Found: C, 33.2; H, 4.0; N, 6.7; S, 20.5%.

**Dicarbonylbis(N,N-dimethyldithiocarbamato)triphenylphosphinetungsten(II)**

A solution of W(S_{2}CNMe_{2})_{2}(CO)_{3} (0.10 g, 0.2 mmol) in dichloromethane (2 mL) was treated with triphenylphosphine (0.053 g, 0.2 mmol) in dichloromethane (2 mL). After standing (with occasional swirling) for 1 hr, n-hexane was added to precipitate the red complex. The crystals were filtered off, washed with n-hexane and dried under vacuum. The yield was 0.126 (85%).

**Anal.** Calcd. for C_{26}H_{27}N_{3}O_{2}PS_{4}W: C, 42.0; H, 3.7; N, 3.8; S, 17.3. Found: C, 41.1; H, 3.7; N, 3.6; S, 17.0%.

**Dicarbonylbis(N,N-diethyldithiocarbamato)triphenylphosphinetungsten(II)**

An orange solution of W(S_{2}CNEt_{2})_{2}(CO)_{3} (0.15 g, 0.27 mmol) in dichloromethane (1.5 mL) was added to triphenylphosphine (0.07 g, 0.27 mmol). Gas evolution occurred to produce a red solution. After standing for 1 hr, the solution was evaporated to dryness in a stream
of N₂. The solid was purified by precipitation from dichloromethane/\( n \)-hexane and then recrystallised from dichloromethane by slow addition of ether. The yield was 0.12 g (60%).

**Anal.** Calcd. for \( \text{C}_{30}\text{H}_{35}\text{N}_{2}\text{O}_{2}\text{PS}_{4}\text{W} \): C, 45.1; H, 4.4; N, 3.5; S, 16.1.

Found: C, 45.6; H, 5.0; N, 3.2; S, 15.3%.

\( n^2 \)-acetylene-dicarboxylbis(\( N,N \)-diethylthiocarbamato)tungsten(II)

\( \text{W(S}_2\text{CNET}_2)_2(\text{CO})_3 \) (0.5 g, 0.9 mmol) was dissolved in dichloromethane (12 mL) and treated with acetylene gas for 30 minutes. The green solution was filtered in air, treated with \( n \)-hexane (50 mL) and cooled overnight. The small amount of brown material formed was filtered off and discarded. The filtrate was treated with \( n \)-hexane (100 mL) and cooled to yield green crystals. Upon isolation the compound was recrystallised from dichloromethane/\( n \)-hexane. Yield 0.3 g (64%).

**Anal.** Calcd. for \( \text{C}_{13}\text{H}_{22}\text{N}_{2}\text{OS}_4\text{W} \): C, 29.1; H, 4.5; N, 5.2; S, 23.9.

Found: C, 27.2; H, 4.3; N, 5.1; S, 23.8%.

### 4.2.3 Characterization of Complexes

#### 4.2.3.1 Infrared Spectra

The infrared spectra of the complexes in various media are summarised in Table 4.1. The infrared spectra of \( \text{W(S}_2\text{CNR}_2)_2(\text{CO})_3 \) and \( \text{cis-W(S}_2\text{CNR}_2)_2(\text{CO})_2 \) are presented for discussion in Figures 4.4 and 4.5 respectively.

#### 4.2.3.2 \( ^1 \text{H} \) N.M.R. Spectra

The \( ^1 \text{H} \) n.m.r. spectra of the complexes are summarised in Table 4.2.

#### 4.2.3.3 \( ^{13} \text{C}-\{^1 \text{H}\} \) N.M.R. Spectra

The \( ^{13} \text{C}-\{^1 \text{H}\} \) n.m.r. of \( \text{W(S}_2\text{CNR}_2)_2(\text{CO})_3 \) and \( \text{W(S}_2\text{CNET}_2)_2(\text{CO})(\text{C}_2\text{H}_2) \)
### Table 4.1.
Infrared Spectral Data \(^a\) (cm\(^{-1}\))

<table>
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<tr>
<th>Complex</th>
<th>(\nu(CO))</th>
<th>(\nu(CN))</th>
<th>(\nu(NC_2))</th>
<th>(\nu(C=S))</th>
<th>(\nu(NH))</th>
</tr>
</thead>
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<td>(W(S_2CNMe_2)_2(CO)_2) (^b)</td>
<td>2006w, 1925s</td>
<td>1880sh, 1795s, 1785sh</td>
<td>1540s</td>
<td>1253m</td>
<td>1050w</td>
</tr>
<tr>
<td>(W(S_2CNEt_2)_2(CO)_2) (^b)</td>
<td>2006w, 1910s</td>
<td>1835sh, 1820s</td>
<td>1505s</td>
<td>1150m</td>
<td>1000w</td>
</tr>
<tr>
<td>(W(S_2CNEt_2)_2(CO)_2) (^c)</td>
<td>2010w, 1930s</td>
<td>1915s, 1826s</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(W(S_2CNEt_2)_2(CO)_3)</td>
<td>2020s, 1935sh, 1915s, 1885s, 1870sh</td>
<td>1530s</td>
<td>1253m</td>
<td>1050w</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)_2(CO)_3)</td>
<td>2020s, 1937s, 1917s, 1902s, 1886s</td>
<td>1508s</td>
<td>1150w</td>
<td>1005w</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)_2(CO)_2NH_2NHMe)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)_2(CO)_2NH_2NHCOPh)</td>
<td>2020s, 1930s, 1905s</td>
<td>1530s</td>
<td>1253m</td>
<td>1050w</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)(CO)_2N_2H_2NHMe)</td>
<td>2020w, 1927s, 1826s</td>
<td>1530s</td>
<td>1253m</td>
<td>1050w</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)(CO)_2NH_2NMe)</td>
<td>2020s, 1910br s, 1818s</td>
<td>1503s</td>
<td>1150s</td>
<td>1000m</td>
<td></td>
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<tr>
<td>(W(S_2CNEt_2)(CO)_2NH_2NMe_2)</td>
<td>2020s, 1915s, 1824s</td>
<td>1530s</td>
<td>1253m</td>
<td>1050w</td>
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<tr>
<td>(W(S_2CNEt_2)(CO)_2NH_2NMe_2)</td>
<td>2020s, 1920s, 1818s</td>
<td>1530s</td>
<td>1253m</td>
<td>1050w</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)(CO)_2NH_2NHCOPh)</td>
<td>2020w, 1937s, 1812s, 1675s (^d)</td>
<td>1530s</td>
<td>1250m</td>
<td>1050w</td>
<td></td>
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<tr>
<td>(W(S_2CNEt_2)(CO)_2NH_2NHCOPh)</td>
<td>2020m, 1912s, 1805s, 1680s (^d)</td>
<td>1510s</td>
<td>1150m</td>
<td>1000s</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)(CO)_2NH_2NH_2SO_2PhMe)</td>
<td>2015s, 1915s, 1830s</td>
<td>1525s</td>
<td>1253m</td>
<td>1050w</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)(CO)_2NH_2NH_2SO_2PhMe)</td>
<td>2015s, 1910s, 1818s</td>
<td>1505s</td>
<td>1150s</td>
<td>1002w</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)(CO)_2NH_3)</td>
<td>2020w, 1893s, 1807s</td>
<td>1535s</td>
<td>1253m</td>
<td>1058w</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)(CO)_2NH_3)</td>
<td>2020s, 1895br s, 1815s</td>
<td>1505s</td>
<td>1150m</td>
<td>1005w</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)(CO)_2py)</td>
<td>2020w, 1912s, 1820s</td>
<td>1525s, br</td>
<td>1233m</td>
<td>1045w</td>
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<td>(W(S_2CNEt_2)(CO)_2py)</td>
<td>2020a, 1900s, 1818s</td>
<td>1505s</td>
<td>1150m</td>
<td>1005w</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)(CO)_2PPh_3)</td>
<td>1915s, 1830s</td>
<td>1525s</td>
<td>1253m</td>
<td>1050w</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)(CO)_2PPh_3)</td>
<td>1926s, 1832s</td>
<td>1505s</td>
<td>1150m</td>
<td>1005w</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)(CO)(C_2H_2))</td>
<td>1946s, 1925s</td>
<td>1500s</td>
<td>1145m</td>
<td>1005w</td>
<td></td>
</tr>
<tr>
<td>(W(S_2CNEt_2)(CO)(C_2H_2)) (^c)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) In CsI, s = strong, m = medium, w = weak, br = broad, sh = shoulder. Dithiocarbamato-ligand assignments follow Reference 222.

\(^b\) In Nujol.

\(^c\) In CH_2Cl_2 solution (W(S_2CNMe_2)_2(CO)_2 insoluble). \(^d\) from NH_2NHCOPh.
Complex | Chemical Shifts, δ | Assignment | Complex | Chemical Shifts, δ | Assignment
--- | --- | --- | --- | --- | ---
W(S₂CNMe₂)₂(CO)₂ | s 3.25 | CH₃ | W(S₂CNET₂)₂(CO)₂NH₂NHCOPh | t 1.18 | CH₃CH₂
 | t 1.28 | CH₃CH₂ | q 3.57 | NH₂ | s 8.27 | NH
 | q 3.69 | CH₃CH₂ | s 5.29 | NH₂ | m 7.84-7.43 | Ph
W(S₂CNET₂)₂(CO)₂ | s 3.26 | CH₃ | W(S₂CNET₂)₂(CO)₂NH₂NHSO₂PhMe | s 2.45 | NH₂NHSO₂PhCH₃
 | s 3.68 | NH₂ | s 3.39 | NH₂ | m 7.85-7.25 | Ph
W(S₂CNET₂)₂(CO)₂ | t 1.32 | CH₃CH₂ | W(S₂CNET₂)₂(CO)₂NH₂NHSO₂PhMe | t 1.28 | CH₃CH₂
 | q 3.72 | CH₃CH₂ | s 3.26 | NH₂ | m 3.68 | NH₂
 | | | | | |

Table 4.1. 

¹H N.M.R. Data

<table>
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<tr>
<th>Complex</th>
<th>Chemical Shifts, δ</th>
<th>Assignment</th>
</tr>
</thead>
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<tr>
<td>W(S₂CNMe₂)₂(CO)₂</td>
<td>s 3.25</td>
<td>CH₃</td>
</tr>
<tr>
<td>W(S₂CNET₂)₂(CO)₂</td>
<td>t 1.28</td>
<td>CH₃CH₂</td>
</tr>
<tr>
<td></td>
<td>q 3.69</td>
<td>CH₃CH₂</td>
</tr>
<tr>
<td>W(S₂CNET₂)₂(CO)₂</td>
<td>s 3.26</td>
<td>CH₃</td>
</tr>
<tr>
<td>W(S₂CNET₂)₂(CO)₂</td>
<td>t 1.32</td>
<td>CH₃CH₂</td>
</tr>
<tr>
<td></td>
<td>q 3.72</td>
<td>CH₃CH₂</td>
</tr>
<tr>
<td>[W(S₂CNMe₂)₂(CO)₂]₂-µ-N₂H₄</td>
<td>insoluble</td>
<td></td>
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<tr>
<td>[W(S₂CNET₂)₂(CO)₂]₂-µ-N₂H₄</td>
<td>t 1.28</td>
<td>CH₃CH₂</td>
</tr>
<tr>
<td></td>
<td>q 3.61</td>
<td>CH₃CH₂</td>
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<tr>
<td></td>
<td>s 5.42</td>
<td>NH₂</td>
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<td>[W(S₂CNMe₂)₂(CO)₂]₂-µ-en</td>
<td>s,br 2.76</td>
<td>CH₃ of en</td>
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<tr>
<td></td>
<td>s 3.13</td>
<td>CH₃</td>
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<tr>
<td></td>
<td>s 3.23</td>
<td>NH₂</td>
</tr>
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<td>t 1.19</td>
<td>CH₃CH₂</td>
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<td>s,br 2.76</td>
<td>CH₃ of en</td>
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<td>s 3.17</td>
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<td>q 3.58</td>
<td>CH₃CH₂</td>
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<td>W(S₂CNET₂)₂(CO)₂</td>
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<td>NH₂NHCH₃</td>
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<td>NH₂NHCH₃</td>
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<td></td>
<td>s,br 3.26</td>
<td>NH₂</td>
</tr>
<tr>
<td>W(S₂CNET₂)₂(CO)₂</td>
<td>t 1.26</td>
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<tr>
<td></td>
<td>s 2.71</td>
<td>NH₂NHCH₃</td>
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<td>q 3.63</td>
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<td>s,br 3.90</td>
<td>NH₂</td>
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<td>W(S₂CNET₂)₂(CO)₂</td>
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<td>NH₂N(C₃H₃)₂</td>
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<tr>
<td>W(S₂CNET₂)₂(CO)₂</td>
<td>s 2.67</td>
<td>NH₂N(C₃H₃)₂</td>
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<td></td>
<td>s 3.63</td>
<td>NH₂</td>
</tr>
<tr>
<td>W(S₂CNET₂)₂(CO)₂</td>
<td>t 1.28</td>
<td>CH₃CH₂</td>
</tr>
<tr>
<td></td>
<td>s 2.49</td>
<td>NH₂N(C₃H₃)₂</td>
</tr>
<tr>
<td></td>
<td>q 3.38</td>
<td>CH₃CH₂</td>
</tr>
<tr>
<td></td>
<td>q 3.68</td>
<td>CH₃CH₂</td>
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<tr>
<td>W(S₂CNET₂)₂(CO)₂</td>
<td>s 3.08</td>
<td>NH₂</td>
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<tr>
<td></td>
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<td>NH₂</td>
</tr>
<tr>
<td></td>
<td>m 7.85-7.25</td>
<td>Ph</td>
</tr>
</tbody>
</table>

a) Chemical shifts relative to Me₄Si in CDC1₃; s, singlet; t, triplet; q, quartet; br, broad; p, pair of; ne, non-equivalent. Correct alkyl-group assignments refer to S₂CNMe₂ unless specified. b) Some nitrogen-donor ligand loss accompanies dissolution. c) Equivalent intensity for non-equivalent resonances. d) In (CD₃)₂SO.
are summarised in Table 4.3. $^{13}$C-$^{1}$H N.m.r. spectra of
$\sigma$-$\delta$-$W(S_{2}CNR_{2})_{2}(CO)_{2}$ could not be recorded due to the complexes' poor
solubility/stability.

Table 4.3
$^{13}$C-$^{1}$H N.M.R. of Selected Complexes$^a$

<table>
<thead>
<tr>
<th>Complex</th>
<th>Chemical Shift $\delta$, ppm (Relative Intensity, %)</th>
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<tbody>
<tr>
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<td>CH$_3$</td>
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<tr>
<td>W(S$_2$CNMe$_2$)$_2$(CO)$_3$</td>
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<tr>
<td>W(S$_2$CNET$_2$)$_2$(CO)$_3$</td>
<td>12.51(68)</td>
</tr>
<tr>
<td>W(S$_2$CNET$_2$)$_2$(CO)$_3$ $^b$</td>
<td>12.42(100)</td>
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<td>W(S$_2$CNET$_2$)$_2$(CO)(C$_2$H$_2$)</td>
<td>12.02(75)</td>
</tr>
<tr>
<td></td>
<td>12.12(100)</td>
</tr>
<tr>
<td></td>
<td>12.54(46)</td>
</tr>
</tbody>
</table>

$^a$ At 30°C, $\delta$ relative to Me$_4$Si in CH$_2$Cl$_2$/Cr(acac)$_3$. Pulse width
15 µsec, pulse delay 1 s at 80 MHz. $^b$ At -60°C.

4.2.3.4 X-Ray Powder Pattern Data

The x-ray powder diffraction patterns of selected compounds
are given in Table 4.4. The patterns for $W(S_{2}CNMe_{2})_{2}(CO)_{3}$ and
$[W(S_{2}CNET_{2})_{2}(CO)_{2}]_{2}-\mu-N_{2}H_{4}.CH_{2}Cl_{2}$ are in excellent agreement with those
calculated from the unit cell dimensions of $W(S_{2}CNMe_{2})_{2}(CO)_{3}$$^{328}$
and the molybdenum complex $[Mo(S_{2}CNET_{2})_{2}(CO)_{2}]_{2}-\mu-N_{2}H_{4}.CH_{2}Cl_{2}$$^{331}$
respectively.$^{340}$
Table 4.4

X-Ray Powder Pattern Data

<table>
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<tr>
<th>Interplanar Spacings, d (Å)</th>
<th>( R = \text{Me} )</th>
<th>( R = \text{Et} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-( W(S_2CNR_2)_2(CO)_2 )</td>
<td>7.76s 14.61m</td>
<td>12.11w</td>
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<tr>
<td>13.70w</td>
<td>7.31s 9.77w</td>
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<td>7.14s</td>
<td>6.56s 8.98s</td>
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<td>6.35s</td>
<td>5.95m 7.50s</td>
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<td>5.81m 7.58s</td>
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<td>5.16w</td>
<td>5.45m 6.61w</td>
<td>7.25m</td>
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<td>6.61w</td>
<td>3.87w 4.82m</td>
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4.2.3.5 Electronic Spectra

The electronic spectra of \( W(S_2CNR_2)(CO)_n \) (\( n = 2,3 \)) are shown in Figure 4.1 and are summarised in Table 4.5.

Table 4.5

Electronic Spectra of \( W(S_2CNR_2)_2(CO)_n \) (\( n = 2,3 \)) Complexes\(^a\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \lambda_{\text{max}}, \text{nm} ) (( \varepsilon, \text{lc}^{-1}\text{mole}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>cis</strong>-( W(S_2CNMe_2)_2(CO)_2 )</td>
<td>360 (( \sim 3200 )), 500 (( \sim 700 )), 699 (( \sim 1700 ))</td>
</tr>
<tr>
<td><strong>cis</strong>-( W(S_2CNET_2)_2(CO)_2 )</td>
<td>368 (( \sim 3400 )), 500 (( \sim 380 )), 690 (( \sim 2500 ))</td>
</tr>
<tr>
<td><strong>cis</strong>-( W(S_2CNET_2)_2(CO)_2 ) (^b)</td>
<td>375 (( \sim 3900 )), 497 (( \sim 1100 )), 702 (( \sim 2800 ))</td>
</tr>
<tr>
<td>( W(S_2CNMe_2)_2(CO)_3 )</td>
<td>360 (sh), 450 (940)</td>
</tr>
<tr>
<td>( W(S_2CNET_2)_2(CO)_3 )</td>
<td>360 (sh), 450 (970)</td>
</tr>
</tbody>
</table>

\(^a\) In \( \text{CH}_2\text{Cl}_2 \)  \(^b\) In thf.
Figure 4.1. The electronic spectra of a) cis-W(S$_2$CNMe$_2$)$_2$(CO)$_2$ b) cis-W(S$_2$CNEt$_2$)$_2$(CO)$_2$ c) W(S$_2$CNMe$_2$)$_2$(CO)$_3$ and d) W(S$_2$CNEt$_2$)$_2$(CO)$_3$ in dichloromethane (CO saturated for c,d).

Electronic spectral changes indicate rapid (ca. 5 min) decomposition of cis-W(S$_2$CNR$_2$)$_2$(CO)$_2$ in dichloromethane; ε values are therefore approximate. Also, the absorption bands of these complexes do not obey Beer's Law. The increased stability of cis-W(S$_2$CNEt$_2$)$_2$(CO)$_2$ in tetrahydrofuran allows more accurate ε values to be determined but unfortunately, cis-W(S$_2$CNMe$_2$)$_2$(CO)$_2$ is even more rapidly decomposed in this solvent. Again the absorption bands of cis-W(S$_2$CNEt$_2$)$_2$(CO)$_2$ in thf do not follow Beer's Law. Solutions of W(S$_2$CNR$_2$)$_2$(CO)$_3$ in CO saturated dichloromethane are stable and exhibit
absorption bands which obey Beer's Law over the concentration range $1.5 \times 10^{-4}$ to $2.3 \times 10^{-3}$ M.

4.2.4 The Oxidation of $[\text{W(S}_2\text{CNEt}_2\text{)}_2(\text{CO})_2]_2-\mu-\text{N}_2\text{H}_4$ with $\text{Cu}^{2+}/\text{H}_2\text{O}_2$

A mixture of $[\text{W(S}_2\text{CNEt}_2\text{)}_2(\text{CO})_2]_2-\mu-\text{N}_2\text{H}_4$ (0.25 g, 0.23 mmol) and anhydrous Na$_2$SO$_4$ (1.71 g) were treated with tetrahydrofuran and the suspension cooled to -78°C. A solution of CuSO$_4$ (0.72 M, 0.04 mL) and a solution of H$_2$O$_2$ (27%, 0.03 mL) were added and the mixture allowed to warm to 0°C over a 10 min period. The volume of the mixture was reduced to dryness at 0°C, then maintained under vacuum at room temperature for 3 hrs. The solid was extracted with thf (8 mL) and filtered to yield a purple solid ($\sigma\pi$-$\text{W(S}_2\text{CNEt}_2\text{)}_2(\text{CO})_2$) and brown filtrate. The solid obtained upon volume reduction was recrystallised from dichloromethane/nu-hexane and was identified as $\text{W(S}_2\text{CNEt}_2\text{)}_2(\text{CO})_3$. A similar reaction was observed when all manipulations were performed at 0°C.

4.3 DISCUSSION

The orange seven-coordinate complexes, $\text{W(S}_2\text{CNR}_2\text{)}_2(\text{CO})_3$, are readily prepared by the reaction of $\text{WBr}_2(\text{CO})_4$ and $\text{NaS}_2\text{CNR}_2$ in methanol (Equation 36). The method is analogous to that described by Colton et al. for the preparation of the molybdenum complexes $\text{W(S}_2\text{CNR}_2\text{)}_2(\text{CO})_n$ ($n = 2,3$). Similarly, the preparation of the complexes, $\text{W(S}_2\text{CNR}_2\text{)}_2(\text{CO})_3$ ($R = \text{Me, Et, CH}_2\text{Ph}$; $R_2 = (\text{CH}_2)_5$), by the reaction of $\text{WI}_2(\text{CO})_4$ and Na$_2$S$_2$CNR$_2$ has recently been reported by Templeton et al. In contrast to the rather complex procedures used by these authors, the preparations described in this thesis are simple and produce the desired products in high yield and purity. The compounds are slightly...
air and moisture sensitive, decomposing over a period of days into yellow/green uncharacterised materials.

The complexes show an enhanced affinity for CO when compared to their molybdenum analogues.\textsuperscript{329} Under vacuum, the molybdenum complexes \( \text{Mo(S}_2\text{CNR}_2\text{)}_2\text{(CO)}_3 \) \((\text{R} = \text{Me, Et, Ph})\) lose carbon monoxide to form six-coordinate \( \text{cis-Mo(S}_2\text{CNR}_2\text{)}_2\text{(CO)}_2 \) complexes. Methanol moistened \( \text{Mo(S}_2\text{CNR}_2\text{)}_2\text{(CO)}_2 \) readily reacts with CO to re-form \( \text{Mo(S}_2\text{CNR}_2\text{)}_2\text{(CO)}_3 \)\textsuperscript{329}

In contrast, the \( \text{W(S}_2\text{CNR}_2\text{)}_2\text{(CO)}_3 \) complexes show no carbonyl ligand loss when stored under vacuum, nor is this ligand readily lost in solution at room temperature. However, the six-coordinate dicarbonyl species, \( \text{cis-W(S}_2\text{CNMe}_2\text{)}_2\text{(CO)}_2 \) (green) and \( \text{cis-W(S}_2\text{CNEt}_2\text{)}_2\text{(CO)}_2 \) (purple), can be prepared from the corresponding tricarbonyl complexes by reflux in methanol (Equation 37). Impure \( \text{W(S}_2\text{CNMe}_2\text{)}_2\text{(CO)}_2 \) has previously been prepared by heating solid \( \text{W(S}_2\text{CNMe}_2\text{)}_2\text{(CO)}_3 \) under vacuum at 170°C for 2 hrs.\textsuperscript{327} Carbonyl ligand loss from \( \text{W(S}_2\text{CNR}_2\text{)}_2\text{(CO)}_3 \) is in the order \( \text{S}_2\text{CNET}_2 > \text{S}_2\text{CNMe}_2 \), suggesting weaker binding of the third CO ligand with increasing size and steric bulk of the \( \text{S}_2\text{CNR}_2 \) alkyl groups. Indeed, the isopropyl derivative \( \text{W(S}_2\text{CNPr}_2\text{)}_2\text{(CO)}_3 \) appears to be very unstable and neither it nor the corresponding dicarbonyl complex could be prepared. Although Templeton \textit{et al.}\textsuperscript{328} have reported the complexes \( \text{W(S}_2\text{CNR}_2\text{)}_2\text{(CO)}_3 \) \((\text{R} = \text{CH}_2\text{Ph}, \text{R}_2 = (\text{CH}_2)_5)\), the stability of these complexes was not commented on. The loss of carbon monoxide from \( \text{W(S}_2\text{CNR}_2\text{)}_2\text{(CO)}_3 \) is reversible; both in the solid state and in suspension, the dicarbonyl complexes readily react with carbon monoxide to regenerate the soluble monomeric tricarbonyl complexes. Thus, the \( \text{W(S}_2\text{CNR}_2\text{)}_2\text{(CO)}_n \) \((n = 2, 3)\) complexes display 'carbon monoxide carrier' properties similar to those observed for \( \text{Mo(S}_2\text{CNR}_2\text{)}_2\text{(CO)}_n \) \((n = 2, 3)\);
R = Me, Et, Ph) and other Mo(II) carbonyl complexes. Nevertheless, reversible carbon monoxide binding is less facile in the tungsten system due to the enhanced stability of the tricarbonyl complexes. The complexes W(S\(_2\)CNR\(_2\))\(_2\)(CO)\(_2\) slowly decompose in air (1-2 days).

The chemistry of these tungsten complexes closely parallels that of their previously described molybdenum counterparts. The coordinatively unsaturated 16-electron W(S\(_2\)CNR\(_2\))\(_2\)(CO)\(_2\) complexes bind an additional ligand with remarkable ease to yield the diamagnetic complexes W(S\(_2\)CNR\(_2\))\(_2\)(CO)\(_2\)L (L = CO, N\(_2\)H\(_3\)Me, NH\(_2\)NMMe\(_2\), NH\(_3\), NH\(_2\)NHCOPh, C\(_5\)H\(_5\)N, NH\(_2\)NHOSO\(_2\)PhMe and PPh\(_3\)) and [W(S\(_2\)CNR\(_2\))\(_2\)(CO)\(_2\)]\(_2\)-µ-B (B = N\(_2\)H\(_4\), NH\(_2\)CH\(_2\)CH\(_2\)NH\(_2\)). These compounds can also be formed from the tricarbonyl complexes by carbonyl ligand displacement, this being the preferred route if the free ligand is appreciably soluble in the mixed solvent from which the complex is precipitated. Where this is not the case or with extremely labile ligands, the reaction of W(S\(_2\)CNR\(_2\))\(_2\)(CO)\(_2\) with the stoichiometric amount or excess of ligand, respectively, was employed (see Section 4.2.2). The orange-red complexes are extremely air and moisture sensitive in solution but are only moderately sensitive in the solid state.

The reaction of W(S\(_2\)CNR\(_2\))\(_2\)(CO)\(_3\) with hydrazine in dichloromethane/methanol yields bright red crystals of the µ-hydrazine complexes [W(S\(_2\)CNR\(_2\))\(_2\)(CO)\(_2\)]\(_2\)-µ-N\(_2\)H\(_4\). The ethyl derivative is isomorphous with its molybdenum analogue (Section 4.2.3.4), the molecular structure of which is shown in Figure 4.2. Thus, a molecular structure similar to that shown in Figure 4.2 is predicted for [W(S\(_2\)CNR\(_2\))\(_2\)(CO)\(_2\)]\(_2\)-µ-N\(_2\)H\(_4\). A µ-ethylenediamine complex is formed by the reaction of W(S\(_2\)CNR\(_2\))\(_2\)(CO)\(_2\) with ethylenediamine and is likely to possess a similar bridged structure.
Figure 4.2. Molecular structure of [Mo(S₂CNEt₂)₂(CO)₂]₂-µ-N₂H₄. For clarity, the ethyl groups of S₂CNEt₂ and the hydrogen atoms of N₂H₄ have been omitted. Only one position of the disordered N₂H₄ ligand is shown.³³²

When reacted with W(S₂CNR₂)₂(CO)ₙ (n = 2,3), the remaining N-donor ligands form monomeric seven-coordinate complexes of the form W(S₂CNR₂)₂(CO)₂L, in which only weak coordination of the co-ligand is observed. However, the complexes are more stable than their molybdenum analogues³³¹ as only the more sterically hindered complexes of NH₂NMe₂, py and NH₂NH₂SO₂PhMe show appreciable ligand loss under vacuum. The immediate colour change of these orange complexes upon dissolution and their methods of preparation indicate the solution equilibrium shown in Equation (38).

\[
W(S₂CNR₂)₂(CO)₂L \rightleftharpoons W(S₂CNR₂)₂(CO)₂ + L \quad \text{green}
\]

orange

L = NH₂NMe₂, py and NH₂NH₂SO₂PhMe.
The W(S$_2$CNR$_2$)$_2$(CO)$_3$ complexes react readily with PPh$_3$ to form the known W(S$_2$CNR$_2$)$_2$(CO)$_2$PPh$_3$ complexes.\textsuperscript{343,344} The reaction of W(S$_2$CNEt$_2$)$_2$(CO)$_3$ with acetylene leads to the formation of W(S$_2$CNEt$_2$)$_2$(CO)(C$_2$H$_2$).\textsuperscript{345} However, the green crystalline solid displays infrared spectra which differ from those reported previously.\textsuperscript{345} In contrast to the reported band at 1960 cm$^{-1}$ (KBr) the complex obtained in this work shows bands at 1945 and 1925 cm$^{-1}$ in CsI and 1915 cm$^{-1}$ in solution. Elemental analysis and $^1$H and $^{13}$C-$^1$H n.m.r. spectra are, however, consistent with the formulation W(S$_2$CNEt$_2$)$_2$(CO)(C$_2$H$_2$). The infrared discrepancy may indicate the existence of various isomers of this complex.

The facile tendency of W(S$_2$CNR$_2$)$_2$(CO)$_2$ to form seven-coordinate complexes reflects the stability of the resulting 18-electron species. The attainment of an 18-electron valence shell in the d$^4$ Mo(II) and W(II) systems requires the donation of seven electron pairs from the coordination sphere and accounts for the extensive seven-coordination chemistry of Mo(II) and W(II).\textsuperscript{342} The recently reported crystal structure of cis-Mo(S$_2$CNPr$_2$)$_2$(CO)$_2$,\textsuperscript{346} shown in Figure 4.3., suggests that the coordination sphere expansion of monomeric M(S$_2$CNEt$_2$)$_2$(CO)$_2$ (M = Mo,W) complexes may also be sterically favoured. The unusual and rather open trigonal prismatic structure provides a steric environment favourable to the coordination of an additional donor atom at site A (Figure 4.3).

The presence of three $\nu$(CO) bands in the solution infrared spectra of W(S$_2$CNR$_2$)$_2$(CO)$_3$ (Figure 4.4a) is indicative of a facial arrangement of carbonyl ligands in these complexes. For octahedral fao-tricarbonyl complexes of $C_3$ symmetry, the $a$, and $e$ normal modes
Figure 4.3. The molecular structure of $\text{cis-Mo(S}_2\text{CNPr}_2\text{)}_2(\text{CO})_2$ showing the available coordination site, A.

produce two allowed infrared absorptions. In the $\text{W(S}_2\text{CNR}_2\text{)}_2(\text{CO})_3$ complexes, the departure from $C_3$ symmetry splits the two components of the degenerate e mode to produce three $\nu(\text{CO})$ bands. On the other hand, five $\nu(\text{CO})$ bands appear in the solid state infrared spectra of these complexes. (Figure 4.4b). Here, local site symmetry effects in the solid state would account for the increased number of bands over that of the solution spectra. The two major $\nu(\text{CO})$ bands in the solid state spectra of $\text{W(S}_2\text{CNR}_2\text{)}_2(\text{CO})_2$ indicate a $\text{cis-}$ configuration of the carbonyl ligands in these complexes (Figure 4.5b). Additional bands indicate the presence of isomers or solid state interactions as the solution spectrum of $\text{W(S}_2\text{CNEt}_2\text{)}_2(\text{CO})_2$ shows only two major bands (Figure 4.5a). The observed carbonyl ligand configurations are electronically favoured as the mutually $\text{cis-}$ arrangement minimises carbonyl ligand competition for $d\pi$-electron density.
With the exception of the triphenylphosphine complexes, the infrared spectra of the adduct complexes of $W(S_2CNR_2)_2(CO)_2$ exhibit three rather than two $\nu(CO)$ bands (Table 4.1). Three bands are also observed in the solution infrared spectra and therefore solid state effects are not responsible for the increased number of bands. The presence of two strong carbonyl bands and a third of variable intensity ($2020 \text{ cm}^{-1}$) suggests the presence of various isomers, isolable
Figure 4.5. The infrared spectra of $W(S_2CNR_2)_2(CO)_2$ in the $\nu(CO)$ region. a) $R = Et$ in dichloromethane solution, b) $R = Me$, ---; $R = Et$, ----- in CsI.

in the solid state and observable in solution on the infrared timescale ($10^{-11}$ s$^{-1}$). The structure of these isomers, also observed in the analogous molybdenum complexes, $^{331,332}$ warrants some discussion.

The examination and rationalization of the coordination geometry in seven-coordinate complexes is of intrinsic interest and
the topic has recently been reviewed.\textsuperscript{232,233} The geometry of seven-coordinate complexes is most frequently described in terms of ideal polyhedra, the most important of which are shown in Figure 4.6.

Most complexes of the type $\text{M(monodentate)}_3(\text{bidentate})_2$ display PB coordination\textsuperscript{233} with the two bidentate ligands in the pentagonal plane; in terms of energy minimization calculations such a structure is generally favoured.\textsuperscript{232} However, surprisingly few cases\textsuperscript{350} of PB geometry are known for Mo(II) and W(II) carbonyl complexes. On the other hand, many examples of CTP and CO geometry have been reported for Mo(II) and W(II) carbonyl complexes\textsuperscript{232} and thus the polytypal and stereochemical isomers of these polyhedra most likely represent the isomers of $\text{M(S}_2\text{CNR}_2)_2(\text{CO})_2\text{L}$ and $[\text{M(S}_2\text{CNR}_2)_2(\text{CO})_2]_2-\mu-\text{B}$ ($\text{M} = \text{Mo, W}; \text{L and B as previously defined}$)
For the molybdenum complexes, several possible isomers can be derived from the trigonal prismatic precursor, \(\sigma\sigma\sigma\)-Mo\((S_2CNPr_2)\)\(_2\)\((CO)\)\(_2\).\(^{3,4,6}\) Here, coordination of the incoming ligand to the site \(\text{trans}\) to the carbonyl ligands (site A, Figure 4.3), or coordination followed by ligand rearrangement leads to Isomers I and II, shown in Figure 4.7.

Figure 4.7. Possible isomers of the complexes M\((S_2CNR_2)\)\(_2\)(CO)\(_2\)L. These isomers also represent the possible metal coordination spheres in the complexes \([M(S_2CNR_2)\)\(_2\)(CO)\(_2\)]\(_2\)\(\mu\)-B. \((S\ S = S_2CNR_2; M = Mo, W)\).

The stability of these CTP isomers will depend on the donor/acceptor nature of the incoming ligand. Since the stereochemistry of I and II permits competition between L (or B) and CO for \(\pi\)-electron density, Isomers I and II would be stabilised by weak \(\pi\)-acceptor ligands such as the N-donor ligands used in this study. Indeed, the structure of \([Mo(S_2CNEt_2)\)\(_2\)(CO)\(_2\)]\(_2\)\(\mu\)-N\(_2\)H\(_4\) (Figure 4.2) can be described in terms of Isomer I. The absence of the 2020 cm\(^{-1}\) band in the infrared spectrum of the \([Mo(S_2CNEt_2)\)\(_2\)(CO)\(_2\)]\(_2\)\(\mu\)-N\(_2\)H\(_4\).CH\(_2\)Cl\(_2\) crystals used in this compound's crystal structure analysis,\(^{3,2}\) assigns this band to Isomer II. A similar statement applies to the other N-coligand complexes. In Isomer I, the \(\sigma\sigma\sigma\) configuration of the carbonyl ligands enhances its stability over
Isomer II, as evidenced by the dominance of bands attributable to Isomer I in the infrared spectra. The stability of Isomer I is further supported by the thermodynamic stability of $\text{cis-}[\text{MoBr(CO)}_2-(\text{dpmm})_2]\text{Br}_3$ compared to the trans- isomer. Similar isomers have been shown to exist in the related complexes $[\text{Mo(CO)}_2(\text{dppe})_2]^n$ and $[\text{Mo(CO)}_2(\text{dpmm})_2]^n$ ($n = 0, +1, +2$). Similar sets of isomers may be derived for the N-donor ligand complexes of tungsten assuming a structural similarity between monomeric $\text{cis-}[\text{W(S}_2\text{CNR}_2]_2(\text{CO})_2$ and $\text{cis-}[\text{Mo(S}_2\text{CNR}_2]_2(\text{CO})_2$ complexes. Certainly, the presence of similar isomers in both the molybdenum and tungsten complexes is supported by spectroscopic evidence (cf. Ref. 331 and Section 4.2.3).

Isomers I and II become less favourable when $L$ is a strongly $\pi$-accepting ligand since direct competition between $L$ and CO for $d\pi$-electron density can occur. In this case an isomer with facial $\pi$-accepting ligands (viz. CO and $L$) would be preferred, e.g. Isomer III in Figure 4.7. For the complexes $\text{W(S}_2\text{CNR}_2]_2(\text{CO})_2L$, triphenylphosphine is the only strong $\pi$-accepting ligand studied and interestingly $\text{W(S}_2\text{CNR}_2]_2(\text{CO})_2\text{PPh}_3$ exhibit only two bands in their infrared spectra (2020 cm$^{-1}$ band absent), indicating the presence of only one isomeric form. The crystal structures of $\text{W(S}_2\text{CNMe}_2]_2(\text{CO})_3$ and $\text{W(S}_2\text{CNET}_2]_2-(\text{CO})_2\text{PPh}_3$ support the assignment of structure III (Figure 4.7) to this unique isomer.

The effect of the dithiocarbamato-ligand substituent on the infrared frequencies in the carbonyl region is not substantial except in the complexes $\text{W(S}_2\text{CNR}_2]_2(\text{CO})_2$ where $\Delta \nu$ (the separation between the two carbonyl bands) is 130 cm$^{-1}$ for $R = \text{Me}$ and 90 cm$^{-1}$ for $R = \text{Et}$. This feature may be related to the presence of monomeric and dimeric complexes in the crystalline forms of $\text{W(S}_2\text{CNMe}_2]_2(\text{CO})_2$ and $\text{W(S}_2\text{CNET}_2]_2-(\text{CO})_2$, respectively (see later).
It is also interesting to compare the $v$(CO) frequencies of the tungsten complexes with those of their molybdenum analogues. In every case, the substitution of tungsten for molybdenum leads to a lowering of $v$(CO). The low frequency shift is in the range of 15-35 cm$^{-1}$ and reflects the more effective $\pi$-electron donation from tungsten to the antibonding orbitals of the carbonyl ligands. The remaining infrared bands are characteristic of bidentate dithiocarbamato-ligands and the N- and P- coligands.

The $^1$H n.m.r. spectra of the complexes, with one exception, show equivalence of the dithiocarbamato-ligand substituents. Since rotation about the C=N bond is unlikely at 30°C, the equivalence of the ligand substituents indicates fluxionality of the complexes in solution. Thus, although inequivalent resonances may be expected for the various isomers observable by infrared spectroscopy (time scale $10^{-11}$ s), fluxionality results in the observation of an averaged ligand environment on the n.m.r. timescale ($10^{-2}$ to $10^{-5}$ s). For the W(S$_2$CNR$_2$)$_2$(CO)$_2$ complexes, equivalence of the dithiocarbamato-resonances may also be explained by a trigonal prismatic solution structure. Stereochemical non-rigidity is a frequent property of similar seven-coordinate complexes and Templeton et al. have reported detailed $^{13}$C-dynamic n.m.r. studies of W(S$_2$CNR$_2$)$_2$(CO)$_3$ and W(S$_2$CNR$_2$)$_2$(CO)$_2$PPh$_3$. The $^{13}$C-$^1$H n.m.r. spectra, summarised in Table 4.3, are in good agreement with the corresponding studies of Templeton et al. and show only one CO resonance and equivalent dithiocarbamato-ligand resonances even at -50°C. For W(S$_2$CNMe$_2$)$_2$(CO)$_2$PPh$_3$, inequivalent dithiocarbamato-ligand resonances suggest the maintenance of a unique ground state structure (Isomer III, Figure 4.7) in solution (while exchange of identical ligands between nonequivalent
sites occurs in the fast exchange limit\(^{354}\)). The absence of a band at 2020 cm\(^{-1}\) in the infrared spectra of \(W(S_2CNR_2)_2(CO)_2PPh_3\) is consistent with this conclusion. The observation of well resolved n.m.r. spectra indicate that all complexes are diamagnetic due to spin pairing of the \(d^4\) systems.

The electronic spectra of the \(W(S_2CNR_2)_2(CO)_3\) and \(W(S_2CNR_2)_2(CO)_2\) complexes (Table 4.5, Figure 4.1) are distinctly different. In the tricarbonyl complexes, the presence of one absorption band \((\lambda_{\text{max}} = 450 \text{ nm})\) which follows Beer's Law is consistent with the presence of monomeric species in CO saturated solutions. In contrast, dichloromethane solutions of \(W(S_2CNR_2)_2(CO)_2\) exhibit absorption bands at \(\alpha\alpha\). 360, 500 and 690 nm, these being relatively intense compared to the bands of \(W(S_2CNR_2)_2(CO)_3\) and the molybdenum complexes \(Mo(S_2CNEt_2)_2(CO)_2\)\(^{146}\) and \(Mo(S_2PPr_2)_2(CO)_2\).\(^{145}\) The bands do not follow Beer's Law and reliable calculations of \(\varepsilon\) are prevented by decomposition of the complexes in solution. Measurements in tetrahydrofuran, in which \(W(S_2CNEt_2)_2(CO)_2\) is more stable, also indicate deviation from Beer's Law as does the concentration dependent colour of \(W(S_2CNEt_2)_2(CO)_2\) solutions, \(\text{viz.}\) purple at high complex concentrations, green at low concentrations.

The green coloration of dilute solutions is associated with the monomeric species \(W(S_2CNR_2)_2(CO)_2\) which are favoured at low concentrations. In concentrated solutions of \(W(S_2CNEt_2)_2(CO)_2\), the reversible equilibrium (Equation 39) is shifted to the right, resulting in the purple coloration characteristic of the dimer.

\[
2W(S_2CNEt_2)_2(CO)_2 \rightleftharpoons [W(S_2CNEt_2)_2(CO)_2]_2
\]

(green) \hspace{2cm} (purple)  (39)
The correlation of solid and solution colours (green $\text{W(S}_2\text{CNMe}_2\text{)}_2\text{(CO)}_2$ and green dilute solutions, $R = \text{Me, Et};$ purple $\text{W(S}_2\text{CNEt}_2\text{)}_2\text{(CO)}_2$ and purple concentrated solutions, $R = \text{Et}$) provides evidence for the existence of $\text{W(S}_2\text{CNMe}_2\text{)}_2\text{(CO)}_2$ monomers and $[\text{W(S}_2\text{CNEt}_2\text{)}_2\text{(CO)}_2]^2_2$ dimers in the solid state. In the absence of such a structural difference, it is unlikely that the variation in ligand substituent would produce the striking colour difference of the $\text{W(S}_2\text{CNR}_2\text{)}_2\text{(CO)}_2$ complexes. The low solubility of $\text{W(S}_2\text{CNMe}_2\text{)}_2\text{(CO)}_2$ prevents the observation of purple dimer-containing solutions of this complex and explains its precipitation from solution as a monomer.

The presence of $\mu$-dithiocarbamato-ligands in $[\text{W(S}_2\text{CNEt}_2\text{)}_2\text{(CO)}_2]^2_2$ is favoured by spectroscopic studies. In the infrared spectra of dilute (monomer) and concentrated (dimer) solutions of the complex, a significant difference in the $\nu$(CO) region is expected if dimerization takes place $\nu\mu\alpha$ the carbonyl ligands. Since the spectra are virtually identical, the presence of $\mu$-CO ligands in $[\text{W(S}_2\text{CNEt}_2\text{)}_2\text{(CO)}_2]^2_2$ can be discounted. A slight splitting ($\approx 10 \text{ cm}^{-1}$) of the $\nu$(CN) mode in the infrared spectrum of dimer containing solutions provides evidence for the presence of bridging and non-bridging dithiocarbamato-ligands. Slight splitting of the $\nu$(CN) mode in solid $[\text{W(S}_2\text{CNEt}_2\text{)}_2\text{(CO)}_2]^2_2$ is also observed but is absent in the spectra of $\text{W(S}_2\text{CNMe}_2\text{)}_2\text{(CO)}_2$. The $^1\text{H}$ n.m.r. spectra of monomer and dimer containing solutions of $\text{W(S}_2\text{CNEt}_2\text{)}_2\text{(CO)}_2$ are also identical but fluxionality of the species present is a likely explanation for this similarity. Mass spectra of the complexes are uninformative.

Known seven-coordinate dimers exhibit a variety of structures, the geometry of which can be described in terms of edge or corner linked ideal seven-coordinate polyhedra. Generally, bridge
formation ensures that the favoured coordination geometry of the metal remains relatively undisturbed. In view of the CTP and CO coordination geometries of many seven-coordinate Mo(II) and W(II) carbonyl complexes, a µ-dithiocarbamato- CTP or CO structure is proposed for \([W(S_2CNMe_2)_2(CO)_2]_2\). The recently reported structure of \([Mo(MeNC(S)PPh_2)_2(CO)_2]_2\) has established the possible dimerization of coordinatively unsaturated Mo(II) and W(II) carbonyl complexes. The complex is comprised of two CTP Mo(II) moieties bridged via tridentate MeNC(S)PPh\(_2\) ligands; the carbonyl ligands are cis-to one another. The characterization of this complex further supports the likely dimeric structure of \([W(S_2CNMe_2)_2(CO)_2]_2\). To date no tungsten or molybdenum µ-dithiocarbamato- complexes have been structurally characterised but \(\eta^2\)-bridging ligands have been proposed for \(Mo_2(S_2CNMe_2)_6\). The determination of the x-ray crystal structures of both \(W(S_2CNR_2)_2(CO)_2\) complexes is planned.

The preparation and reactions of hydrazine and diimine containing carbonyl-complexes of the Group VIa metals have been described. Sellmann et al. have isolated and studied a series of mononuclear and dinuclear complexes of the form \([M(CO)_5]_2-\mu-N_2H_2\), \([M(CO)_5]_2-\mu-N_2H_4\), \(M(CO)_5N_2H_4\) and \(M(CO)_5NH_3\). Recently Ackermann et al. have reported similar complexes of the related ligands \(\sigma\)- and \(\tau\)-1,2-diisopropyl-diimine, 1,2-diisopropylhydrazine, \(\sigma\)- and \(\tau\)-1,2-dimethylidiimine and 1,2-dimethylhydrazine (the larger isopropyl-ligands do not form bridged complexes). In these studies the diimine complexes have been prepared from the hydrazine complexes by reaction with oxidants such as \(H_2O_2/Cu^{2+}\), HgO and MnO\(_2\). In comparison to the complexes of chromium and tungsten, the molybdenum complexes are highly unstable and very reactive. The complexes of tungsten are the most stable products. This fact suggested that it might be possible to isolate a stabilised µ-diimine complex via the oxidation of \([W(S_2CNMe_2)_2(CO)_2]_2-\mu-N_2H_4\). Such a reaction
fails in the corresponding molybdenum system presumably due to the decomposition of the μ-diimine complex formed.

Attempts to prepare stable μ-diimine complexes via the oxidation of \([W(S_2CN\text{Et}_2)_2(CO)_2]_2-\mu-N_2H_4\) with \(H_2O_2\) using \(Cu^{2+}\) as catalyst were, however, unsuccessful. At or above 0°C, the diimine complex, if formed, is unstable and decomposes to the simple tungsten carbonyl complexes \(W(S_2CN\text{Et}_2)_2(CO)_n\) \((n = 2,3)\). As in the molybdenum case, tungsten is incapable of stabilising the highly reaction diimine ligand in \([M(S_2CN\text{Et}_2)_2(CO)_2]_2-\mu-N_2H_2\) type complexes.
CHAPTER FIVE

MOLYBDENUM AND TUNGSTEN COMPLEXES OF
MULTIDENTATE THIAETHER AND THIOLATO- LIGANDS

5.1 INTRODUCTION

Two areas of investigation are described in this chapter. Firstly, the preparation and characterization of molybdenum and tungsten carbonyl complexes of the macrocyclic tetrathiaether ligands 1,4,8,11-tetrathiacyclotetradecane (L₁) and 3,6,10,13-tetrathiabicyclo[13.4.0]nona-1,16,18-triene (L₂) is presented. Secondly, the attempted preparation of molybdenum and iron complexes of 1,4,8,11-tetrathiaundecane (L₃) is described. The ligands L₁, L₂ and L₃ are shown in Figure 5.1.

![Figure 5.1](image)

Figure 5.1. The sulphur-donor ligands 1,4,8,11-tetrathiacyclotetradecane (L₁), 3,6,10,13-tetrathiabicyclo[13.4.0]nona-1,16,18-triene (L₂) and 1,4,8,11-tetrathiaundecane (L₃).
5.1a Macrocyclic Tetrathiaether Complexes of Molybdenum(0) and Tungsten(0)

Soft\(^{361}\) Mo(0) and W(0) centres and \(\pi\)-accepting phosphine coligands pervade the chemistry of dinitrogen complexes.\(^{9,153,155}\) The preferential binding of thiaether ligands to soft metal centres and their considerable \(\pi\)-acceptor properties suggest that Mo(0) and W(0) thiaether complexes may also be capable of binding dinitrogen. However, the unstable \(\sigma\tilde{\tau}s\)-Mo(N\(_2\))\(_2\)(PMe\(_2\)Ph)\(_2\)(PhSCH\(_2\)CH\(_2\)SPh) complex is the only known example of such a compound.\(^{156}\) The possible relevance of low oxidation state molybdenum-sulphur chemistry to nitrogen fixation prompted the investigation of the Mo(0) and W(0) complexes described in this chapter. These studies sought to prepare metal complexes in which four coordination sites were occupied by sulphur atoms, and to investigate the chemistry of the remaining sites.

In their metal complexes, L\(^1\) and L\(^2\) exhibit highly variable and often novel modes of coordination. Structure determinations have been reported for several complexes of L\(^1\)\(^{363-368}\) and for the free ligand itself.\(^{362}\) The free ligand exists in two forms, both of which display an exodentate conformation; in this conformation the sulphur atoms are at the corners of rectangular molecules and their lone-pair electrons point out of the macrocyclic cavity.\(^{362}\) In its metal complexes, L\(^1\) exhibits both exodentate and endodentate conformations. The structurally characterised metal complexes of L\(^1\) and their ligand coordination modes are summarised below and some examples are given in Figure 5.2.

\[[\text{Cu}(L^1)](\text{ClO}_4)_2,^{363} [\text{Ni}(L^1)](\text{BF}_4)_2^{364} \text{ and } [\text{Hg}(L^1)(\text{H}_2\text{O})](\text{ClO}_4)_2^{366}\]

are mononuclear complexes in which L\(^1\) encircles the metal ion and exhibits an endodentate conformation.

\[[\text{Cu}(L^1)]\text{ClO}_4^{367}\] In this complex L\(^1\) acts as a bridging ligand with three sulphur atoms coordinated to one copper atom and the
Figure 5.2. Examples of the variable coordination modes of $L^1$.

a) $[\text{Hg}(L^1)(\text{H}_2\text{O})]^2+,$  

b) $[\text{HgCl}_2]_2-\mu-L^1,$  
c) $[\text{Cu}(L^1)]^+, $  
d) $[\text{NbCl}_5]_2-\mu-L^1.$

fourth coordinated to an adjacent copper atom. The copper atoms have irregular tetrahedral geometries.

$[\text{HgCl}_2]_2-\mu-L^1.$ Here, two HgCl$_2$ moieties are bridged by $L^1$, which functions as a bidentate ligand to each mercury atom. The ligand is exodentate.

$[\text{NbCl}_5]_2-\mu-L^1.$ The bridging $L^1$ ligand in this complex is exodentate and acts as a monodentate ligand to each NbCl$_5$ moiety.

In these complexes the ligand binding modes appear to be controlled by a combination of factors which include, metal ion size (in relation to the cavity size of the macrocycle), the presence of competing ligands and the electronic nature of the metal ions. The
influence of the metal ion size on the ligand binding mode appears to be minimal, for although L¹ is capable of encircling metal ions up to 1.10 Å in radius, e.g. Hg(II), it frequently fails to adopt such a conformation with smaller metal ions. Even in complexes of the same metal ion, variable binding may occur, as in the mercury complexes [Hg(L¹)(H₂O)]²⁺ and [HgCl₂]₂-µ-L¹.³⁶⁵,³⁶⁶ For these complexes, the influence of competing ligands is paramount. Ligand competition is also important in the complex [NbCl₅]₂-µ-L¹ where the preferential binding of the strong σ- and π-donor chloro- ligands to the Nb(V) centre restricts the binding of L¹ to one coordination site only.³⁶⁸ Ligand competition in this case is enhanced by the electronic nature of the metal ion. The binding mode of L¹ in the complexes [Cu(L¹)]ClO₄³⁶⁷ and [Cu(L¹)](ClO₄)₂³⁶³ is determined solely by the electronic nature of the metal ions. While L¹ is capable of encircling both Cu(I) and Cu(II) ions, such a conformation is possible only in square-planar complexes such as [Cu(L¹)]²⁺. The electronically favoured tetrahedral coordination geometry of [Cu(L¹)]⁺ prevents the tetradsentate coordination of the ligand to a single Cu(I) ion, and thus determines the unusual bridging mode observed in this complex.

Complexes of L¹ and L² which have been reported but not structurally characterised include [Ni(L²)]²⁺,³⁶⁹ [NiX₂(L¹)] (X = NCS⁻, Cl⁻, Br⁻, I⁻³⁷⁰), cis-[MX₂(L¹)]⁺ (M = Co, X = Cl⁻, Br⁻, NCS⁻, NO²⁻, oxalate²⁻; M = Rh, X = Cl⁻, Br⁻, I⁻³⁷⁰), trans-[MX₂(L¹)]⁺ (M = Co, X = I⁻³⁷⁰; M = Rh, X = Cl⁻³⁷¹; M = Ru, X = Cl⁻³⁷²), trans-[MX₂(L²)]⁺ (M = Co, X = Cl⁻, Br⁻³⁷⁰), [Rh(L¹⁺²)]⁺,³⁷¹ cis-[RuCl₂(L²)]Cl³⁷² and trans-[RuCl₂(L¹⁺²)].2H₂O.³⁷²

Molybdenum or tungsten complexes of L¹ or L² have not been described, however, three molybdenum complexes of the related ligand,
1,5,9,13-tetrathiacyclohexadecane have been reported.\textsuperscript{57,379} In these complexes, the Mo(II) and Mo(IV) ions are readily accommodated in the central cavity of the 16-membered ligand. The absence of competing ligands leads to such a ligand conformation in all three complexes. Also, the complexes [Mo(CO)]\textsubscript{4} \textsubscript{2-}µ-L, [W(CO)]\textsubscript{4} \textsubscript{2-}µ-L and [W(CO)]\textsubscript{5} \textsubscript{2-}µ-L (L = 2,6,15,19-tetrathia[7.7]paracyclophane) were recently reported.\textsuperscript{380} Stereochemical restraints in the ligand framework, in combination with the strong binding of carbonyl ligands to the Mo(0) and W(0) centres, restricts the binding of the S\textsubscript{4}-ligand to a maximum of two coordination sites in these complexes. Complexes of related polythiaether complexes have been reported.\textsuperscript{373-378}

5.1b Molybdenum Complexes of 1,4,8,11-Tetrathiaundecane

Recent efforts to mimic the molybdenum site of nitrogenase have been directed towards the preparation and study of Fe-Mo-S cluster compounds, several examples of which have now been reported (see Chapter 1). Relatively few studies have centred on the investigation of multidentate alkylthiolato- complexes of iron and molybdenum. The recent studies of Zubieta \textit{et al.}\textsuperscript{381} and Rakowski DuBois \textit{et al.}\textsuperscript{382-384} suggest that this area is attracting increased attention and is capable of exhibiting fascinating chemistry. Part Two of this chapter briefly describes the attempted preparation of molybdenum and iron complexes of \textit{L}\textsuperscript{3}, undertaken with the aim of producing Fe-Mo complexes which incorporate the features of thiolato- ligation. This work does not represent the full scope of possible reactions or approaches to such complexes but is included here as a record for future workers.

The coordination chemistry of thiolato- ligands is complicated by two features. Firstly, thiolato- ligands show a marked tendency to function as bridging ligands and frequently form oligomeric or polymeric materials. These materials are particularly undesirable.
in six-coordinate metal systems where three-dimensional polymers may form. Secondly, with high oxidation state metal ions the ligands are often oxidised to the appropriate disulphide with concomitant reduction of the metal. Polymer formation and ligand oxidation reactions have restricted the coordination chemistry of \( L^3 \) to complexes of Ni(II), Pd(II) and Zn(II),\(^{385,386}\) the successful isolation of these complexes being primarily due to their square-planar kinetically inert nature. The ligand coordination mode observed in \([\text{Ni}_3(L^3)_2]^{2+}\)\(^{385}\) is most common in these complexes (see Figure 5.3). Only one mononuclear

\[
\begin{align*}
\text{M} & = \text{M'} = \text{Ni(II), Zn(II)} \\
\text{M} & = \text{Pd(II)}, \text{M'} = \text{Ni(II)}
\end{align*}
\]

Figure 5.3. Known complexes of \( L^3 \).\(^{385,386}\)

complex of \( L^3 \) has been reported;\(^{386}\) the reaction of palladium acetate with \( L^3 \) in ethylacetate or methanol yields this yellow complex, Pd(\( L^3 \)). The tendency of the thiolato- sulphur atoms to participate in bridge formation is reflected in the reaction of Pd(\( L^3 \)) and \([\text{Ni(H}_2\text{O})_6]^{2+}\) to form the mixed-metal complex, \([\text{Ni[Pd}(L^3)]_2]^{2+}\).\(^{386}\) Recently, an iron carbonyl complex containing the related ligand 1,4,7,10-tetrathiadecane has been prepared and structurally characterised.\(^{387}\)
5.2 EXPERIMENTAL SECTION

5.2a Macro cyclic Tetrathiaether Complexes of Molybdenum(0) and Tungsten(0)

5.2a.1 Materials and Methods

The compounds Mo(CO)$_6$ and W(CO)$_6$ (Aldrich Chemicals, Milwaukee and Fluka Chemicals, Switzerland, respectively) were used without further purification. The method of Wilkinson et al.$^{388}$ was used to prepare RhCl(PPh$_3)_3$.

Except where specified, all preparative procedures were performed under dinitrogen using deoxygenated solvents. With the exception of the $^1$H n.m.r. of $cis$-W(CO)$_4$L$_2$, L$^1$ and L$^2$ (Varian CFT-20), all n.m.r. spectra were obtained on the Bruker HFX-270 instrument. Melting points were determined using a Gallenkamp melting point apparatus.

**Preparation of Ligands.** The ligands L$^1$ and L$^2$ were prepared by the method of Rosen and Busch$^{369}$ via the intermediate, L$^3$. (Figure 5.4)

L$^1$: Obtained as white crystals, m.p. 120°C.

**Anal.** Calcd. for C$_{10}$H$_{20}$S$_4$: C, 44.8; H, 7.5; S, 47.8.

Found: C, 45.0; H, 7.6; S, 47.6%.

Infrared spectrum: 2960s, 2940s, 2920s, 1435m, 1435s, 1350w, 1275w, 1260w, 1210s, 1145s, 1040w, 1025w, 1010w, 920w, $\nu$(CSC) 795s and 708s, 405w cm$^{-1}$.

$^1$H n.m.r. spectrum, 80 MHz (CDC$_3$): $\delta$1.93 (4H, p, J = 6.2 Hz, $\beta$-CH$_2$) overlapping 2.67 (t, J = 7.3 Hz) and 2.77 (s), total 16H, $\alpha$-CH$_2$.

$^{13}$C-$^1$H n.m.r. spectrum, 20 MHz (CD$_2$Cl$_2$): $\delta$30.08 (s, $\alpha$- and $\beta$- propano-), 31.29 (s, $\alpha$- ethano-)

Mass spectrum: m/e 270(11%), 269(9), 268 (M$^+$, 57), 136(3), 135(8), 134(27), 133(31), 121(2), 120(9), 119(7), 108(12), 107(30), 106(100), 105(13), 101(5), 100(4), 87(10), 75(5), 74(18), 73(23), 64(12), 61(28),
Figure 5.4. The preparation of ligands L₁, L₂ and L₃.

L₂: Obtained as white crystals, m.p. 85°C.

Found: C, 54.6; H, 6.7; S, 38.8%.

Infrared spectrum: 2920s, 2840w, 1485w, 1450m, 1430s, 1415s, 1405s, 1345w, 1310w, 1270s, 1250m, 1200s, 1150w, 1070w, 940w, 930w, 865m, 773s, 768s, 720s, v(CSC) 710s and 680s, 668w, 560w, 465w, 425w cm⁻¹.

¹H n.m.r. spectrum, 80 MHz (CDCl₃): 61.89 (2H,p, J = 6.8 Hz, β-CH₂), overlapping 2.71 (t, J = 6.6 Hz) and 2.86 (s) total 12H, α-CH₂, 3.97 (4H,s,benzylic H), 7.32-7.26 (m, aromatic H plus CHCl₃).
\(^{13}\)C-{\(^{1}\)H} n.m.r. spectrum, 20 MHz (CD\(_2\)Cl\(_2\)): δ30.18 (s, β-CH\(_2\)); 30.48, 32.55, 33.20, 33.81 (s, α-CH\(_2\)); 127.48, 130.14 (s, aromatic CH); 136.00 (s, quaternary aromatic C).

Mass Spectrum: m/e 332(9%), 331(8), 330(M\(^{+}\), 36), 195(6), 169(4), 168(4), 167(26), 147(8), 146(11), 145(100), 144(14), 107(22), 106(17), 105(8), 104(23), 103(10), 91(13), 78(9), 73(10), 61(11), 60(8), 59(8), 45(13), 41(13).

5.2a.2 Preparation of the Complexes

fac-Tricarbonyl(1,4,8,11-tetra thiacyclotetradecane)molybdenum(O)

A mixture of Mo(CO)\(_6\) (0.10 g, 0.38 mmol) and L\(^1\) (0.114 g, 0.35 mmol) in ethanol (10 mL) was refluxed for 2.5 hrs. The solid formed was isolated by filtration of the hot solution in air. The light yellow crystals were washed with hot ethanol and dried under vacuum. The yield was 0.136 g (80%).

Anal. Calcd. for C\(_{13}\)H\(_{20}\)MoO\(_3\)S\(_4\): C, 34.8; H, 4.5; N, nil; Mo, 21.4; O, 10.7; S, 28.6. Found: C, 35.10; H, 4.6; N, nil; Mo, 21.3; O, 10.8; S, 28.4%.

fac-Tricarbonyl(3,6,10,13-tetra thiabicyclo[13.4.0]nona-1,16,18-triene)molybdenum(O)

A mixture of Mo(CO)\(_6\) (0.10 g, 0.38 mmol) and L\(^2\) (0.125 g, 0.38 mmol) in ethanol (15 mL) was refluxed for 2 hrs. The light yellow crystals which precipitated were collected by filtration of the hot solution in air, washed with hot ethanol and dried under vacuum. The yield was 0.19 g (80%).

Anal. Calcd. for C\(_{15}\)H\(_{22}\)MoO\(_3\)S\(_4\): C, 42.3; H, 4.3; N, nil; Mo, 18.8; O, 10.2; S, 25.1. Found: C, 42.4; H, 4.4; N, nil; Mo, 18.9; O, 10.5; S, 24.8%.

µ-1,4,8,11-Tetra thiacyclotetradecanebis[tetracarbonyltungsten(O)]

A mixture of W(CO)\(_6\) (0.10 g, 0.28 mmol) and L\(^1\) (0.04 g,
0.15 mmol) in ethanol (5 mL) was refluxed under constant irradiation from a Wotan XBO 150 W Lamp. After 7 hrs, a yellow solid precipitated and was filtered, in air, from the hot solution. The solid was washed with ethanol, then dichloromethane and dried under vacuum. The yield was 0.06 g (43%).

**Anal.** Calcd. for C₁₉H₂₆O₆S₄W₂: C, 25.1; H, 2.4; N, nil; S, 14.7. Found: C, 25.6; H, 2.8; N, nil; S, 14.7%.

**Tetracarbonyl-cis-(3,6,10,13-tetrathiabicyclo[13.4.0]nona-1,16,18-triene)tungsten(0)**

A suspension of W(CO)₆ (0.10 g, 0.28 mmol) and L² (0.11 g, 0.33 mmol) in ethanol (10 mL) was refluxed under constant irradiation from a Wotan XBO 150 W Lamp for 4 hrs. Slow evaporation of the resulting solution (in air) to a volume of ca. 5 mL resulted in the precipitation of several substances, which were isolated by filtration. Clusters of yellow crystals were separated by hand and recrystallised from dichloromethane/n-hexane. The yield was 0.044 g (25%).

**Anal.** Calcd. for C₂₃H₂₂O₆S₄W₂ ([W(CO)₄]₂-µ-L²): C, 29.9; H, 2.4; N, nil; 0, 13.9; S, 13.9. Calcd. for C₁₉H₂₂O₆S₄W (W(CO)₄L²): C, 36.4; H, 3.5; N, nil; 0, 10.2; S, 20.5. Found: C, 36.4; H, 3.6; N, nil; 0, 10.4; S, 20.5%.

### 5.2a.3 Characterization of the Complexes

#### 5.2a.3.1 Physical Properties

Some physical properties of the complexes are given in Table 5.1.

**fac-Mo(CO)₃L¹:** The compound is soluble in many organic solvents with the exception of alcohols, ether and n-hexane. Solutions in non-coordinating solvents (CH₂Cl₂, CH₃NO₂, acetone) are stable for a number of days. Treatment with strongly coordinating solvents (dmf, CH₃CN, H₂O) causes the decomposition of the complex.
Table 5.1
Physical Properties of the Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>m.p. (°C)</th>
<th>$A_0$ (cm$^{-1}$ mol$^{-1}$)</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>fac-Mo(CO)$_3$L$^1$</td>
<td>180$^a$</td>
<td>0.1</td>
<td>451 (448)</td>
</tr>
<tr>
<td>fac-Mo(CO)$_3$L$^2$</td>
<td>195$^a$</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>[W(CO)$_4$]$^2$-µ-L$^1$</td>
<td>200$^a$</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>cis-W(CO)$_4$L$^2$</td>
<td>185$^a$</td>
<td>0.1</td>
<td>650 (626)</td>
</tr>
</tbody>
</table>

a) Decomposes. b) Insufficient solubility prevents measurement.
c) The typical $A_0$ range for 1:1 electrolytes in CH$_3$NO$_2$ is 60-115 cm$^{-1}$ mole$^{-1}$.$^{220}$

fac-Mo(CO)$_3$L$^2$: The complex is only slightly soluble in the above solvents and is also decomposed by coordinating solvents.

[W(CO)$_4$]$^2$-µ-L$^1$: The complex is very insoluble.

cis-W(CO)$_4$L$^2$: Solubility properties similar to fac-Mo(CO)$_3$L$^1$. The ligand is not readily replaced by solvents.

The mass spectra of the complexes are identical to those of the respective free ligands.

5.2a.3.2 Infrared Spectra

The important solution and solid state infrared bands of the complexes are given in Table 5.2. The spectra are presented for discussion in Section 5.3a. Additional ligand vibrations are listed below (unless specified, all bands are weak compared to $\nu$(CO) and are in cm$^{-1}$).


fac-Mo(CO)$_3$L$^2$: 2910m, 1485, 1450, 1430m, 1420m, 1410m, 1295, 1265,
1235, 1150, 1120, 1115, 1070, 1020, 925, 910, 890, 880, 865, 850, 840, 780, 760, 710, 470.

\[ [\text{W(CO)}_4]_\text{2} - \mu - \text{L}^1: \quad 2920, 1445, 1415\text{m}, 1410\text{m}, 1335, 1295, 1275, 1260, 1250, 1170, 1140, 1110, 1030, 1005, 970, 920, 900, 835, 725, 500. \]

\[ \text{cis-}[\text{W(CO)}_4] \text{L}^2: \quad 2920, 1485, 1450, 1430, 1405, 1300, 1265, 1230, 1160, 1110, 970, 900, 860, 850, 780, 770, 750, 715, 500, 445. \]

### Table 5.2

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \nu(\text{CO}) )</th>
<th>( \delta(\text{M-CO}) )</th>
<th>( \nu(\text{M-S}) )</th>
<th>( \nu(\text{M-CO}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{fac-Mo(CO)}_3\text{L}^1 )</td>
<td>1925s, 1810sh, 1790s</td>
<td>647s, 615s, 522sh, 518s</td>
<td>470w</td>
<td></td>
</tr>
<tr>
<td>( \text{fac-Mo(CO)}_3\text{L}^1 )</td>
<td>1935s (a(_1)), 1820s (e)</td>
<td>I(<em>e/I</em>{a_1}) = 2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{(CH}_2\text{Cl}_2) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{fac-Mo(CO)}_3\text{L}^2 )</td>
<td>1928s, 1818s, br</td>
<td>647s, 615s, 518s</td>
<td>470w</td>
<td></td>
</tr>
<tr>
<td>( \text{fac-Mo(CO)}_3\text{L}^2 )</td>
<td>1940s (a(_1)), 1825s (e)</td>
<td>I(<em>e/I</em>{a_1}) = 2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{(CH}_2\text{Cl}_2) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( [\text{W(CO)}<em>4]</em>\text{2} - \mu - \text{L}^1 )</td>
<td>2010s, 1880s, br, 1850sh</td>
<td>610s, 570s, 560sh</td>
<td>465w, 385s</td>
<td></td>
</tr>
<tr>
<td>( \text{cis-W(CO)}_4\text{L}^2 )</td>
<td>2010s, 1900sh, 1875s, 1840s</td>
<td>610s, 575s</td>
<td>470w, 380w</td>
<td></td>
</tr>
<tr>
<td>( \text{cis-W(CO)}_4\text{L}^2 )</td>
<td>2020s (a(_1)), 1895s, 1865s</td>
<td>(a(_2), b(_1), b(_2))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{(CH}_2\text{Cl}_2) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{cis-W(CO)}_4\text{L}^2 )</td>
<td>2020 (a(_1)), 1910s, 1890s</td>
<td>(a(_2), b(_1), b(_2))</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) In CsI unless specified; s, strong; br, broad; w, weak; sh, shoulder; I, intensity. Vibration modes are given in parentheses for solution spectra.
5.2a.3.3 $^1$H and $^{13}$C-$^1$H N.M.R. Spectra

The n.m.r. spectra of the soluble $^{\text{faco-Mo(CO)}_3L^1}$ and $^{\text{cis-W(CO)}_4L^2}$ complexes are given in Table 5.3. The spectra are presented for discussion in Section 5.3a.

### Table 5.3

$^1$H and $^{13}$C-$^1$H N.M.R. Spectra of $^{\text{faco-Mo(CO)}_3L^1}$ and $^{\text{cis-W(CO)}_4L^2}$

<table>
<thead>
<tr>
<th>Nucleus, complex</th>
<th>$\delta$ (ppm)$^a$</th>
<th>Assignment$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$C, $^{\text{faco-Mo(CO)}_3L^1}$ ($25^\circ$C)</td>
<td>25.47, 26.21, 26.51, 30.11, 32.19, 33.95, 35.34, 38.10, 44.35</td>
<td>CH$_2$</td>
</tr>
<tr>
<td></td>
<td>223.14</td>
<td>CO</td>
</tr>
<tr>
<td>$^{13}$C, $^{\text{faco-Mo(CO)}_3L^1}$ ($-70^\circ$C)</td>
<td>24.53, 25.22, 25.89, 29.50, 31.50, 31.71, 33.95, 34.47, 38.51, 43.95</td>
<td>CH$_2$</td>
</tr>
<tr>
<td></td>
<td>223.09</td>
<td>CO</td>
</tr>
<tr>
<td>$^{13}$C, $^{\text{cis-W(CO)}_4L^2}$</td>
<td>29.94, 32.03, 32.47, 33.64, 34.16, 34.98, 35.80, 40.25, 45.54</td>
<td>CH$_2$</td>
</tr>
<tr>
<td></td>
<td>128.50, 129.02, 129.51, 131.52, 134.77, 135.81, 134.77, 135.81, 204.70</td>
<td>$^2$° aromatic C, 3° aromatic C</td>
</tr>
<tr>
<td></td>
<td>204.70</td>
<td>CO</td>
</tr>
</tbody>
</table>

---

a) In CD$_2$Cl$_2$ or CH$_2$Cl$_2$, relative to Me$_4$Si: br, broad; m, multiplet; s, singlet. All $^{13}$C resonances are singlets. The free ligand spectra are given in Section 5.2a.1. b) Resonating nuclei are underlined.
The resonances of the very complex $^1$H n.m.r. spectrum of $\text{fac-Mo(CO)}_3L^1$ are listed below.

$\text{fac-Mo(CO)}_3L^1$: $^1$H n.m.r. spectrum, 270 MHz (CD$_2$Cl$_2$, 25°C), $\delta$ (ppm) (relative intensity, %) 2.03(16), 2.10(46), 2.08(61), 2.12(47), 2.13(26), 2.26(20), 2.27(20), 2.30(20), 2.31(31), 2.36(20), 2.43(25), 2.44(44), 2.46(52), 2.47(62), 2.51(77), 2.51(56), 2.54(45), 2.56(27), 2.57(23), 2.79(81), 2.81(59), 2.82(58), 2.83(71), 2.88(37), 2.90(22), 2.93(45), 2.97(44), 2.99(36), 3.03(25), 3.05(38), 3.06(27), 3.11(100), 3.14(78), 3.16(95), 3.17(64), 3.20(44), 3.21(44), 3.25(55), 3.26(36) 3.30(17), 3.32(20).

5.2.3.4 Electronic Spectra

The electronic spectra of $\text{fac-Mo(CO)}_3L^1$ and $\text{cis-W(CO)}_4L^2$ are shown in Figure 5.5 and summarised in Table 5.4.

![Figure 5.5. The electronic spectra of a) fac-Mo(CO)$_3$L$^1$ and b) cis-W(CO)$_4$L$^2$ in dichloromethane. For the dashed line portion of spectrum b, the $\varepsilon$ scale should be doubled.](image-url)
Table 5.4
Electronic Spectral Data

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ ($1\text{cm}^{-1}\text{mole}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{fac-Mo(CO)}_3\text{L}^1$</td>
<td>332</td>
<td>6680</td>
</tr>
<tr>
<td>$\text{cis-W(CO)}_4\text{L}^2$</td>
<td>372</td>
<td>1990</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>10700</td>
</tr>
</tbody>
</table>

5.2b Molybdenum Complexes of 1,4,8,11-Tetrathiaundecane

5.2b.1 Materials and Methods

The ligand $\text{L}^3$ was prepared by the method of Rosen and Busch\textsuperscript{369} given in Figure 5.4.

$L^3$: Obtained as a colourless liquid.

*Anal.* Calcd. for $\text{C}_7\text{H}_{16}\text{S}_4$: C, 36.8; H, 7.1; S, 56.1.

Found: C, 37.0; H, 7.0; S, 56.1%.

Infrared spectrum (neat): broad bands at 2920s, 2840m, $\nu$(S-H) 2540m, 1425s, 1385w, 1270s, 1260s, 1210s, 1140w, 960w, 850w, 770w, 700m cm$^{-1}$.

Mass spectrum: m/e 228(M$^+$, 19%), 168(15), 167(30), 108(6), 107(59), 106(9), 105(10), 75(10), 74(12), 73(17), 61(100), 60(10), 59(12), 47(20), 46(10), 45(22), 41(18), 39(7), 35(10).

The following starting materials were prepared by literature methods: $\text{cis-MoO}_2(\text{acac})_2$,$^389$ $\text{MoCl}_4(\text{CH}_3\text{CN})_2$,$^390$ $\text{K}_4[\text{MoO}_2(\text{CN})_4].6\text{H}_2\text{O}$,$^391,392$

$\text{MoO(S}_2\text{CNET}_2)_2$,$^{125}$ $\text{MoCl}_3(\text{thf})_3$,$^{393}$ $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$,$^{394}$ $\text{Mo}_2(\text{O}_2\text{CH})_4$,$^{395}$

$\text{MoBr}_2(\text{CO})_4$,$^{396}$ $\text{FeCl}_2.2\text{H}_2\text{O}$,$^{397}$ $\text{(NH}_4)_2[\text{MoO}_2\text{S}_2]$,$^{216}$ $\text{(Et}_4\text{N})_2[\text{MoO}_2(\text{NCS})_4]$,$^{398}$

and $\text{K}_2[\text{MoO(SCH}_2\text{CH}_2\text{S})_2].2\text{EtOH}$.$^{399}$

Unless specified, all reactions were performed under dinitrogen using deoxygenated solvents.
5.2b.2 The Direct Reaction of \( \text{L}^3 \) or \( \text{Na}_2(\text{L}^3) \) with Metal Complexes

The reactions of \( \text{L}^3 \) and \( \text{Na}_2(\text{L}^3) \) with various molybdenum and iron starting materials are summarised in Table 5.5. The general methods used were as follows.

**Method A:** Direct Addition of \( \text{L}^3 \). In these reactions a solution of the metal complex in the specified solvent was treated with \( \text{L}^3 \) in the same solvent. Other reaction conditions are given in Table 5.5. The products precipitated from solution, were collected, washed with the solvent and dried under vacuum.

**Method B:** Direct Addition of Methanolic \( \text{Na}_2(\text{L}^3) \) Solutions. A solution of the metal complex in the specified solvent was treated with \( \text{Na}_2(\text{L}^3) \) in methanol (formed by the reaction of \( \text{L}^3 \) and sodium metal in methanol). Other reaction conditions are given in Table 5.5 and the products were formed and isolated as per Method A.

**Method C:** Addition of Solid \( \text{Na}_2(\text{L}^3) \). Solid \( \text{Na}_2(\text{L}^3) \) was prepared as follows. A suspension of \( \text{L}^3 \) (5.0 g, 22 mmol) in 50 mL of methanol containing sodium methoxide (formed by the addition of sodium (1.0 g, 45 mmol) to the \( \text{L}^3 \)/methanol suspension) was stirred for 2 hrs. The volume of the solution was then reduced to ca. 15 mL and ether (80 mL) was added to precipitate \( \text{Na}_2(\text{L}^3) \). After cooling at 4°C for 24 hrs, the solid was filtered, washed with ether and dried under vacuum. In Method C, a solution of the metal complex in the specified solvent was stirred with suspended \( \text{Na}_2(\text{L}^3) \) for 24 hrs. The insoluble product was filtered, washed with methanol and dried under vacuum.

5.2b.3 Template Assisted Synthesis of \( \text{L}^3 \) Complexes

In an attempt to prepare precursor bis(ethanedithiolato)-complexes for further reaction with \( \text{C}_3\text{H}_6\text{Br}_2 \) (see Section 5.3b) the following two reactions were performed.
### Table 5.5
Reactions of $L^3$ or $Na_2(L^3)$ with Molybdenum and Iron Complexes$^a$

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>Method</th>
<th>Solvent</th>
<th>Other Conditions</th>
<th>Product$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$MoO_2(acac)_2$</td>
<td>A</td>
<td>$CH_3OH$</td>
<td>Slow addition at room temperature</td>
<td>Red solid, $Mo_2(L^3)_3, \nu(Mo-O) \ 925 \ \text{cm}^{-1}$.</td>
</tr>
<tr>
<td>$MoO_2(acac)_2$</td>
<td>A</td>
<td>thf</td>
<td>Addition at $-15^\circ C$, warm to room temperature</td>
<td>Red solid, $Mo_2(L^3)_3, \nu(Mo-O) \ 925 \ \text{cm}^{-1}$.</td>
</tr>
<tr>
<td>$MoO_2(acac)_2$</td>
<td>B</td>
<td>$CH_3OH$</td>
<td>Slow addition at $-15^\circ C$, warm</td>
<td>Red solid, $Mo_2(L^3)_3, \nu(Mo-O) \ 925 \ \text{cm}^{-1}$.</td>
</tr>
<tr>
<td>$MoCl_4(CH_3CN)_2$</td>
<td>B</td>
<td>$CH_2Cl_2$</td>
<td>Slow addition</td>
<td>Dark brown solid, $Mo(L^3)Cl$</td>
</tr>
<tr>
<td>$MoCl_3(thf)_3$</td>
<td>B</td>
<td>$CH_2Cl_2$</td>
<td>Fast addition</td>
<td>Dark brown solid, $Mo(L^3)Cl$</td>
</tr>
<tr>
<td>$MoCl_3(thf)_3$</td>
<td>C</td>
<td>$C_6H_6$</td>
<td>Slow addition</td>
<td>Brown solid, $Mo(L^3)Cl_3$</td>
</tr>
<tr>
<td>$MoCl_3(thf)_3$</td>
<td>C</td>
<td>$C_6H_6$</td>
<td>Solid washed with water to remove NaCl, filter wash</td>
<td>Brown solid, $Mo_2(L^3)_2Cl_3$</td>
</tr>
<tr>
<td>$MoCl_3(thf)_3$</td>
<td>C</td>
<td>$CH_2Cl_2$</td>
<td>to warm to room temperature</td>
<td>Brown solid, $Mo_2(L^3)_2Cl_3$</td>
</tr>
<tr>
<td>$Mo_2(acetate)_4$</td>
<td>A</td>
<td>thf</td>
<td>$-15^\circ C$, warm to room temperature</td>
<td>No reaction</td>
</tr>
<tr>
<td>$Mo_2(acetate)_4$</td>
<td>B</td>
<td>$CH_3OH$</td>
<td>Slow addition</td>
<td>Purple solid*, $Mo(L^3)_2$</td>
</tr>
<tr>
<td>$Mo_2(formate)_4$</td>
<td>A</td>
<td>thf</td>
<td>Slow addition</td>
<td>No reaction</td>
</tr>
<tr>
<td>$MoBr_2(CO)_4$</td>
<td>A</td>
<td>$CH_3OH$</td>
<td></td>
<td>Grey solid*, $Mo_1.25(L^3)_2$, no $\nu(CO)$</td>
</tr>
<tr>
<td>$MoBr_2(CO)_4$</td>
<td>B</td>
<td>thf</td>
<td>Addition at $-78^\circ C$, then allowed</td>
<td>Grey solid, as above</td>
</tr>
<tr>
<td>$MoBr_2(CO)_4$</td>
<td>B</td>
<td>$CH_3OH$</td>
<td>to warm to room temperature</td>
<td>Black solid, as above</td>
</tr>
<tr>
<td>$K_4[MoO_2(CN)_4].6H_2O$</td>
<td>A</td>
<td>$H_2O$</td>
<td></td>
<td>No reaction</td>
</tr>
<tr>
<td>$FeCl_3$</td>
<td>A</td>
<td>$CH_3CH_2OH$</td>
<td>Suspension of solid and $L^3$ treated</td>
<td>White solid, disulphide</td>
</tr>
<tr>
<td>$FeCl_2.2H_2O$</td>
<td>-</td>
<td>$CH_3CH_2OH$</td>
<td>with NaOEt/EtOH, then filtered</td>
<td>Brown solution, solid not isolable.</td>
</tr>
</tbody>
</table>

$^a$ The stoichiometry of the reactions was metal:$L^3 = 1:1$, solution volume not critical. $^b$ Products formulated on the basis of analysed elements only. Analyses do not closely match any reasonable formulation. * = air sensitive.
The Reaction of (Et₄N)₂[MoO₂(NCS)₄] and Na₂(SCH₂CH₂S)

This reaction was performed in air. A solution of 0.18 M Na₂(SCH₂CH₂S) in methanol (20 mL) was added dropwise over a period of 1 hr to a solution of (Et₄N)₂[MoO₂(NCS)₄] (1.0 g, 1.61 mmol) in dichloromethane (150 mL). After stirring for 1 hr, the solution was washed with 2x70 mL portions of water and the organic phase was dried over sodium sulphate (anhyd.). Following filtration of the organic phase, the volume of the filtrate was reduced to ca. 20 mL and ether (100 mL) was added. Cooling at 2°C overnight produced a small yield of orange crystals which were recrystallised from dichloromethane/ether.

Anal. Calcd. for C₁₅H₃₅Mo₂NO₃S₆: C, 27.2; H, 5.3; N, 2.1; S, 29.1.
Found: C, 27.3; H, 5.2; N, 2.0; S, 28.9%.

Infrared spectrum: 2980m*, 2940m, 2915m, 2900m, 2800w, 1460br m*, 1410m*, 1320m*, 1285w, 1275w, 1260m, 1183s*, ν(C-O) 1075s and 1067s, 1030w*, ν(Mo=O₄) 932s, 922s and 910s, 840w, 800w*, 425w, ν(Mo-S) 365s, 350s and 315m cm⁻¹ (* from Et₄N⁺)

The Reaction of cis-MoO₂(acac)₂ and Na₂(SCH₂CH₂S)

This reaction was performed in air. A solution of 0.23 M Na₂(SCH₂CH₂S) in methanol (70 mL) was added dropwise over a period of 1 hr to a solution of cis-MoO₂(acac)₂ (2.6 g, 7.98 mmol) in methanol (200 mL). After stirring for 2 hrs, the mixture was filtered and the filtrate was reduced to dryness on a rotary evaporator. The residue was suspended in water (10 mL) and filtered. A solution of PPh₄Cl (0.4 g) in water (4 mL) was added to the filtrate to precipitate an orange solid which was filtered, washed with water and air dried. The solid was recrystallised from methanol by the addition of a solution of PPh₄Cl in methanol. The yield of orange crystals was 0.25 g. The compound may be further purified by recrystallization from dichloromethane/ether.
**Analysis**

Calcd. for $\text{C}_5\text{H}_5\text{Mo}_2\text{O}_3\text{P}_2\text{S}_6$, (PPh$_4$)$_2$[Mo$_2$O$_3$(SCH$_2$CH$_2$S)$_3$]:

C, 54.3; H, 4.4; S, 16.1.

Calcd. for $\text{C}_5\text{H}_4\text{Mo}_2\text{O}_2\text{P}_2\text{S}_6$, (PPh$_4$)$_2$[Mo$_2$O$_2$S$_2$(SCH$_2$CH$_2$S)$_2$]: C, 54.3; H, 4.2; S, 16.7.

Found: C, 53.5; H, 4.2; S, 16.0%.

Infrared spectrum: 3050w*, 2900m, 2820w, 1585w*, 1480m*, 1435s*, 1320w, 1270m, 1110s*, 1000s*, $\nu$(Mo=O$_{\text{t}}$) 918s and 885m, 760sh, 750m*, 720s*, 690s*, 545sh, 530s*, $\nu$(Mo=S) 360w, 340m and 310w cm$^{-1}$ (* from PPh$_4^+$).

---

**The Reaction of K$_2$[MoO(SCH$_2$CH$_2$S)$_2$.2EtOH and Br(CH$_2$)$_3$Br**

A solution of Br(CH$_2$)$_3$Br (0.088 g, 0.43 mmol) in dimethylsulphoxide (5 mL) was added to a solution of K$_2$[MoO(SCH$_2$CH$_2$S)$_2$.2EtOH (0.188 g, 0.40 mmol) in the same solvent (4 mL). The mixture was allowed to stand for 1 hr, then water (15 mL) was added to precipitate a white solid. The solid was filtered, washed with water and dried under vacuum.

**Analysis**

Calcd. for $\text{C}_7\text{H}_{14}\text{MoOS}_4$: C, 25.0; H, 3.6; S, 38.1; Mo, 28.5.

Found: C, 24.7; H, 4.1; S, 39.2; Mo, 26.0%. The analysis indicates slight contamination with dimethylsulphoxide.

Infrared spectrum: 2940w, 2905w, 2895w, 1430w, 1420w, 1415w, 1295w, 1285w, 1275w, 1265w, 1195w, 1030w, $\nu$(Mo=O$_{\text{t}}$) 860s and 853s, $\nu$(Mo=S) 355m and 330m cm$^{-1}$.

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**5.3 DISCUSSION**

5.3a Macro cyclic Tetrathiaether Complexes of Molybdenum(0) and Tungsten(0)

In comparison to other transition metals, relatively few macrocyclic tetrathiaether complexes of molybdenum and tungsten are known. Although attempts to prepare such complexes with high oxidation state molybdenum and tungsten centres have been unsuccessful, the preferential binding of the soft thiaether donor atom to soft metal ions may be expected to favour complex formation
with low oxidation state molybdenum and tungsten. Indeed, the reactions of \( \text{M(CO)}_6 \) (\( \text{M} = \text{Mo}, \text{W} \)) and the ligands \( \text{L}^1 \) and \( \text{L}^2 \) leads to the ready formation of the new complexes \( \text{faa-Mo(CO)}_3\text{L}^1\cdot\text{L}^2 \), \( \text{cis-W(CO)}_4\text{L}^2 \) and \( \text{[W(CO)}_4\text{]}_2\cdot\mu-\text{L}^1 \). Under dinitrogen, the formation of the molybdenum complexes proceeds smoothly in refluxing ethanol, however, photolysis of the reaction mixture is also required in the preparation of the tungsten complexes.

The complexes are air stable light yellow (\( \text{M} = \text{Mo} \)) or yellow (\( \text{M} = \text{W} \)) crystalline solids. Elemental analysis and conductivity and molecular weight measurements indicate that, with the exception of \( \text{[W(CO)}_4\text{]}_2\cdot\mu-\text{L}^1 \), the complexes are neutral monomeric species in solution. The complexes \( \text{faa-Mo(CO)}_3\text{L}^1 \) and \( \text{cis-W(CO)}_4\text{L}^2 \) exhibit negligible solution conductivities and molecular weights which are in good agreement with those calculated for their respective formulae. On the basis of its spectroscopic similarity to \( \text{faa-Mo(CO)}_3\text{L}^1 \), \( \text{faa-Mo(CO)}_3\text{L}^2 \) is also assigned a neutral monomeric structure, despite an inability to perform the above mentioned solution measurements on this sparingly soluble complex. The empirical formula and high insolubility of \( \text{[W(CO)}_4\text{]}_2\cdot\mu-\text{L}^1 \) suggests that this complex is a neutral dimer.

Two structural types may be envisaged for these complexes, \textit{viz.} high coordination number complexes in which full tetradeutate coordination of the \( \text{S}_4 \)-ligand (\textit{i.e.} \( \text{L}^1 \) or \( \text{L}^2 \)) occurs, or six coordinate complexes in which partial coordination of the \( \text{S}_4 \)-ligand occurs. In the majority, zerovalent molybdenum and tungsten complexes obey the E.A.N. rule and display an octahedral coordination sphere about the 18-electron metal atom.\textsuperscript{400} In following this precedent, the \( \text{Mo(0)} \) and \( \text{W(0)} \) complexes of \( \text{L}^1 \) and \( \text{L}^2 \) are required to display
partial coordination of the potentially tetradentate $S_4$-ligands. Indeed, the spectroscopic properties of the complexes show them to be octahedral complexes in which the $L^1$ and $L^2$ ligands exhibit partial and unprecedented binding modes.

The infrared spectra of the complexes provide valuable structural information.

**Solution Infrared Spectra**

$2000 - 1700 \text{ cm}^{-1}$ $\nu$(CO) Region: The solution infrared spectra of octahedrally substituted carbonyl complexes have been extensively studied. Compounds of the type $\text{fac-M(CO)}_3L_3$ are reported to exhibit two bands resulting from the $\nu$(CO) modes shown in Figure 5.6.

![Diagram](image)

Figure 5.6. Carbonyl stretching vibrations for complexes of the type $\text{fac-M(CO)}_3L_3$.

$\text{mer-M(CO)}_3L_3$ complexes exhibit three infrared and Raman active $\nu$(CO) bands ($2a_1$, $b_1$). The infrared spectra of $\text{fac-Mo(CO)}_3L^1,^2$ in dichloromethane (Figure 5.7) show two intense bands in the $\nu$(CO) region, consistent with a *facial* tricarbonyl configuration. The bands at 1940 cm$^{-1}$ in both complexes are assigned to the $a_1$ mode, the bands at lower frequency being assigned to the $e$ mode. As predicted for this substitution pattern, the degenerate mode is roughly twice the intensity of the $a_1$ mode. Broadening of the $e$ mode due to partial lifting of the degeneracy, by either asymmetric $S_4$-ligand binding or solvent interactions, is also
observed. The facial tricarbonyl configuration of the Mo(CO)$_3$L$_1$,$^2$ complexes is preferred since the strongly π-accepting carbonyl ligands can avoid competition for d-orbital electron density. Bands of similar position have been reported for the complexes $\text{fac-Mo(CO)}_3$L ($L = 3,6,9$-trithiaundecane$^{349}$) and $\text{fac-Mo(CO)}_3$L$_3$ ($L = \text{SMe}_2$, $^{401}$SEt$_2$, $^{402}$ and S$^{403}$).

Figure 5.7. Solution infrared spectra in the ν(CO) region. a) dichloromethane, b) $\text{fac-Mo(CO)}_3$L$_1$ in dichloromethane, c) $\text{fac-Mo(CO)}_3$L$_2$ in dichloromethane, d) $\text{cis-W(CO)}_4$L$_2$ in benzene and e) $\text{cis-W(CO)}_4$L$_2$ in dichloromethane.

For complexes of the type $\text{cis-M(CO)}_4$L$_2$, the ν(CO) modes shown in Figure 5.8 are predicted. For such complexes the high frequency
Figure 5.8. Carbonyl stretching vibrations for complexes of the type \( \text{cis-M(CO)}_4\text{L}_2 \).

The \( a_1(1) \) mode is usually sharp and of medium intensity while the remaining bands are more intense and show a resolution which is generally solvent dependent. The complexes \( \text{trans-W(CO)}_4\text{L}_2 \) exhibit only one \( \nu(\text{CO}) \) band. The presence of four \( \nu(\text{CO}) \) bands in the infrared spectrum of \( \text{cis-W(CO)}_4\text{L}_2 \) in benzene establishes its structural type (Figure 5.7). According to calculations for \( \text{cis-W(CO)}_4(\text{dppe}) \), the band at 2020 \( \text{cm}^{-1} \) for \( \text{cis-W(CO)}_4\text{L}_2 \) can be assigned to the \( a_1(1) \) mode. The low frequency bands cannot be assigned with present information. The insolubility of \( [\text{W(CO)}_4]_2-\mu-L \) prevents its study by solution infrared spectroscopy.

**Solid State Spectra.** The infrared spectra of the complexes in CsI are given in Figures 5.9 and 5.10.

2000 - 1700 \( \text{cm}^{-1} \) \( \nu(\text{CO}) \) Region: Two strong \( \nu(\text{CO}) \) bands are observed in the spectra of \( \text{fac-Mo(CO)}_3\text{L}_1\text{L}_2 \), the low frequency band being significantly split by solid state interactions. These bands are also Raman active, as predicted for the \text{facial} isomer. In the spectrum of \( \text{cis-W(CO)}_4\text{L}_2 \), the sharp \( \nu(\text{CO}) \) band at 2010 \( \text{cm}^{-1} \) may be assigned to the \( a_1(1) \) vibration while the clearly resolved low frequency bands represent the \( a_2(2) \), \( b_1 \) and \( b_2 \) vibration modes. Also, the grossly similar \( \nu(\text{CO}) \) pattern for both tungsten complexes supports a \( \text{cis-} \) configuration for the sulphur donor atoms in \( [\text{W(CO)}_4]_2-\mu-L \).
Figure 5.9. The infrared spectra of: I, $\text{fac-Mo(CO)}_3\text{L}^1$ in CsI; II, $\text{fac-Mo(CO)}_3\text{L}^2$ in CsI. An insert in the 700 - 600 cm$^{-1}$ region of both spectra shows the $\nu$(CSC) bands of the appropriate free ligand.
Figure 5.10. The infrared spectra of: I, \([\text{W(CO)}_4]_2-\mu-L^1\) in CsI; II, \(\text{cis-W(CO)}_4L^2\) in CsI. An insert in the 700 - 600 cm\(^{-1}\) region of both spectra shows the \(\nu(\text{CSC})\) bands of the appropriate free ligand.
1700 - 650 cm\(^{-1}\) Region: The infrared spectra in this region are indicative of thiaether coordination. The major feature in this region is the almost complete absence of the strong free ligand \(\nu\)(CSC) bands which occur in the 690 - 675 cm\(^{-1}\) region. This results from a decrease in the frequency and intensity of the \(\nu\)(CSC) modes upon coordination and has been used as evidence for sulphur coordination in complexes of thioxane,\(^4\) 404 pentamethylene sulphide\(^4\) 405 and \(L^1\) and \(L^2\).\(^3\) A reduction in the intensity of other ligand associated bands in this region also occurs upon ligand coordination.

650 - 250 cm\(^{-1}\) Region: Bands due to \(\delta\)(MCO), \(\nu\)(M-CO) and \(\nu\)(M-S) vibrations occur in this spectral region.\(^3\) While a marked difference in the \(\delta\)(MCO) and \(\nu\)(M-CO) bands of the molybdenum and tungsten complexes is expected to result from their disparate carbonyl ligand configurations, the \(\nu\)(M-S) bands of these complexes are likely to be similar. Consequently, the weak bands at ca. 470 cm\(^{-1}\) which are common to the spectra of all the complexes are assigned to \(\nu\)(M-S).

The \(\nu\)(M-CO) and \(\delta\)(MCO) modes of metal carbonyl complexes have been extensively studied.\(^3\) For octahedrally substituted carbonyl complexes these bands are generally observed in the following regions: \(\nu\)(M-CO), 428 - 366 cm\(^{-1}\); \(\delta\)(MCO), 787 - 468 cm\(^{-1}\). For complexes of the type \(\text{fac-M(CO)}_3L_3\), three \(\delta\)(MCO) and two \(\nu\)(M-CO) bands are predicted. In the complexes \(\text{fac-Mo(CO)}_3L^1L^2\), bands at 647, 615 and 518 cm\(^{-1}\) may be attributed to \(\delta\)(MoCO) in good agreement with literature values for complexes of the type \(\text{fac-Mo(CO)}_3L_3\) (\(L = \) phosphine ligand).\(^3\) The almost identical infrared spectra of \(\text{fac-Mo(CO)}_3L^1\) and \(\text{fac-Mo(CO)}_3L^2\) in this region confirms the presence of an identical donor atom set in these complexes. In the \(\nu\)(Mo-CO) region, no strong bands are observed.
For the tungsten complexes, six $\delta$(WCO) and four $\nu$(W-CO) modes are predicted for the $\text{cis-W(CO)_4L}_2$ type structure.\cite{347} In this region, strong bands at 615, 575, 565sh and 390 cm$^{-1}$ are observed for the tungsten complexes. The bands at 615, 575 and 565 cm$^{-1}$ may be assigned to $\delta$(WCO). These values compare well with those observed for $\text{cis-W(CO)_4L}_2$ (L = phosphine ligand) complexes where less than the six predicted bands are also observed due to band degeneracy.\cite{347} In contrast to $\text{fac-Mo(CO)_3L}_1$, a very strong band in the $\nu$(M-CO) region is observed for the tungsten complexes at ca. 380 cm$^{-1}$. Again, the identical band pattern in the spectra of the two tungsten complexes indicates a similar coordination environment about the metal atoms.

The structural features determined above dictate tridentate and bidentate coordination of L$_1$\textsuperscript{2} in the molybdenum and tungsten complexes respectively. In the cases of $\text{fac-Mo(CO)_3L}_1$ and $\text{cis-W(CO)_4L}_2$, the ligand conformations can be studied by $^1$H and $^{13}$C-$^1$H n.m.r. spectroscopy.

The $^1$H and $^{13}$C-$^1$H n.m.r. spectra of $\text{fac-Mo(CO)_3L}_1$, shown in Figures 5.11 and 5.13 respectively, are extremely complex in comparison to the simple spectra of the free L$_1$ ligand. This complexity results from the methylene group inequivalence produced by the unsymmetrical tridentate coordination of the S$_4$-ligand. The presence of geometrical isomers may be discounted as tridentate ligand coordination through any S$_3$-donor set produces equivalent structures due to carbonyl ligand fluxionality (see later).

The most discernable resonance in the $^1$H n.m.r. spectra of $\text{fac-Mo(CO)_3L}_1$ is the well defined pentuplet at $\delta$2.08, assigned to a $\beta$-propano- methylene group. The resolution and relatively small low field shift of this resonance (cf. L$_1$, $\delta$L.93) suggests a
\[ T = 5^\circ C \]
\[ T = 25^\circ C \]

Figure 5.11. The \(^1\text{H n.m.r.}\) spectra of \(\text{fac-Mo(CO)}_3\text{L}^1\) in \(d^2\)-dichloromethane (270 MHz)

character essentially similar to that of free \(\text{L}^1\), for this group.

Consideration of the tridentate coordination mode of \(\text{L}^1\), Figure 5.12,

Figure 5.12. The proposed structure of \(\text{fac-Mo(CO)}_3\text{L}^{12}\). The exact ligand conformation is unknown.
shows that one \(\beta\)-methylene group (A) is locked into a static conformation by the bonding of S-1 and S-11 to the metal, whereas \(\beta\)-methylene-B is relatively free-ligand-like in nature. These two groups would be expected to differ markedly in chemical shift, that of \(\beta\)-CH\(_2\)-A being at relatively low field due to the increased deshielding induced by the binding of both S-1 and S-11. The \(\beta\)-CH\(_2\)-A resonances may also be split due to inequivalence of the protons in the locked conformation. From the above considerations, the \(\delta\)2.08 pentuplet is assigned to \(\beta\)-CH\(_2\)-B; the relatively low field \(\beta\)-CH\(_2\)-A resonances being contained in the \(\delta\)2.53 resonance envelope. The remaining resonances are due to inequivalent \(\alpha\)-CH\(_2\) protons. Compared to those of the free ligand, these resonances are all shifted to low field depending on the deshielding caused by proximal sulphur coordination. The complexity of the spectra, not atypical of complexes of L\(^1\),\(^{369,379}\) prevents further interpretation.

The \(^{13}\)C-{\(^1\)H} n.m.r. spectrum of \(\text{fac}^\circ\text{Mo(CO)}\(_3\)L\(^1\) (Figure 5.13), consistent with the unsymmetrical coordination of L\(^1\) in this complex, exhibits ten resonances attributable to the ten inequivalent methylene groups of the S\(_4\)-ligand. The \(^{13}\)C-{\(^1\)H} n.m.r. spectra of a variety of cyclic polythiaether ligands and some of their metal complexes have been reported\(^{379,406}\) and it has been suggested that the carbon atoms adjacent to coordinated sulphur atoms resonate at lower field than those of the free ligand.\(^{379}\) While this may be the case, assignment of the resonances in \(\text{fac}^\circ\text{Mo(CO)}\(_3\)L\(^1\) is not feasible with present data. The presence of only one carbonyl ligand resonance (\(\delta\)223.1) indicates fluxionality of the tricarbonyl ligand set. Similar chemical shifts have been reported for other \(\text{facial}\) tricarbonyl-molybdenum(0) complexes.\(^{497}\) The variation in n.m.r. linewidth with temperature indicates considerable ligand motion at ambient
As shown in Figure 5.14, a significant splitting of the singlet benzylic proton resonance of $L^2$ occurs upon coordination in the complex $\sigma\delta\sigma$-$W(CO)_4 L^2$. In the $^1H$ n.m.r. spectrum of $\sigma\delta\sigma$-$W(CO)_4 L^2$, the resonances at $\delta 4.25$ and $\delta 4.46$ may be assigned to a benzylic $\text{CH}_2$ group.
Figure 5.14. The $^1$H n.m.r. spectra of a) $L^2$ and b) $cis$-$W$(CO)$_4$L$^2$ in $d^2$-dichloromethane (80 MHz).

which is adjacent to a coordinated sulphur atom, the low field of these resonances being due to the deshielding influence of the sulphur atom. The resonances at δ3.81 and δ3.82 may be attributed to a benzylic CH$_2$ group which is adjacent to an uncoordinated sulphur atom. The inequivalence of the benzylic CH$_2$ protons accounts for the presence of two resonances for each of these groups. Other resonances represent aliphatic CH$_2$ and aromatic protons.

The $^{13}$C-$^1$H n.m.r. spectrum of $cis$-$W$(CO)$_4$L$^2$, shown in Figure 5.15, clearly indicates unsymmetrical binding of the ligand in this complex. In the aliphatic CH$_2$ region of the spectrum, nine resonances attributable to nine inequivalent carbon atoms are observed. Also, four secondary aromatic and two tertiary aromatic carbon resonances are present, indicating the absence of a symmetry
Figure 5.15. The $^{13}$C-$\{^1H\}$ n.m.r. spectrum of cis-W(CO)$_4$L$_2$ in d$_2$-dichloromethane (68 MHz).

plane bisecting the C-1-C-15 and C-17-C-18 bonds of the benzene ring of L$_2$. This feature discounts the binding of L$_2$ through S-3,S-13 or S-6,S-10 donor atom combinations.

The structure of cis-W(CO)$_4$L$_2$ must also account for the inability of the uncoordinated sulphur atoms to bind another W(CO)$_4$ moiety. Examination of molecular models suggests that the structure shown in Figure 5.16 provides the steric constraints most likely to prevent dimer formation (cf. ligand binding through S-3,S-6).
investigation of this interesting conformational aspect by x-ray crystallography was initiated but suitable single crystals proved difficult to obtain.

Figure 5.16. Proposed structure of cis-W(CO)$_4$L$^2$. The exact ligand conformation is unknown.

The ligand coordination modes in the L$^{1,2}$ complexes, with the exception of [W(CO)$_4$]$_2$-μ-L$^1$ (cf. [HgCl$_2$]$_2$-μ-L$^{1366}$ and [W(CO)$_4$]$_2$-μ-\(C_{22}H_{28}S_4^{380}\)) are unprecedented in the coordination chemistry of these ligands. Both the size and the electronic requirements of the Mo(0) and W(0) centres are important factors influencing these coordination modes. While the metal sizes (ca. 1.3 Å radii) make their encirclement by the ligands unlikely, the instability of the complexes formed upon further carbonyl ligand loss also prevents the tetradeinate coordination of the ligands. The reactivity of the complexes supports the contention that they represent the limit to which carbonyl ligand displacement may proceed before rendering the complexes unstable. The reaction of fac-Mo(CO)$_4$L$^{1,2}$ with NOPF$_6$ or RhCl(PPh$_3$)$_3$ results in carbonyl ligand loss followed by decomposition of the resulting complex. Upon CO loss, further coordination of
the $S_4$-ligand or dinitrogen is not observed.

The inability of the thiaether ligands to stabilize Mo(0) and W(0) centres in the absence of strong π-accepting ligands has prevented the full realization of the aim of this investigation. Even upon partial (as observed) $L^1$ and $L^2$ ligation, reactions directed at the remaining carbonyl ligand sites leads to complex decomposition.

5.3b Molybdenum Complexes of 1,4,8,11-Tetrathiaundecane

The direct reaction of $L^3$ or its disodium salt with various molybdenum and iron containing starting materials failed to yield simple, characterizable complexes under the conditions employed in this study. In all cases the reactions led to highly insoluble and often air sensitive materials. The techniques available for the characterization of these compounds were severely limited (to elemental analysis and infrared spectroscopy) owing to their extreme insolubility. Although the compounds remain partially characterised because of this, it is evident that they are polymeric materials formed by the participation of $L^3$ in extensive thiolato-bridge formation. Considerable variation in the reaction conditions, \textit{e.g.} rate and order of reactant addition, increased dilution and reaction temperature, did not improve the nature of the reaction products. Polymerization in this system appears to be an intrinsic tendency. Also, where the metallic starting material contains high oxidation state metal ions, $L^3$ oxidation to form polymeric disulphides accompanies the reduction of the metal ion. The inherent difficulties of thiolato-chemistry, \textit{viz.} polymerization and disulphide formation, are particularly prevalent in the chemistry of the large flexible tetradeinate $L^3$ ligand.
The chemistry of L\(^3\) contrasts with that of related aminothiolato-ligands,\(^{498}\) such as \(N,N'\)-dimethyl-\(N,N'\)-bis(2-mercaptoethyl)ethylenediamine, where mononuclear and dinuclear complexes are readily formed. While the strong coordination of the N-donor atoms of these ligands would enhance rapid chelation, the inability of the thiaether donor atoms to follow suite may inhibit the rapid chelation of L\(^3\) and thus promote polymer formation with this ligand.

Since polymerization prevents the isolation of monomeric or simple oligomeric complexes by the reaction of L\(^3\) or Na\(_2\)(L\(^3\)) with various starting materials, the feasibility of a template synthesis of molybdenum-L\(^3\) complexes was investigated. As shown in Equation (40),

\[
\begin{align*}
\text{Br} & \quad + \quad \text{Br} \\
\text{S} & \quad \text{S} \\
\text{L}_{\text{n}'} & \quad \text{S} \\
\text{Mo} & \quad \text{S} \\
\text{S} & \quad \text{S} \\
\rightarrow & \\
\text{Br} & \quad + \quad 2\text{Br}^-
\end{align*}
\]

the rationale of this approach involves the preparation of precursor bis(ethanedithiolato)- complexes and their subsequent reaction with 1,3-dibromopropane, C\(_3\)H\(_6\)Br\(_2\), to form mononuclear L\(^3\) complexes. Similar reactions have been recently reported for iron carbonyl systems, for example, the formation of Fe(CO)\(_2\)(1,4,7,10-tetrathiadecane) from the reaction of [Fe(SCH\(_2\)CH\(_2\)S)\(_2\)(C0)\(_2\)]\(^{2-}\) and C\(_3\)H\(_6\)Br\(_2\).\(^{387}\)

Attempts to prepare precursor bis(ethanedithiolato)- complexes from Mo(VI) starting materials resulted in the formation of dinuclear Mo(V) complexes presumably due to the reducing properties of the thiolato- ligands; direct substitution products such as [MoO\(_2\)(SCH\(_2\)CH\(_2\)S)]\(^{2-}\) were not obtained.
The reaction of \((\text{Et}_4\text{N})_2\text{[MoO}_2\text{(NCS)}_4]\) with \(\text{Na}_2\text{(SCH}_2\text{CH}_2\text{S)}\) resulted in the isolation of the orange crystalline compound \((\text{Et}_4\text{N})\text{[MoO}_2\text{(OMe)(SCH}_2\text{CH}_2\text{S)}_3]\). The infrared spectrum of the compound, shown in Figure 5.17, displays several strong bands characteristic\(^{409}\)

\[\text{v(Mo-S)}\]

\[\text{v(C-O)}\]

\[\text{v(Mo-O)}\]

\[1600\ 1400\ 1200\ 1000\ 800\ 600\ 400\]

Wavenumber (cm\(^{-1}\))

Figure 5.17. The infrared spectrum of \((\text{Et}_4\text{N})\text{[MoO}_2\text{(OMe)(SCH}_2\text{CH}_2\text{S)}_3]\) of methoxy- ligation at 1075 and 1067 cm\(^{-1}\). The complex is likely to possess a triply bridged structure similar to that shown in Figure 5.18,

\[\begin{align*}
\text{CH}_2\text{S} & \quad \text{O}_t \quad \text{CH}_3 \\
\text{CH}_2\text{S} & \quad \text{Mo} \quad \text{S} \quad \text{Mo} \quad \text{S} \quad \text{CH}_2 \\
\end{align*}\]

Figure 5.18. The proposed structure of \([\text{MoO}_2\text{(OMe)(SCH}_2\text{CH}_2\text{S)}_3]\)\(^{-}\)
where the bridge atoms are the methoxo-oxygen atom and the sulphur donor atoms of one ethanedithiolato ligand. This structure is analogous to that of the related complex \([\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]^{2-}\), the crystal structure of which has been reported by Dance and Landers.\(^90\)

In its various salts, this complex also exhibits an infrared spectrum similar to \([\text{Mo}_2\text{O}_2(\text{OME})(\text{SCH}_2\text{CH}_2\text{S})_3]^-\) in the \(\nu(\text{Mo-O}_t)\) region.

Boyd et al.\(^8\) have also reported the formation of \([\text{Mo}_2\text{O}_2(\text{OME})(\text{SCH}_2\text{CH}_2\text{S})_3]^-\) by the reaction of \(\text{HSCH}_2\text{CH}_2\text{SH}, \text{Et}_3\text{N}\) and \(\text{MoOCl}_3(\text{thf})_2\) in dimethylformamide/methanol.

The reaction of \(\sigma\text{is-MoO}_2(\text{acac})_2\) and \(\text{Na}_2(\text{SCH}_2\text{CH}_2\text{S})\) also results in the isolation of an orange crystalline solid upon the addition of \(\text{PPh}_4^+\). In its infrared spectrum (Figure 5.19), this compound exhibits two \(\nu(\text{Mo-O}_t)\) bands at 918 and 885 \(\text{cm}^{-1}\). Although such a band pattern is typical of the \(\sigma\text{is-MoO}_2\) moiety, elemental analysis

![Figure 5.19. The infrared spectrum of '(PPh$_4$)$_2$[Mo$_2$O$_2$S$_2$(SCH$_2$CH$_2$S)$_2$]'](image)
is not consistent with the formulation \((\text{PPh}_4)_2[\text{MoO}_2(\text{SCH}_2\text{CH}_2\text{S})_2]\).

Rather, the elemental analysis is compatible with two possible dinuclear Mo(V) formulations, \(\text{viz.} \ (\text{PPh}_4)_2[\text{Mo}_2\text{O}_2\text{S}_2(\text{SCH}_2\text{CH}_2\text{S})_2]\) or \((\text{PPh}_4)_2[\text{Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{S})_3]\). The infrared spectrum of the compound is significantly different to those of various cyclic secondary ammonium salts of \(\text{[Mo}_2\text{O}_3(\text{SCH}_2\text{CH}_2\text{O})_3]^{2-}\) and that of \(\text{syn-Mo}_2\text{O}_2\text{S}_2(\text{S}_2\text{CNEt}_2)_2;\) upon this comparison, analogous formulations for the ethanedithiolato- complexes are discounted. The \(\nu(\text{Mo-O}_2^-)\) band pattern of the complex is, however, similar to that observed in the complexes \(\text{anti-Mo}_2\text{O}_2\text{S}_2(\text{C}_6\text{H}_5)_2;\) \(\text{anti-Mo}_2\text{O}_4(\text{C}_6\text{H}_5)_2;\) and thus the ethanedithiolato- complex is tentatively assigned the formulation \(\text{anti-}[\text{Mo}_2\text{O}_2\text{S}_2(\text{SCH}_2\text{CH}_2\text{S})_2]^{2-}\).

Examination of the structures of the above ethanedithiolato- complexes suggests that they would be unlikely to produce monomeric \(\text{L}^3\) complexes upon reaction with \(\text{C}_3\text{H}_6\text{Br}_2\). Their further characterization was, therefore, not pursued.

The facile reduction of Mo(VI) centres to dinuclear Mo(V) centres suggested that the preparation of monomeric bis(ethanedithiolato)- complexes might be better approached from low oxidation state starting materials. Recently, the reaction of such a material, \(\text{K}_2\text{[MoO}_2(\text{CN})_4].6\text{H}_2\text{O}\), with HSCH\(_2\)CH\(_2\)SH has been reported to produce the interesting complex \(\text{K}_2\text{[MoO}(\text{SCH}_2\text{CH}_2\text{S})_2]\).2EtOH. A square pyramidal structure for this complex would facilitate the template synthesis of \(\text{L}^3\) upon further reaction with \(\text{C}_3\text{H}_6\text{Br}_2\). The reaction yields a white compound which appears to be a simple molybdenum complex of \(\text{L}^3\). Elemental analysis of the product is consistent with the formulation MoO(\(\text{L}^3\)) and its infrared spectrum (Figure 5.20) exhibits a strong split \(\nu(\text{Mo-O}_2^-)\) band centred at 857 cm\(^{-1}\). Solid state effects may be responsible for the splitting of the predicted single \(\nu(\text{Mo-O}_2^-)\) band.
Figure 5.20. The infrared spectrum of 'MoO(L³)').

The presence of two $\nu$(Mo-S) bands, at 345 and 330 cm$^{-1}$, is consistent with both thiaether and thiolato- donor atom coordination. This material remains partially characterised and its reactions with iron-containing materials, i.e. FeCl$_2$·2H$_2$O and (Et$_4$N)$_2$[FeCl$_4$] have not produced pure characterisable products.

In summary, the prospect for quality chemistry in the L³ system is limited by the complexity of the ligand and its chemical nature.
APPENDIX I

Construction and Operation of Schlenk Line Apparatus

The Schlenk Line Apparatus shown schematically in Figure I.1 was designed and constructed to facilitate rapid chemical manipulations under anaerobic conditions.

The Line consists of two reservoirs, one containing high purity dinitrogen (N) and the other a high vacuum (V), which are employed to alternately evacuate/purge reaction vessel configurations through a series of double oblique gas taps (T1-T4).

High purity cylinder dinitrogen is introduced into the Line at point A via a copper tube gas line. The sections of copper tubing are connected and various specialised switches are incorporated into the gas line by the use of gas tight Swagelok connections. Copper-to-glass joints were clamped flat flange joints sealed by rubber o-rings. Glass-to-glass joints were of a similar construction. The dinitrogen passes through switch S1 into a column of BASF R3-11 (oxygen scavenging) catalyst § (C).

The dinitrogen then flows through a series of bubblers into reservoir N. An adjustable head of mercury (H) incorporated into the dinitrogen supply line provides a ready means of adjusting the gas pressure and provides a safe outlet for excess dinitrogen upon the attainment of the desired gas pressure.

§ The R3-11 catalyst, supplied in the oxidised form, is activated by reduction with 10% H₂ in N₂. The procedure used is as follows. The 10% H₂/N₂ gas is passed into line B and when tap S2 is closed the gas is directed down the length of the column, and with switch S1 in the appropriate position, exits at point C. A heating tape placed around the column provides the 250°C temperature required for regeneration. Upon regeneration, switches S1, S2 and S3 allow the removal of the 10% H₂/N₂ source and reconnection of the dinitrogen source.
Figure I-1. Schematic diagram of the Schlenk line apparatus. A cross-section X-X shows the construction of the double oblique taps (T1-T4).
The vacuum reservoir is connected directly to a vapour trap (VT) operated at liquid nitrogen temperatures and a diffusion pump vacuum source by glass-to-glass joints.

The reaction vessels are connected to the line by lengths of high vacuum tubing attached to the double oblique taps T1-T4. A series of outlet bubblers (O) are available to allow the continual flushing of reaction vessels by dinitrogen should this be desired.

Sections of the Line and accessory equipment are securely attached to a solid benchtop grid constructed of aluminium rod.
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**APPENDIX II**

\[ \text{Mo}_2\text{O}_5\text{S}_2\text{CNET}_2\text{BF}_6 \] Observed and Calculated Structure Factor Amplitudes.
REFERENCES AND NOTES


151. A.E. Shilov, ibid., p.121.


281. The density was calculated using the equation

\[ D = D_{20^\circ} \times \frac{1 + \alpha x 20}{1 + \alpha t} \]

where \( D_{20^\circ} = 1.595 \text{ gcm}^{-3}, \alpha = 1.18384 \times 10^{-3} \) and \( t \) was measured to be 37.5°C.


290. G.M. McLaughlin, D. Taylor and P.O. Whimp, 'The ANUCRYST Structure Determination Package', Research School of Chemistry, The ANU, P.O. Box 4, Canberra, ACT, 2600, Australia.


340. Values of 2θ were calculated from unit cell dimensions using program POWDER by M. Sterns, Chemistry Department, Faculty Science, The ANU, Canberra, 2600, Australia.


360. For example, the structures in Refs. 201, 205 and 212. Also, in the complexes $\text{cis-Mo(S}_2\text{CNET}_2\text{)}_2(\text{NO})_2$ and $\text{Mo(S}_2\text{CNET}_2\text{)}_3(\text{SO}_2)$, M. Sterns, private communication.


