STUDY OF REACTIONS OF MOLYBDENUM(II) AND TUNGSTEN(II) HALOCARBONYLS WITH NITROGEN BASES

BY

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JULY 2009

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To my dear parents, Mr. Micah Nyawade and Mrs. Apeles A. Nyawade, my beloved son, Dennis and daughter, Sharon

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LIST OF ABREVIATIONS

ADP - Adenosine diphosphate

$AsMe_3$ - Trimethylarsine

$AsPh_3$ - Triphenylarsine

ATP - Adenosine tri-phosphate

dam - Bis (diphenylarsino)methane

Diars - O-phenyl bis(dimethylarsine)

DEA - Diethylamine

Diglyme - Diethyeneglycoldimethylether

diphos - 1,2 - bis(diphenylphosphino)ethane

dppm - bis(diphenylphosphino)methane

IR - Infrared

MA - Methylamine

MeCN - Acetonitrile

NCR - nitrile

NMR - Nuclear Magnetic Resonance

Pip - Piperidine

PPh_3 - Triphenylphosphine

RCN - Isonitrile

Redox - Reduction- oxidation process

THF - Tetrahydrofuran

TMEDA- Tetramethylethylenediamine

TMS - Tetramethylsilane

ABSTRACT

The study focused on the possible oxidation of various nitrogen bases by molybdenum(II) and tungsten(II) halocarbonyls, formation of zerovalent aminecarbonyl metal complexes and mode of coordination of nicotine to molybdenum and tungsten. Aminecarbonyls of the type $M(CO)_3L_3$ (M=Mo, W; L= CH_3NH_2, $CH_3CH_2)_2NH$), $M(CO)_4$TMEDA and $M(CO)_5$nicotine were prepared by a reaction of the halocarbonyls $[M(CO)_4X_2]_2$ (M=Mo, W; X=Br or Cl) with selected nitrogen bases. The crystal structurse of $Mo(CO)_4$TMEDA and $W(CO)_5$nicotine were obtained by X-ray diffraction confirming the structures of the compounds. Nicotine coordinated to the metal through the imine nitrogen, as shown seen in the crystal structure, to form $M(CO)_5$(nicotine) (M=Mo, W). The amine carbonyl compounds were isolated by filtration while the organic by-products, were isolated from the filtrate by column chromatography. The nitrogen bases were oxidized by the halocarbonyls to imines which may have been hydrolyzed by water to an amine and an aldehyde or a ketone. This was shown by the presence of IR bands in the region of $1740cm^{-1}$ in the infrared spectra of all the oily by-products from reaction of $M(CO)_4X_2$ (M=Mo, W; X=Br or Cl) with N,N-diethylamine. The ethylenamine was hydrolysed to methanal and methylamine. The presence of a new IR band at $1651.9cm^{-1}$ in the IR spectrum of the oily by-product from reaction of nicotine with the tetrahalocarbonyls suggested that nicotine was oxidized by the tetrahalooctacarbonylmetal(II) $M(CO)_4X_2$ (M=Mo, W; X=Br or Cl). ^{1}H NMR, ^{13}C NMR, infrared spectroscopy, melting point and elemental analysis were used to characterize the products. The halides were determined gravimetrically as the silver halides, AgX (X=Br or Cl) while molybdenum and tungsten were determined by weighing as the oxides MO_3 (M=Mo, W). The results confirmed that the reactions of the halocarbonyls $[M(CO)_4X_2]_2$ (M=Mo, W; X=Br or Cl) with the nitrogen bases studied takes place via a redox mechanism.

All preparative work was done in an atmosphere which was dry and oxygen-free.

CHAPTER 1

INTRODUCTION

1.1 Background

The focus of this study was to investigate the reactions of halocarbonyls $[M(CO)_4X_2]_2$ (M=Mo, W; X=Br or Cl) with nitrogen bases to help understand the chemistry of molybdenum(II) and tungsten(II). Tungsten (W) and the chemically analogous metal molybdenum (Mo) have a wide range of oxidation states from –2 to +6 and are abundant

elements in this planet (Johnson *et al.*, 1996; Kletzin and Adams, 1996). The chemistry of molybdenum has been of particular interest to researchers seeking to understand the "Biological Nitrogen Fixation".

In particular, the chemistry of molybdenum especially in low oxidation states is of special interest because together with iron, it is a constituent of nitrogenase, an enzyme, which is responsible for converting atmospheric nitrogen to ammonia. Conversion of dinitrogen to ammonia is required for all life since ammonia is the raw material used by plants to synthesize nitrogen-containing compounds such as proteins, which are essential for proper growth and development of living organisms. The interest in biological nitrogen fixation arises from being a relatively inexpensive process compared to the Haber-Bosch process for manufacture of ammonia. The conversion by the metallo-enzyme, nitrogenase, is on a scale of approximately 10^8 tons/year. This is equivalent to that of the Haber-Bosch process (Jennings, 1991) for making ammonia from nitrogen and hydrogen gases at high temperatures of 350-550 ^oC and pressures of 150-350 atmospheres (equation 1.1).

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \text{Equation 1.1}$$

The Haber-Bosch process, which consumes more than 1% of the energy consumed by human and, in these days of energy concerns, it is an expensive process (Schrock, 2006).

It further requires special equipment that can withstand these conditions. These factors make the ammonia plant an expensive one, which, therefore, requires big capital investment. Perhaps this partly explains why many developing nations, that need nitrogenous fertilizers so much, cannot build such plants. The initial cost involved is high and yet the local market is not always big enough to attract would-be investors. Therefore, there is definitely a need to develop a catalytic process that would mimic nature's method of converting dinitrogen to ammonia and reduce dinitrogen at 0.78 atmospheres N_2 pressure and ambient temperatures

to bring down efforts and costs involved to a minimum. A system that works under mild conditions of temperature and pressure the way nitrogenase would be preferable and molybdenum is therefore seen by many to be an essential element in life processes (Burns and Hardy, 1975).

Currently, there are many dinitrogen complexes that are known (Baker, 1998; Baker *et al., 1986).* Unfortunately, most of these are stabilized by tertiary phosphine ligands. Yet, nitrogenase does not contain phosphorous-donor atom ligands but sulphur. Hence the complexes are not realistic models of nitrogenase. Although there are complexes that produce ammonia, they have not been shown to work catalytically and may not therefore be realistic models of nitrogenase. In order to make realistic models, knowledge of the chemistry of molybdenum especially in low oxidation states, is very essential.

The discovery of the first dinitrogen complex by Allen and Senoff (1965) raised the expectation that eventually mankind might be able to understand how to activate and reduce dinitrogen to ammonia using molybdenum or tungsten complexes as catalyst under mild conditions. This has not been achieved due to missing information on the chemistry of molybdenum in low oxidation state. The current study sought to investigate the reaction of halocarbonyls $[M(CO)_4X_2]_2$ (M=Mo, W; X=Br or Cl) with nitrogen bases at room temperature and pressure to help understand the chemistry of molybdenum and tungsten in low oxidation states. In biological nitrogen fixation molybdenum is oxidized and reduced in a cyclic process (Fig. 1.2) and hence findings will probably contribute to knowledge required to come up with realistic processes that can produce ammonia at ambient conditions of temperature and pressure

Biological nitrogen fixation can be represented by equation 1.2 in which two moles of ammonia are produced from one mole of nitrogen gas, at the expense of 16 moles of ATP and a supply of eight moles of electrons and eight moles of protons (hydrogen ions).

$$N_2 + 8H^+ + 8e^- + 16\,ATP \longrightarrow 2NH_3 + H_2 + 16ADP + 16\,Pi \qquad \text{Equation 1.2}$$

The enzyme nitrogenase catalyzes the reduction of N_2 to ammonia at 0.78 atmospheres pressure in aqueous environment at a pH near 7 and at about 298K in the absence of air (Greenwood, 1997; Fujita, 2000; Dixon, 1986; Emerich *et al.*, 1981; Mishitin *et al.*, 1971). This reaction is performed exclusively by prokaryotes (the bacteria and related organisms), using the enzyme complex nitrogenase.

The Molybdenum-containing enzyme, nitrogenase, that catalyses the ATP-dependent reduction of nitrogen to ammonia during the process of dinitrogen fixation contains two distinct proteins. The smaller Iron (Fe)-protein contains iron but no molybdenum and, therefore, known as "Fe-protein". Its molecular weight is approximately 60,000 Daltons and its structure has a Fe_4S_4, cluster. The Fe-protein couples hydrolysis of ATP to electron transfer during the biological nitrogen fixation (Rees *et al*, 1992). The other protein contains both molybdenum and iron and is known as "Mo-Fe protein".

The molybdenum-iron protein contains the dinitrogen-binding site (Yandulov *et al*., 2003, Schrock, 2006). The structures of Mo/7Fe/10S nitrogenases from *Azotobacter vinelandii* (Rees *et al*, 1992) and *Clostridium pastuerianum* (Bolin *et al.*, 1993) have been solved and refined (Fig. 1.1).

STRUCTURE OF THE NITROGENASE CORE (iii)

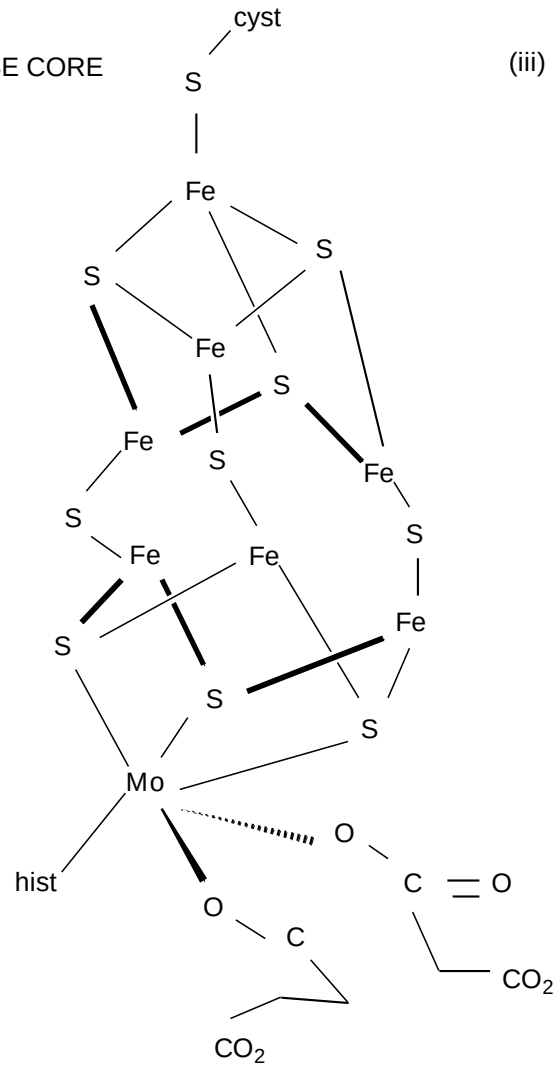


Figure 1.1: Structure of the Mo-Fe-S cluster in Nitrogenase (Rees and Kim, 1992)

An interesting observation that suggests very strongly that during biological nitrogen fixation, molecular nitrogen is coordinated to one of the metals in the metallo-enzymes is the reaction of isonitriles with the enzyme. An isonitrile is converted to a primary amine and methane as shown in equation 1.3. However, when the isonitrile is reduced with sodium borohydride, it is converted to a secondary amine (Eq 1.4). It is found that the enzyme reaction can be reproduced if just before adding sodium borohydride, a solution of some transition metal such as iron(II) is added (Equation 1.5)

$$RNC + Nitrogenase \longrightarrow RNH_2 + CH_4 \qquad 1.3$$

$$RNC + NaBH_4 \longrightarrow RNHCH_3 \qquad 1.4$$

$$RNC + \text{Transition metal ions} \longrightarrow RNH_2 + CH_4 \qquad 1.5$$

It is known that isonitriles are good σ-donors. It is, therefore, clear that in reaction 1.5, the reducing agent is acting on a co-ordinated ligand. It is reasonable therefore to assume that in the enzyme reaction 1.3, a similar mechanism is operative i.e. the isonitrile is reduced when it is co-ordinated to a metal ion. By extension, it is indeed reasonable to assume that in biological nitrogen fixation, a similar mechanism is operative i.e. the dinitrogen is co-ordinated to a metal ion during reduction process.

In the biological nitrogen fixation process electrons donated by ferredoxin first reduces the Fe-protein. Then the reduced Fe protein binds adenosine tri-phosphate (ATP) and reduces the molybdenum-iron protein, which donates electrons to N_2, producing HN=NH. In two further cycles of this process (each requiring electrons donated by ferredoxin) HN=NH is reduced to $H_2N\text{-}NH_2$, and this in turn is reduced to $2NH_3$ (Yandulov *et al*., 2003). Three orbitals, two π and one σ or combinations are sufficient to bind all N_xH_y intermediates (Fig.1.2).

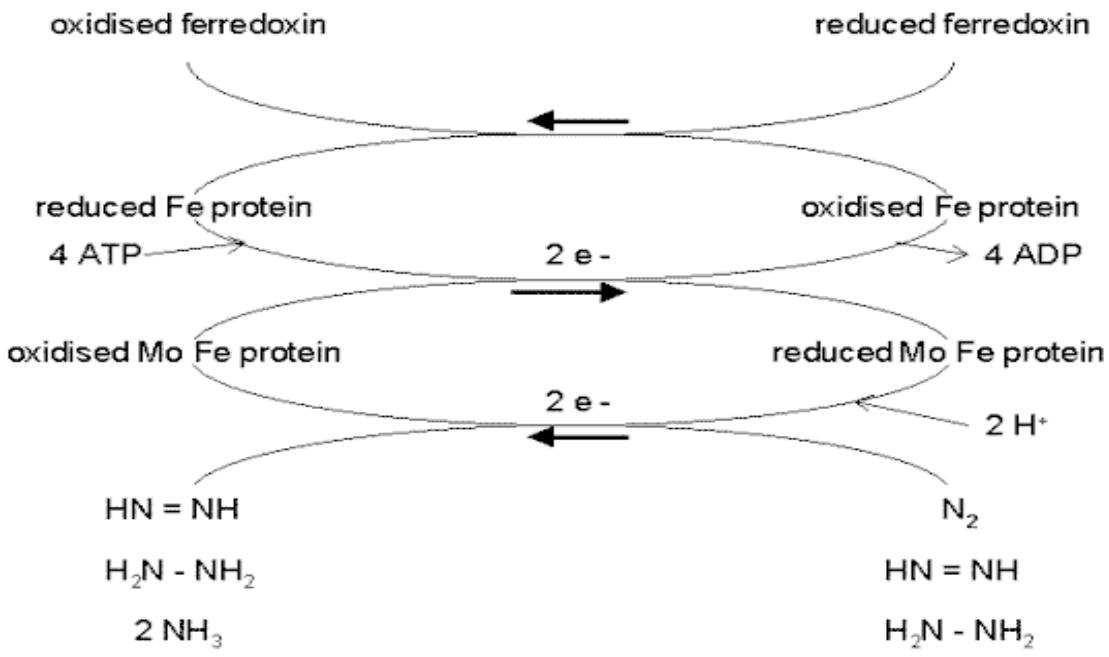


Figure 1.2: Proposed mechanism of reduction of dinitrogen at a single metal-center (Yandulov *et al*., 2003)

1.2 Problem Statement and Justification

The chemistry of transition metals is of interest to many researchers. In particular as explored above, the possible role of molybdenum and tungsten in the biological fixation of nitrogen has been of special interest. The halocarbonyl compounds of the type, $M(CO)_4X_2$, (M=Mo; X=Cl or Br), have been shown to react with alkylamines to give alkyl aminecarbonyls of the type $M(CO)_3L_3$ or $M(CO)_4L_2$ (L=alkylamine) depending on the nature of alkylamine (Andala, 2003; Muriithi, 1993). In such reactions the amines are oxidized to imines, which readily tautomerizes to enamines. The base piperazine reacts with the halocarbonyls to form products of the type $M(CO)_3$(piperazine)X_2 (M=Mo or W; X=Cl or Br), even when the reaction was carried out in boiling n-propanol. This observation is of interest because it shows that these halocarbonyls do not oxidize all nitrogen bases.

As the amines are oxidized in these reactions, the corresponding metals are usually reduced from oxidation state +2 to 0. However, the observation that piperazine is not oxidized by the

halocarbonyls shows that there is need to investigate the reactions of halocarbonyls with more nitrogen bases. In particular nicotine was chosen because it contains both imine and amine nitrogens. The mode of coordination to the metal ions should also be of interest because it is known that in hemoglobin, the globin is coordinated to the iron through the imine nitrogen of the imidazole ring and not via the amine nitrogen. The findings of this investigation should contribute positively to the existing database of chemistry of molybdenum and tungsten in low oxidation state. Further, the conclusions drawn fro here would contribute to the understanding of the chemistry of biological nitrogen fixation.

1.3 Hypothesis

i) Noting that the redox mechanism gives aminecarbonyls of the type $M(CO)_3L_3$ (M=Mo, W; L=alkylamines at room temperature which cannot be obtained via thermal reactions, the same mechanism may give similar products when $M(CO)_4X_2$ is reacted with low molecular weight amines such as methylamine at very low temperature.

ii) The presence of both amine and imine nitrogen atoms on nicotine may show different types of mechanisms e.g. simple substitutions, redox reactions or a mixture of the two types of reactions.

iii) Nicotine which has both amine and imine nitrogen will co-ordinnate to molybdenum or tungsten via the imine nitrogen as is the case in haemoglobin where the globin is coordinated to the iron through the imine nitrogen of the imidazole ring and not via the amine nitrogen.

1.4 Objectives of the study

General objective

To study the reaction between the halocarbonyl complexes, $[M(CO)_4X_2]_2$ (M=Mo, W; X=Cl, Br), and various nitrogen bases.

Specific objectives

i. To investigate how Molybdenum(II) or tungsten(II) halocarbonyls, $M(CO)_4X_2$ (M=Mo, W; X=Br, Cl) react with the low molecular weight nitrogen bases such as methylamine, diethylamine, the polydentate ligand N,N,N',N'-tetramethylethylenediamine, and nicotine.

ii. To investigate whether nicotine reacts with halocarbonyl complexes, $[M(CO)_4X_2]_2$ (M=Mo, W; X=Cl, Br), via a substitution, redox reaction or a mixture of the two reactions.

iii. To investigate whether nicotine coordinates to tungsten or molybdenum through the amine or imine nitrogen.

CHAPTER 2

LITERATURE REVIEW

This chapter provides a review of literature on the chemistry of divalent molybdenum and tungsten, with particular reference to halocarbonyls with the general formula, $[M(CO)_4X_2]_2$ (M=Mo, W; X=Cl or Br).

2.1 Chemistry of Divalent Molybdenum and Tungsten

The molybdenum(II) and tungsten(II) halides exist as cluster complexes. Thus, molybdenum and tungsten with empirical formulae, MX_2 (M=Mo,W;X=Cl, Br, I) are cluster complexes whose correct formulation is M_6X_{12} . These contain the complex cation, $[M_6X_8]^{4+}$ (Meyer *et al*., 1978), with the structure shown in Fig. 2.1

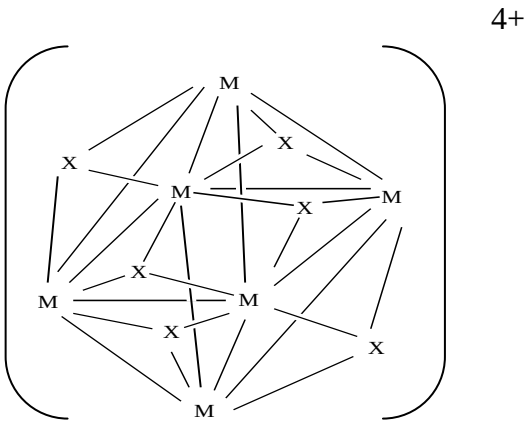


Figure 2.1: Structure of $[M_6X_8]^{4+}$ (M=Mo, W; X=Cl or Br) (Greenwood, 1997).

Mononuclear complexes of these elements are obtained when the metals are complexed to bulky and simple ligands especially those with good π-acceptor ability such as the carbonyls (Colton and Tomkins, 1966) isonitriles (Bonati and Minghetti, 1970), cyclopetadienyls and tertiary phosphines and arsines (Nyholm *et al.*, 1960; Moss, *et al.*, 1970).

The Molybdenum(II) and tungsten(II) halocarbonyls, $M(CO)_4X_2$ (M=Mo, W; X=Br, Cl) have been chosen for study because they do not contain metal-metal bond. These

halocarbonyls react with tertiary phosphines and tertiary arsines to give seven coordinate similar to those prepared by Nyholm and Co-workers (1960) and Moss and co-workers. Nyholm and Co-workers showed that the hexacarbonyls, $M(CO)_6$ [M=Mo, W] react with diarsine to form complexes of the type $M(CO)_4Diars$ or $M(CO)_2(Diars)_2$ [Diars= diarsine, $C_6H_4(AsMe_2)$]. When these partially substituted compounds were reacted with stoichiometric amounts of bromine or iodine, they gave seven-coordinate diamagnetic complexes of the type $M(CO)_3DiarsX_2$ or $M(CO)(Diars)_2X_2$. The reactions are illustrated by the following equations:

1. $Mo(CO)_6 + diars \xrightarrow{\text{suitable solvent/reflux}} Mo(CO)_4(diars) + 2CO$ 2.1

2. $Mo(CO)_4(diars) + X_2 \longrightarrow MO(CO)_4(diars)X_2$ (X=Br, I) 2.2

Similar complexes were made using tertiary phosphine ligands for example, $Mo(CO)_3(PEt_2Ph)_2X_2$ (X=Cl, Br) (Moss, et al, 1970). A controlled amount of chlorine or bromine was used to avoid oxidizing the metal to higher oxidation state, as CO groups are lost (Moss *et al.*, 1970). At times the phosphine ligand is oxidized by excess halogen (Nyholm *et al.*, 1960; Stiddard *et al.*, 1962), as in Equation 2.3 (Fujita *et al*., 2000).

$Mo(CO)_4(diars) + \text{excess } Br_2 \longrightarrow Mo(diars)_2Br_4 + 4CO$ 2.3

2.2 Preparation and Properties of $[M(CO)_4X_2]_2$ (M=Mo, W; X=Cl or Br)

Previously, halocarbonyls of the type $[M(CO)_4X_2]_2$ (M=Mo,W; X=Cl, Br) have been prepared by previous researchers using various procedures (Colton and Tomkins, 1966; Anker *et al.*, 1967; Schmidt and co-workers (1975). Colton and Tomkins (1966) showed that molybdenum hexacarbonyl, $Mo(CO)_6$, reacts with liquid chlorine at –78 ^oC to give $[Mo(CO)_4Cl_2]_2$. They prepared the bromo-complex, $[Mo(CO)_4Br_2]_2$ by adding bromine to a

suspension of $Mo(CO)_6$ in dichloromethane that had been cooled to –78 ^oC. The tungsten complexes $[W(CO)_4X_2]_2$ (X=Cl or Br) were prepared using the same procedure as that used to prepare $[Mo(CO)_4X_2]_2$ (X=Cl or Br) (Anker *et al.*, 1967). It is worth noting that $M(CO)_6$ reacts with halogens at room temperature with complete loss of carbonyl group to form metal halides (Cook *et al.*,1965). Equations 2.7 to 2.12 show some reactions of $M(CO)_6$ with halogens that lead to complete and partial substitution of the carbonyls.

$Mo(CO)_6 + Cl_2 \xrightarrow{\text{Room temperature}} MoCl_5 + 6CO$ 2.7

$Mo(CO)_6 + Br_2 \xrightarrow{\text{Room temperature}} MoBr_4 + 6CO$ 2.8

$W(CO)_6 + 3Cl_2 \xrightarrow{\text{Room temperature}} WCl_6 + 6CO$ 2.9

$W(CO)_6 + 5/2Br_2 \xrightarrow{\text{Room temperature}} WBr_5 + 6CO$ 2.10

$Mo(CO)_6 + I_2 \xrightarrow{\text{Elevated temperature}} MoI_2 + 6CO$ 2.11

$M(CO)_6 + X_2 \xrightarrow{\text{-78 }^0C} M(CO)_4X_2 + 2CO$ 2.12

An alternative method for making these halocarbonyls was reported by Schmidt and co-workers (1975). They showed that molybdenum hexacarbonyl, $Mo(CO)_6$, reacts with SiI_4 to give $[Mo(CO)_4I_4]_2$.

Whereas it is reported in literature that the reaction in equation 2.12 takes place at -78^oC, the exact temperature at which the reaction takes place needs to be confirmed since carbon monoxide gas starts being evolved only when the cold tube with a mixture of the hexacarbonyl and liquid chlorine is allowed to warm up slowly.

The structure and properties of halocarbonyls have been widely investigated (Anker *et al.*, 1967; Cotton *et al.*, 1985; Holste and Schafer, 1970). The halo-complexes were found to be diamagnetic and neutral (Anker *et al.*, 1967), and confirmed to have a dimeric formulation $[M(CO)_4X_2]_2$ using solution molecular weight determination (Holste and Schafer, 1970). Figure 2.2 shows the dimeric formulation of $[M(CO)_4X_2]$

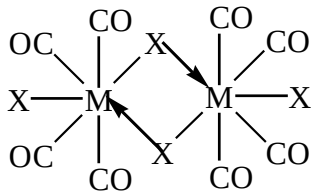


Figure 2.2: Structure of $[M(CO)_4X_2]_2$, [M=Mo, W; X=Cl, Br]

The molecular structure of the tungsten bromo-bridged dimer determined crystallographically shows each tungsten atom to be in a capped octahedral environment with the carbonyl group capping an octahedral face (Cotton *et al.*, 1985).

The halocarbonyls were also found to be thermally unstable (Anker *et al.*, 1967; Colton *et al.*, 1967). For example, Holste and Schafer (1970) showed that the thermal decomposition of $[Mo(CO)_4Cl_2]_2$ gives $MoCl_2$. The halocarbonyl complexes $[M(CO)_4X_2]_2$ were further found to be highly reactive.

The halocarbonyls $[M(CO)_4X_2]_2$, [M=Mo, W; X=Cl, Br] are convenient starting materials for studying the reaction of Molybdenum(II) and tungsten(II) with various bases. For instance they have been used to prepare a wide range of substituted seven-coordinate halocarbonyls such as $Mo(CO)_3(PPh_3)_2Cl_2$ and $Mo(CO)_3(AsPh_3)_2Cl_2$ (Colton *et al.*, 1966). Table 2.1 gives a summary of some of the findings in reactions of the halocarbonyl complexes of Mo and W with some good π-ligands at room temperature.

Table 2.1: Studies on reactions of the halocarbonyl complexes of Mo and W with some good π-acids at room temperature

Reactants	Reaction Conditions/solvent	Products	Ref
$[[Mo(CO)_4Cl_2]_2 + 2PPh_3$	CH_2Cl_2	$Mo(CO)_3(PPh_3)_2Cl_2$	Colton & Tomkins (1966)
$[Mo(CO)_4Br_2]_2 + 2AsPh_3$	Me_2CO	$Mo(CO)_3(AsPh_3)_2Br_2$	Colton & Tomkins, 1966
$[W(CO)_4I_4]_2 + 2dppm$	CH_2Cl_2	$[W(CO)_3(dppm)_2I]I$	Colton & Tomkins, 1968
$[Mo(CO)_4Cl_2]_2 + H_2S_2Ph_2$	MeOH	$Mo(CO)_3(S_2PPh_2)_2$	Chou, C.Y., Maata, E. A. (1984)
$[Mo(CO)_4Cl_2]_2 + dam$	CH_2Cl_2	$Mo(CO)_3(dam)_2Cl_2$	Anker *et al.*, 1968
$[Mo(CO)_4X_2]_2 + btp$	EtOH	$Mo(CO)_2(btp)_2X_2$	Colton *et al.*, 1968
$[Mo(CO)4Cl_2]_2 + As\text{-}N$	CH_2Cl_2	$Mo(CO)_3(As\text{-}N)Cl_2$	Broadbent and Kingston, 1970
$[Mo(CO)_4Cl_2]_2 + RNC$	Excess ligand	$Mo(CNR)_5Cl_2$	Bonati and Minghetti, 1970
$[Mo(CO)_4X_2]_2 + NCR$	CH_2Cl_2	$Mo(CO)_3(NCR)_2X_2$	Muriithi, 1972
$[W(CO)_4Br_2]_2 + Et_4NBr$	CH_2Cl_2	$Et_4N[W(CO)_4Br_3]^-$	Colton *et al.*, 1968
$[W(CO)_4Cl_2]_2 + 2PPh_3$	Me_2O	$W(CO)_3(PPh_3)_2Cl_2$	Anker *et al.*, 1967
$[Mo(CO)_4Cl_2]_2 + 2Py$	CH_2Cl_2	$Mo(CO)_3Py_2Cl_2$	Colton and Tomkins, 1967

The mononuclear complexes, which are reported in the Table 2.1, have also been prepared by other methods. For example, Brencze (1970) reported that the reduction of $MoCl_4(PPh_3)_2$ and $WOCl_4$ with $EtAlCl_2$ in the presence of PPh_3 and CO lead to the formation of $Mo(CO)_3(PPh_3)Cl_2$ and $W(CO)_3(PPh_3)_2Cl_2$, respectively. Szymanska-Buzar (1989) reported the photochemical oxidation of $W(CO)_6$ with CCl_4 to $[W(CO)_4Cl_2]_2$, an active alkene metathesis, arene alkylation and alkyne polymerization catalyst.

Colton and co-workers observed that when $[M(CO)_4X_2]_2$ (M=Mo, W; X=Cl, Br) complexes were treated with diphos or dppm in the ratio of 1:4 at room temperature, only complexes of the type $MX_2(CO)_2$(diphos) were formed and not $M(diphos)_2X_2$ which would be formed if all carbonyl groups were replaced (Anker *et al.*, 1968).

Westland and Muriithi (1973) described the reaction of halogen-bridged dimers $[Mo(CO)_4X_2]_2$ (X=Cl, Br) with weaker field ligands such as pyridine, tetrahydrofuran and acetonitrile, which eventually gave the non-carbonyl containing products $[MoX_3L_3]$ and zero-valent $[Mo(CO)_6]$ via disproportionation of the six-coordinated molybdenum(II) intermediates, $[MoX_2(CO)_2L_2]$ (Equation 2.14).

$$[Mo(CO)_4X_2]_2 + \text{Neat ligand(L)} \longrightarrow MoX_3L_3 + Mo(CO)_6 + 2CO \qquad 2.14$$

The reaction of $[Mo(CO)_4X_2]_2$ with neat $P(OMe)_3$ gave complexes of the type $Mo(CO)_2[P(OMe)_3]_3X_2$. Use of PhNC in 1:3 ratio and 1:4 ratio gave complexes of the type $Mo(CO)_2L_2X_2$ and $Mo(CO)L_4X_2$ respectively (L=isocyanide; X=Cl, Br). The aim of their study was to find out the degree of substitution of CO ligands by other ligands.

The specific reactions that gave the non-carbonyl containing products $[MoX_3L_3]$ and zero-valent $[Mo(CO)_6]$ via disproportionation of the six-coordinated molybdenum(II) intermediates are tabulated in table 2.2.

Table 2.2: Some reactions yielding MoX_3L_3

$Mo(CO)_4Br_2 + (CH_3)_3CCN$	$\longrightarrow MoBr_3((CH_3)_3CCN)_3$
$Mo(CO)_4Br_{2+} + CH_3(CH_2)_3CN$	$\longrightarrow MoBr_3(NC(CH_2)_3CH_3)_3$
$Mo(CO)_4Cl_2CH_3(CH_2)_2CN$	$\longrightarrow MoCl_3(CH_3(CH_2)_2CN)_3$
$Mo(CO)_4Cl_2 + CH_3CN$	$\longrightarrow MoCl_3(CH_3CN)_3$
$Mo(CO)_4Cl_2 + 3PhCN$	$\longrightarrow MoCl_3(PhCN)_3$
$Mo(CO)_4Br_2 + C_4H_8S$	$\longrightarrow MoBr_3(C_4H_8S)_3$
$Mo(CO)_4Cl_2 + C_4H_8O$	$\longrightarrow MoCl_3(C_4H_8O)_3$
$Mo(CO)_4Cl_2 + C_5H_5N$	$\longrightarrow MoCl_3(C_5H_5N)_3$

Bonati and Minghetti (1970) reported that the halocarbonyl, $[Mo(CO)_4X_2]_2$ (X=Cl, Br, I) react with excess isocyanides to form seven coordinate mononuclear complexes of the type MoL_5X_2 where all CO groups are replaced and the metal remains in oxidation state +2.

The procedures for preparation of complexes in table 2:2 have been followed in present study but with some modifications (see experimental section), e.g. preparation of standard bromine solution on page 24.

2.3 Dinitrogen Complexes

The dinitrogen complexes of transition metals seem to hold the key to understanding how to activate and reduce dinitrogen to ammonia using molybdenum or tungsten complexes as a catalyst under mild conditions (Allen *et al*., 1965).

Dinitrogen, N_2, behaves as a weak σ-donor and a good π-acceptor though much weaker than carbon monoxide in both respects (Cotton *et al*., 1980). The dinitrogen complexes are generally prepared by reaction of dinitrogen with preformed complexes with replacement of labile neutral or anionic ligands (Masanobu *et al*., 2001). The involvement of molybdenum as a dinitrogen binding site in nitrogenases has attracted many workers to investigate possible ways of making models for nitrogenases. In addition to molybdenum, tungsten is also used in the studies because it has chemical properties similar to those of molybdenum (Hidai *et al.*, 1995). Many metal complexes of stoichiometry $M(N_2)_2L_4$ (M=Mo, W; L=monodentate tertiary phosphine) are known. Equations 2.5 and 2.6 show formation of some of these metal complexes.

$$WCl_4(PMePh)_2 + 2N_2 \xrightarrow{\text{Excess } PMe_2Ph,\ Na/Hg} W(N_2)_2(PMePh)_4 \qquad 2.15$$

$$MoCl_5 + 4R_3P + 2N_2 \xrightarrow{THF,\ Na/Hg} Mo(N_2)_2(R_3P)_4 \qquad 2.16$$

(Me=CH_3, Ph=C_6H_5).

The *bis*-N_2 complexes give ammonia on treatment with protic acid or on acylation and may be definitive evidence of model systems appropriate for dinitrogenases (Masanobu *et al*., 2001). The mechanism of splitting N_2 and the nature of the resulting metal species are not known. However, since monomeric species such as $Cp^*Me_3W{=}NNH_2$ and $[Cp^*Me_3Mo(\eta^2\text{-}N_2H_4)]^+$ react under the same conditions to yield almost two equivalents of ammonia, probably two metals are not required (Schrock, 1997). This study proposes that a single electron site is sufficient to split the N-N bond and that η^2-hydrazine complexes are crucial intermediates in the N-N bond splitting reaction.

2.4 Alkylaminemolybdenum Carbonyls

Molybdenumhexacarbonyl(0) reacts with ethylamine, isopropylamine or cyclohexylamine on heating in evacuated sealed tubes to give mono-, di- and tri-substituted products depending on temperature and time (Tipathi and Srivastava, 1970) as described in Equation 2.17

$$Mo(CO)_6 + nL \longrightarrow L_n(CO)_{6-n} + nCO \qquad 2.17$$

Where n=1, 2 or 3

Piperazine reacts with hexacarbonylmolybdenum(0), $Mo(CO)_6$, to form piperazinedimolybdenum decacarbonyl, $Mo_2(CO)_{10}$(piperazine). In sealed tube reactions with piperazine, bis(piperazinemolybdenumtricarbonyl), $Mo(CO)_3(piperazine)_2$, is formed where only one piperazine molecule acts as a bridging molecule the other being monodentate. Ethylenediamine reacts with haxacarbonylmolybdenum(0) to form

bis(ethylenediamine)molybdenumtricarbonyl. Studies on reaction of haxacarbonylmolybdenum with alkylamines have shown that there is no change in oxidation state of the metal. This may suggest that there is no reduction or oxidation. However, findings in later work seem to provide mixed results. The main objective of the current work was to investigate whether the halocarbonyl complexes, $M(CO)_4X_2$ (M=Mo, W; X=Cl, Br) reacts with the selected nitrogen bases by a redox mechanism.

2.5 Reaction of $[Mo(CO)_4X_2]_2$ with alkylamines

The halocarbonyl, $[Mo(CO)_4X_2]_2$ (X=Cl, Br) react with primary amines to give zero-valent complexes of the type $M(CO)_3L_3$ (L=propylamine, butyl amine and cyclohexylamine) under mild conditions (Muriithi *et al.,* 1993). Piperidine reacts with $Mo(CO)_4X_2$ complexes to form zero-valent complexes of the type, $Mo(CO)_4L_2$ (L=piperidine and other monocyclic secondary amines) (Muriithi, 1972).

A redox mechanism has been proposed for this reaction where Mo(II) is reduced to Mo(0) while the amine is oxidized either to an imine or an enamine (Heyns *et al,* 1976). The redox mechanism has found further support in the work of Andala (2003) who studied the reaction of $M(CO)_4X_2$ (M=Mo,W; X=Cl, Br) with monocyclic secondary amines. Andala observed that the molybdenum complexes obtained did not contain any halogen. It was further showed that the halocarbonyls $[M(CO)_4Br_2]_2$ [M=Mo,W; X=Cl, Br] do not oxidize piperazine to the expected pyrazine. This finding seem to go against earlier work suggesting that the reaction between halocarbonyl complexes $M(CO)_4X_2$ (M=Mo, W; X=Cl, Br) and alkylamines takes place by a redox mechanism (Heyns *et al,* 1976).

The present study was undertaken with the following objectives: - First, it was of interest to find out whether, zero-valent amine carbonyls of the type $M(CO)_3L_3$ (M=Mo, W; L=low molecular weight amine such as CH_3NH_2 and $(CH_3CH_2)_2NH$) are formed when Molybdenum(II) or tungsten(II) halocarbonyls, $M(CO)_4X_2$ (M=Mo, W; X=Br or Cl) react with the low molecular weight nitrogen bases, methylamine and N,N-diethylamine. Secondly, it was of interest to investigate whether nicotine reacts with halocarbonyl complexes, $[M(CO)_4X_2]_2$ (M=Mo, W; X=Cl, Br), via a substitution, redox reaction or a mixture of the two reactions. Thirdly, it was of interest to investigate whether nicotine coordinates to tungsten or molybdenum through the amine or imine nitrogen and finally, to investigate whether methylamine will be oxidized to the radical $^{\cdot}CH_2NH_2$ that may dimerize to $H_2NCH_2CH_2NH_2$.

CHAPTER 3

METHODS AND MATERIALS

This chapter presents the methods used to study the reactions of molybdenum(II) and tungsten(II) halocarbonyls with selected nitrogen bases. All preparations were done in an atmosphere of dry, oxygen-free nitrogen to prevent oxidation and hydrolysis of the main and intermediate products.

3.1 Experimental techniques

The experimental techniques discussed in this section include the cleaning of apparatus, purification of organic solvents and the nitrogen bases used, preparation of sodium naphthalide solution, purification of nitrogen, preparation of reagents, preparation of standard bromine solution, preparation of dry chlorine gas, methods of handling air-sensitive compounds, and analytical techniques.

3.1.1 Cleaning of Apparatus

3.1.1.1 Glassware

Glassware with no grease was washed with a liquid detergent and tap water. The glassware was then filled with chromic acid and left overnight. The chromic acid was removed and the glassware washed with tap water, rinsed several times with distilled water and dried in an electric oven at 130 ^{o}C for three hours. Small glassware items such as test tubes and adapters were immersed in chromic acid and left overnight. They were then washed, rinsed with distilled water and dried in an electric oven at 130 ^{o}C.

Glassware with grease or any other water-insoluble impurities from joints was washed off using halogenated organic solvents such as chloroform or dichloromethane. The glassware

was then washed with detergent and tap water. They were filled with freshly prepared chromic acid or immersed in it and kept overnight. The filtration apparatus could not hold chromic acid in both chambers at the same time. Therefore, one chamber was filled with the acid that was allowed to pass through the glass frit and the process repeated for the second chamber. The apparatus was washed with tap water, rinsed thoroughly with distilled water and then dried in an electric oven at 130 ^{o}C for three hours.

3.1.1.2 Sintered Glass Filter Crucibles

To ensure that the surface of sintered glass crucibles was clean prior to analysis, the surface was cleaned using liquid detergent and tap water and then rinsed with plenty of distilled water. Each crucible was placed on a holder in a suction flask, where, with gentle suction several portions of distilled water were drawn through the frit. The crucibles were then placed in a beaker, covered with a watch glass and put in an oven for three hours at 130 ^{o}C. The hot crucibles were transferred into a desiccator containing phosphorous pentoxide powder and cooled before use.

After the analysis the cake of the analyzed sample was removed and the crucible placed in a beaker where about 6 cm^3 of concentrated ammonia was put in each crucible and the beaker covered with a watch glass. After 10-15 minutes, the crucibles were transferred to the crucible holder in a suction flask and washed with several portions of distilled water. In case the frit appeared dark after washing, a few millimeters of concentrated nitric acid was passed through by suction and then washed thoroughly with distilled water.

3.1.1.3 Infra Red Cells and NMR Tubes

IR cells and NMR tubes were washed with dichloromethane, to ensure no interference with the samples to be used during analysis. NMR Tubes were washed with detergent and tap water. They were rinsed thoroughly with distilled water and dried in an electric oven at 130 ^{o}C for 4 hours, to ensure that they were free of water.

3.1.2 Purification of Organic Solvents and Nitrogen Bases

This was done following literature method (Keese *et al.,* 1982) as most of the intermediate products and final products in the preparations carried out were oxygen and water-sensitive. The solvents were dried and kept in an inert atmosphere. All the solvents were first treated with anhydrous magnesium sulphate to remove the bulk of the water before further treatment.

The flow of dry, oxygen-free nitrogen through the refluxing and distillation apparatus was monitored by use of rubber tubing and a glass tube dipped in liquid paraffin.

The solvents purified included dichloromethane, alcohols, Diethyleneglycoldimethylether (diglyme), THF, diethylether and nitrogen bases. Dichloromethane was refluxed over phosphorous pentoxide for 40 minutes and distilled in an atmosphere of dry, oxygen-free nitrogen to further remove any traces of water. Methanol and Ethanol obtained after treatment with anhydrous magnesium sulphate was refluxed over calcium oxide in an atmosphere of dry, oxygen-free nitrogen for 20 hours to further remove traces of water. The alcohol was distilled under dry, oxygen-free nitrogen. Magnesium turnings and a little iodine were added to the distillate and the mixture refluxed for 5 hours. It was then distilled and collected in an atmosphere of dry, oxygen-free nitrogen. Diglyme was refluxed over

sodium metal in an atmosphere of dry, oxygen-free nitrogen for 40 minutes, distilled in an inert atmosphere and used to prepare sodium naphthalide used in removing oxygen form the nitrogen gas. Tetrahydrofuran (THF) was refluxed for 40 minutes over sodium metal, distilled in an inert atmosphere and the middle portion used. Diethylether was refluxed over sodium metal for 40 minutes to remove oxygen and then distilled in an inert atmosphere.

The nitrogen bases, N,N,N',N'-tetramethylethylenediamine and diethylamine were refluxed over calcium oxide for 40 minutes in an inert atmosphere to remove water, distilled and collected in an inert atmosphere. Other amines were Analar grade chemicals and were used without further purification.

3.1.3 Preparation of Sodium Naphthalide

The purified diglyme was used to dissolve naphthalene crystals in an atmosphere of dry, oxygen-free nitrogen to enable it react with sodium metal. Sodium metal was cut into small pieces and dissolved in the diglyme. A dark green solution of sodium naphthalide was formed. It formed a whitish solid on exposure to air. Formation of white solid served to confirm whether any air leaking, indicated when the solution had expired.

3.1.4 Purification of nitrogen

Dry, oxygen-free nitrogen was obtained by passing white spot nitrogen obtained from British Oxygen Company (Kenya) Limited through two columns packed with phosphorous pentoxide supported on dry pumice.

Nitrogen gas was dried over phosphorous (V) oxide. The dry nitrogen was bubbled through a solution of sodium naphthalide in diglyme to remove oxygen.

3.1.5 Preparation of Reagents

The reagents required for the study included hexacarbonylmetal(0), Chlorine gas and Hydrogen halides. The first two were used as starting materials while the third was used during analysis to establish the boiling point of the aminium halides formed. Hexacarbonylmolybdenum(0) and hexacarbonyltungsten(0), obtained commercially, were separately ground thoroughly in a mortar and dried over phosphorous pentoxide in a dessicator overnight. They were kept in bottles that were tightly screwed and kept in the dessicator to prevent entry of moisture and oxygen.

Chlorine gas was generated by the action of Analar grade concentrated hydrochloric acid on a manganese (IV) oxide. The gas was dried by passing it through a flask containing concentrated sulphuric acid and finally through a **U**-tube of phosphorous pentoxide.

The two hydrogen halides prepared were hydrogen chloride and hydrogen bromide. Hydrogen chloride was generated using Analar grade sodium chloride and concentrated sulphuric acid. Hydrogen bromide was prepared by reacting tetrahydronaphthalene (tetralin), $C_{10}H_{12}$ with Analar grade bromine (B.D.H). The gas was passed through two conical flasks containing tetralin to remove excess bromine, and a coiled glass in ice mixture to trap any moisture.

Dry Methylamine Solution in THF was prepared by distilling methylamine obtained after treatment with anhydrous magnesium chloride in a dry oxygen-free atmosphere. The methylamine vapour produced were dried by passing through U-tubes packed with calcium oxide and collected in a receiver dipped in dry-ice/acetone bath. This was necessary because methylamine has a very low boiling point of about -8 ^{o}C. About 100ml of methylamine were

recovered. About 300ml of THF was cooled in dry-ice/acetone bath for 20 minutes and added to the cold methylamine while the receiver was still in dry ice/acetone bath

3.1.6 Preparation of Standard Bromine Solution

To prepare standard bromine solution, a 100-ml volumetric flask was filled with 50ml of freshly distilled dichloromethane, the stopper replaced and weighed. About 16ml of analytical grade bromine (B.D.H) were added to the flask. The stopper was quickly replaced and weighed again. The flask was filled to the mark with freshly distilled dichloromethane, the stopper replaced and thoroughly shaken. The concentration of the solution made was 0.453g/ml

3.1.7 Methods of Handling Air-Sensitive Compounds

Filtration of air-sensitive compounds was done in nitrogen using the modified Fritz apparatus (Figure 3.1) (Fritz *et. al,* 1959)**.** As evident in the Figure the storage and handling of the sample was made possible by its retention in part C of the apparatus during filtration.

As nitrogen gas was flowing through the system, an ampoule (Fig 3.2) was fitted on the filtering apparatus at B and the gas flow stopped. The sample was transferred to the ampoule and the system purged with nitrogen. The ampoule was quickly detached and sealed. The samples were recovered from the ampoule by transferring a desired amount to one of the side tubes. The other tubes were dipped in dry-ice/acetone mixture in a Dewar flask and the tube with the desired amount of sample cut off from the rest with a blowtorch.

To carry out physical measurement or elemental analysis, the tube was broken open while inside a 1½m x 1m polythene bag through which nitrogen gas was passing.

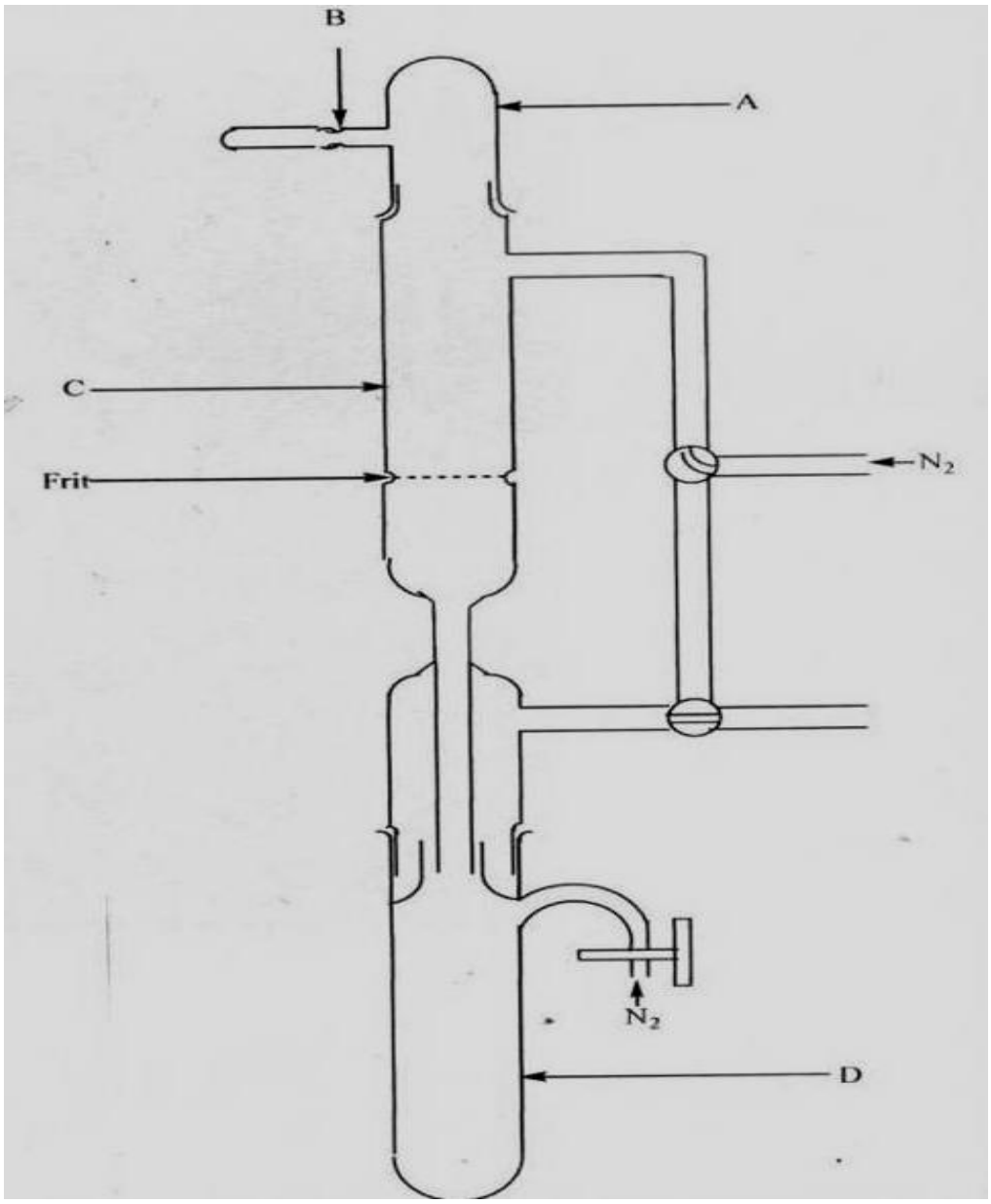


Figure 3.1: Apparatus for filtration under nitrogen

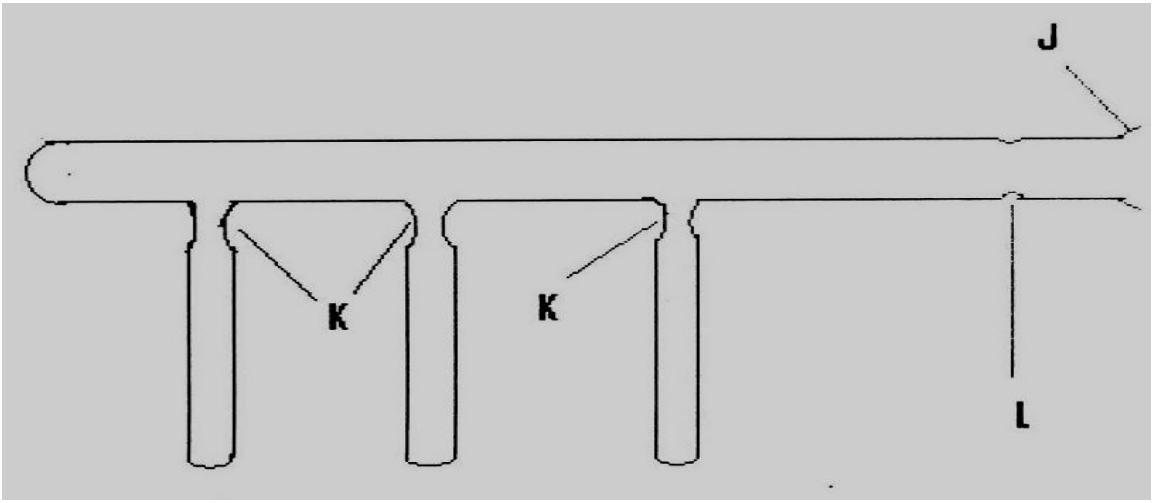


Figure 3.2: Ampuole for storing air-sensitive compounds

NB: J = Joint 14/23 K = Constriction by blow torch for detaching the arms containing desired amount of sample;
L = Constriction by blow torch for sealing ampuole

3.1.8 Physical Measurements

The physical measurement involved obtaining UV spectra, Fourier Transform Infrared (FTIR) spectra, and Nuclear Magnetic Resonance (NMR) spectra. UV spectra were recorded on a UV spectrophotometer model CECIL CE 2041 with a wavelength range of 190nm to 1000nm. Samples were dissolved in suitable solvent and the solution put in solution cells. The UV spectra were obtained using the solvent to set the baseline and hence as the reference.

Fourier Transform Infrared (FTIR) spectra were recorded in the range 4000cm^{-1} to 400cm^{-1} on an FTIR-8400 Shimadzu spectrometer. The regions of interest were between 2200 cm^{-1} and 1600 cm^{-1} for inorganic ν(CO), 1680cm^{-1} -1620cm^{-1} for the ν(C=C), and 3100cm^{-1} to 3000cm^{-1} for the ν(=C-H). Solid samples were molded into KBr discs by grinding them (0.1– 0.2%) with KBr into fine powder which was then pressed into a transparent discs, mounted onto the spectrometer and scanned. The spectra were recorded. Liquid samples

were dissolved in suitable organic solvents and the solution put into KBr cells, which were mounted onto the spectrometer, and the samples scanned.

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian Quadruple 200Mz Mercury VX spectrophotometer using deuterated chloroform, $CDCl_3$, as the solvent and thus the reference.

X-ray structures of some compounds were obtained using a Bruker APEX II, 4K CCD Detector at 100(2) K. The low temperature was obtained by kryoflex (90K to 300K). The machine uses Cu K alpha radiations, which give absolute configuration as opposed to Mo K alpha radiation (McArdle, 1993; Walker and Stuart, 1983)

3.1.9 Analytical Techniques

3.1.9.1 Chromatography and Elemental Analysis

Chromatography was done using an analytical thin layer chromatography (TLC) on Kieselgel 60 F_{24} (Merk) silica gel pre-coated aluminium plate with fluorescent indicator UV_{254}. Column chromatography was carried out on neutral alumina (particle size 0.063 – 0.2mm, 70-230 mesh, Aldrich) packed in a 30mm by 500mm long column. This technique was used to find out whether the resulting filtrate had more than one component. Elemental analyses were done on a Leco CHNS analyzer, at the school of Chemistry, University of Kwa-Zulu Natal, South Africa to determine carbon, hydrogen and nitrogen content of the samples.

3.1.9.2 Gravimetric determination of halides as silver halides using 0.1M $AgNO_{3\,(aq)}$ (Basset, *et al;* 1978)

The halogens were determined gravimetrically by weighing as the silver halide. The sample containing either chloride or bromide ions were accurately weighed put in a 250-ml beaker and digested using 5ml of Analar grade concentrated nitric acid. About 100ml of distilled water were added to the mixture followed by about 2g of zinc powder, added a little at a time to reduce any chlorate, ClO_3^-, to chloride ions and bromate ions, BrO_3^- to bromide ions. The solution was allowed to cool and then filtered into a 250-ml volumetric flask. It was made to the mark.

100ml of the solution were transferred into a 250-ml beaker. 30ml of 0.1M $AgNO_3$ from a burette were added to the solution drop by drop while stirring until no more precipitate formed. The beaker was covered with a watch glass and wrapped with an aluminium foil to prevent photodecomposition of the silver halide precipitate. The precipitate was coagulated by gently warming it on a hot plate for 30 minutes. When the supernatant was clear, a few drops of 0.1M $AgNO_3$ were added to test whether there were halide ions in solution. When no turbidity was seen, the beaker was kept in a dark cupboard to cool for two hours and the filtrate separated by filtration in a pre-weighed G-4 sintered glass crucible.

The residue was washed several times with very dilute nitric acid until the filtrate gave no turbidity with 0.1M HCl. The residue on the sintered glass crucible was dried in an electric oven at 140 ^{0}C, cooled in a desiccator containing phosphorous pentoxide and weighed. The process of heating, cooling and weighing was repeated until a constant weight was obtained. The determinations were carried out in duplicates to compare the accuracy of the analysis results.

3.1.9.3 Determination of Molybdenum and Tungsten by weighing as MO_3

Molybdenum was determined following literature methods (Bnasset *et. al*, 1978)). A known amount of the sample was put into a cool, dry pre-weighed porcelain crucible which had been heated in a muffle furnace at 550 ^{0}C for two hours to dehydrated it and decompose all the organic matter on its surface. The crucible was cooled in a desiccator containing phosphorous pentoxide. The sample was digested using concentrated Analar grade nitric acid. The digestion was done by adding drops of the concentrated acid to the sample until present in excess and then gently warmed on a hot plate.

Once the excess acid had evaporated, the crucible and its contents was heated in a muffle furnace at about 550 ^{0}C for molybdenum and 750 ^{0}C for tungsten to dehydrate the acids formed. It was cooled in a desiccator containing phosphorous pentoxide and weighed. The process of heating, cooling and weighing was repeated to obtain a constant weight. The determinations were carried out in duplicates to compare the accuracy of results.

3.2 Preparative Work

The Preparative work, described in this section, provided the results needed to achieve the set objectives. It involved preparing tetrahalooctacarbonylmetal(II) complexes, and their reactions with tetramethylethylenediamine, methylamine, diethylamine, and 1-methyl-2-(3-pyridyl)-pyrrolidine at room temperature. Stoichiometric amounts of the metal hexacarbonyls and nitrogen bases were used in all the preparations described in this section.

3.2.1 Preparation of tetrabromooctacarbonylmetal (II), $[M(CO)_4Br_2]_2$ (M=Mo, W)

The procedure by Colton and Tomkins (1966) was carried out in Schlenk tube shown in Figure 3.3. The Schlenk tube was dried in an electric oven at 120 ^{o}C for one hour and cooled by flushing it with dry, oxygen-free nitrogen through stopcock $\mathbf{T_2}$. The joints of the cool

Schlenk tube and stopper **S** were lightly greased with silicon grease. As dry, oxygen-free nitrogen was passing through the system, accurately weighed amounts of well pulverized and dry hexacarbonylmetal(0), ($Mo(CO)_6$ or $W(CO)_6$), were put into the Schlenk tube. About 15ml of dry freshly distilled dichloromethane was added. A Teflon coated bar magnet was put in the Schlenk tube, the stopper replaced and the mixture stirred.

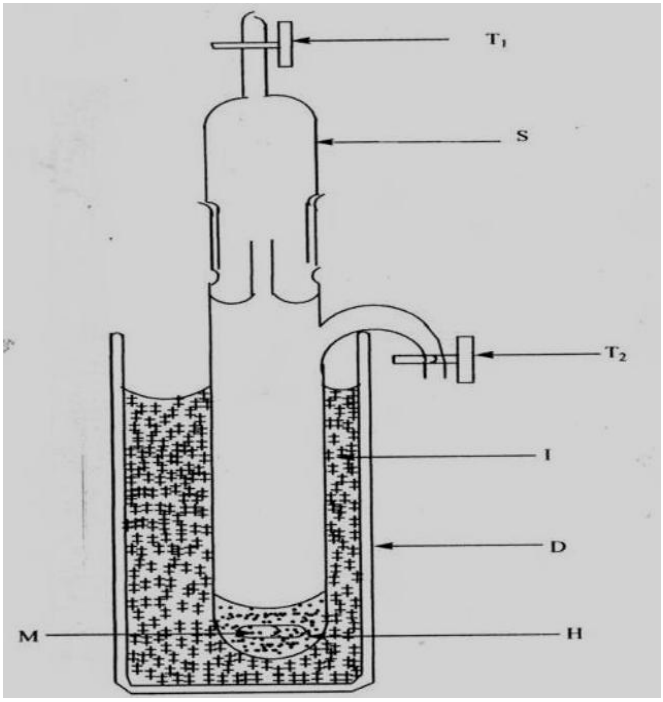


Figure 3.3: Apparatus for the preparation of tetrabromooctacarbonylmetal(II), $[M(CO)_4Br_2]_2$

NOTE: T_1, T_2 = Stopcock S = Stopper I = Dry ice/acetone mixture
D = Dewer flask M = Magnetic stirrer bar H = $M(CO)_6$/Bromine (M=Mo,W)

The tube was briefly evacuated by use of a vacuum pump connected to stopcock $\mathbf{T_1}$ and the system filled with dry, oxygen-free nitrogen through stopcock $\mathbf{T_2}$**.** The Schlenk tube was placed in dry-ice/acetone bath and cooled for at least 30 minutes. A stoichiometric amount of standard bromine solution (section 3.6) was accurately measured with a pipette and added to the cold suspension of the hexacarbonylmetal (0), $M(CO)_6$, while dry oxygen-free nitrogen was passing through stopcock $\mathbf{T_2}$**.** The stopper of the Schlenk tube was quickly replaced and the tube cooled for a few minutes.

The tube was removed from the dry-ice/acetone bath and the contents stirred vigorously as the tube was allowed to warm up to room temperature. There was effervescence as a colourless gas, carbonmonoxide was evolved and a dark orange solid was formed. When effervescence stopped, stopcock $\mathbf{T_2}$ was closed and all the dichloromethane pumped off.

Samples of the dark orange solid formed were taken for metal and bromine analysis. Elemental analysis results (table 3.1) showed that the products in each case had empirical formula $MC_4O_4Br_2$ (M=Mo or W). The molecular formula for the compound had been shown to be $[Mo(CO)_4Br_2]_2$ (Stykes *et al*, 1987).

3.2.2 Preparation of Tetrachlorooctacarbonylmetal (II), $[M(CO)_4Cl_2]_2$ (M=Mo or W)

The procedure by Colton and Tomkins (1966), for preparing tetrachlorooctacarbonylmetal (II), was carried out in Schlenk tube.

$[M(CO)_4Cl_2]_2$ was prepared by transferring accurately weighed finely powdered hexacarbonyl, $(MCO)_6$ (M=Mo,W), in a clean dry Schlenk tube. A 2cm long teflon coated bar magnet was put into the Schlenk tube and the stopper replaced. The tube was briefly evacuated through $\mathbf{T_1}$ and then filled with dry, oxygen-free nitrogen. The stopper was removed as nitrogen continued to flow and a dry glass tube that was connected to a chlorine source was put into the Schlenk tube. The mouth of the Schlenk tube was lightly plugged with dry glass wool so that nitrogen flow could continue but air could not get into the tube.

The Schlenk tube was immersed in a dry-ice/acetone bath and cooled for at least half an hour after which chlorine generated as described in section 3.5.2 was condensed on the walls of the Schlenk tube until liquid chlorine was visible. The Schlenk tube was then

removed from the bath and allowed to warm up slowly as the contents were gently stirred. There was effervescence as a colourless gas, carbon monoxide, was evolved and the solid turned orange. When effervescence stopped, excess chlorine was flushed off the system by dry, oxygen-free nitrogen, which also provided an inert atmosphere. Samples of the dark orange solid left were taken for metal and chlorine analysis.

Elemental analysis results (table 3.1) showed that the products in each case had empirical formula $MC_4Cl_2O_4$ (M=Mo or W). The molecular formula for the compound had been shown to be $[Mo(CO)_4Cl_2]_2$ (Stykes A. G. *et al*, 1987).

Table 3.1: Analysis results for the metal and halogen in halocarbonyl complexes

Compound	**% composition**	
	M	X
$C_4Br_2MoO_4$	25.89 (26.09)	43.20 (43.45)
$C_4Br_2WO_4$	39.98 (40.34)	34.88 (35.07)
$C_4Cl_2MoO_4$	34.35 (34.38)	25.42 (25.47)
$C_4Cl_2WO_4$	48.98 (50.12)	18.94 (19.33)

NOTE: The values in brackets are the calculated for the compounds

3.2.3 Reaction of tetrabromooctacarbonylmolybdenum(II) with neat diethylamine

THE hexacarbonylmolybdenum(0) (12.8 mmol) were used to prepare tetrabromooctacarbonylmolybdenum(II) as described in section 3.2.1. Dry diethylamine (64.0 mmol) was added to cool dark orange crystals of $[Mo(CO)_4Br_2]_2$ and the mixture stirred for 16 hours under dry, oxygen-free nitrogen. A dark brown precipitate was formed and was separated by suction filtration in an inert atmosphere. The precipitate was washed with dry diethylamine and rinsed with dry diethyl ether. It was dried and weighed. Qualitative analysis was done to determine the presence of molybdenum in the product. The percentage molybdenum in the product was determined immediately after preparation and

four days later because the colour of the solid product changed from orange to grey. Some of the dark brown solid product was stored in an ampoule and used for IR and elemental analysis. Elemental analyses results (Table 3.2) showed that the product had the empirical formula $MoO_3C_{15}H_{33}N_3$ while an IR spectrum (Fig. 3.4) gave peaks in the region of 2000.0cm^{-1} to 1800.0cm^{-1}, an indication that there were coordinated inorganic CO groups.

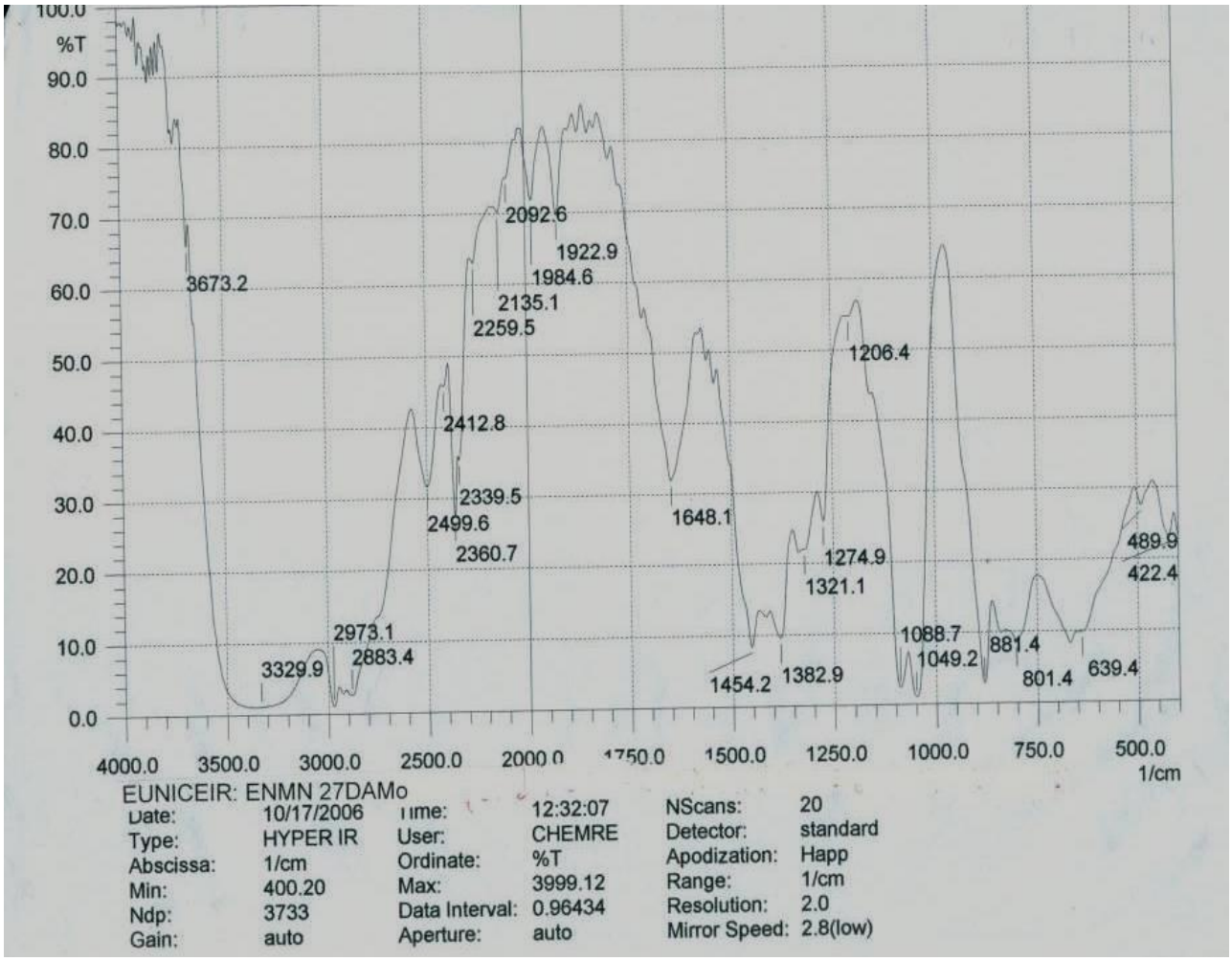


Figure 3.4: Infrared spectrum of $Mo(CO)_3$(N,N-diethylamine)$_3$ complex formed

3.2.3.1 Isolation of Compounds in the filtrate obtained from reaction of $[Mo(CO)_4Br_2]_2$ with diethylamine.

The filtrate obtained from section 3.2.3 was concentrated by pumping off excess solvent at reduced pressure. IR spectra (Fig. 3.5 & 3.6) of the distillate and the concentrated filtrate were obtained by scanning in the spectral range 4000-200cm^{-1}. Thin layer chromatography

gave three bands on the silica gel pre-coated aluminium plate. The concentrated filtrate was eluted in a column packed with neutral alumina and dry methanol used as the eluting solvent. Three major fractions were separated.

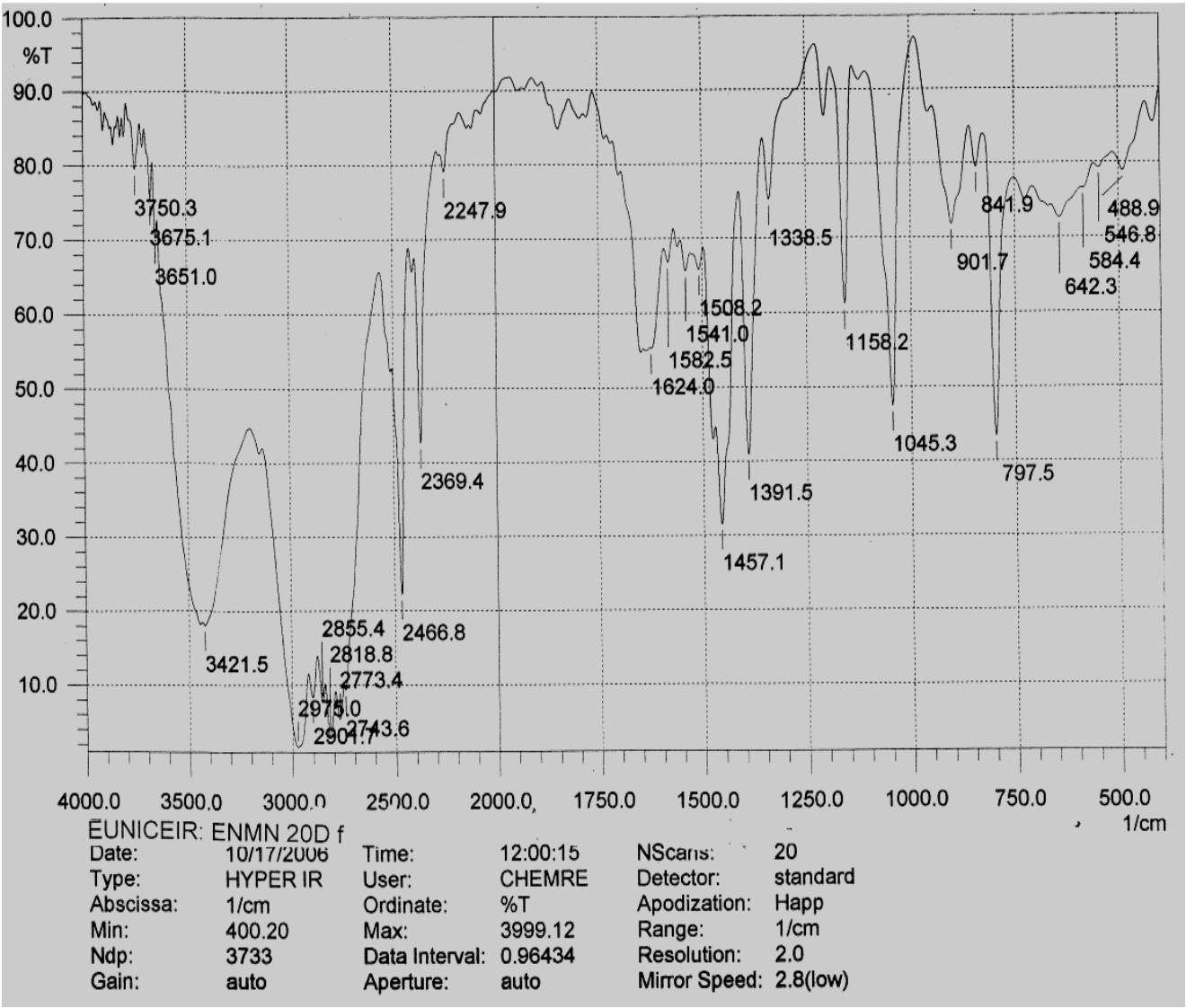


Figure 3.5: Infrared spectrum of distillate obtained from diethylamine + $Mo(CO)_4Br_2$

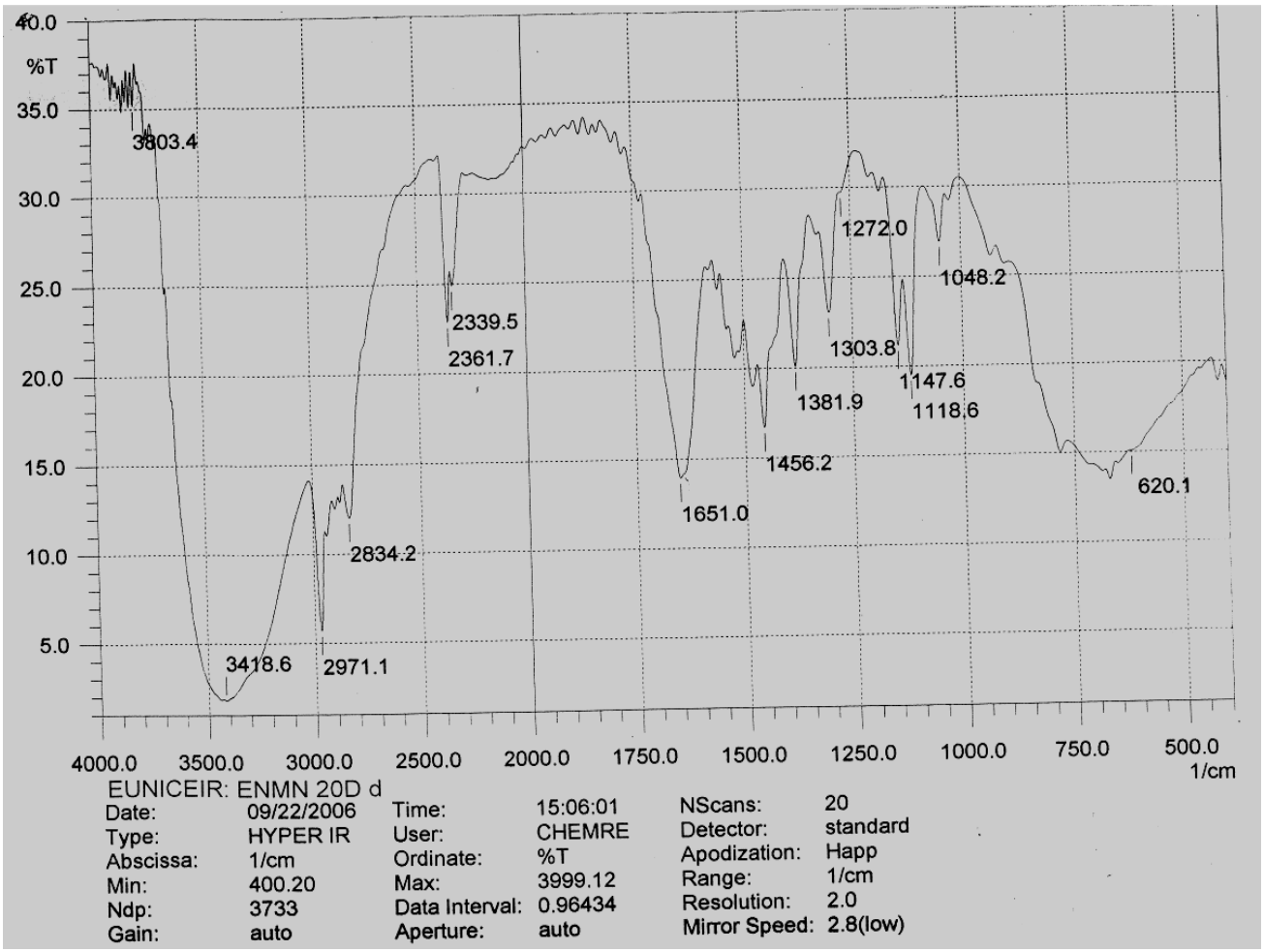


Figure 3.6: Infrared spectrum of filtrate obtained from diethylamine + $Mo(CO)_4Br_2$

The first portion was yellow in colour and halogen-free. This portion was concentrated by pumping out excess methanol using a vacuum pump. When the concentrated yellow solution was left in a desiccator, a dark brown solid was formed. An IR spectrum of dark brown solid was similar to that of the brown solid obtained in section 3.2.3 of this thesis. Percentage molybdenum present in the dark brown solid was found to be the same as that for the solid obtained in section 3.2.3.

The second portion was colourless and tested positive for halogen. It was concentrated in a rotary evaporator and white needle-shaped crystals appeared on cooling. Elemental analysis was done. The elemental analysis results (Table 3.3) and the empirical formula deduced suggested that the white needle-shaped crystals diethyl ammonium hydro bromide. It melted

at 217^{o}C while the pure solid melts at 220^{o}C. This is an indication that the salt formed was fairly pure.

The third portion was a reddish brown oily liquid and tested positive for halogen. An IR spectrum (Fig. 3.7) of this liquid obtained showed bands at 1741.6 cm^{-1}, 1699.2 cm^{-1} and 1625.25 cm^{-1}. The spectrum suggests that the compound is an oxidized diethyl amine that has been hydrolyzed to methylamine and methanal. The spectrum will be discussed further in section 4.2.2.1 of this thesis.

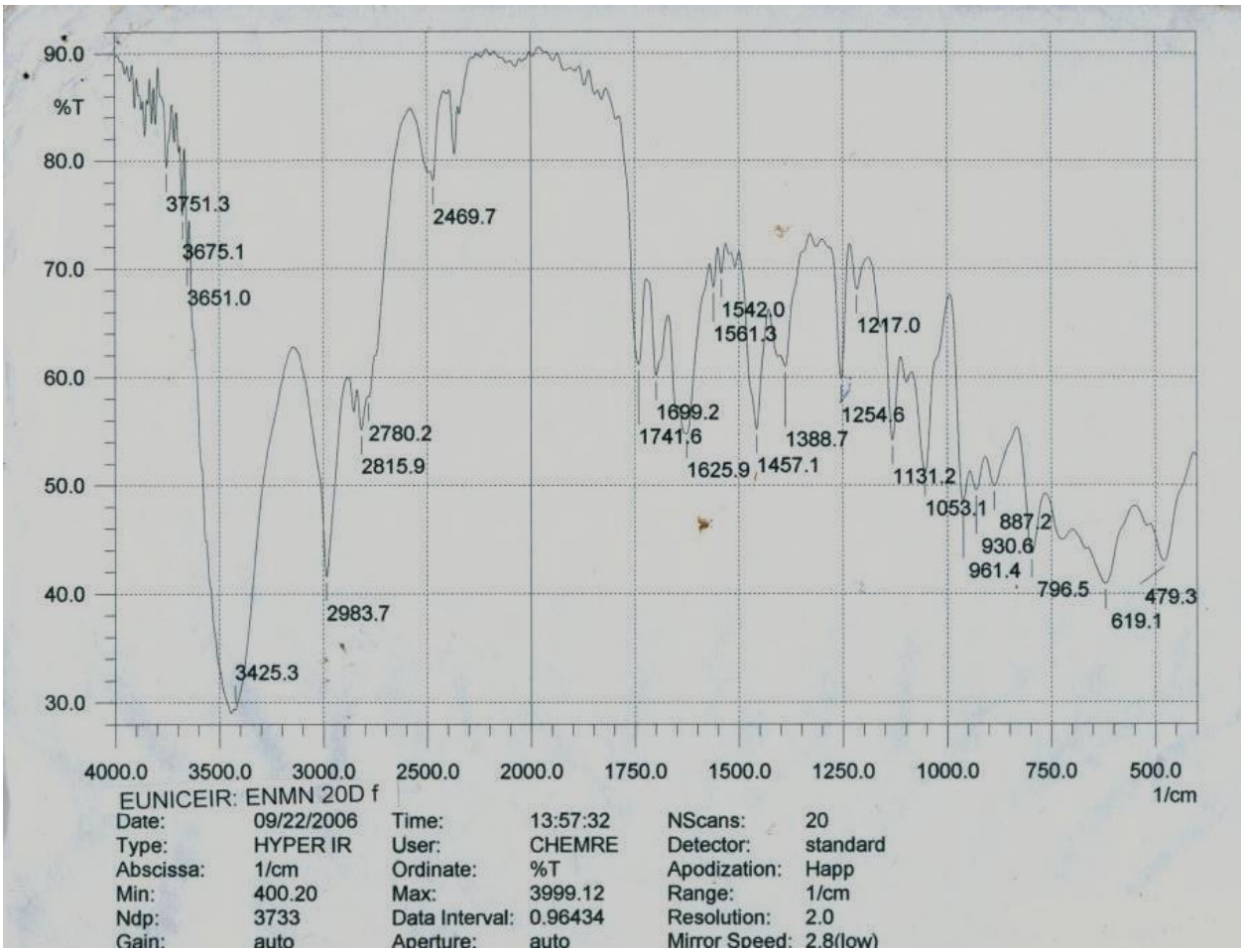


Figure 3.7: Infrared spectrum of oily product obtained from diethylamine + $Mo(CO)_4X_2$

3.2.4 Reaction of Tetrabromooctacarbonyltungsten(II) with Diethylamine

Hexacarbonyltungsten(0), $W(CO)_6$, (14.66 mmol) were used to prepare $W(CO)_4Br_2$ as described in section 3.2.1. The dark orange crystals obtained were cooled in dry-ice/acetone

bath for about 15 minutes. Dry diethylamine (73.3mmol) added and the mixture stirred for 16 hours. There was effervescence when the amine was added as a colourless gas was evolved. A yellow solid was precipitated. The precipitate was separated by suction filtration under nitrogen. It was washed with diethylamine, rinsed with diethyl ether, dried by suction and weighed. The filtrate was kept aside for further analysis. The solid obtained was stored in an ampoule from where some were immediately used to determine the tungsten and the remaining used for the determination of carbon, nitrogen and hydrogen. An IR spectrum (Fig 3.8) of the solid indicated that the compound had co-ordinated CO groups as well as co-ordinated bases. The elemental analysis results (Table 3.2) suggested that the compound has the empirical formula $WO_3C_{15}H_{33}N_3$.

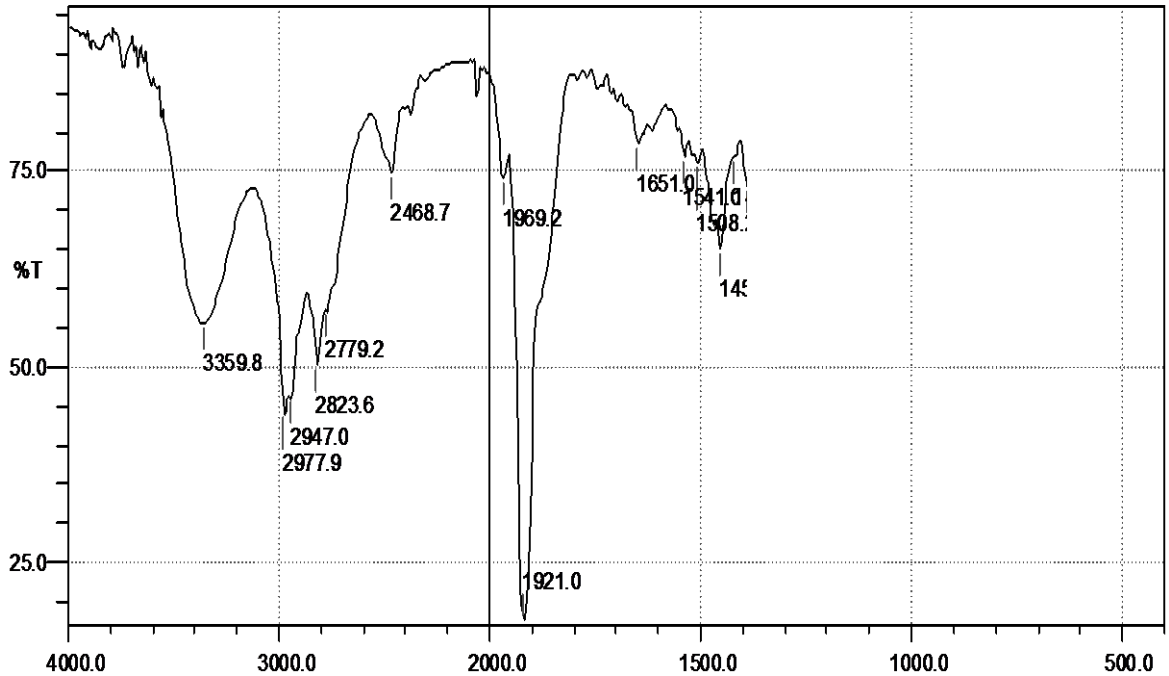


Figure 3.8: Infrared spectrum of $W(CO)_3$(N,N-diethylamine)$_3$ complex

3.2.4.1 Isolation of compounds from the filtrate obtained from the reaction of tetrabromooctacarbonyltungsten (II) with diethylamine

The filtrate was concentrated by distillation under nitrogen. Thin layer chromatography showed that the filtrate had two components. The filtrate was further concentrated and

eluted with methanol in a column packed with neutral alumina. Three different fractions were obtained.

3.2.4.1.1 Fraction 1

This portion was yellow in colour and halogen-free. It was concentrated, vacuum-dried and weighed. A yellow solid was obtained. Elemental analysis gave 38.06% tungsten; the calculated value for tungsten based on the formula $WO_3C_{15}H_{33}N_3$ is 37.73%. This was an indication that the product was similar to that obtained in section 3.2.4.

3.2.4.1.2 Fraction 2

This portion was colourless and tested positive for halide ions. It was concentrated in a rotary evaporator. Long white needle-shaped crystals were obtained. They melted at 218^0C while the theoretical melting point is 220^oC for diethylammonium bromide. Elemental analysis results (Table 3.3) for the crystals suggested that they had the empirical formula $C_4H_{12}NBr$

3.2.4.2.2 Fraction 3

The third portion was reddish brown and tested positive for halogen. It gave an oily liquid on concentration. An IR spectrum (Fig. 3.9) of this liquid showed peaks at 1635.5 cm^{-1} and 1635.5 cm^{-1} suggesting that diethylamine may have been oxidized to an enamine.

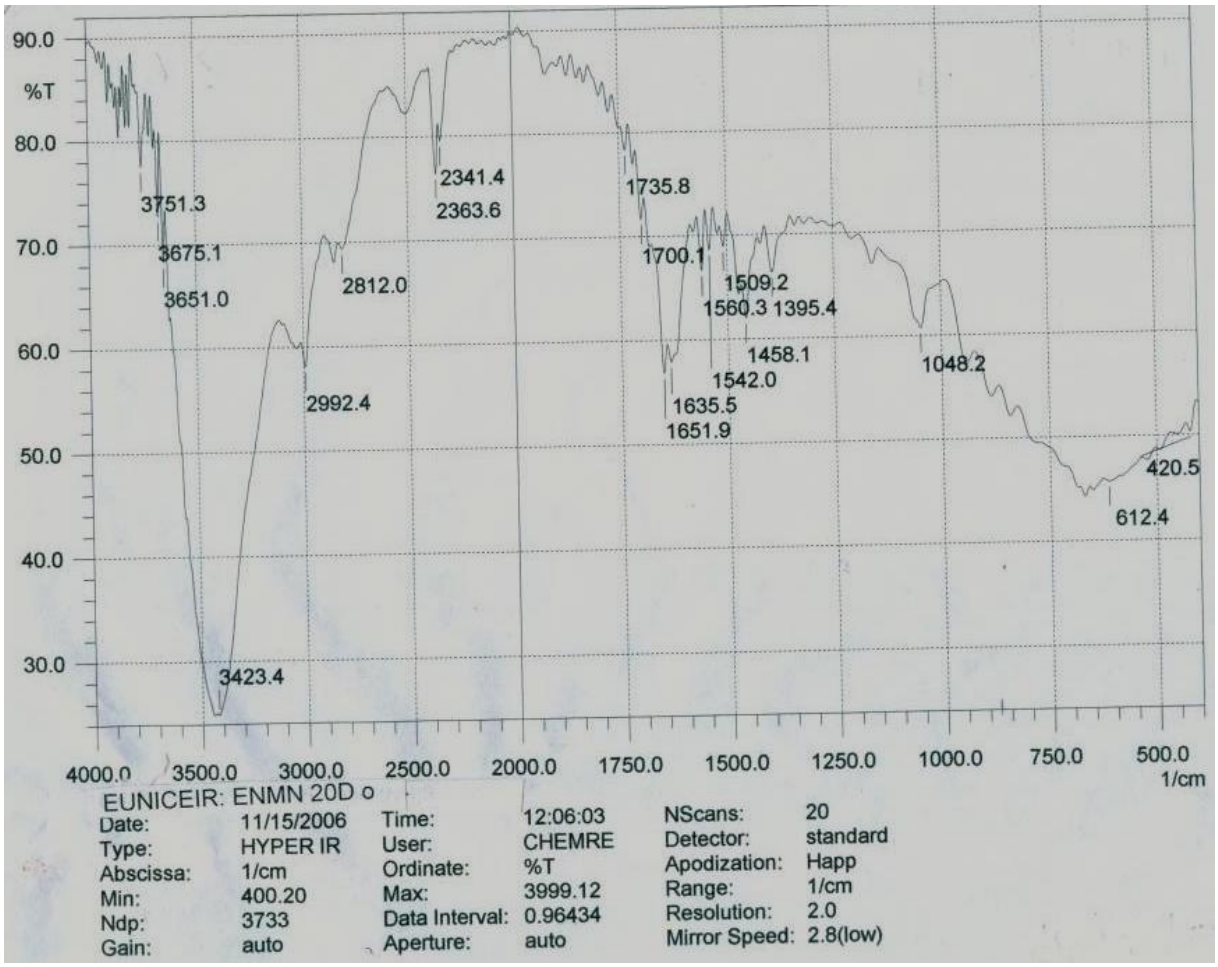


Figure 3.9: Infrared spectrum of oily product obtained from diethylamine + W(CO)4X2

3.2.5 Reaction of Tetrabromooctacarbonylmolybdenum(II), $[Mo(CO)_4Br_2]_2$ with N,N,N',N'-Tetramethylethylenediamine (TMEDA),

Hexacarbonylmolybdenum(0) (16.1 mmol) were used to prepare tetrabromooctacarbonylmolybdenum(II), $Mo(CO)_4Br_2$, in a Schlenk tube as described. The $Mo(CO)_4Br_2$ crystals were cooled in dry-ice/acetone bath for about 20 minutes. About 15 ml of freshly distilled TMEDA were cooled and added to the cold solid. The mixture was stirred vigorously. The Schlenk tube became very warm. There was no effervescence. The reaction mixture was stirred for 16 hours. A yellow solid was formed. The precipitate was separated by suction filtration under dry, oxygen-free nitrogen. The residue was washed with a little TMEDA and rinsed with dry diethyl ether. It was vacuum dried and weighed.

Some of it was stored in an ampoule while the rest was immediately used to determine both molybdenum and bromine content.

Elemental analysis results (Table 3.2) suggest that the compound has the empirical formula $MoO_4C_{10}H_{16}N_2$. The IR spectrum (Fig. 3.10) of the compounds gave three peaks in the region of 1985cm^{-1}, 1858.3cm^{-1} and 1858.3cm^{-1}, an indication that co-ordinated CO was present. The crystal structure of the compound was determined by x-ray diffraction.

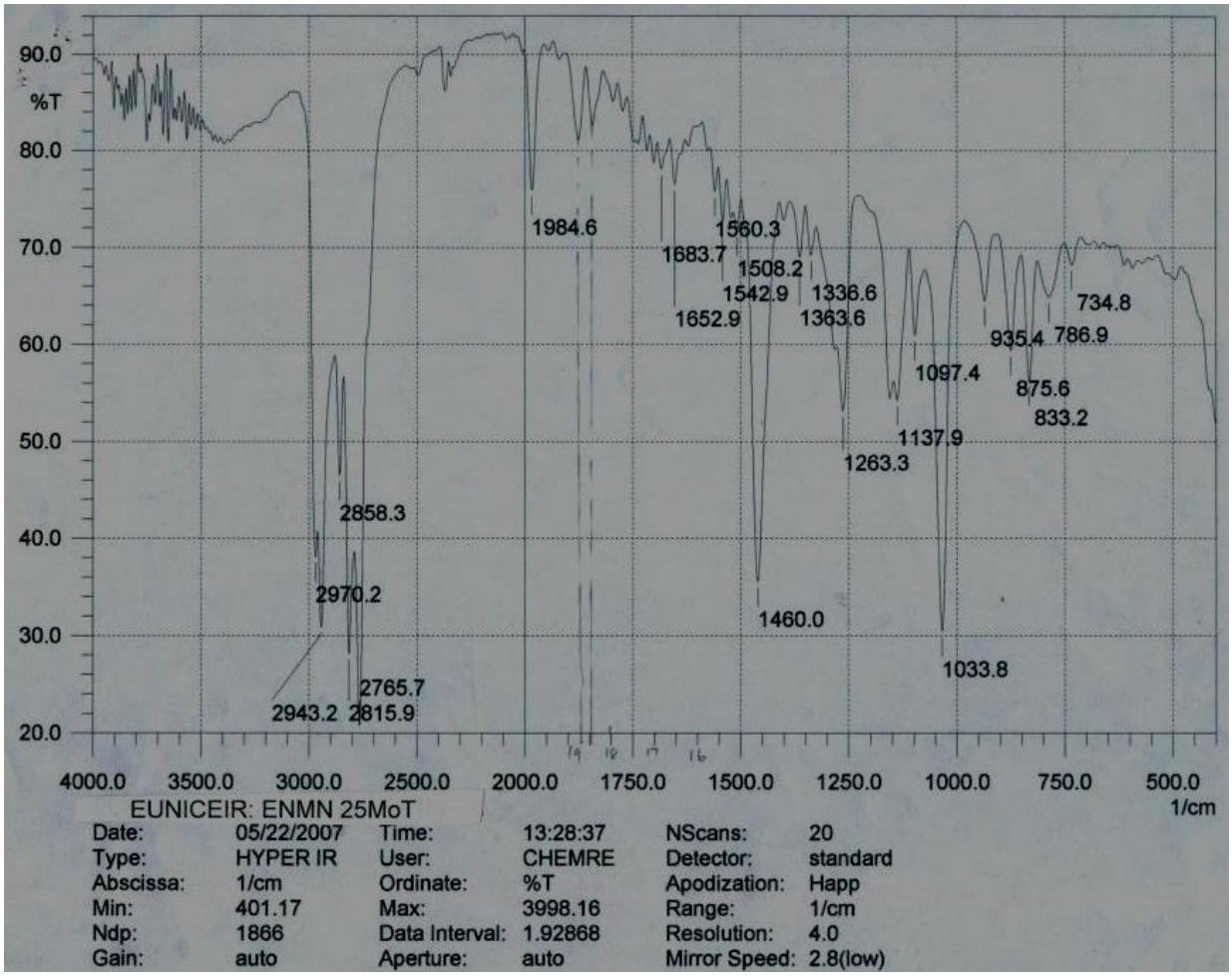


Figure 3.10: Infrared spectrum of $Mo(CO)_4$(N,N,N',N'-tetramethylethylenediamine)

3.2.5.1 Isolation of products from the filtrate obtained from the reaction of Tetrabromooctacarbonylmolybdenum(II), with N,N,N',N'-Tetramethylethylenediamine,

The filtrate was concentrated by vacuum distillation. The mother liqour was eluted in a column packed with neutral alumina. Tetrahydofuran, THF, was used as the eluting solvent. Two fractions were obtained.

3.2.5.1.1 Fraction 1

This was yellow in colour. A qualitative test for halide ions was negative. It was concentrated and vacuum-dried. A yellow solid was formed. Elemental analysis for molybdenum showed that it had the same empirical formula, $MoO_4C_{10}H_{16}N_2$, as the solid formed in section 3.2.5.

An IR spectrum (Fig. 3.10) and ^{13}C NMR spectrum (Fig. 3.11) of the solid were obtained. The ^{13}C NMR gave two peaks at 221.390 and 235.874ppm, an indication that the compound was a *cis*-isomer of the zero-valent complex.

3.2.5.1.2 Fraction 2

This fraction was colourless and tested positive for bromide ions. It was concentrated in a rotary evaporator and dried. Cream-white needle-shaped crystals were formed. Elemental analysis results (Table 3.3) showed that this was the dibromosalt of TMEDA with the empirical formula $C_6H_{18}N_2Br_2$.

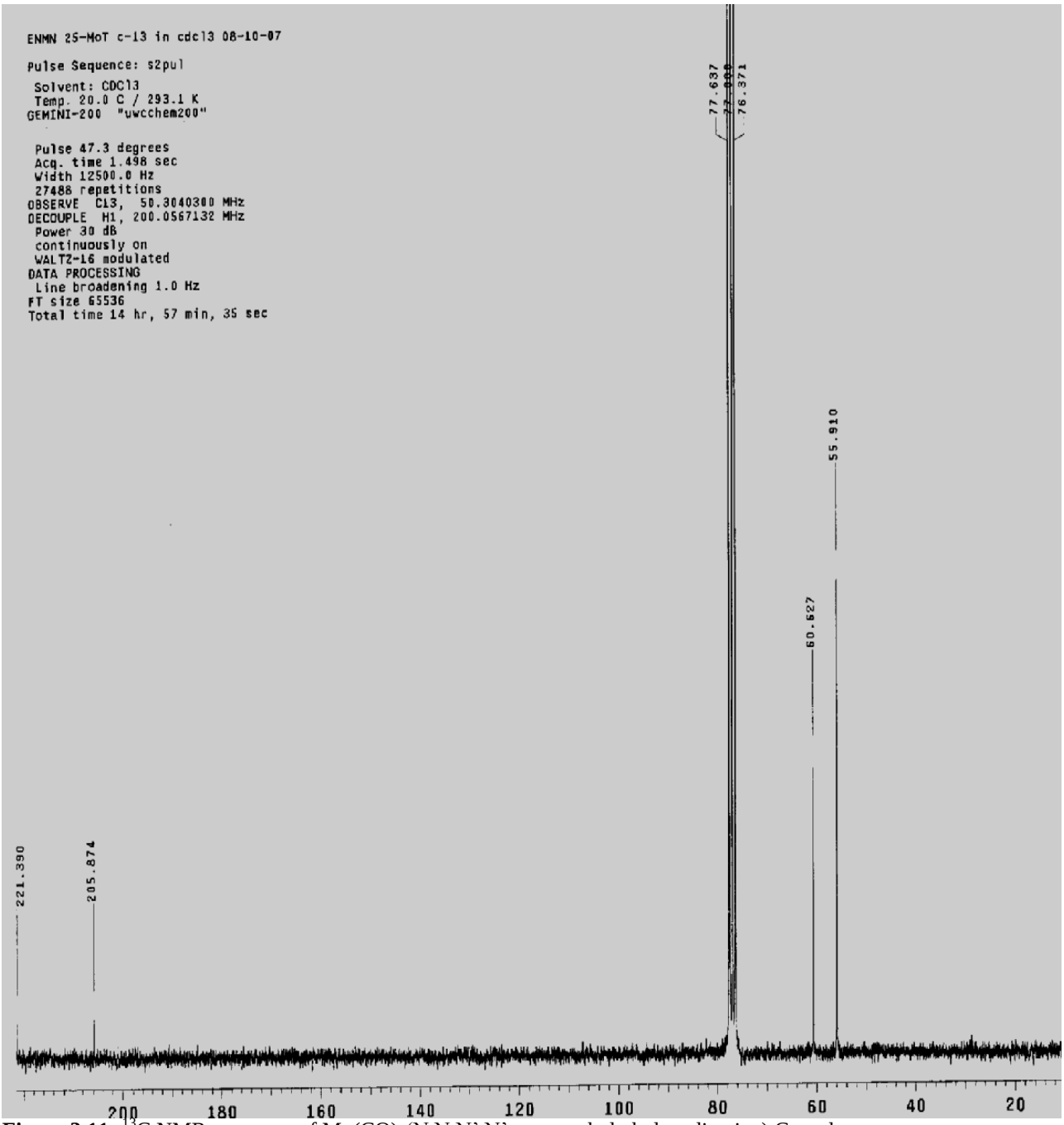


Figure 3.11: ^{13}C NMR spectrum of $Mo(CO)_4$(N,N,N',N'-tetramethylethylenediamine) Complex

3.2.6 Reaction of tetrabromooctacarbonyltungsten (II), $[W(CO)_4Br_2]_2$, with TMEDA

Hexacarbonyltungsten(0), $W(CO)_6$, (11.37 mmol) were used to prepare $W(CO)_4Br_2]_2$ in a Schlenk tube under dry, oxygen-free nitrogen. The dark orange crystals obtained were cooled in dry-ice/ acetone bath for 15 minutes. Freshly distilled TMEDA (34.28 mmol) were cooled and added to the cold $[W(CO)_4Br_2]_2$. As the mixture was stirred, the solid slowly dissolved in the base with the formation of a yellow solid. The Schlenk tube became

quite warm as the reaction continued. The mixture was stirred for 16 hours in an inert atmosphere. There was a sticky brown solid on the sides of the Schlenk tube. About 20 ml of dry diethyl ether were added to the mixture to help form a good suspension of the solid. The solid was separated by suction filtration under dry, oxygen-free nitrogen.

The yellow solid was rinsed with diethyl ether, dried, weighed and stored in an ampoule from where it was used for analysis. Elemental analysis (Table 3.2) suggested that the compound had the empirical formula $WO_4C_{10}H_{16}N_2$

The colour of the compound darkened with time, an indicator that decomposition was taking place. An IR spectrum (Fig. 3.12) of the solid was obtained. It gave IR bands at 1975.0cm.[1], 1930cm^{-1}, 1865.0cm^{-1} and 1832.2cm^{-1}. ^{13}C NMR spectrum (Fig. 3.13) of the solid gave two peaks at 221.314 and 205.723ppm, an indication that the compound had coordinated carbonyls.

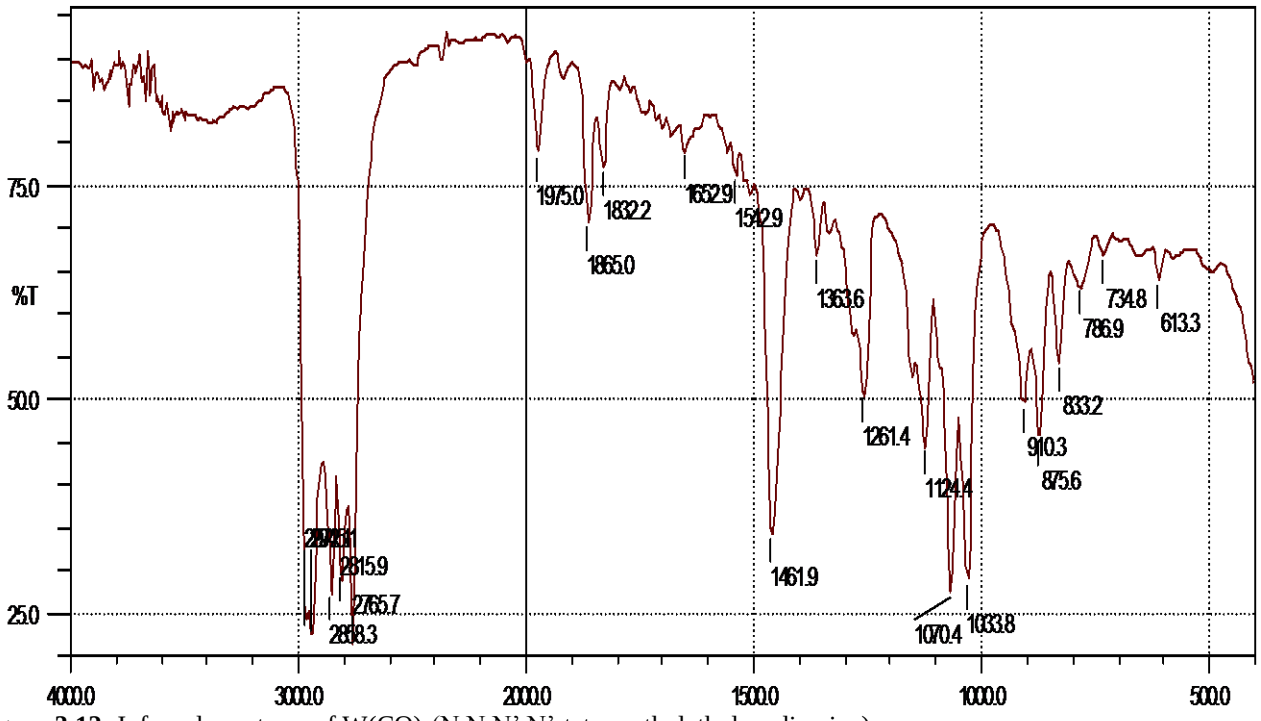
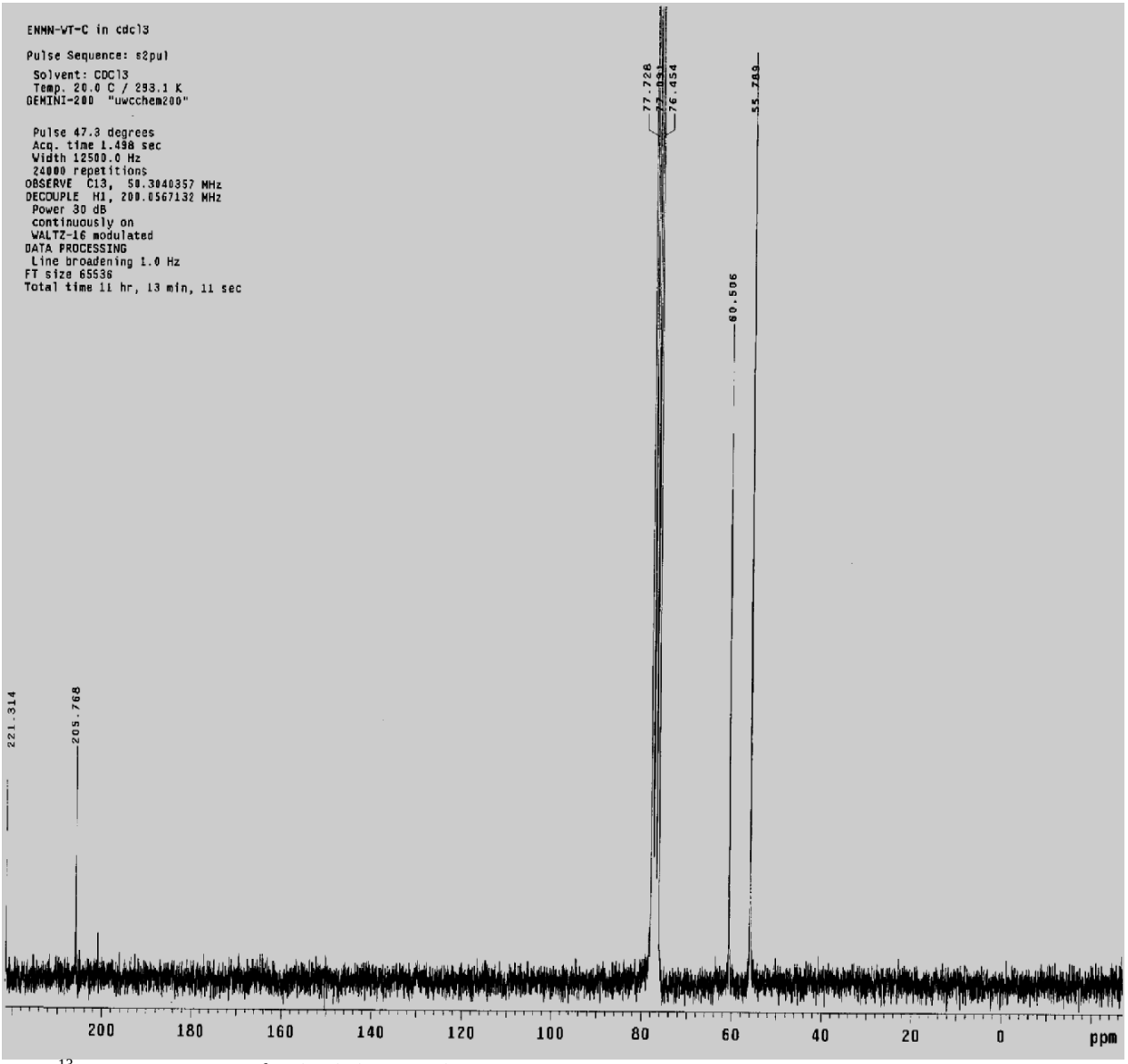


Figure 3.12: Infrared spectrum of $W(CO)_4$(N,N,N',N'-tetramethylethylenediamine)



3.13: ^{13}C NMR spectrum of $W(CO)_4(TMEDA)$

3.2.6.1 Isolation of products in the filtrate of the reaction of tetrabromooctacarbonyltungsten(II), $[W(CO)_4Br_2]_2$, with TMEDA

The filtrate was concentrated and the concentrated filtrate eluted in a column packed with neutral alumina using THF as the solvent. Three fractions were obtained.

3.2.6.1.1 Fraction 1

This portion was yellow. Qualitative test for halide ions was negative. It was concentrated and a yellow solid precipitated. The solid tarnished quite fast on storage. The precipitate was

dried and the percentage tungsten determined immediately. The percentage tungsten (44.9%) suggested that the product was $W(CO)_4C_6H_{16}N_2$.

3.2.6.1.2 Fraction 2

This was colourless and gave a positive test for bromide ions. The fraction was concentrated in a rotary evaporator. Fine needle-shaped crystals were formed. Elemental analysis results (Table 3.3) suggested an empirical formula $C_6H_{18}N_2Br_2$ for the compound.

3.2.6.1.3 Fraction 3

This portion was yellow and tested positive for bromide ions. It was concentrated in a rotary evaporator and a dark yellow oily liquid formed. An IR spectrum (Fig. 3.14) showed a peak in the region of 1650.00cm^{-1} suggesting the presence of a carbon-carbon double bond.

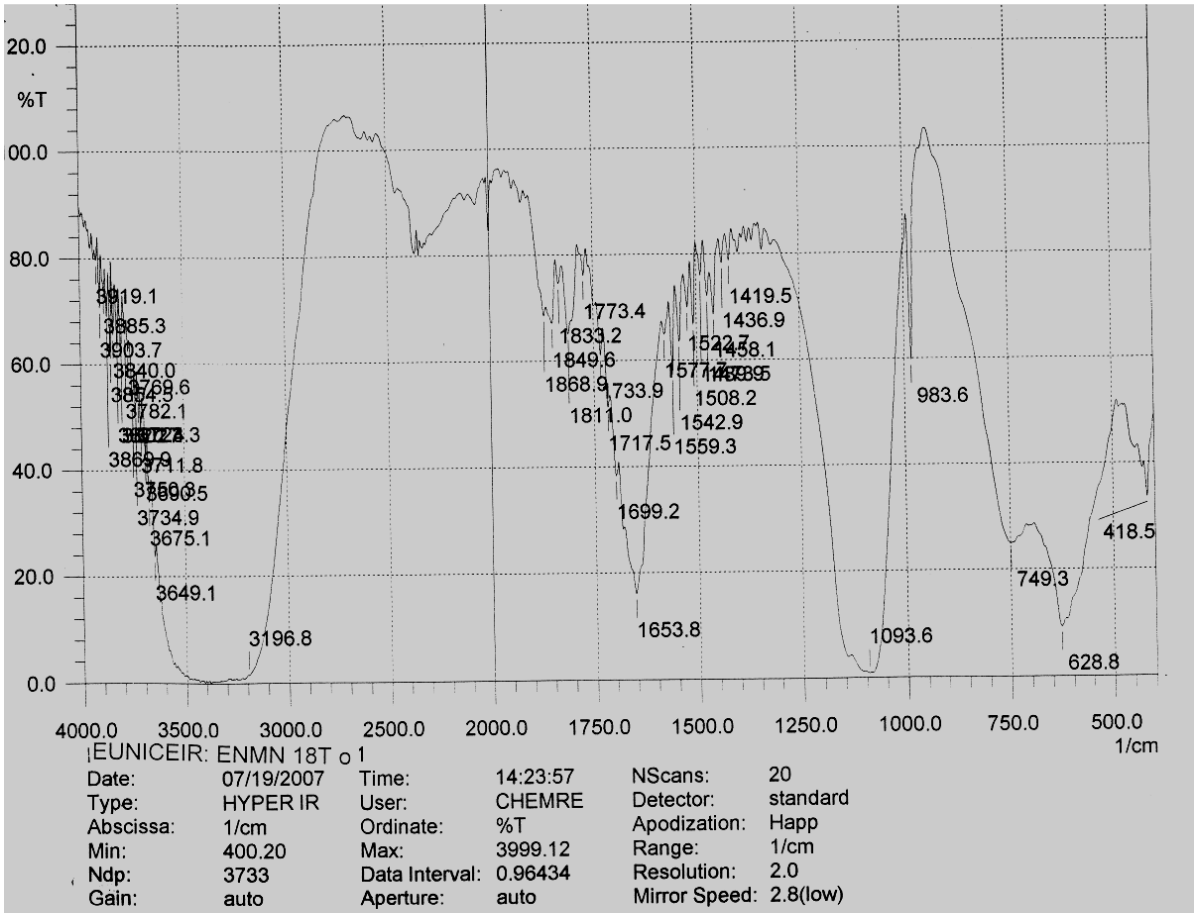


Figure 3.14: Infrared spectrum of oily product obtained from TMEDA + $Mo(CO)_4X_2$

3.2.7 Reaction of tetrabromooctacarbonyltungsten (II) with methylamine in THF

Hexacarbonyltungsten(0) (14.27 mmol) was used to prepare $[W(CO)_4Br_2]_2$. The orange crystals obtained were cooled in dry-ice/acetone bath for 30 minutes. Freshly distilled methylamine solution (99.89 mmol) in THF were cooled in dry-ice/acetone bath for 5 minutes and then added into the Schlenk tube containing $[W(CO)_4Br_2]_2$ crystals. The tube was removed from the dry-ice/acetone bath, the mixture stirred as the tube warmed up. The tube became hot and a vigorous reaction took place with the evolution of a colourless gas.

A yellow solid appeared. The mixture was stirred for 8 hours to allow the reaction to come to completion. The yellow solid was separated by suction filtration under dry, oxygen-free nitrogen, washed with THF, rinsed with diethylether, vacuum dried and weighed. Some of the solid was stored in an ampoule and later used for IR, NMR and elemental analysis. The rest was immediately used to determine the percentage of tungsten. The filtrate was kept aside and used later to isolate other products.

The elemental analysis results (Table 3.2) suggest that the product has the empirical formula $WO_3C_3H_{15}N_3$.These results suggest that the product formed was $W(CO)_3(CH_3NH_2)_3$. The compound was decomposing at a fast rate as registered from the decrease in the amount of C, H and N was noted when elemental analysis was done one week later. IR spectrum (Fig. 3.15) of the product was recorded. It gave peaks in the region of 1990.0cm^{-1} to 1820.0cm^{-1}; a sign that coordinated carbonyl was present.

3.2.7.1 Isolation of products from filtrate obtained from the reaction of tetrabromooctacarbonyltungsten(II) with methylamine in THF

The filtrate was concentrated in a rotary evaporator. Pale white, plate-like crystals were obtained. The mixture was decanted to obtain the crystals, which were then re-crystallized from dry methanol. The elemental analysis results (Table 3.3) suggest that the product has the empirical formula $C_2H_{10}N_2Br_2$. The solid sublimed at temperatures above 340 ^oC.

TLC was carried out on the mother liquor to find out whether it was a mixture or not. There was only one compound in the mother liquor; therefore column chromatography was not necessary. Mother liquor was dried and a yellow solid was formed. Elemental analysis (Table 3.2) suggests the empirical formula $WO_3C_3H_{15}N_3$. The IR spectrum (figure 3.14) showed that the product was similar to the solid obtained from the reaction described in section 3.2.7.

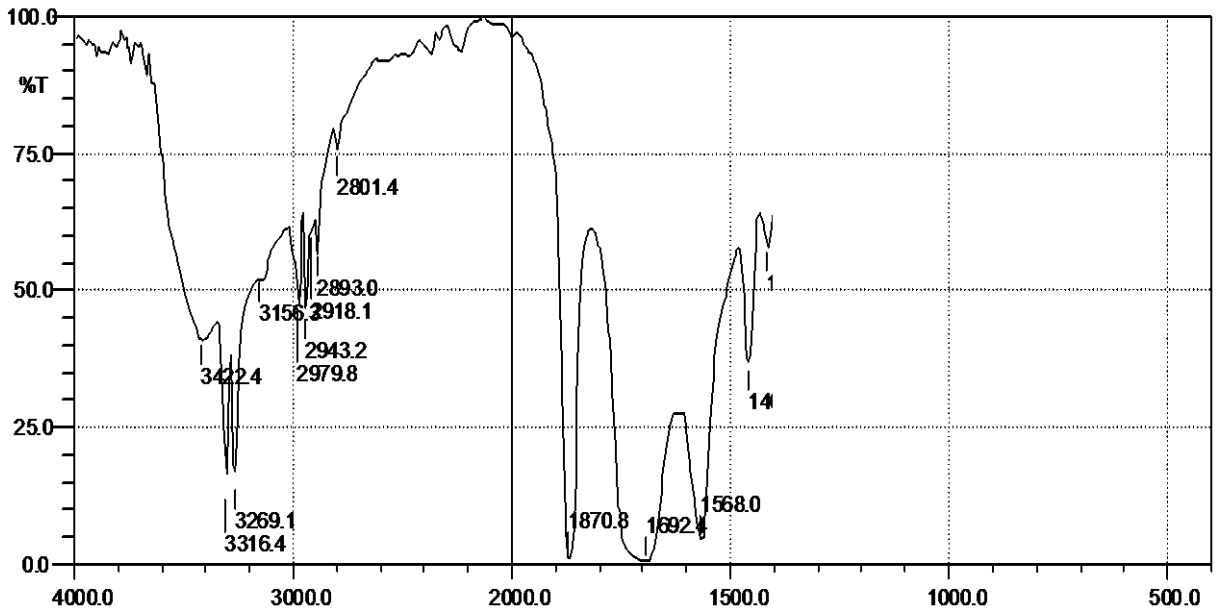


Figure 3.15: Infrared spectrum of $Mo(CO)_3(CH_3NH_2)_3$ complex

3.2.8 Reaction of tetrabromooctacarbonylmolybdenum(II) with methylamine in THF

The procedure followed is the same as the one described in section 3.2.7. Hexacarbonylmolybdenum(0) (19.96 mmol) were used in place of hexacarbonyltungsten(0).

Elemental analysis results (Table 3.2) suggested the empirical formula of the product as $MoO_3C_3H_{15}N_3$.

3.2.8.1 Isolation of products from filtrate

The compounds in the filtrate were isolated following the procedure described in section 3.2.7.2. Elemental analysis results (Table 3.3) suggested that the salt had empirical formula CH_6NBr.

3.2.9 Reaction of tetrabromooctacarbonyltungsten(II) with 1-methyl-2-(3-pyridyl)-pyrrolidine (nicotine)

$W(CO)_6$ (13.33 mmol) were used to prepare $[W(CO)_4Br_2]_2$. Nicotine (39.84 mmol) were added to about 20 ml of THF and the mixture cooled in dry-ice/acetone bath. The cold solution was added to $[W(CO)_4Br_2]_2$ in a Schlenk tube and stirred in an atmosphere of dry, oxygen-free nitrogen gas. The solid dissolved to form a dark-brown solution. The mixture was stirred for about 18 hours and a black mass was formed.

The mother liquor was decanted off and the black mass remained in the Schlenk tube. The solution (mother liquor) was kept for further treatment as described in section 3.2.9.1. Dry petroleum ether was added to the solid and the mixture stirred for one hour. The mixture was filtered by suction, the residue rinsed using dry diethylether, dried and weighed. A brown solid obtained was stored in an ampoule and used for analysis. The percentage tungsten in the product was found to be 39.13%.The IR spectrum (Fig. 3.16) for the sample gave 5 spectral bands at 2009.7 cm^{-1}, 1979.8 cm^{-1}, 1936.4 cm^{-1}, 1887.2 cm^{-1} and 1837.1cm^{-1} for coordinated carbonyl stretching frequency, 3 bands in the region 1067.5 cm^{-1}, 1047.3 cm^{-1} and 1026cm^{-1} for C-N stretches on pyrrolidine ring and 2 peaks around 1600.8 and 1577.7cm^{-} for C=N stretches in pyridine ring

3.2.9.1 Isolation of compounds from the filtrate obtained from the reaction of tetrabromooctacarbonyltungsten (II) with 1-methyl-2-(3-pyridyl)-pyrrolidine (nicotine)

The mother liquor was concentrated by vacuum distillation. An IR spectrum (Fig. 3.17) of the concentrated liquid gave a peak at 1760.9cm^{-1} indicating the presence of a free CO in a ketone. The filtrate was eluted using THF in a column packed with neutral alumina.

3.2.9.1.1 Fraction 1

The first portion was dark brown and was halogen-free. It was concentrated in a vacuum and dried. A dark-brown product was formed. Percentage tungsten in the solid was found to be 42.84%. This suggested that the product was similar to that found in section 3.2.9. An IR spectrum (Fig. 3.16) of the sample was obtained.

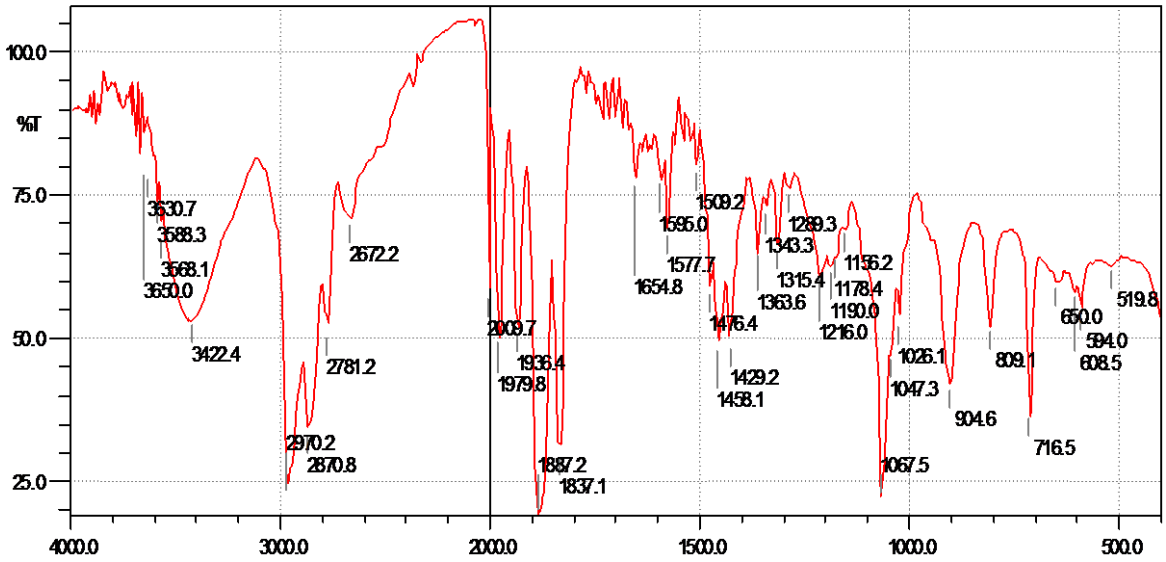


Figure 3.16: Infrared spectrum of $W(CO)_5$(nicotine) complex

3.2.9.1.2 Fraction 2

The second portion was cream-white and tested positive for bromide ions. It was concentrated in a rotary evaporator. Cream-white crystals were formed. They were re-crystallized in methanol and analyzed. The elemental analysis results (Table 3.3) suggest that the product has the empirical formula $C_{10}H_{15}N_2Br$. These results suggest that the compound formed was nicotine hydrobromide, $C_{10}H_{14}N_2.HBr$.

3.2.10 Reaction of tetrabromooctacarbonylmolybdenum (II) with 1-methyl-2-(3-pyridyl)-pyrrolidine (nicotine)

$Mo(CO)_6$ (11.71 mmol) were used to prepare $[Mo(CO)_4Br_2]_2$. 8.0 ml of nicotine (45.80 mmol) was added to the dark-orange solid in a Schlenk tube. A black mass was formed as the tube became quite hot. The mixture was stirred in an atmosphere of dry, oxygen-free nitrogen for 16 hours. The black mass became stickier. About 15 ml of dry, freshly distilled THF was added to the mixture and stirred for 3 hours.

The resulting brown precipitate was separated by suction filtration. The filtrate was kept aside and used to isolate other products while the residue was washed several times with distilled methanol and rinsed with diethylether. The brown solid was dried, weighed and stored in an ampoule from where it was used for analysis. The percentage molybdenum in the product was found to be 25.41%. An IR spectrum (Fig. 3.17) of the solid gave 5 absorption peaks in the region of 2006.0cm^{-1}, 1975.0cm^{-1}, 1925.8cm^{-1}, 1873.7 cm^{-1} and 1834.2cm^{-1}. The peaks fall in the region for inorganic carbonyl groups.

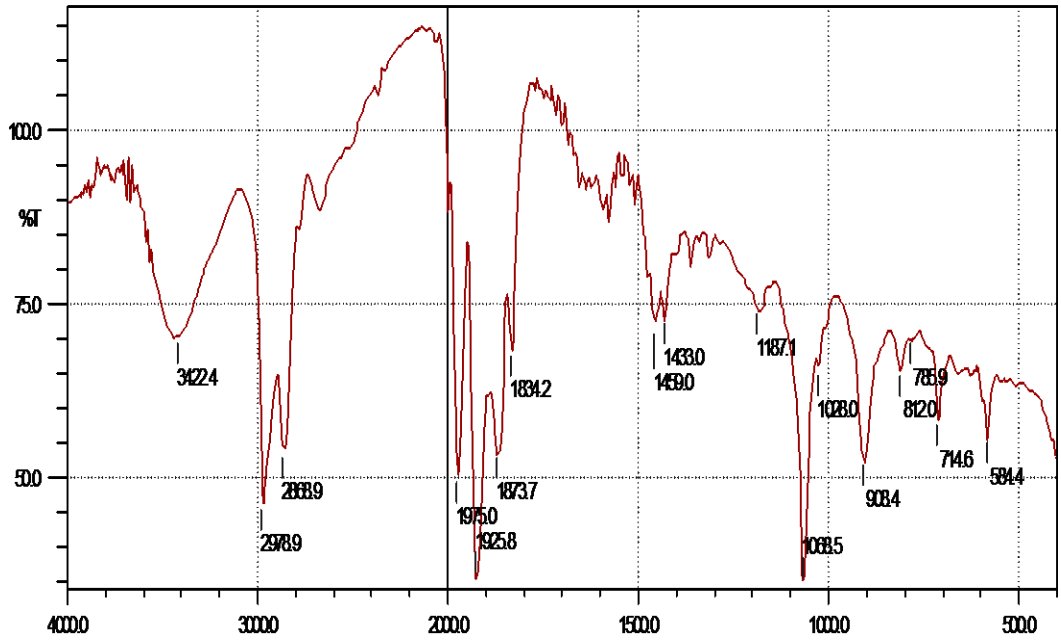


Figure 3.17: Infrared spectrum for $Mo(CO)_5$(nicotine) complex

3.2.10.1 Isolation of other products from the filtrate obtained from the reaction of tetrabromooctacarbonylmolybdenum (II) with 1-methyl-2-(3-pyridyl)-pyrrolidine (nicotine)

The filtrate was concentrated and eluted in a column as described in section 3.2.9.1. Three fractions were recovered. The first fraction was dark brown and halogen-free, the second fraction was cream-white and tested positive for halide ions while the third portion was reddish brown. The fractions were treated as reported in section 3.2.9.1.

Percentage molybdenum found in the sample from the first fraction was found to be 28.84%. This suggested that it had the same empirical formula as the solid formed in the reaction between tetrabromooctacarbonylmolybdenum(II) and 1-methyl-2-(3-pyridyl)-pyrrolidine (nicotine). Elemental analysis results (Table 3.3) for the cream-white solid suggested an empirical formula of $C_{10}H_{15}N_2Br$.This result suggests that the compound formed was nicotine hydrobromide, $C_{10}H_{14}N_2.HBr$.

3.2.11 Reaction of tetrachlorooctacarbonylmolybdenum(II) with 1-methyl-2-(3-pyridyl)-pyrrolidine (nicotine)

Hexacarbonylmolybdenum(0), $Mo(CO)_6$, (7.42 mmol) were used to prepare tetrachlorooctacarbonylmolybdenum(II), $[Mo(CO)_4Cl_2]_2$.

Nicotine (31.13 mmol) was dissolved in 20 ml of freshly distilled methanol and cooled in dry-ice/acetone bath for 15 minutes. The nicotine solution was added to the cold orange crystals of $[Mo(CO)_4Cl_2]_2$ and the mixture stirred as it warmed up. A brown precipitate was formed. The mixture was stirred for 14 hours after which the precipitate was separated by suction under dry, oxygen-free nitrogen. The residue was washed with dry, freshly distilled methanol and rinsed with diethylether. The precipitate was dried, weighed and then stored in an ampoule. The percentage molybdenum was found to be 28.61%. An IR spectrum (Fig. 3.18) of the product showed 5 absorption peaks at 1930.0cm^{-1}, 1899.8cm^{-1}, 1871.8cm^{-1}, 1829.4cm^{-1} and 1817.8.1cm^{-1}. This suggests the presence of inorganic carbonyl in the compound.

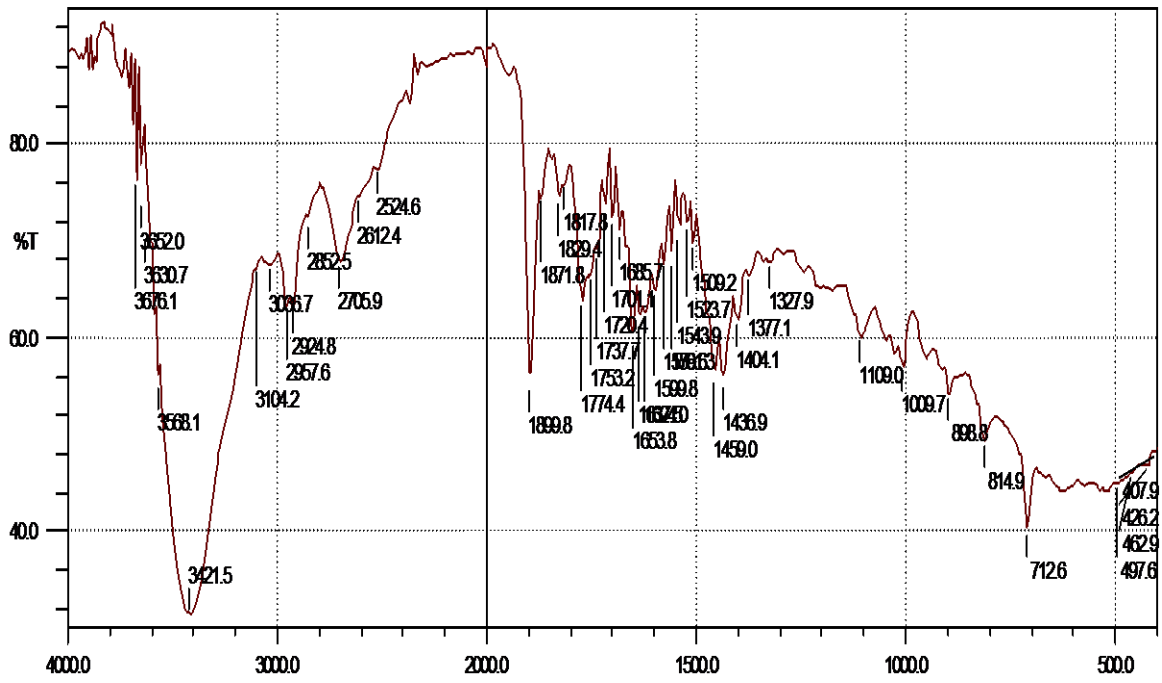


Figure 3.18: IR spectrum for $Mo(CO)_5$(nicotine) complex

3.2.11.1 Isolation of compounds from the filtrate obtained from the reaction of tetrachlorooctacarbonylmolybdenum(II) with 1-methyl-2-(3-pyridyl)-pyrrolidine (nicotine)

The filtrate was concentrated by rotary evaporation. A few drops of the distillate were used for IR analysis. The concentrated filtrate was eluted in a column packed with neutral alumina and methanol used as the eluting solvent. Three portions were obtained. The first portion was dark brown and was halogen free. It was concentrated and vacuum dried. The percentage molybdenum in the solid was found to be 28.52%. The second portion was colourless and tested positive for chloride ions. It was concentrated in a rotary evaporator and the solution allowed to cool slowly. White crystals formed were re-crystallized from methanol. Elemental analysis results (Table 3.3) suggested an empirical formula of the product as $C_{10}H_{15}N_2Cl$.

The third portion was yellow and tested positive for halide ions. It was concentrated in a rotary evaporator and vacuum dried. An oily, yellow liquid was left. An IR spectrum (Fig. 3.19) of the liquid showed a peak at around 1678.0cm^{-1} an indication that there is a new C=C bond that is not associated with the pyridine ring.

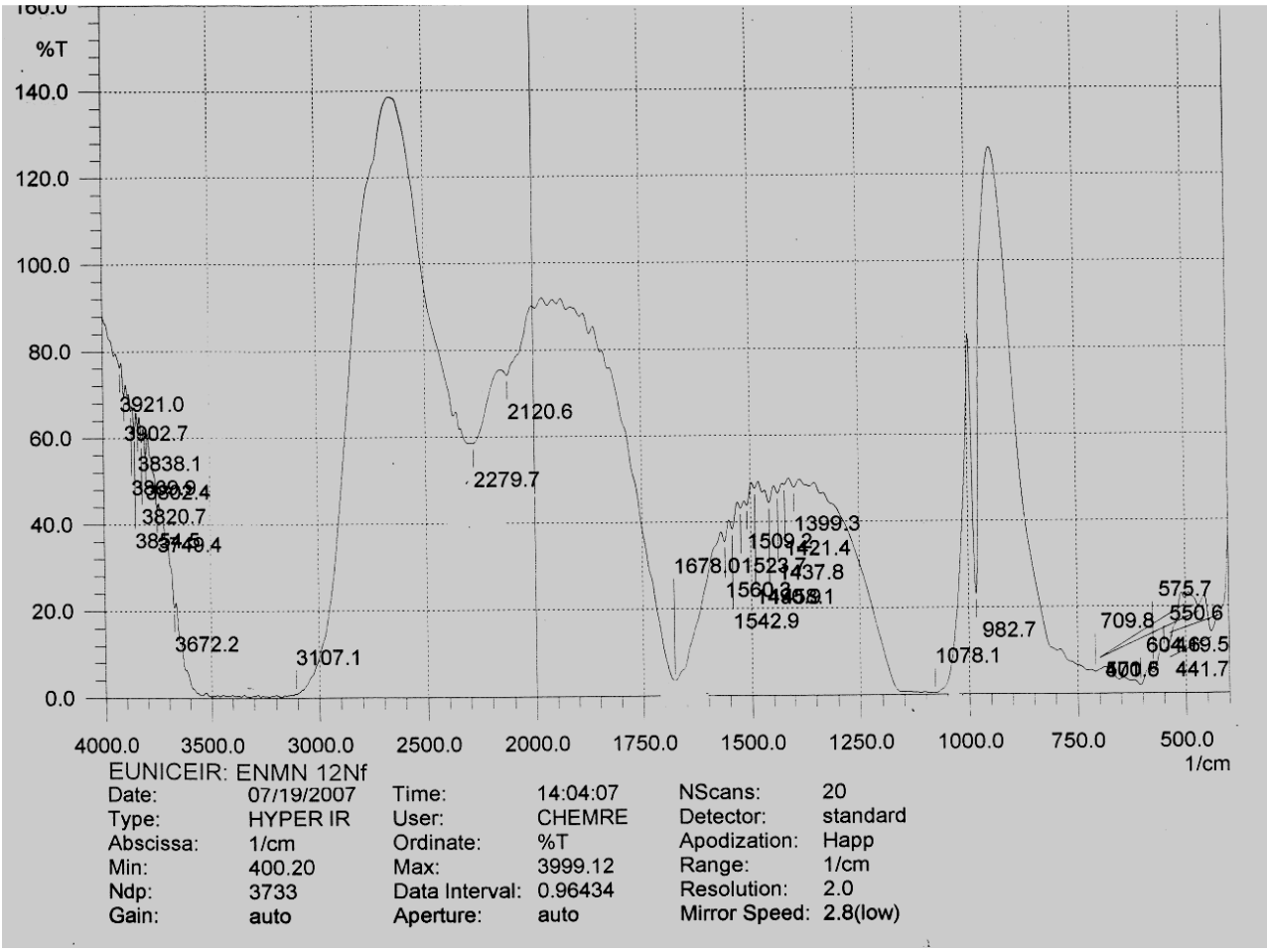


Figure 3.19: Infrared spectrum of oily liquid obtained from nicotine + $Mo(CO)_4Br_2$

3.2.12 Reaction of tetrachlorooctacarbonyltungsten(II) with 1-methyl-2-(3-pyridyl)-pyrrolidine (nicotine)

$W(CO)_6$ (12.62 mmol) were used in this experiment. The procedure followed is the same as the one described in section 3.2.11.1 of this document. The percentage tungsten in the compound was found to be 42.32% while the calculated value for tungsten in $W(CO)_5$nicotine is 45.28%. An IR spectrum (Fig. 3.20) of the product was obtained.

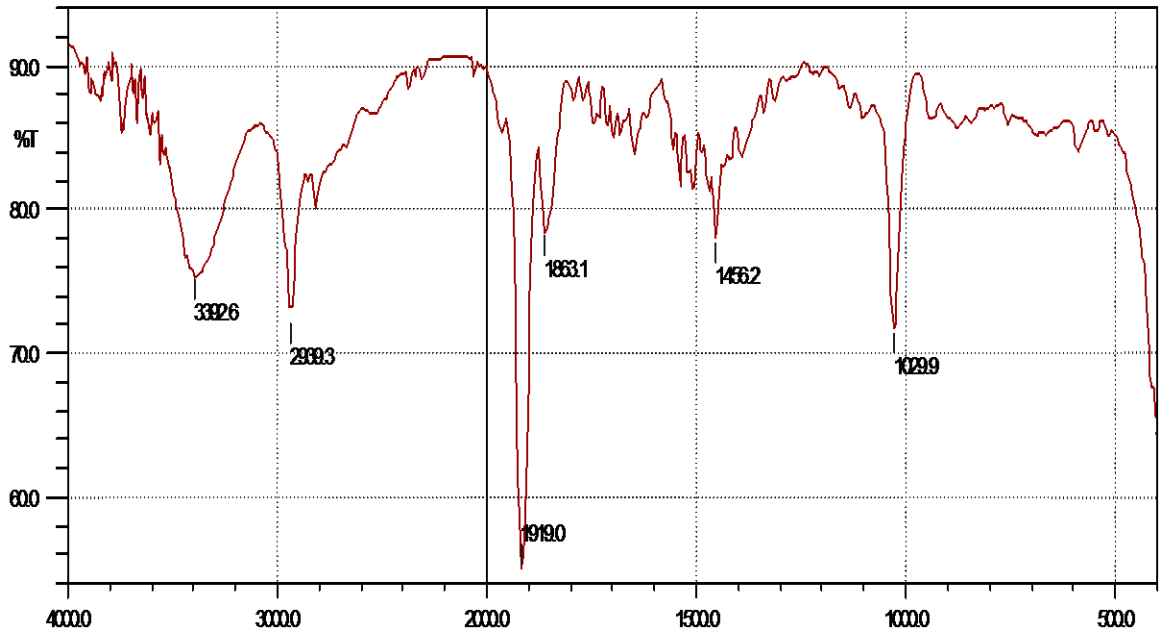


Figure 3.20: IR spectrum for $W(CO)_5$(nicotine) complex

3.2.12.1 Isolation of compounds from the filtrate obtained from the reaction of tetrachlorooctacarbonyltungsten(II) with 1-methyl-2-(3-pyridyl)-pyrrolidine (nicotine)

The filtrate was treated as described in section 3.2.10.2 of this thesis. The percentage tungsten in the product was found to be 43.92%. An IR spectrum (Fig. 3.20) for the product was obtained.

The elemental analysis results (Table 3.3) of white crystals obtained from the second fraction suggested an empirical formula of $C_{10}H_{15}N_2Cl$.

The third portion was yellow and tested positive for halide ions. It was concentrated in a rotary evaporator and vacuum dried. An oily, yellow liquid was left. An IR spectrum of the liquid showed a peak at 1765.0 cm^{-1}, an indication that there is a carbonyl group of a ketone.

Table 3.2: Elemental analysis for the zero-valent compounds

Base (L)	Compound	% composition found and calculated for the compounds			
		M	C	H	N
Diethylamine $C_4H_{11}N$.	$Mo(CO)_3(L)_3$ (A) (B)	24.54 30.20 (24.04)	45.08 35.59 (45.15)	8.40 6.45 (8.32)	9.98 7.65 (10.53)
	$W(CO)_3(L)_3$ (A) (B)	37.92 39.76 (37.72)	36.27 34.87 (36.97)	6.18 5.28 (6.83)	7.91 6.12 (8.62)
TMEDA $C_6H_{16}N_2$	$Mo(CO)_4(L)$	29.45 (29.96	36.87 (37.02	4.63 (4.94)	8.02 (8.64)
	$W(CO)_4(L)$	43.88 (44.62)	28.25 (29.15)	3.28 (3.94)	6.36 (6.79)
Methylamine CH_5N	$Mo(CO)_3(L)_3$	35.22 (35.12)	25.44 (26.38)	5.15 (5.54)	14.92 (15.38
	$W(CO)_3(L)_3$ (A) (B)	50.50 52.13 (50.92)	19.04 18.78 (19.96)	3.78 3.21 (4.19)	10.58 9.74 (11.63)
1,2- ethyldiamine $C_2H_6N_2$	$W(CO)_4(L)$	(51.64)	(20.24)	(2.26)	(7.87)
Nicotine $C_{10}H_{13}N_2$	$Mo(CO)_5(L)$	28.61 (30.15)	(56.65)	(4.43)	(8.81)
	$W(CO)_5(L)$	42.32 (45.28)	(44.35)	(3.47)	(6.89)

NB/ (i) The figures in brackets are the calculated values for the zero-valent complexes
(ii) B values were obtained when analysis was done after a few days' storage

Table 3.3: Elemental analysis for the alkyl ammonium salts

Base	Halocarbonyl	Salt	% composition			
			Br	C	H	N
Diethylamine	$Mo(CO)_4Br_2$	$C_4H_{12}NBr$	49.32	31.63	7.90	9.58
	$W(CO)_4Br_2$	$C_4H_{12}NBr$	50.26	31.12	7.64	9.61
			(51.87)	(31.18)	(7.85)	(9.09)
TMEDA	$Mo(CO)_4Br_2$	$C_6H_{18}N_2Br_2$	56.98	25.73	6.73	9.92
	$W(CO)_4Br_2$	$C_6H_{18}N_2Br_2$	56.90	25.60	6.73	9.8
			(57.47)	(25.92)	(6.57)	(10.07)
Methylamine	$Mo(CO)_4Br_2$	CH_6NBr	71.89	12.301	4.30	12.36
	$W(CO)_4Br_2$	CH_6NBr	71.53	12.26	4.20	12.53
			(71.36)	(10.73)	(5.40)	(12.51)
1,2-ethyldiamine	-	$C_2H_{10}N_2Br_2$	(72.01)	(10.87)	(4.55)	(12.62)
Nicotine	$Mo(CO)_4Br_2$	$C_{10}H_{15}N_2Br$	32.30	48.70	5.89	10.61
	$W(CO)_4Br_2$	$C_{10}H_{15}N_2Br$	32.71	48.93	5.91	10.82
			(32.87)	(49.42)	(6.18)	(11.53)
	$Mo(CO)_4Cl_2$	$C_{10}H_{15}N_2Br$	17.42	60.28	7.38	13.90
	$W(CO)_4Cl_2$	$C_{10}H_{15}N_2Br$	17. 32	60.12	7.38	13.90
			(17.85)	(60.48)	(7.56)	(14.11)

NB/ The figures in brackets are the calculated values for the salts

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the results of the study on the reactions of halocarbonyls, $[M(CO)_4Br_2]_2$ (M=Mo, W), with methylamine, diethylamine, nicotine and N,N,N',N',-tetramethylethylenediamine are reported and discussed.

4.1 Summary of important IR bands and NMR peaks

The IR and NMR data for the zero-valent metal complexes and organic oxidation products isolated in the present work have been summarized in tables 4.1, 4.2, 4.3 and 4.4 of this section for easy reference. As expected, the complexes of diethylamine and methylamine were each found to be highly unstable. They decomposed readily on exposure to air.

Table 4.1: ^{1}H NMR Spectra data

Product	σ (ppm)
$W(CO)_3L_3$ (L=Diethylamine)	CH_3: 1.168-0.598 (1.0), CH_2: 3.186-2.731 (2.59), NH: 5.199 (4.6), C=CH: 3.954-3.568 (4.04-3.99), N=CH: 7.772 (7.5)
$M(CO)_4L$ (L=TMEDA; M=Mo, W)	CH_3: 3.025-2.969 (2.27), CH_2: 2.879 (2.46)
$M(CO)_4L_2$ (L=nicotine; M=Mo, W)	C-6: 8.783-8.660 (8.363-8.298); C-4: 8.528-8.490 (7.533-7.496); C-3: 7.499-7.435 (7.101-7.037); C-7: 4.467-4.429 (3.096-2.869); C-9 4.054 (2.151-2.090), 3.268-3.244 (2.063-1.963), 2.755-2.729 (1.836-1.8.14), C-8: 2.625-2.253 (1.792-1.474)
Oily product from nicotine - $W(CO)_4Br_2$ reaction.	C-6: 8.160-8.079 (8.363-8.297); C-4: 7.323-7.286 (7.533-7.496): C-3: 6.871-6.810 (7.101-7.037); 4.944 (new), C-7: 3.108-2.656 (3.096-2.8690); C-9: 1.934-1.760 (2.151-1.985); C-8: 1.571-1.271 (1.963-1.474)

Note

The values in brackets are peaks for protons in neat nitrogen base

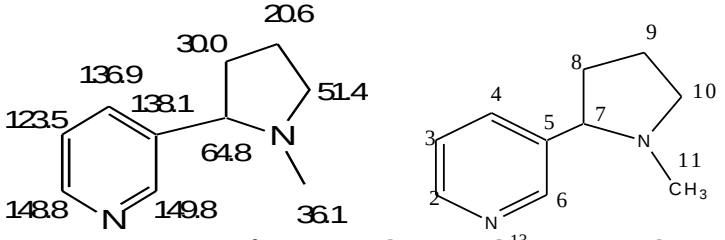


Figure 4.1: Structure of nicotine and estimated ^{13}C NMR peaks BY Chem Draw version 6.0

Table 4.2: ^{13}C NMR data

Product	**□ (ppm)**
$M(CO)_4L$ (L=TMEDA; M=Mo, W)	CO: 221.322 and 205.723; CH_2: 60.483 (57.7); CH_3: 55.796(41.2)
$M(CO)_4L_2$ (L=nicotine; M=Mo, W)	CO: 191.310; 151.723(149.8); 150.631(148.8); 137.005(138.1); 128.144(136.9); 124.723(123.5); 70.501(64.8); 55.920(51.4); 38.046(36.1); 31.795(30.0) & 21.462(20.06)
Oily product from nicotine - $W(CO)_4Br_2$ reaction.	149.349, 148.393, 138.689, 123.258, 68.643, 65.532-64.538, 56.739, 40.026, 35.209, 22.425 & 15.385-15.021

Table 4.3: ν(CO) stretch, ν(N-H) stretch, ν(N-H) bend, ν(N-H) wag and ν(C-N) stretch (cm^{-1})

Complex	ν(CO) stretch	ν(N-H) stretch	ν(N-H) bend	ν(C-N) stretch	ν(N-H) wag
$Mo(CO)_3L_3$ (L =Diethylamine)	2092.6(w) 1984.6(m) 1922.9(m)	3329.9(s) (3278.8(w))	-	1088.7-1049.2 (1138.9)	639.4 (725.2)
$W(CO)_3L_3$ (L=Diethylamine)	1969.2(w) 1921.0(s)	3359.8(m) (3278.8(w))	-	1028.0(m) (1138.9)	796.5(w) 725.2)
$W(CO)_3L_3$ (L=methylamine)	1870.8(s) 2003.0(w)	3316.4(s) 3269.1(s), (3412.8(broad))	1692.4(s) 1568.0(s), (1637.5(s))	1051.1(w) 1065.0	877.6(w) 843.8(w)
$Mo(CO)_4L$ (L=TMEDA)	1984.6(w), 1875.0(w) 1850.0(w)	-	-	1145.0(w), (1149.0(w)) 1137.9(w), (1139.9(w))	-
$W(CO)_4L$ (L=TMEDA)	1975.0(w), 1910.0(w) 1865.0(w), 1832.2(w)	-	-	1124.4(w), (1149.0(w)) 1126.0(w), (1139.9(w))	-
$Mo(CO)_5L$ (L=nicotine)	2009.7(m), 1979.8(m) 1936.4(m), 1887.2(m), 1837.1(m)	-	-	1216.0(w), (1212.2(m)) 1245.0(w), 1315.4(m) 1156.2(w), 1155.3.3(m))	-
$W(CO)_5L$ (L=nicotine)	2006.8(m), 1921.9(w) 1884.3(s), 1816.6(m), 1760.9(m)	-	-	1212.2(w), (1216.0(m))	-

NB**:** s=strong, m=medium and w=weak

Table 4.4: ν(C=C) stretch, ν(=C-H) stretch and ν(=C-H) bend (in cm^{-1})

Product	ν(C=C) stretch	ν(N-H) bend	ν(=C-H) stretch	ν(N-H) stretch	ν(=C-H) bend
Oily product from the reaction of $W(CO)_4Br_2$ with methylamine	1627.8	1572.8	3031.9-2973.1	3416.7-3317.3	921.9
Oily product from the reaction of $W(CO)_4Br_2$ with TMEDA	1653.8	-	3196.8	-	983.8
Oily product from reaction of $Mo(CO)_4Br_2$ with nicotine	1678.0	-	3107.1	-	982.7
Distillate from filtrate in the reaction of $Mo(CO)_4Br_2$ with diethylamine	1651	-	2971.1	3418.6	950.0
Oily product from reaction of $W(CO)_4Br_2$ with diethylamine.	1651.9 and a shoulder at1635.5	-	2992.4	3423.4	875.0

4.2 Formation of Zero-Valent Complexes

The formulae of complexes obtained when the halocarbonyls $M(CO)_4Br_2$(M=Mo,W) react with methylamine, diethylamine, nicotine and tetramethylethylenediamine are described in section 3.2. In this chapter, the Infrared, Ultraviolet, Nuclear Magnetic Resonance, both proton and ^{13}C data, that helped to identify the products formed are discussed. In the case of the molybdenum complex, $Mo(CO)_4$(TMEDA), the structure of the complex was confirmed by means of single a crystal X-ray diffraction study.

4.2.1 Methylamine and Diethylamine Complexes of the type, $M(CO)_3L_3$ M=Mo, W; L=MA or DEA)

Molybdenum and tungsten complexes of the type, $M(CO)_3L_3$ M=Mo, W; L=MA or DMA**)** were prepared using the tetrabromooctacarbonylmetal complexes, $[M(CO)_4Br_2]_2$(M=Mo,W).The analytical data on tables 3.2 suggests that the products are zero-valent complexes that have the general formula $M(CO)_3L_3$ (M=Mo, W; L= diethylamine or methylamine).

4.2.1.1 IR Analysis

Table 4.1 gives a summary of the absorption peaks for all the zerovalent complexes prepared. An IR spectrum of the complex $W(CO)_3((C_2H_5)_2NH)_3$ (Fig. 3.5) shows absorption bands at 1969.2cm^{-1} and 1921.0cm^{-1} as reported in Table 4.1. This suggests that the complex formed in this case is a *fac*-isomer.

The IR spectrum of $Mo(CO)_3((C_2H_5)_2NH)_3$ (Fig. 3.3) showed new absorption bands at 1984.69cm^{-1} and 1922.9cm^{-1} that were absent in the IR spectrum of neat diethyl amine. This

is the region for coordinated inorganic carbonyl groups. The presence of the three peaks strongly suggests that the product is a *fac*-isomer of the complex $Mo(CO)_3((C_2H_5)_2NH)_3$.

The spectrum also shows peaks at 1088.7 cm^{-1} and 1049.2cm^{-1} (C-N stretch), 3329cm^{-1} (N-H stretch) and 639cm^{-1} (C-H wag). The IR spectrum further showed that the ν(C-N) stretch had shifted to lower cm^{-1} as compared to that of neat diethyl amine (Appendix I). The ν(N-H) stretch shifted to higher cm^{-1} while the ν(N-H) wag shifted to lower cm^{-1}. The IR spectrum (Fig. 3.14) of the solid product obtained from the reaction of methylamine with $M(CO)_4Br_2$ (M=W, Mo) shows one absorption peak at 1870.8cm^{-1} which corresponds to coordinated carbonyl stretching frequencies, peaks at 1051.1 cm^{-1} and 1007.7cm^{-1} for C-N bond stretching frequency and N-H stretching frequency at 3316.4 cm^{-1} and 3269.1cm^{-1}. The complex formed is a *mer*-isomer (Fig 3.11) of the complex $W(CO)_3(CH_3NH_2)$

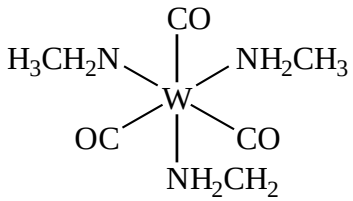


Figure 4.2: *mer*-isomer of the complex $W(CO)_3(CH_3NH_2)$

The spectrum strongly suggests that the solid was a complex with coordinated carbonyl and methylamine.

The IR spectra confirmed that the complexes had coordinated CO and nitrogen bases where the amine was coordinated via the N atom. Alkyl groups have electron inductive effect; they pile electrons on the N-atom, which is a strong σ-donor. The net result is that excess electrons are donated to the central metal leading to strong back-donation. This must have led to significant shift to lower cm^{-1} of ν(C-N) in the IR spectrum.

4.2.1.2.1 NMR analysis

Table 4.3 summarizes the results of NMR analysis. The expected ^{1}H and ^{13}C NMR spectra for neat diethylamine is compared with ^{1}H NMR spectrum for $W(CO)_4((CH_3CH_2)_2NH)_3$ (Fig 4.3).

^{1}H NMR spectrum, (Fig. 4.3 and Table 4.1), of the product obtained from the reaction of $[M(CO)_4Br_2]_2$ (M =Mo, W) with N-diethylamine showed peaks at 2.215ppm (CH_2), and 3.160ppm, 3.270ppm(CH_3). The ^{1}H NMR spectrum for the pure diethylamine showed a tripplet peak at 1.13ppm (CH3) and a quadruplet peak at 2.71ppm.The change in chemical shift to lower field supported the formation of the complex $M(CO)_3$(N,N-diethylamine)$_3$ (M= Mo,W).

The NMR analysis, therefore, showed that the diethylamine detected is coordinated and not free. The N-H proton was expected to appear at 4.6pmm but was not prominent because the hydrogen exchanges with deuterium.

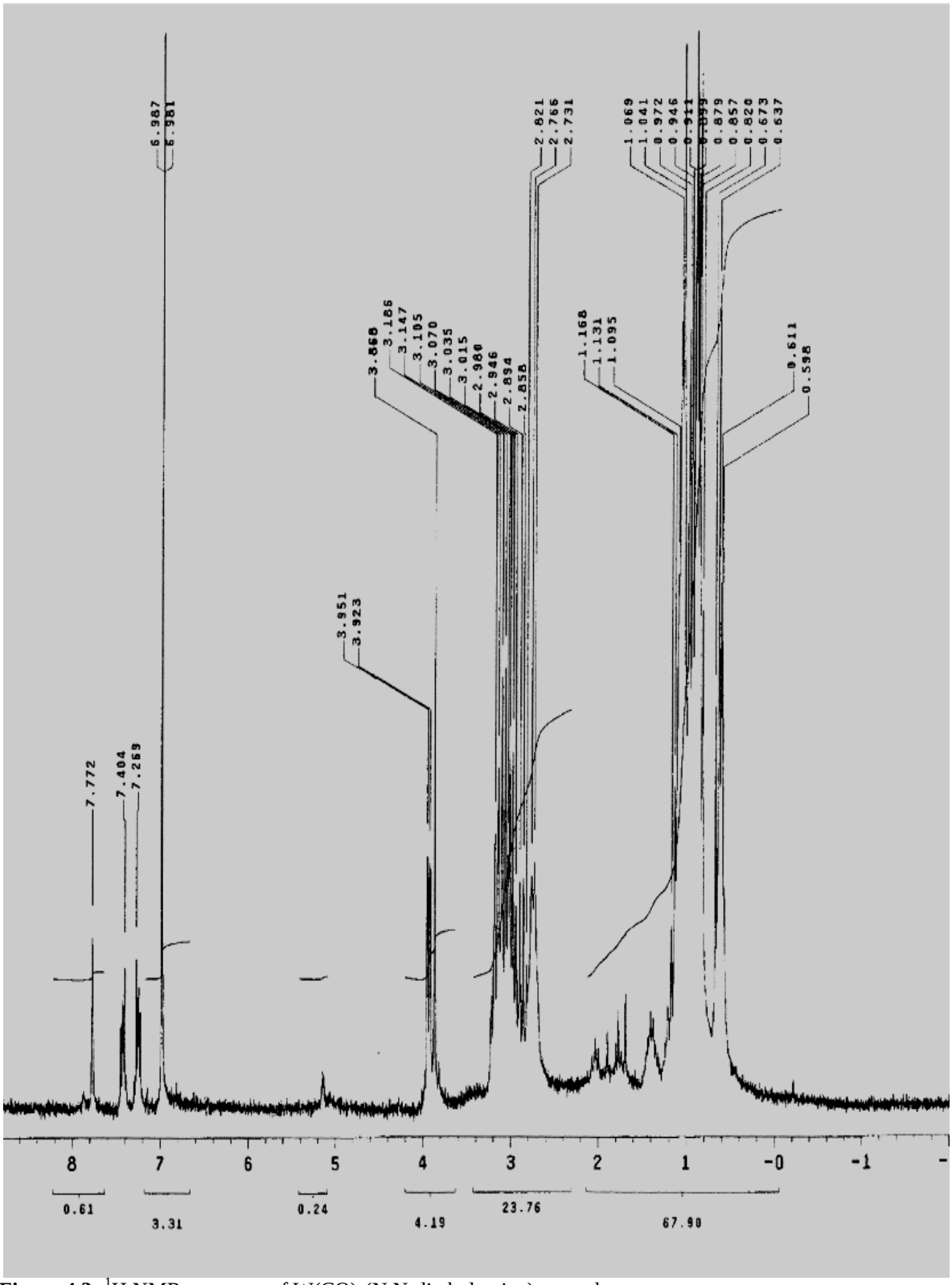


Figure 4.3: ^{1}H NMR spectrum of $W(CO)_3$(N,N-diethylamine)$_3$ complex

4.2.2 Tetramethylethylenediamine complexes of the type $M(CO)_4L$ (M=Mo, W; L= TMEDA)

The elemental analysis for M, C, H and N in the product formed with TMEDA gave the empirical formula $MO_4C_{10}H_{16}N_2$ (M=Mo, W). This is the empirical formula for zero-valent metal complexes whose molecular formula is $M(CO)_4L$ (M=Mo, W; L=TMEDA).

4.2.2.1 IR analysis

Table 4.1 gives a summary of the absorption peaks for all the zerovalent complexes prepared.

An IR spectrum of tetramethylethylenediaminetetracarbonylmolybdenum(0) (Fig. 3.10) showed three inorganic carbonyl peaks at 1984.6 cm^{-1}, 1875.0cm^{-1} and 1850.0cm^{-1} due to inorganic carbonyl groups and 1137.9cm^{-1} and 1145.0 cm^{-1}due to ν(C-N) stretches. In a free amine, the ν(C-N) stretch occurs around 1142.0 $cm^{-1.}$ On coordination of the nitrogen, this peak is lowered by about 2.0cm^{-1}. Alkyl groups have electron inductive effect; they pile electrons on the N-atom, which is a strong σ-donor. The net result is that excess electrons are donated to the central metal leading to strong back-donation. This must have led to significant shift to lower cm^{-1} of ν(C-N) IR absorption peaks. It is therefore reasonable to attribute the peak at 1140 cm^{-1} to ν(C-N) for a coordinated amine, in this case TMEDA.

4.2.2.2 NMR analysis

The ^1H NMR spectra (fig. 4.4) of the product obtained from the reaction of tretrabromooctacarbonylmolybdenum(II) showed a triplet peak (2.969ppm) associated with CH_2 (neat base, 2.40ppm) and a singlet at 1.7ppm associated with CH_3 (neat base, 2.25ppm).

As expected in co-ordinated complexes, there were significant downfield shifts in both of the ^{1}H and ^{13}C NMR spectra. The changes in chemical shifts support zero-valent complex.

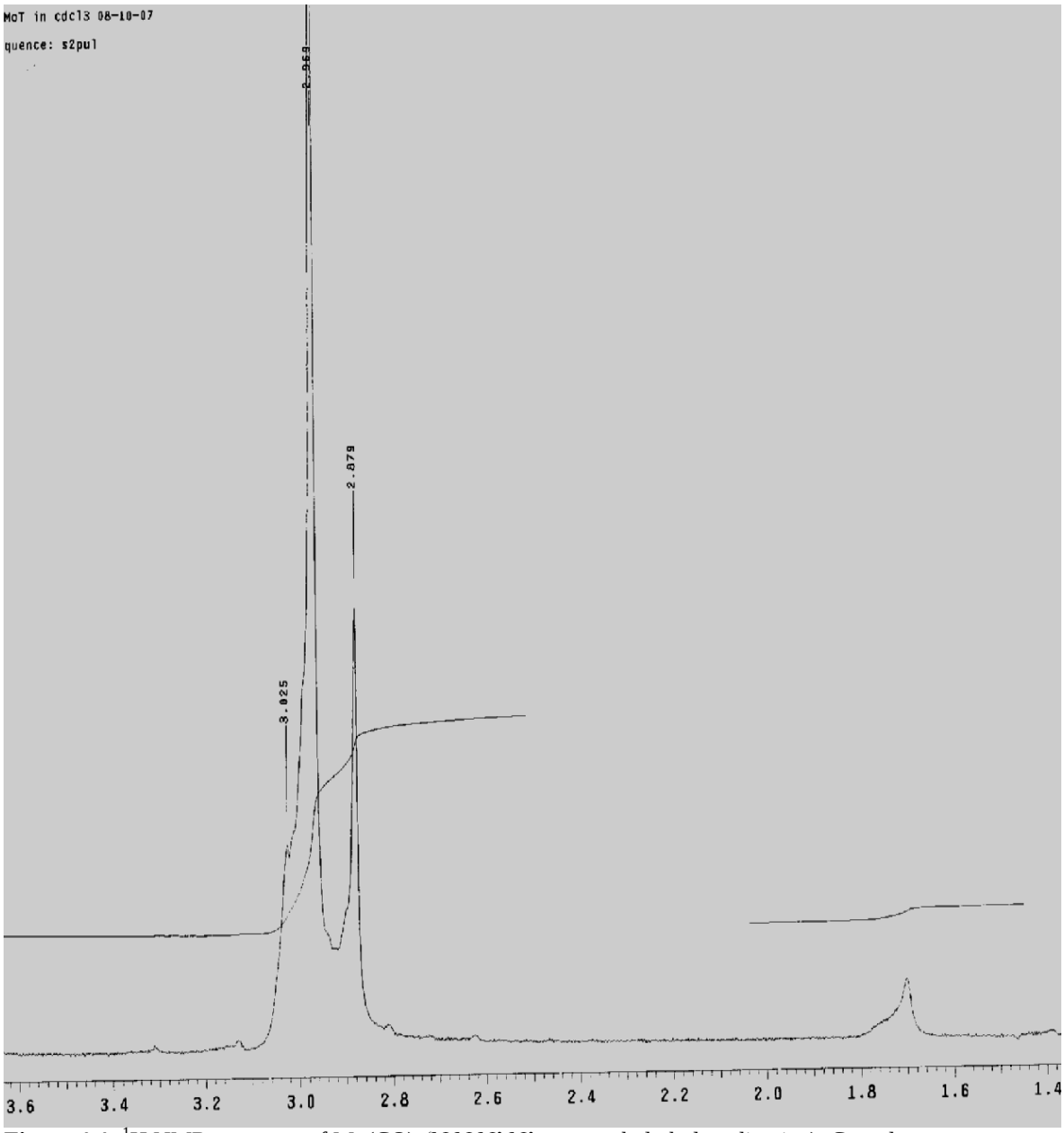


Figure 4.4: ^{1}H NMR spectrum of $Mo(CO)_5$(N,N,N',N'-tetramethylethylenediamine) Complex

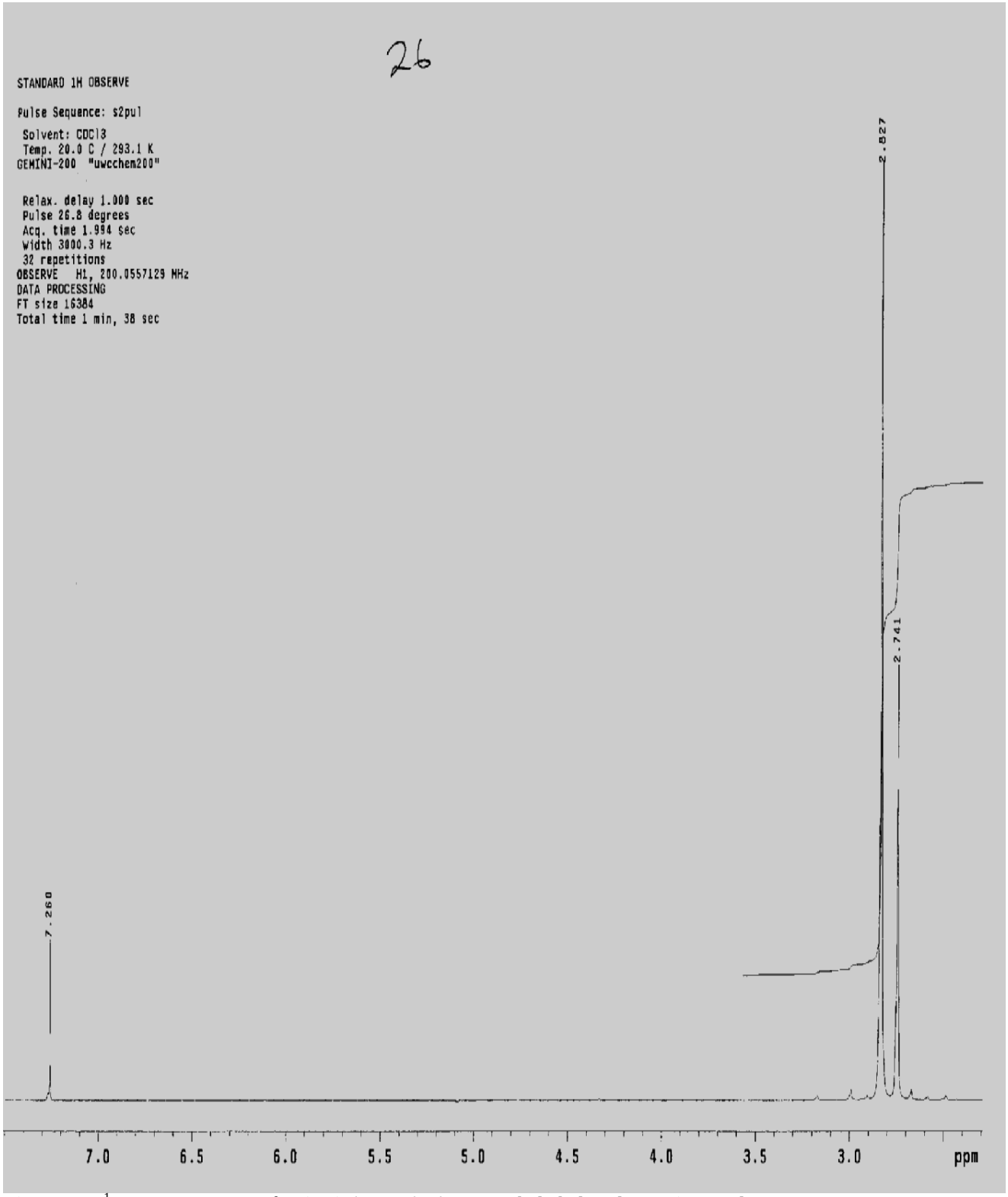


Figure 4.5: ^{1}H NMR spectrum of $W(CO)_4$(N,N,N',N'-tetramethylethylenediamine) Complex

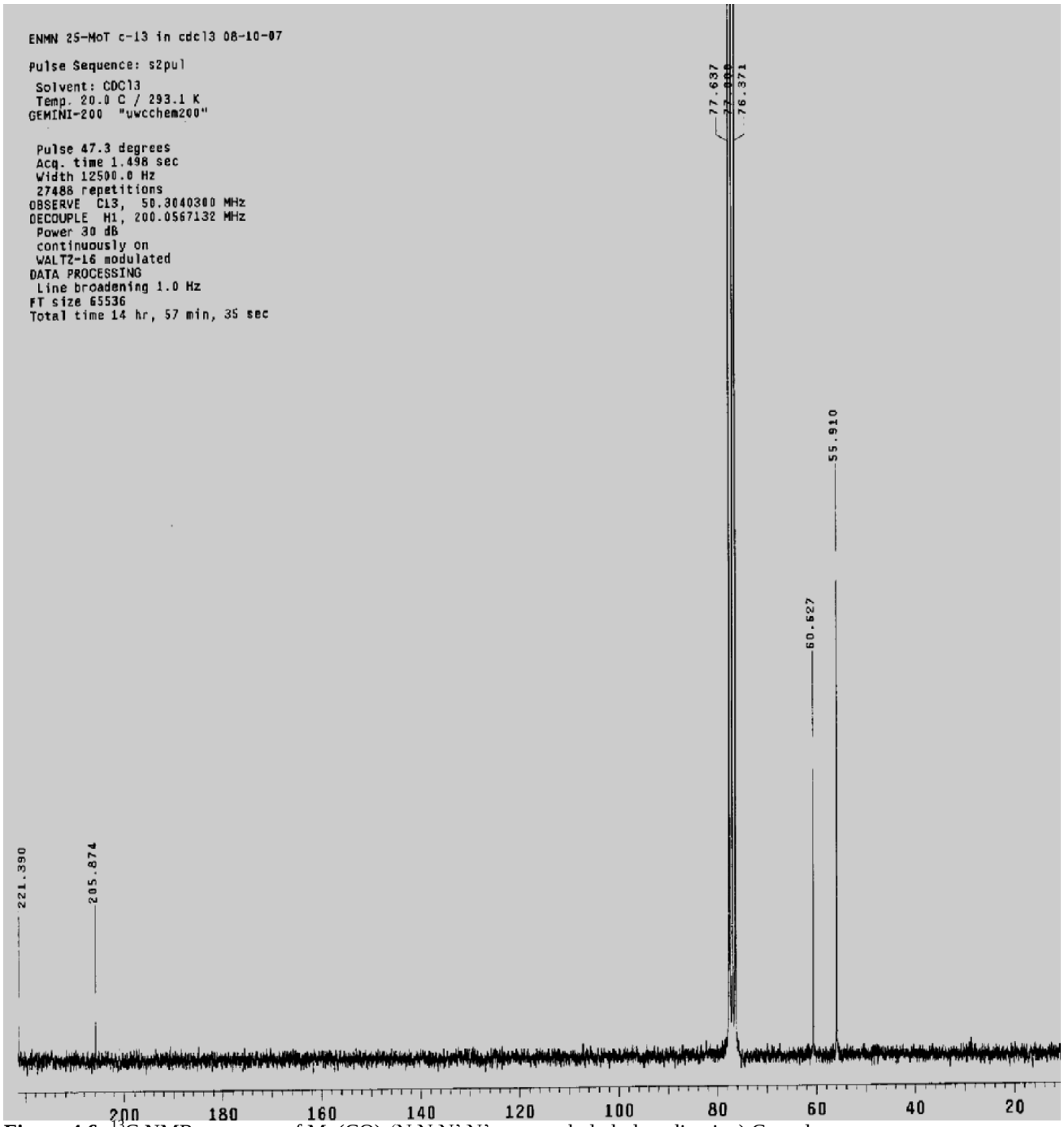


Figure 4.6: ^{13}C NMR spectrum of $Mo(CO)_5$(N,N,N',N'-tetramethylethylenediamine) Complex

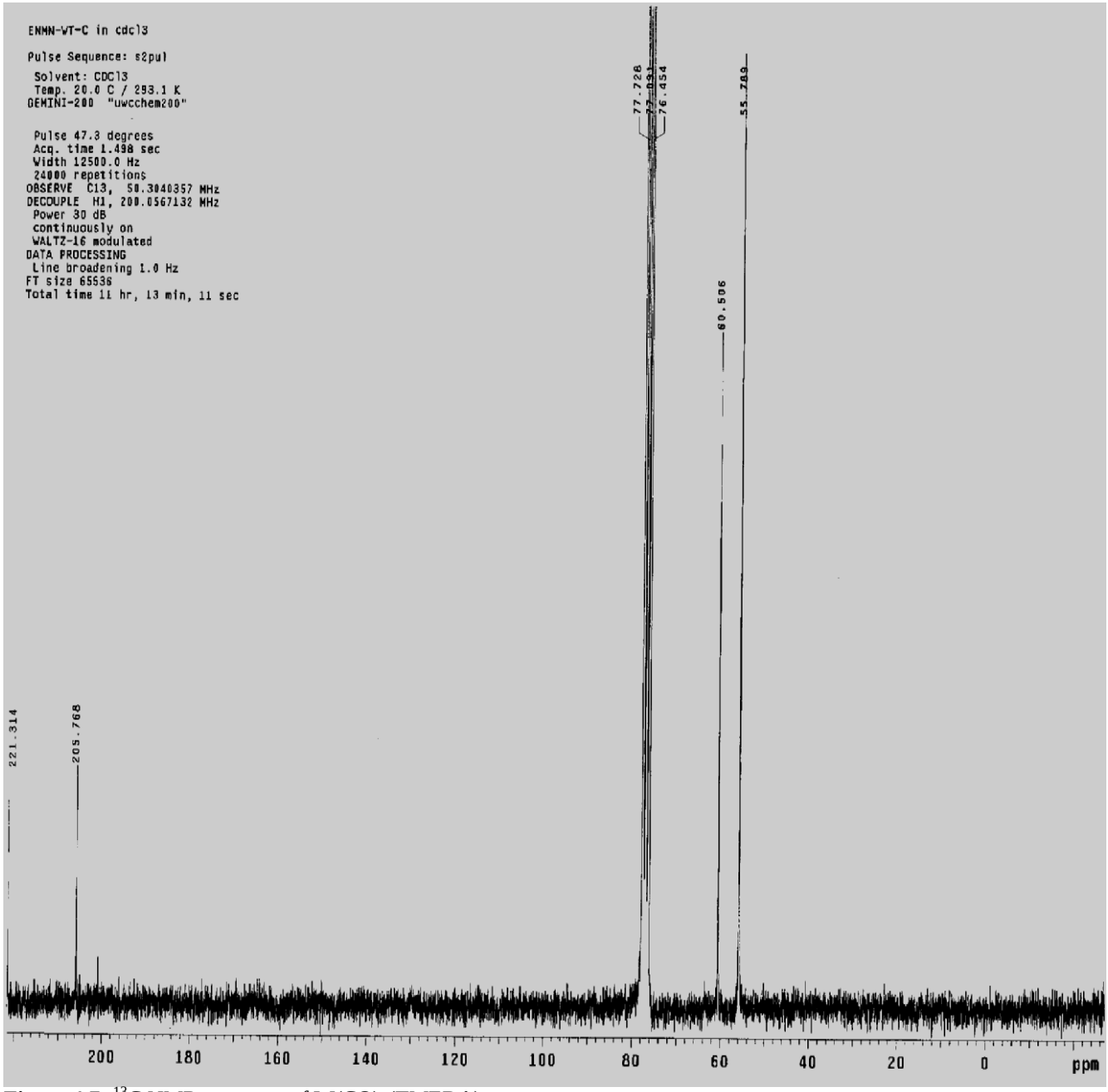


Figure 4.7: ^{13}C NMR spectrum of $W(CO)_5$(TMEDA)

^{13}C NMR spectra (Fig. 4.6 and 4.7) of $M(CO)_5L$ (L=TMEDA and M=Mo, W) gave peaks at 55.91ppm for uncoordinated base, (45ppm) associated with CH_3, 60.627ppm (uncoordinated base, 58ppm) associated with CH_2 and 221.390ppm and 205ppm associated with coordinated carbonyl. The NMR spectra proved that the product was a metal carbonyl complex of TMEDA. The presence of two carbonyl peaks is further proof that the compound has inorganic carbonyl group.

The crystal structure of tetracarbonyl[N,N,N',N'-tetramethylethylenediamine-N,N']-molybdenum complex (Fig. 4.8 and 4.9) was determined. The structure of this molecule confirms the synthesis of the intended of the intended complex and by extension the complexes prepared from the reaction of $M(CO)_4X_2$ (M=Mo,W; X=Cl or Br), with an appropriate amine to give M(0) species.

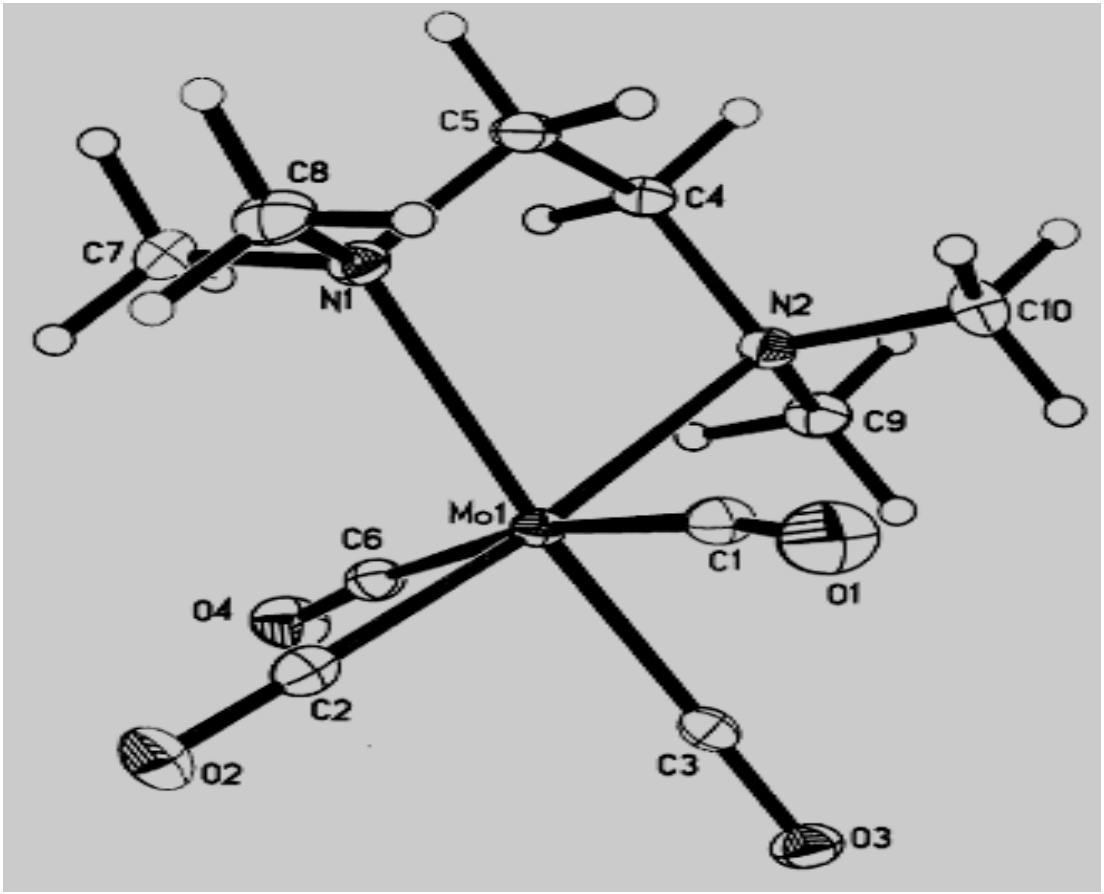


Figure 4.8: Ortep diagram of the x-ray structure of the TMEDA complex. Ellipsoids are contoured at the 35% probability level. H atoms have arbitrary radius of 0.1 angstrom.

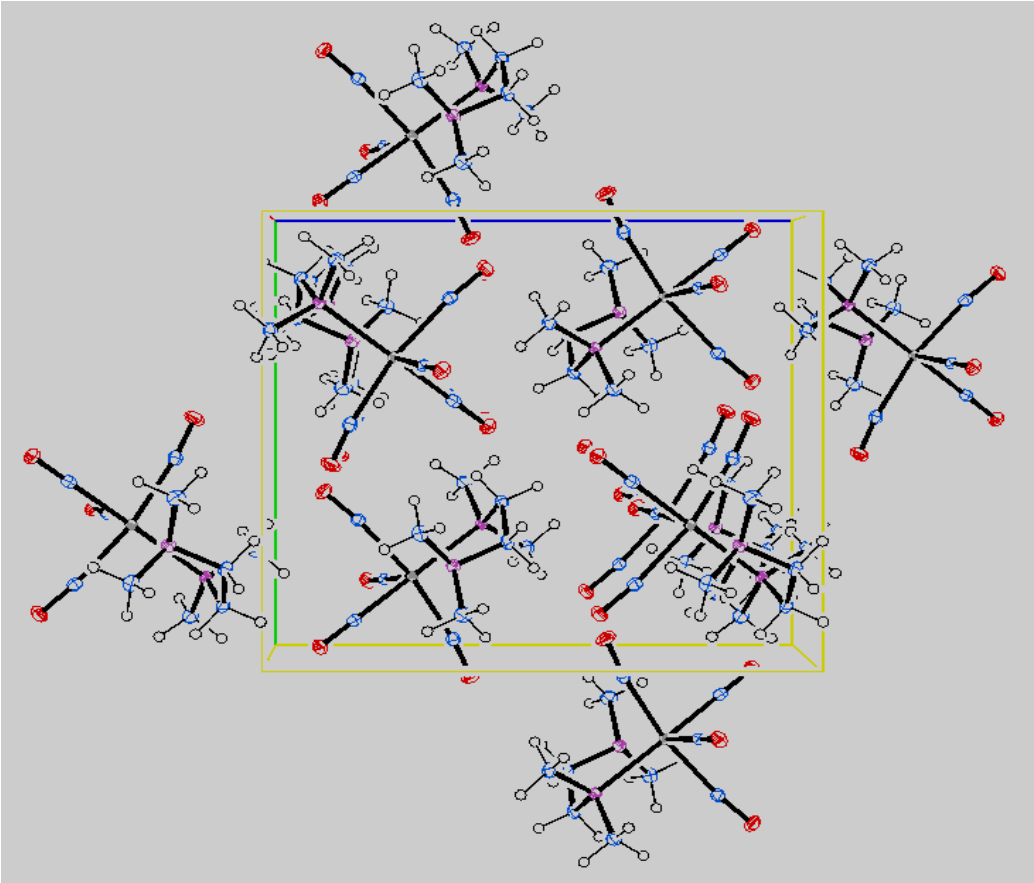


Figure 4.9: Ortep diagram showing the unit cell packing of the TMEDA complex viewed down the crystallographic a-axis. Thermal ellipsoids are contoured at the 35% probability. H atoms have been omitted for clarity.

Table 4.5 gives a summary of Bond lengths (Å) in tetracarbonyl[N,N,N',N'-tetramethyethylenediamine-N,N']molybdenum(0) while table 4.6 gives a summary of Bond angles (^{0}) in the tetracarbonyl[N,N,N',N'-tetramethyethylenediamine-N,N']molybdenum(0). The CIF files for the structure are attached as appendices in this thesis.

Table 4.5: Bond lengths (Å) in tetracarbonyl[N,N,N',N'-tetramethyethylenediamine-N,N']molybdenum(0)

Bond	**Bond length (Å)**	**Bond**	**Bond length (Å)**
Mo1 C3	1.9575(19)	N2 C4	1.493(2)
Mo1 C2	1.9633(19)	N2 C9	1.486(2)
Mo1 N2	2.3284(15)	N1 C5	1.491(2)
Mo1 C1	2.0368(19)	N1 C8	1.489(2)
C1 O1	1.150(2)	N2 C4	1.493(2)
C6 O4	1.146(2)	N1 C7	1.481(2)
C2 O2	1.157(2)	C3 O3	1.163(2)

Table 4.6: Bond angles (^{0}) in the tetracarbonyl[N,N,N',N'-tetramethyethylenediamine-N,N']molybdenum(0)

Bonds	Bond angle (^{0})	Bonds	Bond angle (^{0})
C3 – Mo1 – C2	90.54(7)	O2 – C2 –Mo1	178.93(16)
C3 – Mo1 – C1	86.89(7)	O3 – C3 – Mo1	179.25(15)
C2 – Mo1 – C1	86.09(7)	O1 – C1 – Mo1	172.52(16)
C3 – Mo1 – C6	85.28(7)	N2 – Mo1 – N1	77.96(5)
C2 – Mo1 – C6	86.10(7)	C6 – Mo1 – N1	94.51(6)
C1 – Mo1 – C6	168.89(7)	C1 – Mo1 – N1	94.14(6)
C3 – Mo1 – N2	95.67(6)	C2 - Mo1 N1	95.82(6)
C2 – Mo1 – N2	173.73(6)	C3 Mo1 N1	173.61(6)
C1 – Mo1 – N2	95.13(6)	C6 Mo1 N2	93.48(6)

The TMEDA ligand binds to the metal through the lone-pair orbitals of the two N atoms. The N atoms and the two carbonyl groups can be considered to occupy equatorial positions while the remaining two carbonyl groups are directed towards the axial positions. The axial carbonyl groups bend away from the TMEDA ligand as a result of steric interactions and subtend a C(6) – Mo(1) – C(1) angle of 168.89(7)^0; the angles Mo(1) – C(1) – O(1) and Mo(1) – C(6) – O(4) [O(1) – C(1) – Mo(1)] 172.52(16)^0 and 172.32(16)^0, respectively deviate considerably from linearity (Mohamed *et.al,* 1993). The Mo – C distances in the axial position are slightly longer than those in the equatorial positions, as observed by Mohamed and co-workers (1993) when they obtained a similar crystal structure for the same

compound. It is important to note that even though the structures obtained look similar to structure in literature, the method Mohamed and co-workers used to prepare $Mo(CO)_4$(TMEDA) is different from the method used in this work.

4.2.4 1-methyl-2-(3-pyridyl)-pyrrolidine

Reaction of $[M(CO)_4X_2]_2$ (M=Mo, W; X=Br or Cl) with 1-methyl-2-(3-pyridyl)-pyrrolidine (nicotine) was carried out in freshly distilled methanol as the solvent. The product formed was insoluble in methanol hence separated by filtration. The solid was dissolved in a mixture of diethylether and hexane and solution kept at low temperature. Crystals grew from the mixture and were used for crystallography. The X-ray structure of the product obtained from the reaction of $[W(CO)_4Br_2]_2$ with 1-methyl-2-(3-pyridyl)-pyrrolidine (nicotine) showed that the product has the formula $W(CO)_5$nicotine (Figure 4.11) .

4.2.4.1 IR spectra analysis

The IR spectrum of nicotine has no absorption bands in the inorganic carbonyl region, 2000-1800 cm^{-1}. IR spectrum (Figures 3.16) for the product obtained from the reaction of $[Mo(CO)_4Br_2]_2$, with nicotine shows 5 spectral bands at 2009.9cm^{-1},1979.8 cm^{-1}, 1936.4 cm^{-1}, 1887.2 cm^{-1} and 1837.1cm^{-1} for coordinated carbonyl stretching frequency, 3 bands in the region

1067.5 cm^{-1}, 1047.3 cm^{-1} and 1026cm^{-1} for C-N stretches on pyrrolidine ring and 2 peaks around 1600.8 and 1577.7cm^{-1} for C=N stretches in pyridine ring. The presence of five peaks for coordinated carbonyl in the IR spectra (figures 3.16) could indicate that there is a mixture of products or $Mo(CO)_5$nicotine formed by reaction of unreacted molybdenum hexacarbonyl reacting with a mole of nicotine. The ν(C=N) showed an increase in the stretching frequency compared to the neat nicotine value (1576.7cm^{-1}) (Table 4.1). The

increase in ν(C=N) from 1576.7cm^{-1} to 1577.7cm^{-1} is due to the σ–bonding of the ligand to the metal, which outweighs the back-donation effect. Since the electrons of the non-bonding orbital are involved in hybridization with the anti-bonding pi-orbital (π^*), the removal of the electrons through σ–donation enhances the ν(C=N) value (Muralidharan *et al.*, 1987).

The out-of-plane ring vibrations at 616.2cm^{-1} in free nicotine are shifted to 650.0cm^{-1} (molybdenum) and 628.8cm^{-1} (tungsten). The observed shifts suggest the involvement of nitrogen of pyridine ring in the bonding with the metal atoms. The IR spectrum of neat nicotine also exhibits a medium absorption band at 1315.4cm^{-1} assigned to ν(C-N) of -NCH_3 group of pyrrolidine. The ν(C-N) mode of –NCH_3 group of the pyrrolidine ring shifted from 1315.0 cm^{-1} to 1245.0 cm^{-1} (Table 4.1). These observations may suggest that the imine nitrogen in nicotine was used in coordination. Therefore, as shown in the crystal structure, the product has the formula $W(CO)_5$nicotine.

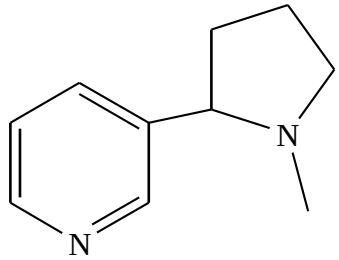


Figure 4.10: Structure of nicotine

The formation of $W(CO)_5$nicotine in the product is supported by the crystal structure (Fig. 4.12) of $W(CO)_5$nicotine grown from the solid obtained. This product has five inorganic carbonyls bonded to the tungsten with nicotine coordinated to the tungsten via the imine nitrogen. This product may have been formed from the reaction of unreacted hexacarbonyltungsten(0), $W(CO)_6$, with nicotine. The coordination of nicotine to tungsten, in this case, is via the imine nitrogen and not amine nitrogen showing similarity to the way the last amino acid, histidine, is joined to iron in hemoglobin and myoglobin. Histidine is

joined to the iron at the fifth co-ordination site of the heme complex via the imine nitrogen of imidazole as shown in figure 4.11.

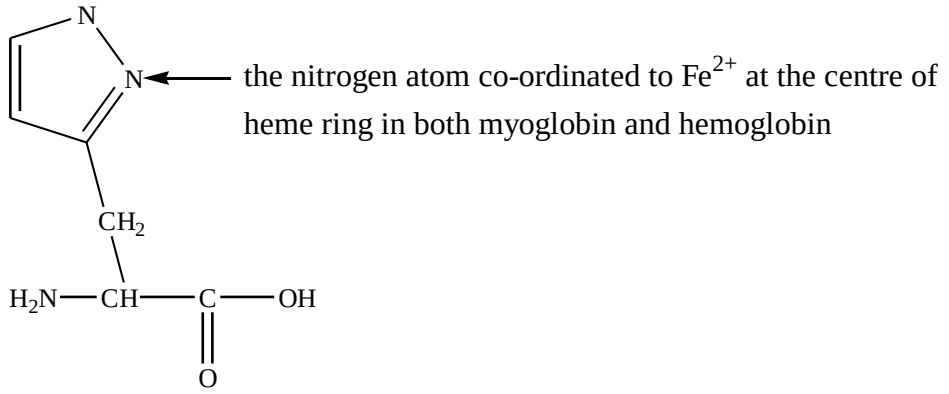


Figure 4.11: Structure of histidine

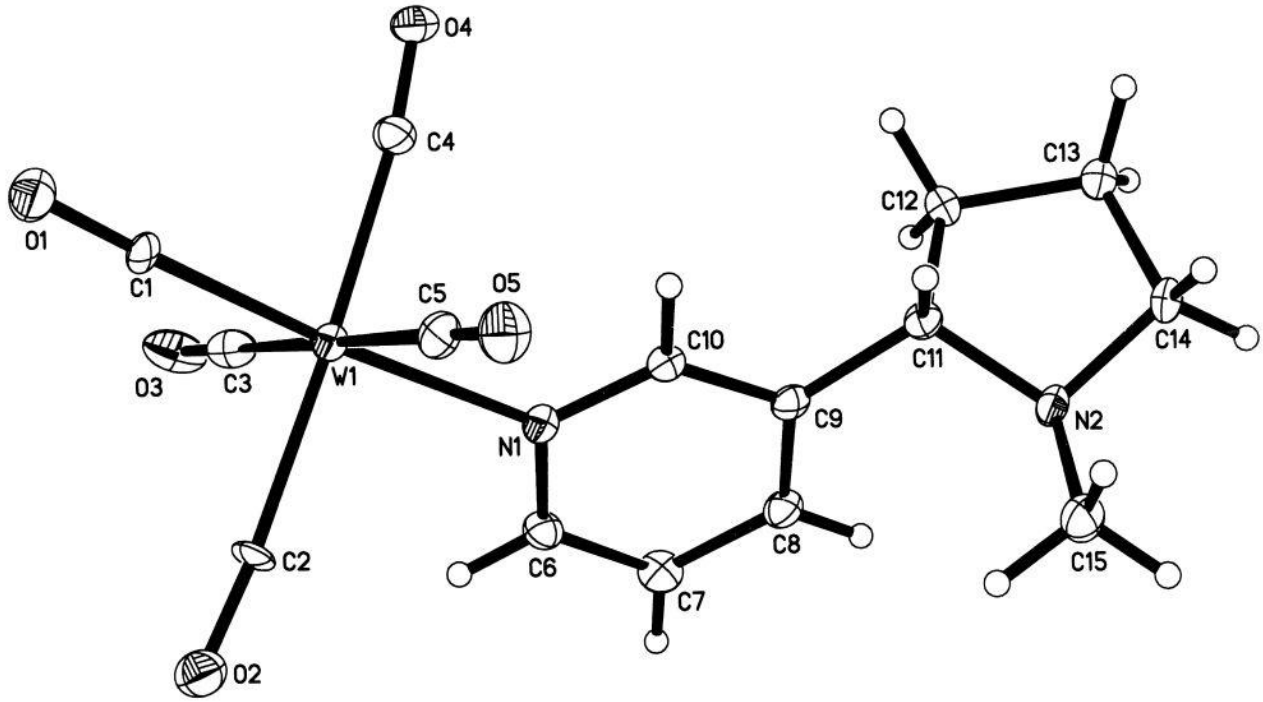


Figure 4.12: Ortep diagram of the x-ray structure of the nicotine complex, $W(CO)_5L$. Ellipsoids are contoured at the 35% probability level. H atoms have arbitrary radius of 0.1 angstrom.

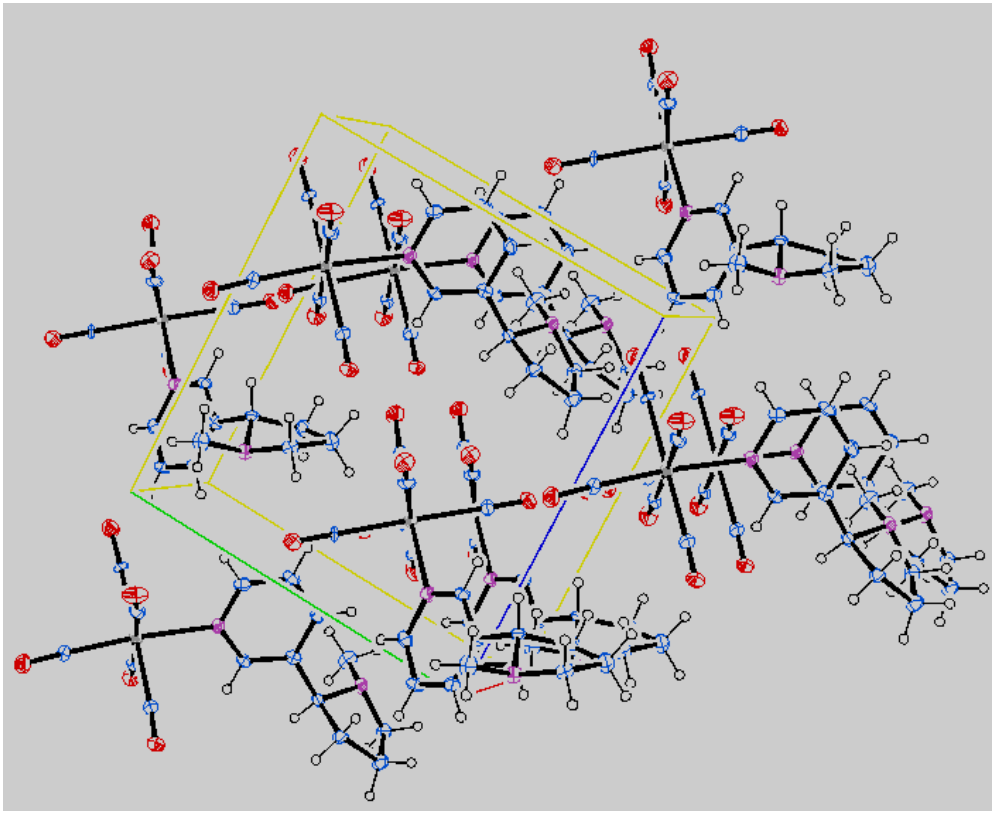
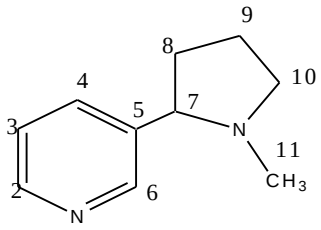


Figure 4.13: Ortep diagram showing the unit cell packing of the nicotine complex, $W(CO)_5L$, viewed down the crystallographic b-axis. Thermal ellipsoids are contoured at the 35% probability. H atoms have been omitted for clarity.

It is worth noting that in the IR spectra (Fig. 3.16 and 3.19) for tungsten complexes, and IR spectra for molybdenum complexes (Fig. 3.17 and 3.18) there are five inorganic carbonyl bands respectively. These observations suggest that the complex has five co-ordinated carbonyls and one mole of nicotine co-ordinated to tungsten via the imine nitrogen. This observation is supported by the crystal structure of $W(CO)_5L$ obtained.

4.2.4.2 NMR spectra analysis



^{1}H NMR spectra of neat nicotine and the nicotine-tungsten complexes (Fig. 4.13) were done to confirm the mode of coordination. The positions of the σ observed for protons 2 and 6 on the ^{1}H NMR spectrum were 8.691-8.660ppm (7.533) and 8.783-8.772ppm (8.368) respectively while for protons 7 and 11 were 4.054ppm (3.050-2.905) and 2.729ppm (1.963). The proton shifts on pyridine ring of nicotine shows that nicotine coordinated to the metal via the imine nitrogen atom in the molecule to form $M(CO)_5L$ (M-Mo, W; L=nicotine). The proton shift on the pyrrolidine ring can be attributed to the effect of the carbonyl from neighbouring $W(CO)_5L$ molecules as shown in the unit cell packing of the nicotine complex, $W(CO)_5L$, viewed down the crystallographic b-axis (Fig. 4.12)

^{13}C NMR spectrum of the solid (figure 4.14) showed a shift downfield for carbon atoms attached to the nitrogen atoms in pyrrolidine as well as pyridine. The carbon peaks were as follows, C-10 55.92ppm (51.4), C-7 70.501ppm (64.8), C-11 38.046ppm (36.1), C-2 150.631ppm (148.8) and C-6 151.723ppm (149.8). The shift on the peaks for the carbon atoms on the pyridine ring shows that coordination was via the imine nitrogen atom. On the other hand, the shift downfield for carbon atoms on pyrrolidine ring may have resulted from their association with CO group from neighbouring $M(CO)_5L$ (M-Mo, W; L=nicotine) (Fig. 4.12).

Presence of a peak at 191.310ppm suggests that the compound had coordinated CO group. In the $M(CO)_5$(nicotine) complex where nicotine is bonded to the metal via the imine nitrogen, at least one carbonyl peak (CO group trans to the imine nitrogen) will be shielded by the ring electrons leading to slow decay. The other inorganic CO peaks may be so close that they appear identical in the spectrum giving only one peak.

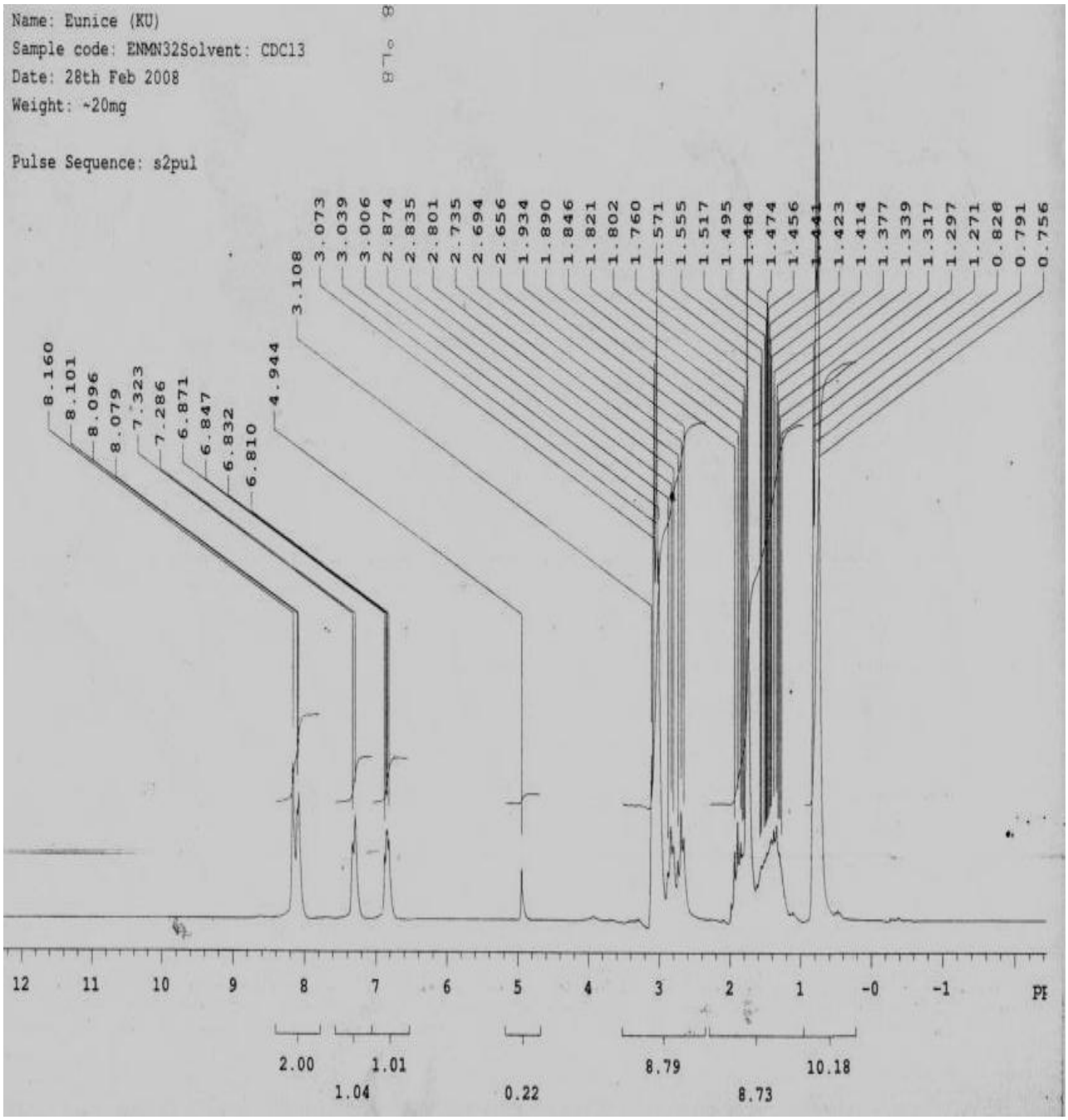


Figure 4.14: ^{1}H NMR spectrum of $W(CO)_5$(nicotine) complex

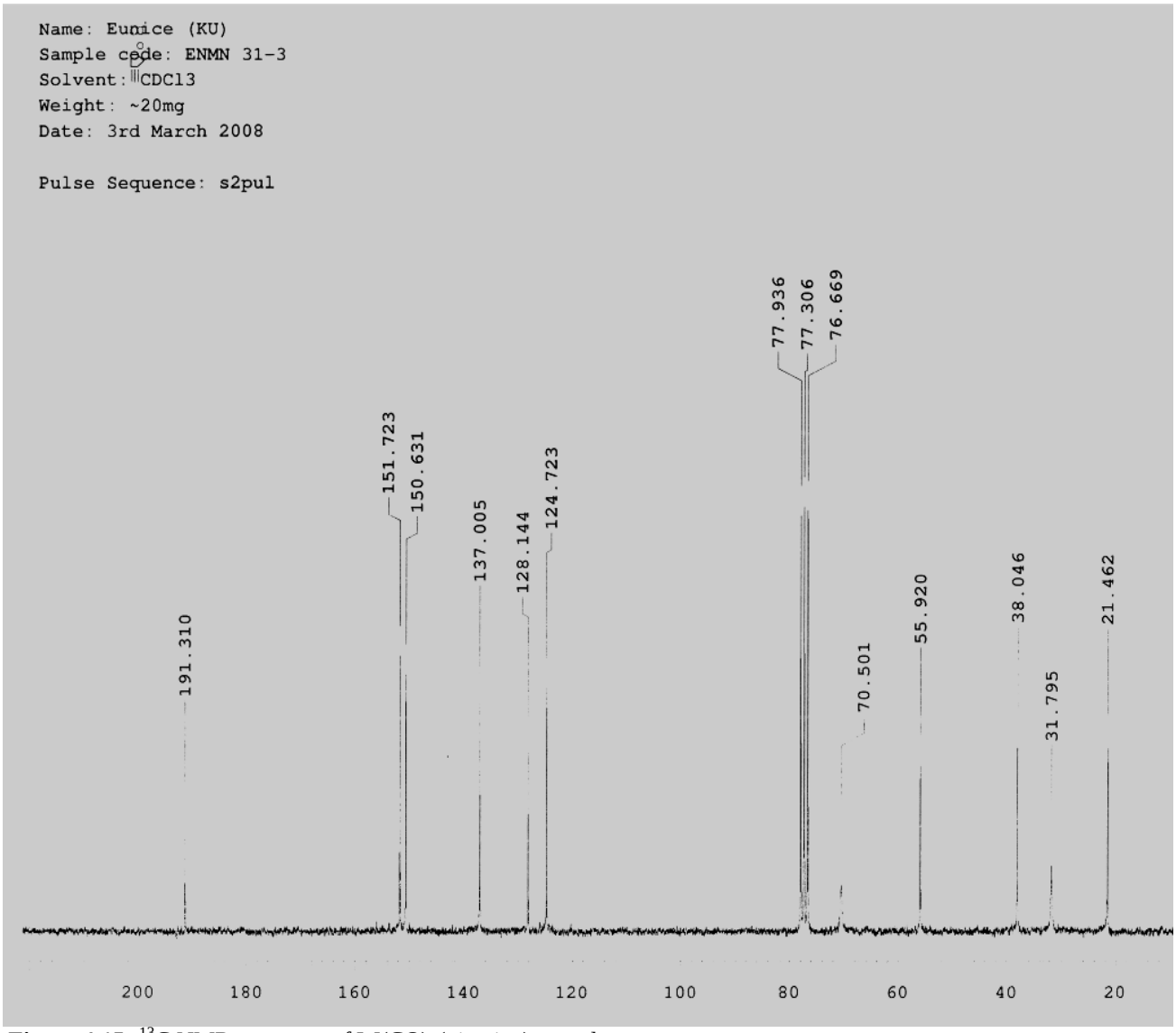


Figure 4.15: ^{13}C NMR spectrum of $W(CO)_5$(nicotine) complex

4.3 Organic products

The reaction of $M(CO)_4X_2$ (M=Mo, W; X-Br or Cl) with the various nitrogen containing bases gave two types of by-products in addition to the metal complexes discussed in section 4.2 of this thesis. These were salts of the nitrogen bases and nitrogen base oxidation products. These are further discussed in sections 4.3.1.

4.3.1 Salts of the nitrogen bases

These were isolated when $[M(CO)_4X_2]_2$ (M=Mo, W; X-Br or Cl) were reacted with N,N diethylamine, N,N,N',N' tetramethylethylenediamine and 1-methyl-2-(3-pyridyl)-

pyrrolidine. The salts were obtained when the nitrogen base were used in slight excess. A slight excess of the base was used absorb any hydrogen halide released during the redox process.

The formation of these salts suggested that the reactions studied were taking place via a redox mechanism where molybdenum(II) and tungsten(II) were reduced to the zero-valent complexes as hydrogen halides were released. The nitrogen base was oxidized by removal of a hydrogen atom that must have combined with the halide ions to form hydrogen halides. The hydrogen halide combined with the base to form the salt.

The reaction of $[M(CO)_4Br_2]_2$ (M=Mo, W) with methylamine formed salts of nitrogen bases. For example, the bromocarbonyl complex gave the salt 1,2-ethyldiammonium dibromide. The formation of this salt instead of the expected methylamine hydrobromide suggests that the reaction may have taken place via a redox mechanism. The proposed mechanism is shown in Figure 4.15.

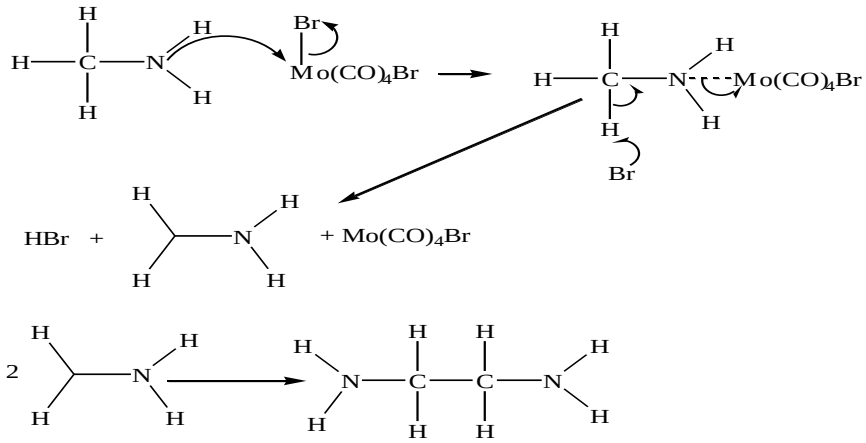


Figure 4.16: Proposed redox reaction mechanism

4.3.2 Nitrogen Base Oxidation Products

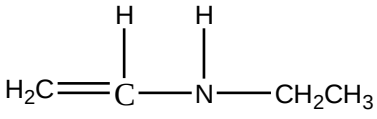
4.3.2.1 Reaction of $[Mo(CO)_4Br_2]_2$ with diethylamine

The filtrate obtained from the reaction of $[Mo(CO)_4Br_2]_2$ with diethylamine was concentrated by pumping off excess solvent at reduced pressure. A UV spectrum of the concentrated filtrate showed new peaks that were absent in diethylamine spectrum at 333.0nm and 414.5nm. These may have been due to the presence of unsaturated compounds.

4.3.2.1.1 IR analysis

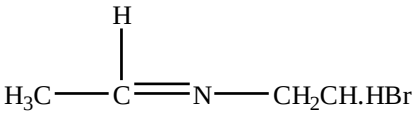
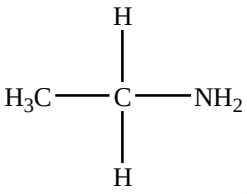
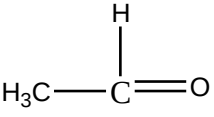
An IR spectrum of the distillate (Fig. 3.6) gave an absorption peak at 1651.0cm^{-1}. This peak is absent in the IR spectrum of neat diethylamine. An IR peak at 1651.0cm^{-1} in the spectrum of the distillate is likely to be a contribution of ν(C=C) bond stretch (Kemp, 1991; Silversten, *et. al.,* 1990). The IR spectrum (Fig. 3.7) of the concentrated filtrate obtained from the reaction between diethylamine and $[Mo(CO)_4Br_2]_2$, showed a peak at 1625.9cm^{-1}. This peak could also be due to ν(C=C) bond stretch (Kemp, 1991; Silverstein, *et. al.,* 1990).

The filtrate is likely to contain some oxidized species of diethylamine,



in addition to other by-products.

The third portion was reddish brown and tested positive for halogen. It gave an oily liquid on concentration, no crystals formed. IR spectrum of this product (Fig. 3.7), showed absorption peak associated with ν(C=C) stretch at 1625.9cm^{-1}. IR peaks at 1741.6 and 1699.2cm^{-1} were also present on the spectrum. The peak at 1741.69cm^{-1} may have been due to the presence of aldehydic ν(C=O) bond stretch (Kemp, 1991; Silversten, *et. al.,* 1990)).

This may suggest that hydrolysis of the salt,  to an amine,  , and an aldehyde,  , may have taken place.

4.3.2.1.2 NMR analysis

The ^{1}H NMR spectrum of this product has a singlet peak at 5.17ppm (figure 4.15). This falls within the region (4.5-6.5ppm) for olefinic protons (Kemp, 1991). The ^{13}C NMR spectrum has peaks that suggest the presence of a mixture of fragments from the oxidized diethylamine and the base.

A UV spectrum of the product gave absorption bands that were absent in UV spectrum for diethylamine at 327.5 and 460.0nm. This suggested the presence of unsaturated compounds.

4.3.2.2 Reaction of $[W(CO)_4Br_2]_2$ with diethylamine

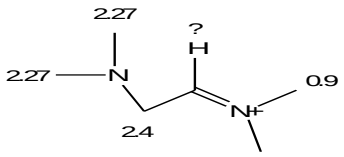
An IR spectrum of the oily product (Fig. 3.9) gave absorption peaks at 1651.9 and 1635.5 cm^{-1} that are typical for ν(C=C) stretches (1680 –1620 cm^{-1}). The ν(=C-H) stretch occurs in the region of 3100-3000cm^{-1}, therefore presence of a peak at 2992.4cm^{-1} is a further suggests the presence of either a C=C bond or a C=N bond.

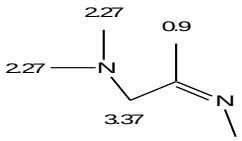
The presence of an IR band on the spectrum at 3423.4cm^{-1} is an indication that there was a N-H bond stretch (Kemp, 1991; Silversten, *et. al.*, 1990). The oily liquid is likely to be a H_2C=CH-NH-CH_2CH_3.

An absorption Spectrum of the product gave two peaks at 327.5nm and 460.0nm. The peaks were absent in a spectrum of diethylamine. The two peaks are attributed to ν(C=C) stretch (Kemp, 1991; Silversten, *et. al.*, 1990).

4.3.2.3 Reaction of $[Mo(CO)_4Br_2]_2$ with TMEDA

In this reaction, no oxidized species was isolated. The only sign of oxidation was seen on the IR spectrum of the zero-valent complex formed in this reaction. Absorption peaks at 1683.7 and 1652.9cm^{-1} suggested that the product may have been contaminated with an oxidized species since C=C or N=N bond stretching frequency fall within this range (Kemp, 1991; Silversten, *et. al.*, 1990).

The ^1H NMR spectrum of the zero-valent complex which gave peaks at 2.969ppm (2.46) for CH_2, 2.879ppm (2.27) for CH_3 and a new peak at 1.7ppm that was absent in the spectrum of TMEDA. The new peaks at 1.7ppm may have been for the proton on $=N(CH_3)_2$ as suggested by ^1H NMR spectrum estimate for the compound 

or 

. This suggests that there is an oxidation product with a C=N bond.

4.3.2.4 Reaction of $[W(CO)_4Br_2]_2$ with TMEDA

An IR spectrum (Fig. 3.14) of the oily product gave an absorption peak at 1653.8cm^{-1} suggesting the presence of a C=C bond stretch, =C-H bends appeared at 983.6cm^{-} and =C-H stretch was seen at 3196.8cm^{-}. These bands suggest the presence of an oxidized species of TMEDA in the yellow oily product. There was also a new absorption peak on the UV

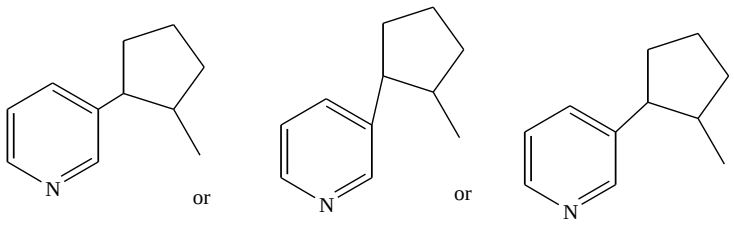
spectrum of the third oily fraction at 404.0nm. These observations strongly suggest that the possible structure of the oxidized TMEDA is $(CH_3)_2N\text{-}CH{=}CH\text{-}N(CH_3)_2$

4.3.2.5 Reaction of $[M(CO)_4X_2]_2$, (M=Mo, W; X=Br or Cl) with 1-methyl-2-(3-pyridyl)-pyrrolidine (nicotine)

4.3.2.5.1 IR analysis

The filtrate obtained from the reaction of $Mo(CO)_4Br_2$ with nicotine was concentrated by use of a rotary evaporator and an oily liquid was formed. The IR spectrum of the oily liquid (figure 3.19) obtained from the reaction of $Mo(CO)_4Br_2$ with nicotine showed a strong IR peak at 1678.0cm^{-1}. This falls in the region for ν(C=C) stretches. Since there is no similar peak in the IR spectrum of the neat base, then this suggests that the oily liquid contained some unsaturated organic product.

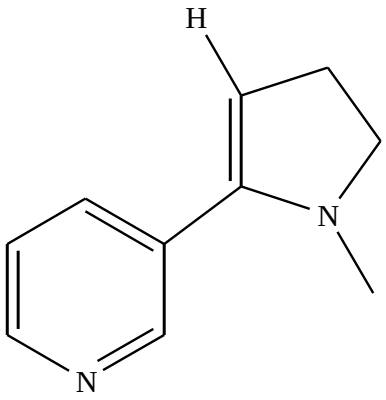
The concentrated filtrate from the reaction of nicotine with tetrabromooctacarbonyltungsten(II) gave a peak at 1651.0cm^{-1}. This suggests that an unsaturated organic product was present. A similar peak was observed at 1654.8cm^{-} on the IR spectrum of $Mo(CO)_5$(nicotine) complex. This shows that the complex was contaminated with some unsaturated organic by-products. A new peak in the (C=C) range at 1678cm^{-1}, that was not present in the IR spectrum of nicotine, may be attributed to oxidation of the pyrrole ring by the metal ion to give either



I II III

4.3.2.5.2 NMR analysis

^{1}H NMR spectrum of the concentrated filtrate obtained from the reaction of nicotine with $Mo(CO)_4X_2$ was obtained and a new singlet peak observed at 5.0ppm (Fig. 4.17). This falls within the region (4.5-6.5ppm) for olefinic protons (Kemp, 1991; Silversten, *et. al.*, 1990) or β-protons in partially reduced pyridines and related compounds (Wenkert E et al 1965; Ziecher et al, 1969). Since the speculated olefinic shift is upfield, the suggested structure of the oxidized nicotine is



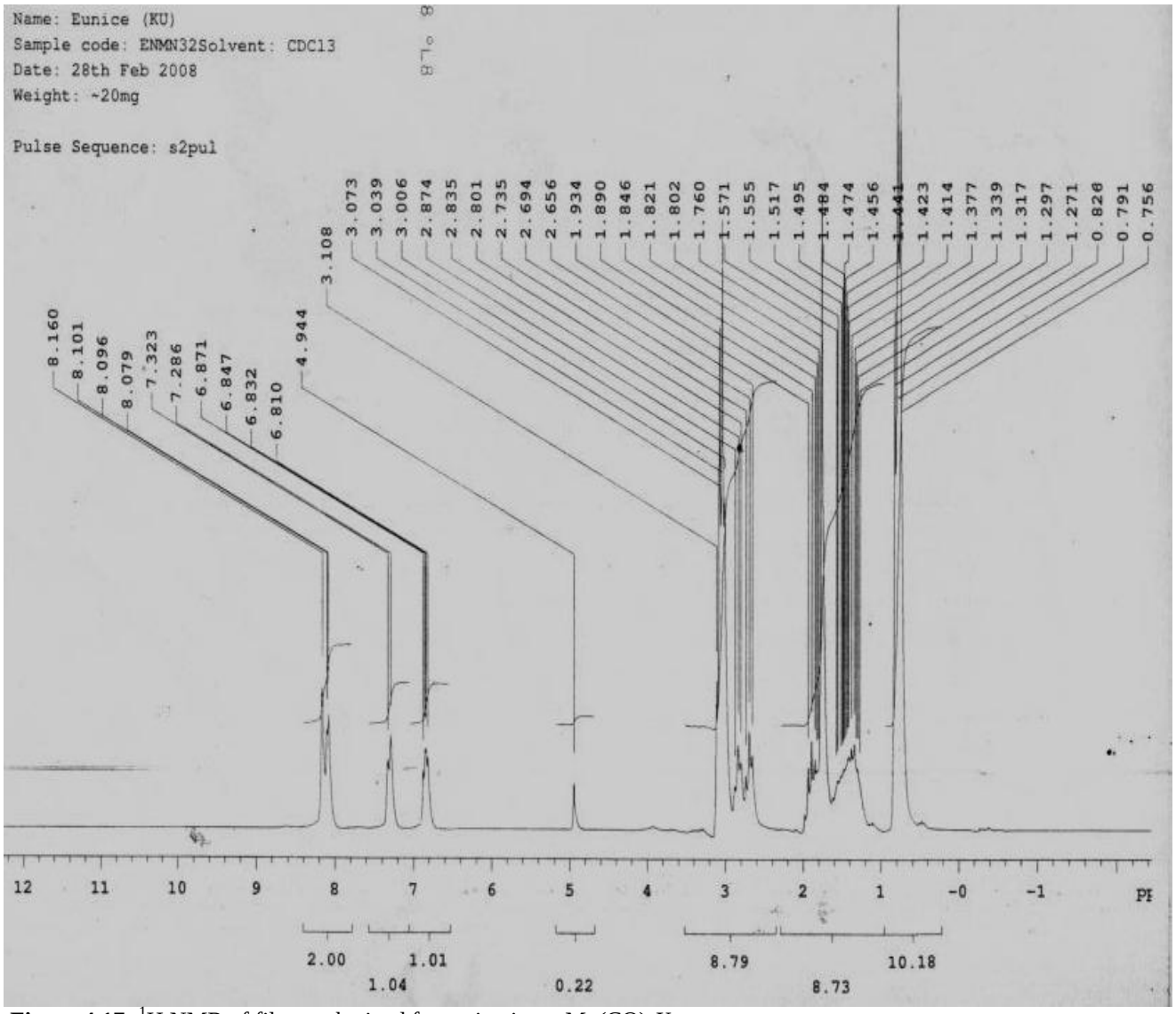


Figure 4.17: ^{1}H NMR of filtrate obtained from nicotine + $Mo(CO)_4X_2$

CHAPTER 5

SUMMARY AND CONCLUSIONS

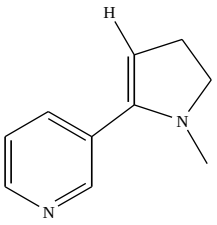
This chapter provides a summary of the results of the study and conclusion. The main objective of the study was to investigate how Molybdenum(II) or tungsten(II) halocarbonyls, $[M(CO)_4X_2]_2$ (M=Mo, W; X=Br, Cl) react with the low molecular weight nitrogen bases, methylamine and N,N-dimethylamine. The other objectives were to investigate whether nicotine coordinates to tungsten or molybdenum through the amine or imine nitrogen.

5.1 Summary of the findings

A key hypothesis was that the redox mechanism gives aminecarbonyls of the type $M(CO)_3L_3$ (M=Mo, W; X=Cl or Br) at room temperature which cannot be obtained via thermal reactions, the same mechanism may give similar products with low molecular weight amines such as methylamine at very low temperature. The results, from this work show that tetrahalooctacarbonylmetal (II), $[M(CO)_4X_2]_2$, (M=Mo, W; X=Br or Cl) react with low molecular weight nitrogen bases such as diethylamine and methylamine to form zero-valent metal complexes, $M(CO)_3L_3$ (L=diethylamine or methylamine) at low temperatures. Tetrahalooctacarbonylmetal (II), $[M(CO)_4X_2]_2$, (M=Mo, W; X=Br or Cl) react with tetramethylethylenediamine to form zero-valent metal complexes $M(CO)_4$TMEDA. The reaction of tetrahalooctacarbonylmetal (II), $[Mo(CO)_4X_2]_2$, (X=Br or Cl) with nicotine formed $M(CO)_5$nicotine.

The results suggest that the nitrogen bases, diethylamine and tetramethylethylenediamine are oxidized by $M(CO)_4X_2$ (M=Mo, W; X=Br or Cl) to imines which may have been hydrolyzed to an amine and an aldehyde or a ketone. The IR bands obtained in the region of $1740cm^{-1}$ for the product in an oily sample from $M(CO)_4X_2$ (M=Mo, W; X=Br or Cl) and

diethylamine reaction supports this suggestion. The imines formed in these reactions should tautomerises to enamines as reported in the case with tetramethylethylenediamine. The suggestion that tetramethylethylenediimine may have tautomerized to tetramethylethylenedienamine is supported by the presence of ν(C=C) bond stretch at 1653.8cm^{-1} on the IR spectrum of the oily product obtained from the reaction of $[W(CO)_4Br_2]_2$ with TMEDA. The results obtained could further suggest that methylamine is oxidized to the radical '$\cdot CH_2NH_2$' which, dimerizes to form 1,2-ethyldiamine, $NH_2CH_2CH_2NH_2$. However, this did not have strong supportive evidence.

The presence of a new IR band at 1651.9cm^{-1} on the spectrum of the oily product from the reaction of nicotine with the tetrahalooctacarbonylmetal (II) $[M(CO)_4X_2]_2$ (M=Mo, W; X=Br or Cl) and a new olefinic type of peak at 5 ppm suggests that nicotine was oxidized to 

. However, the reported IR spectra of $M(CO)_5$(nicotine) showed five coordinated carbonyl peaks. It is therefore not clear whether $M(CO)_5$(nicotine) was formed from the reaction of nicotine with halocarbonyls or with un-reacted hexacarbonylmetal(0). Hence, the mechanism by which $M(CO)_5$(nicotine) was formed is not clear.

The final hypothesis that nicotine which has both amine and imine nitrogen will co-ordinnate to molybdenum or tungsten via the imine nitrogen as is the case in haemoglobin where the globin is coordinated to the iron through the imine nitrogen of the imidazole ring and not via the amine nitrogen is therefore supported by the results. The crystal structure of the tungsten-nicotine complex, $W(CO)_5$nicotine (Fig. 4.10) confirms that nicotine is co-ordinated to tungsten via the imine nitrogen and not the amine nitrogen.

5.2 Conclusion

From the work presented in this thesis, the following conclusions were arrived at;

- Molybdenum(II) and tungsten(II) halocarbonyls, $M(CO)_4X_2$ (M=Mo, W; X=Br, Cl) react with the low molecular weight nitrogen bases; methylamine, N,N-dimethylamine, and the polydentate ligands N,N,N',N'-tetramethylethylenediamine and nicotine to form zero-valent amine carbonyls metal complexes. At the same time the nitrogen bases were oxidized to the imines and enamines.
- Nicotine reacts with halocarbonyl complexes, $[M(CO)_4X_2]_2$ (M=Mo, W; X=Cl, Br), via redox mechanism.
- Nicotine coordinates to tungsten or molybdenum through the imine nitrogen.
- Methylamine is oxidized by halocarbonyl complexes, $[M(CO)_4X_2]_2$ (M=Mo, W; X=Cl, Br), to the radical CH_2NH_2 that dimerizes to $H_2NCH_2CH_2NH_2$.

5.3 Recommendations

The results presented in this study show that the objectives have been successfully achieved. However, the following areas need to be researched on (i) a crystal structure of $W(CO)_4$TMEDA should be attempted, (ii) a reaction of $W(CO)_6$ with nicotine should be attempted to see what products are formed, (iii) isolation and complete characterization of the organic oxidized species or the filtrates should be critically analyzed for any olefins probably by conducting an ac analysis of the products using olefinic standards for a period of 24 hours. (iv) $M(CO)_4X_2$ (M= Mo, W; X= Cl or Br) should further be tested on olefins and alkanes to monitor their reaction transformation abilities.

Further work is required to help understand the mechanism of the reaction between nicotine and halocarbonyl molybdenum(II) or tungsten(II) and establish whether the complex $M(CO)_5$nicotine is formed from these reactions or from the reaction of nicotine and hexacarbonylmetal(0).

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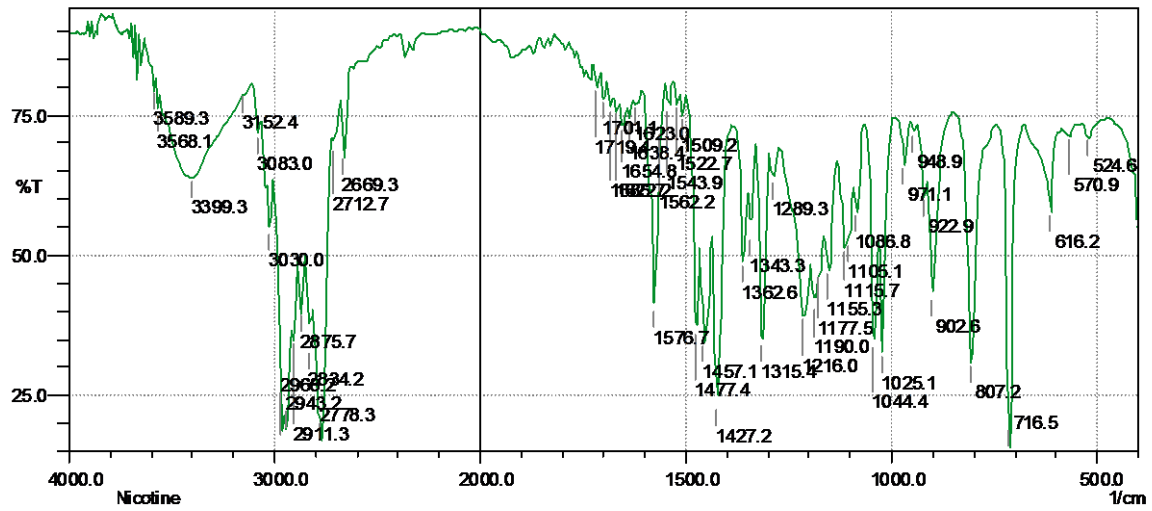
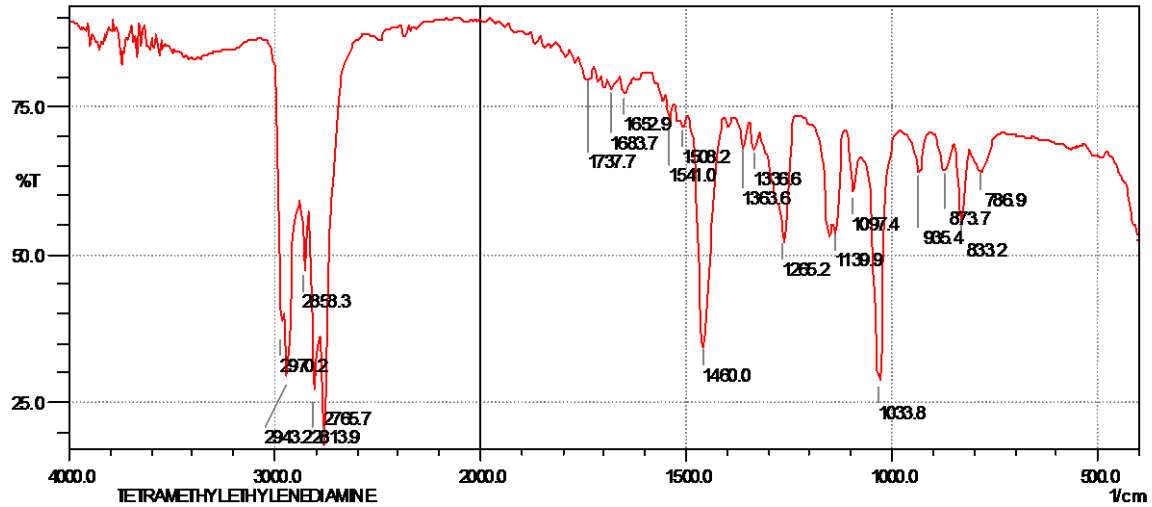
APPENDICES

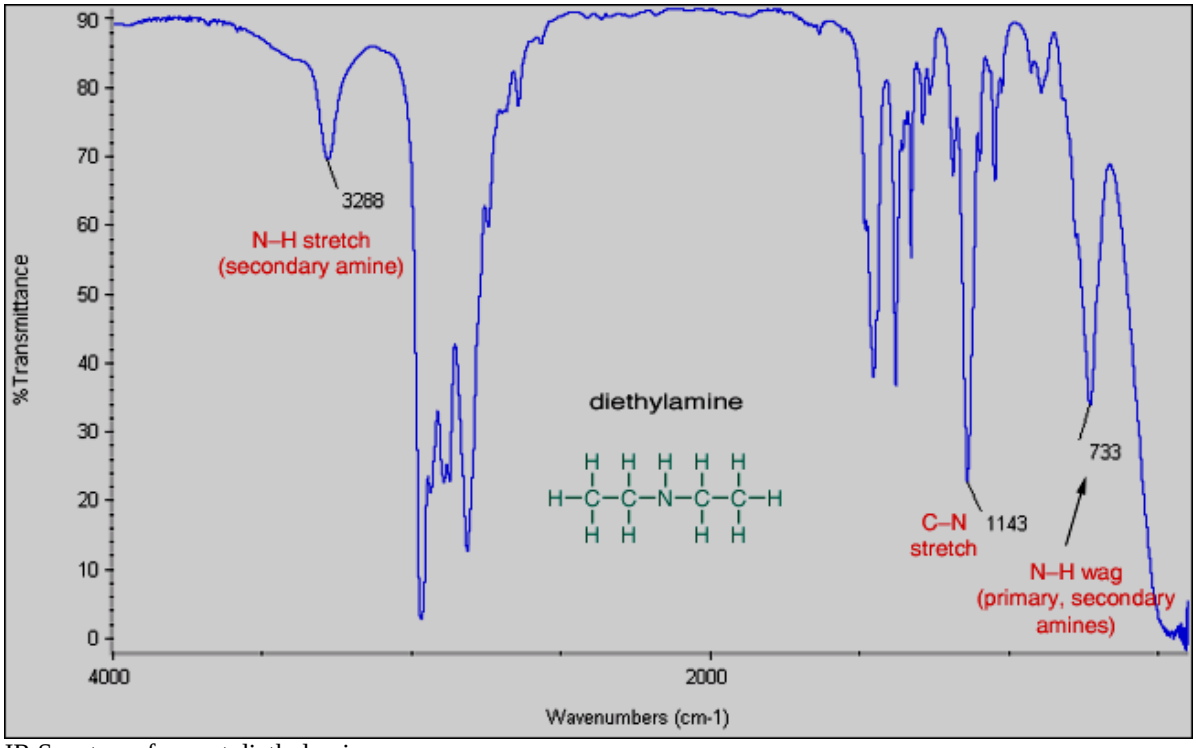
Appendix I: IR spectra of neat bases



IR Spectrum for neat nicotine

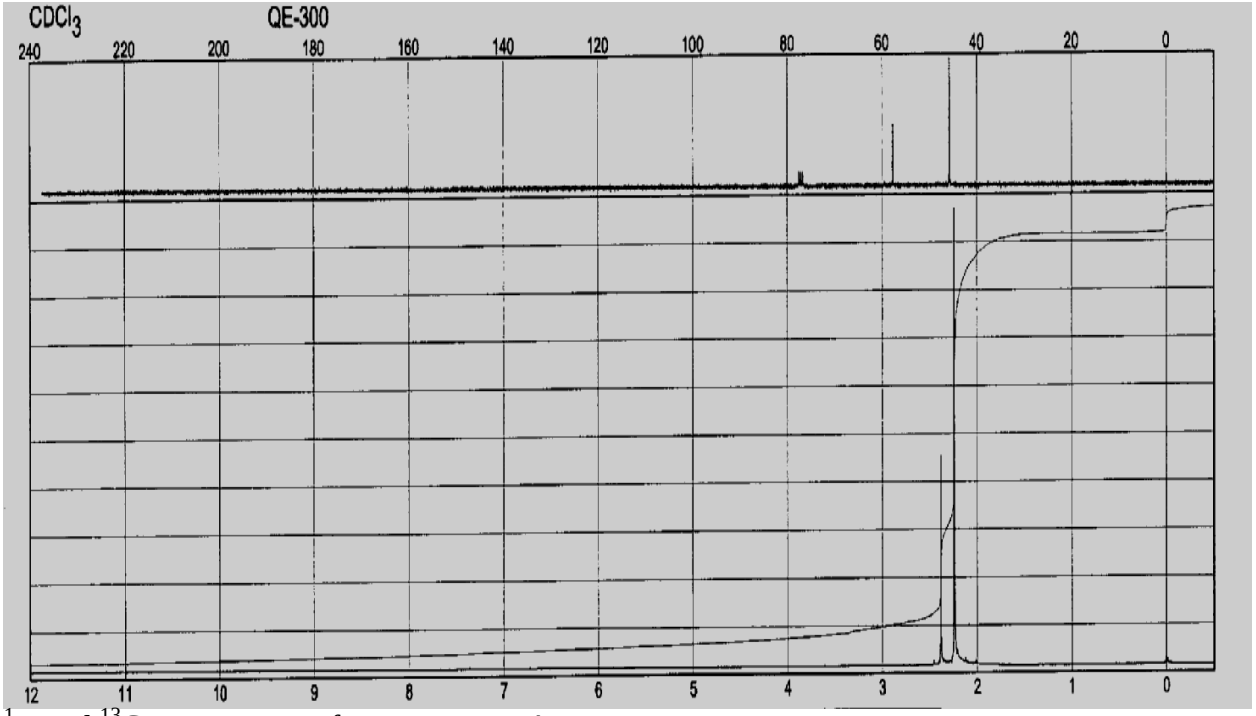


IR Spectrum for neat N,N,N,N’,N’-tetramethylethylenediamine

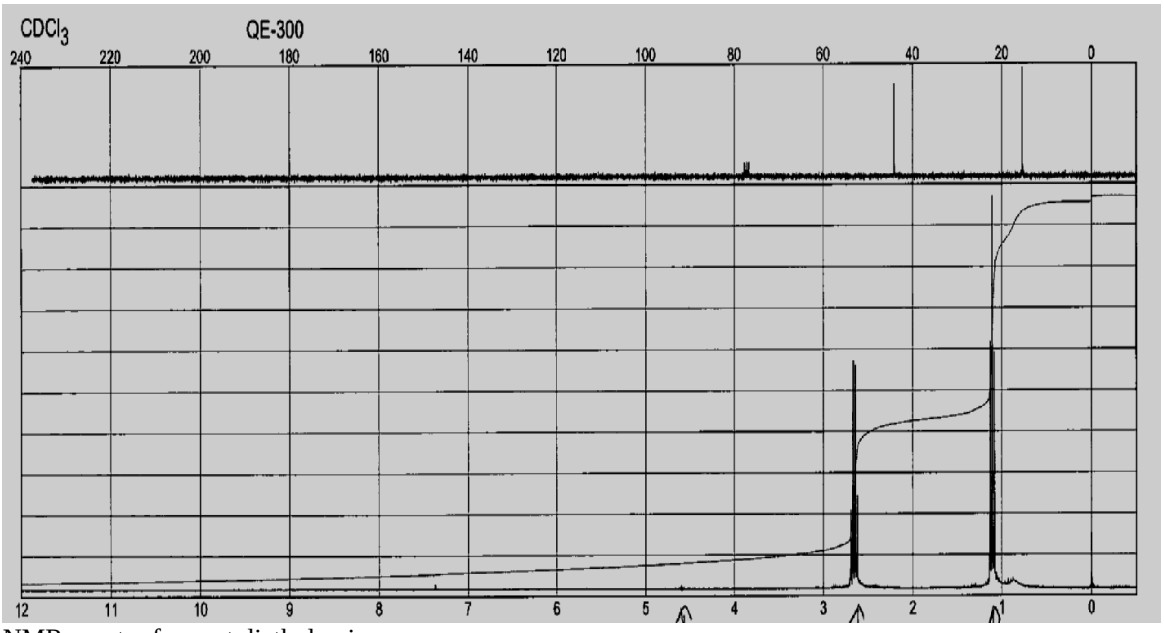


IR Spectrum for neat diethylamine

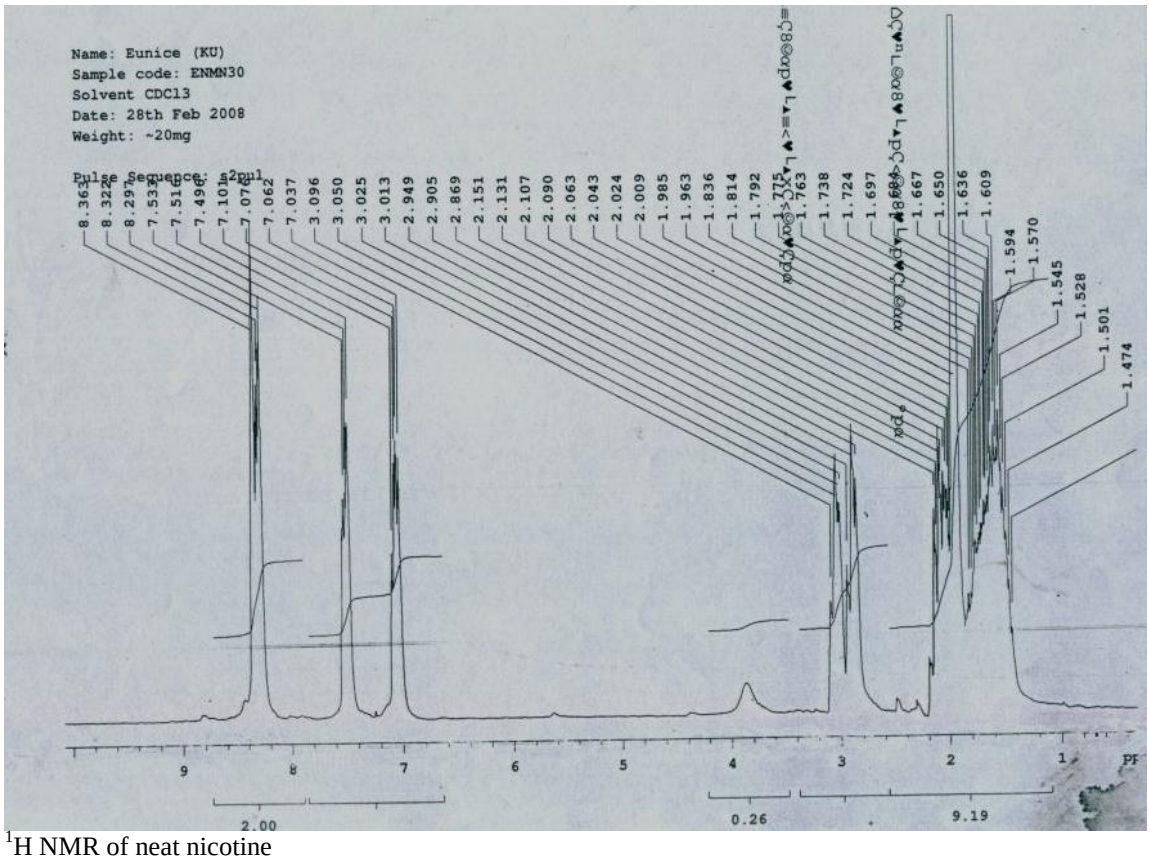
Appendix II: NMR spectra of neat bases



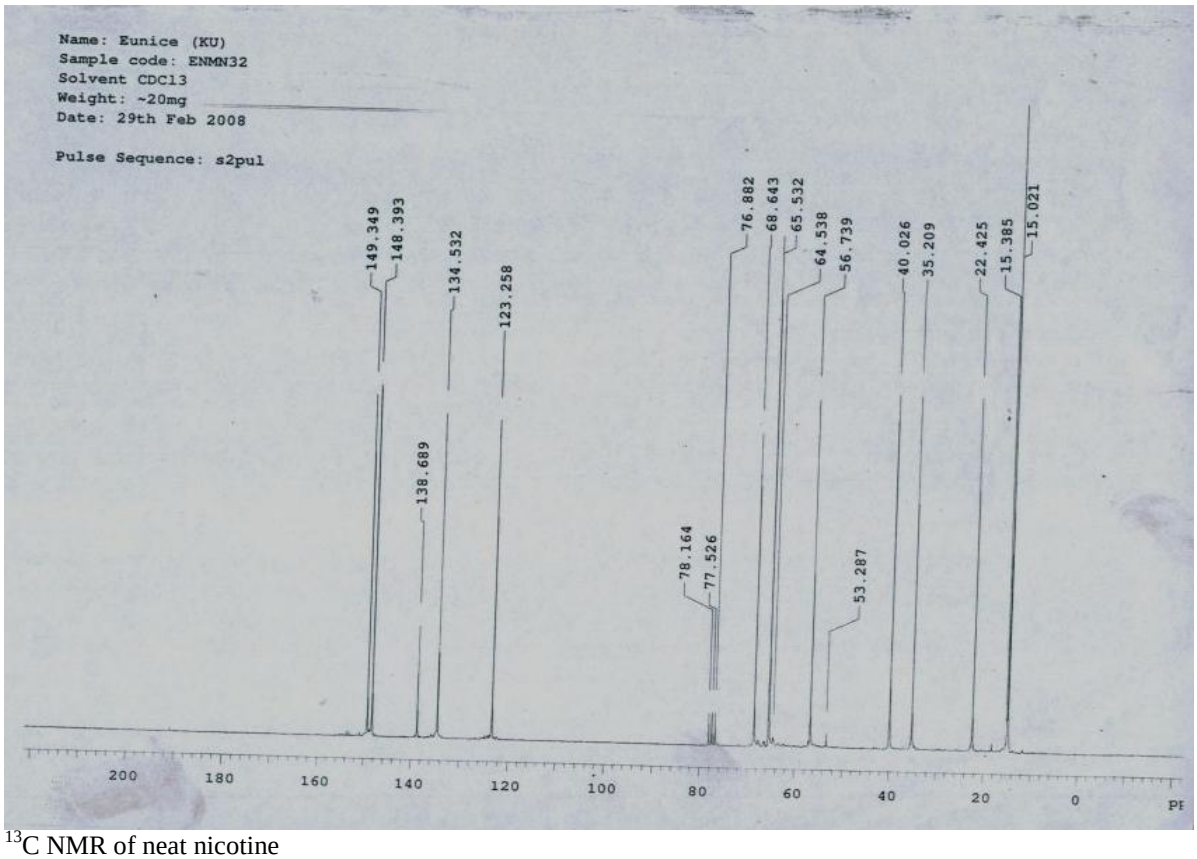
^{1}H and ^{13}C NMR spectra for neat TMEDA



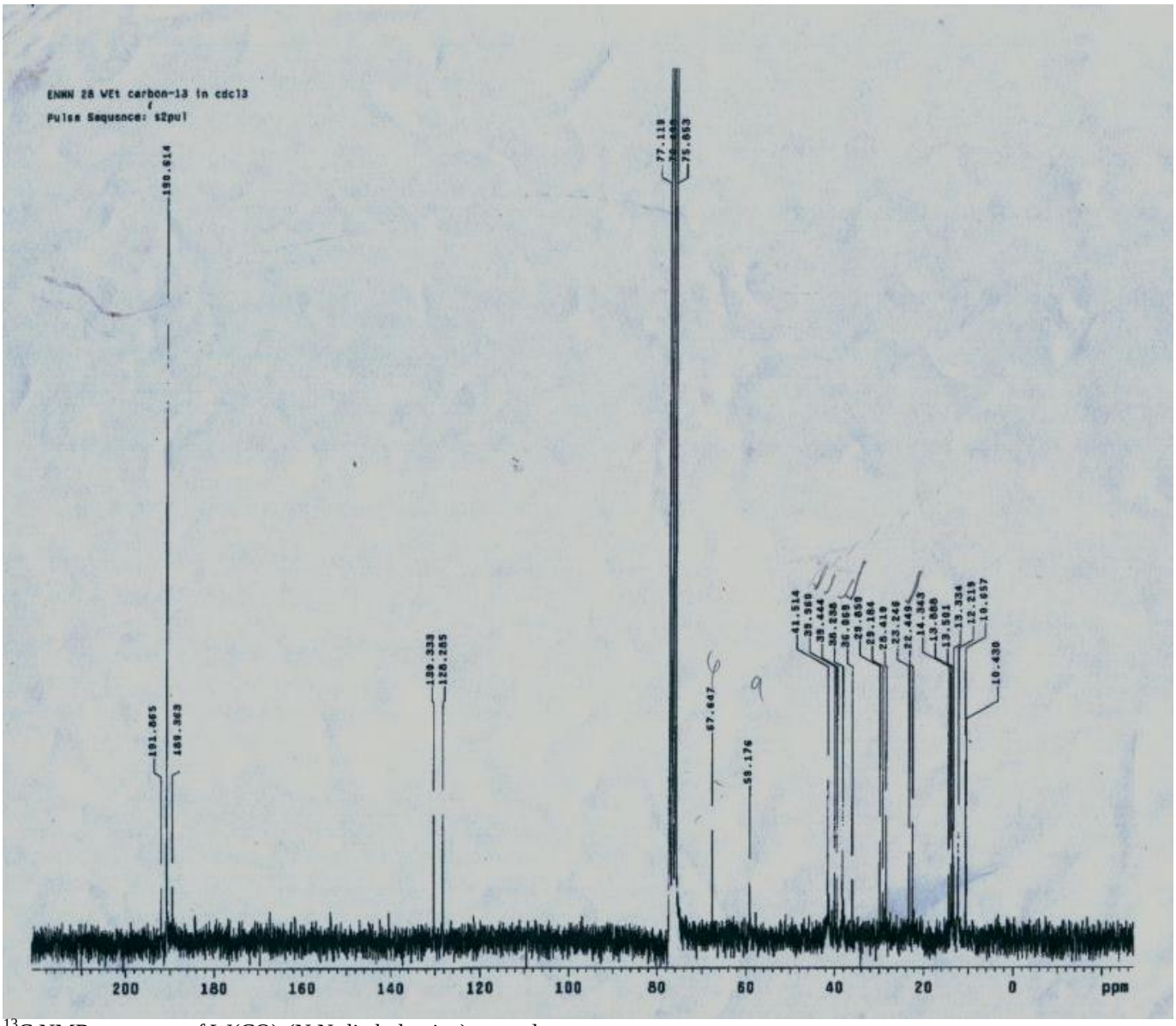
NMR spectra for neat diethylamine



^{1}H NMR of neat nicotine



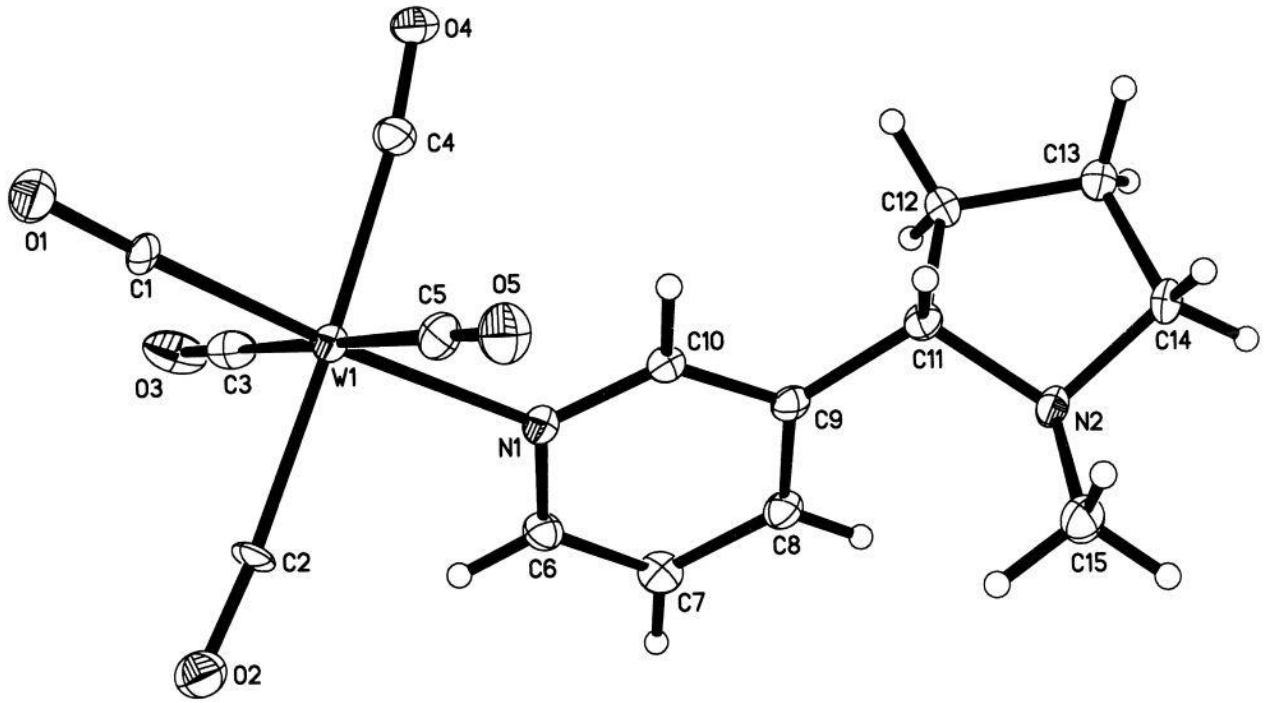
^{13}C NMR of neat nicotine



^{13}C NMR spectrum of $W(CO)_3$(N,N-diethylamine)$_3$ complex

Appendix III: Data collection and refinement information for the Crystal structures of complexes

1-(pentacarbonyltungsten)-2-(1-methylpyrrilidin-2-yi)pyridinium



Crystal data

$C_{15}H_{14}N_2O_5W$
Mr = 486.13

F_{000} = 464
Dx = 1.967 Mg m^{-3}
CuKα radiation
λ=1.544178 Å

a=6.6302 (2) Å
b=10.6722(3) Å
c=11.6768(4) Å
α=90°
β=96.638(2)°
γ=90°
V=820.70 (4) $Å^3$
Z=2

μ = 13.29 mm^{-1}
T=100(2) K

0.28 x 0.25 x 0.19

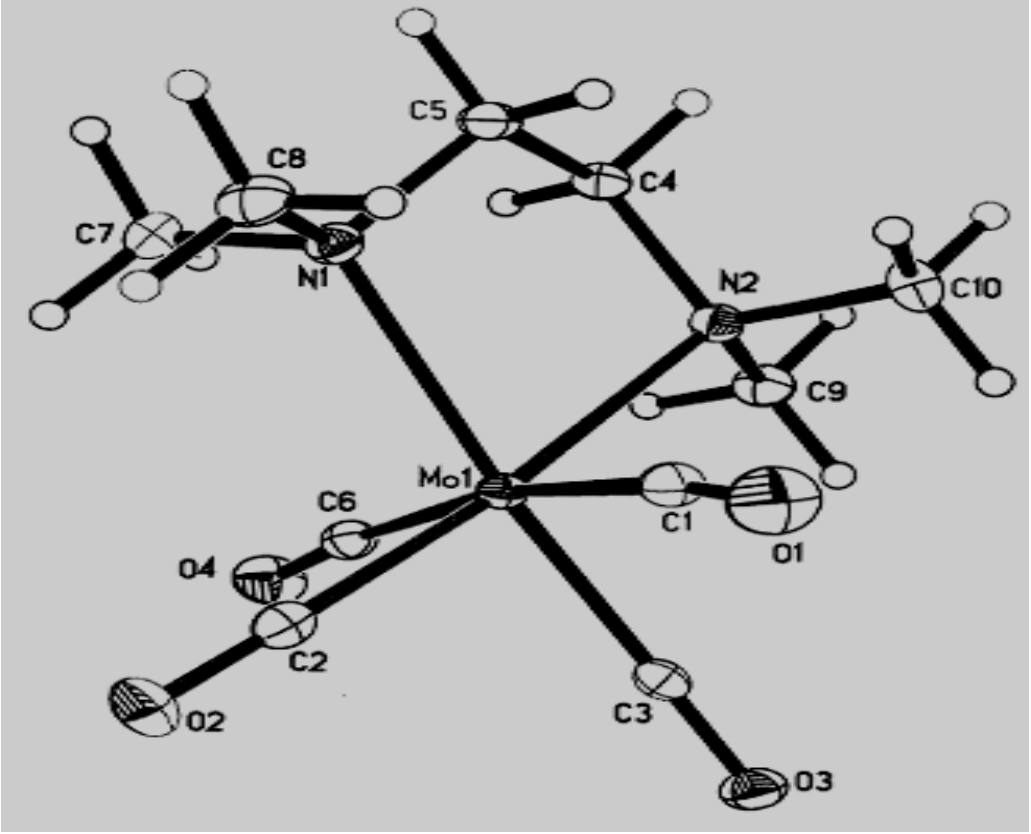
Data collection

Radiation source: fine-focus sealed tube
Monochromator: graphite
T=100(2) K

3467 measured reflections
1727 independent reflections

1726 reflections with 1 >2σ (1)
R_{int}=0.021
θ_{max} = 66.7°
θ_{min} = 3.8°
h=-6 →7
k=-12 →8
l=-11→10

1,1,1,1-tetracarbonyl-2,2,5,5-tetramethyl-1λ^6,2,5-tungsten-2,5-diium



Crystal data

$C_{10}H_{16}N_2O_4M$
Mr = 324.19

a=8.3177 (7) Å
b=11.9311(10) Å
c=13.3517(11) Å
α=90°
β=91.181 (5)°
γ=90°
V=1324.73 (19) Å^3
Z=4

F_{000} = 658
Dx = 1.625 Mg m^{-3}
CuKα radiation
λ=1.54178 Å

μ = 8.17 mm^{-1}
T=100(2) K

Data collection

Radiation source: fine-focus sealed tube
Monochromator: graphite
T=100(2) K

3467 measured reflections
1727 independent reflections

2093 reflections with 1 >2σ (1)
R_{int}=0.023
θ_{max} = 66.9°
θ_{min} = 5.0°
h=-9→9
k=-13 →14
l=-15→15