

**PREPARATION OF TERVALENT MOLYBDENUM COMPLEXES AND A  
STUDY OF THEIR REDUCTION BY ZINC UNDER LOW PRESSURE OF  
CARBON MONOXIDE. //**

**BY**

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tervalent molybdenum*




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## DECLARATION

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## DEDICATION

To my beloved son; Rooney Mwenda, my dear brother Josphat Kaunyangi, my niece Ruth Kinya and all other people who may benefit from this thesis.

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## LIST OF ABBREVIATIONS

$\infty$	Excess ligand
ADP	Adenosine diphosphate
AsPh <sub>3</sub>	Triphenylarsine
bipy	2,2' bipyridyl
btp	N-n-butylthiopicolinamide.
CHP	Cumil Hydroperoxide
CVD	Chemical Vapor Deposition.
dam	Bis(dimethylarsino)methane
diars	1,2-bis(dimethylarsino)benzene
diglyme	Bis(2-methoxyethyl)ether
diphos	1,1 bis(diphenylphosphinomethyl)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
dppae	1-diphenylarsino-2-diphenylphosphinoethane
dppe	1,2-bis(diphenylphosphino)ethane
dtc <sub>2</sub>	dialkyldithiocarbamate.
IR	Infrared
MeCN	Acetonitrile
nbd	Norbornadiene
NCS	N-chlorosuccinimide
PPh <sub>3</sub>	Triphenylphosphine
Phen	1,10-phenanthroline or <i>o</i> -phenanthroline.
pip	Piperidine
py	Pyridine
RCN	Nitrile
RNC	Isonitrile
SbPh <sub>3</sub>	Triphenylstibine
Stoich	Stoichiometric
TBHP	<i>t</i> -butylhydroperoxide
THF	Tetrahydrofuran
Tms	Trimethylsilane

**ABSTRACT**

Previously, molybdenum hexacarbonyl,  $\text{Mo}(\text{CO})_6$  has been prepared by reduction of high oxidation state molybdenum compounds such as  $\text{MoCl}_5$  under high pressure (60-100 atm.) and temperature (20-100°C), carbonylation of metal oxide at very high pressure (2000 atm) and temperature (300°C) or carbonylation of the metal itself at 250 atm pressure and 200°C. Products made under these conditions are very expensive. The present study was aimed at investigating whether  $\text{Mo}(\text{CO})_6$  can be prepared under mild conditions by reducing trihalotris(tetrahydrofuran)molybdenum(III),  $\text{Mo}(\text{THF})_3\text{X}_3$  (X=Cl, Br) with zinc dust at 1 to 2 atmospheres. The results confirm beyond any reasonable doubt that this is possible. Products were isolated using thin layer and column chromatography, and identified using infrared spectroscopy and elemental analysis.

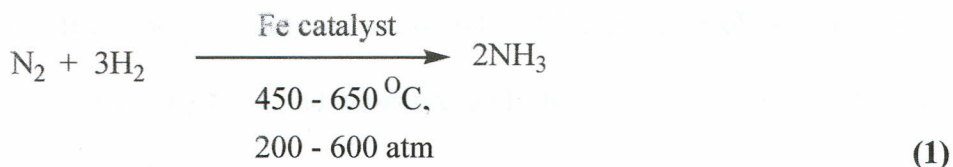
## CHAPTER ONE

### 1.0 INTRODUCTION.

#### 1.1 Background.

Metals of the d-block of the periodic table are extremely important components of many enzymes. Molybdenum is one of these d-block elements, and is apparently necessary for all species including human<sup>1-6</sup>. It is found in many molybdopterin-containing enzymes<sup>7, 8</sup>. Molybdopterin-containing enzymes possess a molybdenum cofactor (Moco) which contains a single molybdenum atom and a pterin ring system substituted at 6-position. Examples of these include: nitrate reductase<sup>9</sup>, sulfite oxidase<sup>10</sup> and xanthine oxidase<sup>11</sup>. Molybdenum occurs at the active site of these enzymes<sup>12, 13</sup> which mediate the metabolism of carbon, nitrogen and sulfur. Nitrogenase<sup>14</sup> is the nitrogen-fixing enzyme which converts molecular nitrogen ( $N_2$ ) to ammonia ( $NH_3$ )<sup>15</sup>. This enzyme is actually a cluster coordination complex<sup>16 - 20</sup> which coordinates molecular nitrogen and in so doing actually facilitates breaking of the ( $N\equiv N$ ) bond, one of the strongest chemical bonds, which requires 946 KJ/mole<sup>21</sup>.

A problem of long-standing interest in inorganic chemistry is that of finding a way to "fix" nitrogen<sup>22</sup>, a process that is currently carried out commercially using the Haber - Bosch process. This is an energy-intensive reaction between nitrogen and hydrogen molecules at very high temperature (450-650 °C) and pressure (200-600 atm)<sup>20, 21, 23</sup>.



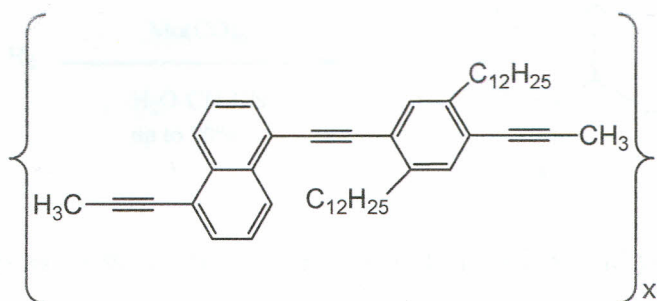
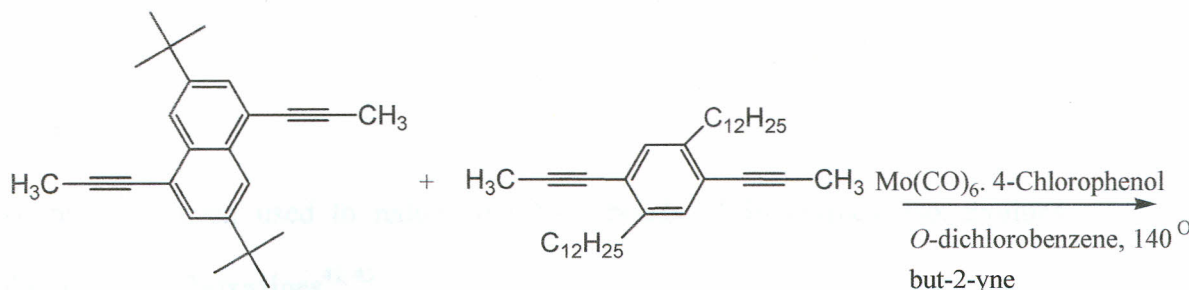
In contrast to the Haber - Bosch process, the reduction of dinitrogen by biological systems (nitrogen fixation) takes place under very mild reaction conditions. Diazotrophs normally fix nitrogen at ordinary temperature and pressure. In nature the nitrogenase plays a key role in the fixation of nitrogen, acting via molybdenum and iron-containing protein<sup>14, 15</sup>.

A lot of effort has been put in attempting to make complexes which can serve as models for the enzyme, and thus give a better understanding of how the enzyme actually functions<sup>12, 24-36</sup>. It is noteworthy that molybdenum hexacarbonyl is one of the most convenient starting material for synthesis of such complexes. It is not only used as starting material for the preparation of other complexes, but also it has many industrial applications among them being:

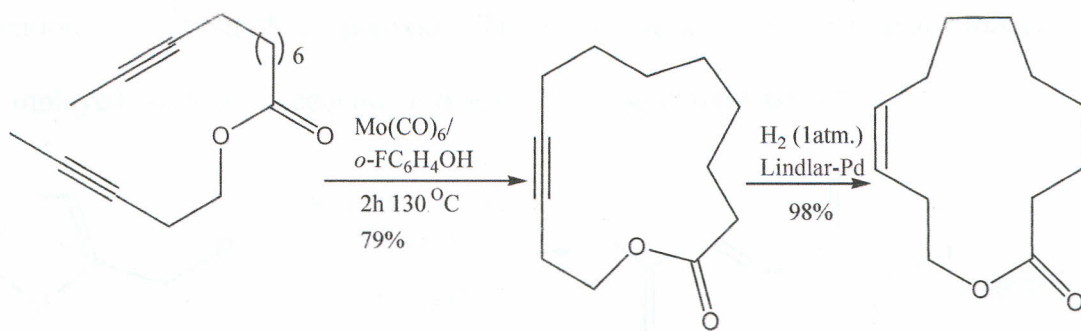
#### (a) Catalysis

$\text{Mo}(\text{CO})_6$  finds use as catalyst in several processes, by itself or tuning its reactivity by ligand exchange. The  $\text{Mo}(\text{CO})_6$ /Phenol system has been known since 1974 when Mortreux used a catalyst formed *in situ* from  $\text{Mo}(\text{CO})_6$ /resorcinol at  $160^\circ\text{C}$  for the cross metathesis of simple disubstituted acetylenes<sup>37, 38</sup>. Later Mori<sup>39</sup> utilized a similar reaction ( $\text{Mo}(\text{CO})_6$ /4-Chlorophenol) for the preparation of unsymmetrically substituted alkynes (equation 2). Recently, Karol Grela and Jolanta Ignatowska described an improved "instant" catalyst for ring-closing alkyne metathesis reaction (equation 3); a catalyst

formed *in situ* from molybdenum hexacarbonyl and 2-fluorophenol. This catalyst can be used without exclusion of air and moisture and shows high activity in metathesis of functionalized dynes<sup>40</sup>.

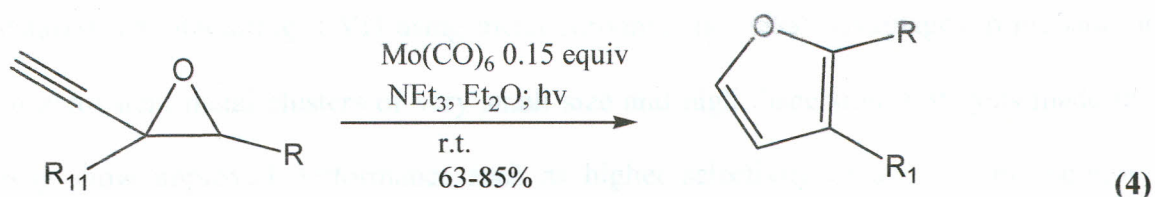


(2)



(3)

$\text{Mo(CO)}_6$  has been used to catalyze the cycloisomerization of 1-alkyn-4-ols to 2,3-dihydrofurans and the isomerization of epoxyalkynes to furans<sup>41</sup> (equation 4).

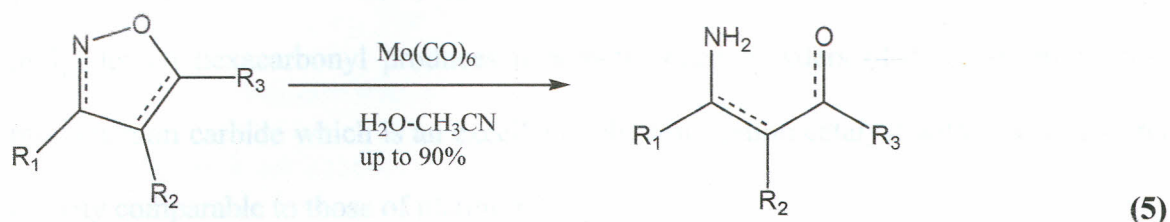


R = CH<sub>2</sub>OH

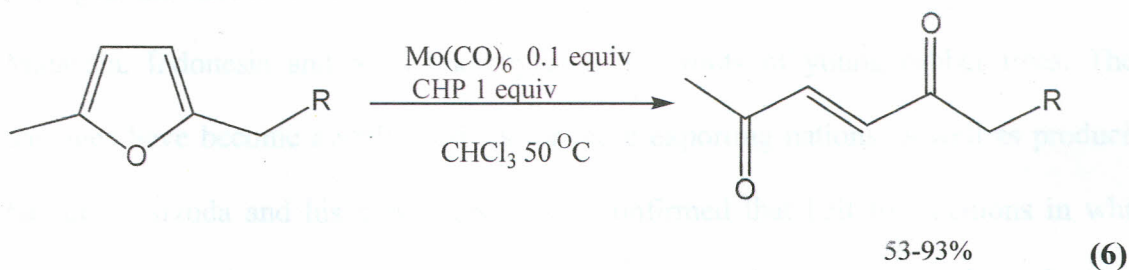
R<sub>1</sub> = CH<sub>3</sub>

R-R<sub>11</sub> = (CH<sub>2</sub>)<sub>4</sub>

Mo(CO)<sub>6</sub> has also been used to reduce the N-O bonds of isoxazoles, isoxazolines, isoxazolidines and 1,2-oxazines<sup>42, 43</sup>.



Mo(CO)<sub>6</sub> behaves as a catalyst for the mild oxidation of 2,5-dialkylfurans (equation 6) to *E* or *Z* (depending on the base used) enediones using cumyl hydroperoxide (CHP). Diones gave peroxyranones in moderate yields, irrespective of the C=C bond configuration, when *t*-butylhydroperoxide (TBHP) was used. This shows that Mo(CO)<sub>6</sub> can be employed not only in reduction processes, but also in oxidations<sup>44</sup>.



(*Z*-product if Na<sub>2</sub>CO<sub>3</sub> is used)

Use of metal carbonyls in chemical vapor deposition (CVD) has been attractive for both the synthesis of supported metal catalysts and the fabrication of electronic devices. In

catalyst manufacturing, CVD using metal carbonyls has clear advantages in preparation of zerovalent metal clusters of very small size and high dispersion. Catalysts made this way show improved performance such as higher selectivity or activity. Furthermore, metal carbonyls provide flexibility in terms of catalyst composition since they are readily available for a broad range of metals. Many studies have focused on finding the decomposition conditions of metal carbonyls for obtaining naked metals and also on the structure and reactivity of the deposited metal clusters or films. Recently, Mo particles have been prepared on Au(III) by  $\text{Mo}(\text{CO})_6$  CVD<sup>45</sup>. Sonochemical decomposition of molybdenum hexacarbonyl produces nanometer-sized powders of face centered cubic molybdenum carbide which is an excellent dehydrogenation catalyst with selectivity and activity comparable to those of platinum<sup>46</sup>.

#### **(b) Termite Control**

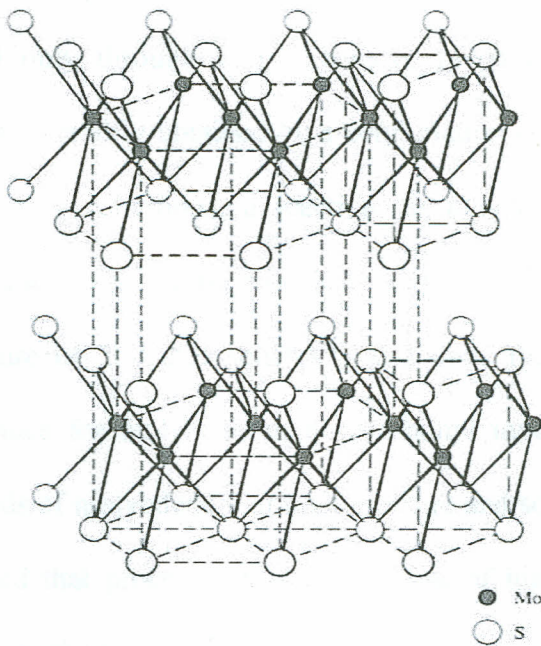
Damages by termites that eat wood or destroy embankment are of social concern, and in particular, the damage of embankment by *Odontotermes formosanus*, *Odontotermes hainanensis*, *Globitermes*, or *Macrotermes* is serious. These kinds of termites have damaged the rubber plantations of hot and humid countries such as Ghana, Thailand, Malaysia, Indonesia and Sri Lanka by attacking roots of young rubber trees. These damages have become awfully serious for these exporting nations as well as producing farmers. Katzuda and his coworkers<sup>47</sup> have confirmed that bait formulations in which molybdenum and tungsten compounds are incorporated eradicate termite colonies of *Macrotermes* and *Odontotermes* which attack rubber trees. These compounds are slow-acting to termites and show high termiticidal efficacy. Termiticidal effectiveness of Molybdenum and tungsten compounds might be much more associated with the



physiological depression caused by the accumulation of their oxides in the body, especially in the fat body, rather than with the influences on the symbiotic intestinal flagellates.

### (c) Lubrication

MoS<sub>2</sub> has been prepared by irradiating a slurry of molybdenum hexacarbonyl and sulfur in 1,2,3,5-tetramethylbenzene (isodurene) with high-intensity ultrasound (20 KHz) under argon<sup>48</sup>. It has a layer structure in which each metal atom has six S neighbours at apices of a trigonal prism (*fig 1*). The long S-S distance between sandwich layer are 366 pm, corresponding to van der Waals interaction<sup>49</sup>. This results in easy cleavage of the MoS<sub>2</sub> crystal making it an excellent solid lubricant especially at high temperatures where normal oil will decompose<sup>50</sup>.



**Fig. 1: Structure of MoS<sub>2</sub>**

#### (d) Metallurgy and Corrosion Inhibition

Molybdenum is a typical transition element with a maximum number of unpaired 4d electrons, which accounts for its high melting point, strength, and modulus of elasticity. The melting point of molybdenum is about 2626 °C, 1100 °C above that of iron. As a result of its high melting temperature, molybdenum metal has strength characteristics at temperatures where most metals are in the molten state. Metallic molybdenum coating which can be deposited onto steel substrates by the thermal decomposition of  $\text{Mo}(\text{CO})_6$  increases the strength and corrosion resistance of the steel because it has a particularly good resistance to corrosion by mineral acids<sup>50</sup>.

From the above discussion, it is obvious that molybdenum hexacarbonyl is one of the most important compounds of molybdenum. Unfortunately, so far, the compound has been obtained only through very expensive preparative routes. Thus, unlike nickel carbonyl which is readily obtained by a combination of CO with elemental nickel under very mild reaction conditions, a reaction discovered by Mond in 1891<sup>51</sup>, elemental molybdenum reacts with carbon monoxide only when heated to a temperature of 200 °C under a pressure of 250 atmospheres<sup>52</sup>, and then, the yield is less than 15%. Other preparative routes for molybdenum hexacarbonyl involve reduction of high-oxidation state compounds of molybdenum at high pressure and sometimes high temperature too. It should be noted that processes that require use of high pressure, high temperature or combination of both are usually very expensive to operate the reason being that, not only does the process consume a lot of energy, but also requires use of expensive construction materials to ensure that the process can be operated safely.

The work reported in this thesis was undertaken in an attempt to gain a better understanding of the chemistry of low-valent molybdenum compounds. Most important types of compounds, their representative synthesis and some of their more important reactions or applications are discussed with special reference to synthesis of  $\text{Mo}(\text{CO})_6$ , which is the useful and indispensable starting material in syntheses of most of these compounds.

## 1.2 Objectives of the Present Study

### General objective

To prepare tervalent complexes of molybdenum and study their reduction by zinc under ordinary conditions of temperature and pressure.

### Specific objectives

1. To synthesize complexes of the type  $\text{MoX}_3\text{L}_3$  ( $\text{X} = \text{Cl}, \text{Br}; \text{L} = \text{THF}$ ) by different routes and carry out infrared examination to show that they do not contain any traces of the coordinated carbonyl groups
2. To reduce these complexes with zinc powder at ordinary pressure of CO and slightly elevated pressure of carbon monoxide (1.5 – 2.0 atm).
3. To investigate whether  $\text{Mo}(\text{CO})_6$  would be among the reduction products formed.

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 Synthesis of Molybdenum Hexacarbonyl $\text{Mo}(\text{CO})_6$

The classical discovery of tetracarbonylnickel[0],  $\text{Ni}(\text{CO})_4$  in 1891<sup>51</sup> by Mond which was followed almost immediately by discovery of pentacarbonyliron[0],  $\text{Fe}(\text{CO})_5$  led to the development of the chemistry of metal carbonyls. Hexacarbonylmolybdenum[0],  $\text{Mo}(\text{CO})_6$  was the first of group 6 metal carbonyl to be prepared in 1906<sup>53</sup>. Since then there has been a continued interest in these compounds, but in the past this was very modest compared with relatively recent activities. The tremendous increase in interest in the molybdenum hexacarbonyl over the last two decades has arisen partly as a result of the discovery of many novel complexes of molybdenum in which a metal carbonyl system forms an integral part of the structure.

Molybdenum hexacarbonyl is prepared by the following methods:

- i. Direct reaction of the metal and gaseous carbon monoxide<sup>52</sup>
- ii. Reductive carbonylation<sup>51, 55-59</sup> and
- iii. Exchange of carbon monoxide molecules<sup>60</sup>.

The percentage yields and conditions under which synthesis by these methods are achieved are given in the table 1.

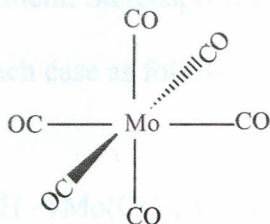
**Table 1. Selected Mo(CO)<sub>6</sub> Syntheses**

Reaction	Conditions	Yield (%)	Ref
Mo + CO (direct reaction)	P <sub>CO</sub> 250 atm; 200 °C	Low(< 15)	52
MoO <sub>3</sub> + CO (direct reaction)	300 °C, P <sub>CO</sub> 2000 atm; 12 hrs.	89	54
MoCl <sub>5</sub> + Zn + CO (Reductive carbonylation)	Ether-benzene; P <sub>CO</sub> 100 atm; 0-10 °C	46	55
MoCl <sub>5</sub> + Al + CO (Reductive carbonylation)	Ether; 3-16 hrs; P <sub>CO</sub> 70 atm 20-100 °C	60-90	56 and 57
MoCl <sub>5</sub> + Et <sub>3</sub> Al + CO (Reductive carbonylation)	Benzene; 3 hrs; P <sub>CO</sub> 70 atm; 50-60 °C	76	58
MoCl <sub>5</sub> + Na+ CO followed by acid hydrolysis (Reductive carbonylation)	DIGLYME; P <sub>CO</sub> 65 atm 20hrs. -20-25 °C	65	59
MoCl <sub>5</sub> + Fe(CO) <sub>5</sub> + CO (Exchange of CO molecule)	Ether; HCl present P <sub>CO</sub> 100 atm	28	60

As can be noted from table 1, the preparative methods used require high CO pressure (65-2000 atm) and, in most cases elevated temperature. In practice the direct procedure is limited to carbonyls of metals which can be obtained in active form by low temperature reduction. For example nickel absorbs carbon monoxide at room temperature and normal pressure to form nickel tetracarbonyl<sup>61</sup>. Preparation of metal carbonyls by reduction of a suitable compound under carbon monoxide is not peculiar to molybdenum. Thus, Cr(CO)<sub>6</sub>, Co<sub>2</sub>(CO)<sub>8</sub>, Mn<sub>2</sub>(CO)<sub>10</sub> and V(CO)<sub>6</sub> are examples of metal carbonyls prepared using this techniques<sup>62, 63</sup>.

## 2.2 Some Properties and Reactions of Molybdenum Hexacarbonyl [Mo(CO)<sub>6</sub>]

Molybdenum hexacarbonyl is colourless, odourless diamagnetic solid that forms orthorhombic crystals with a density of 1.96 g cm<sup>-3</sup>. The crystals are air-stable, hydrophobic and sublime at 150 °C but melt reversibly under vacuum at 146 °C. Molybdenum hexacarbonyl is very slightly soluble in non-polar organic solvents, slightly soluble in polar organic solvents and insoluble in water<sup>64</sup>. It has an octahedral<sup>65, 66</sup> structure (*fig. 2*) in which all six d electrons are involved in  $\pi$ -bonding to the carbonyls. The linkage to the metal is through carbon rather than oxygen<sup>67</sup>.

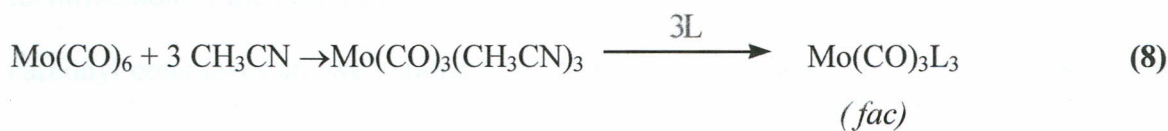
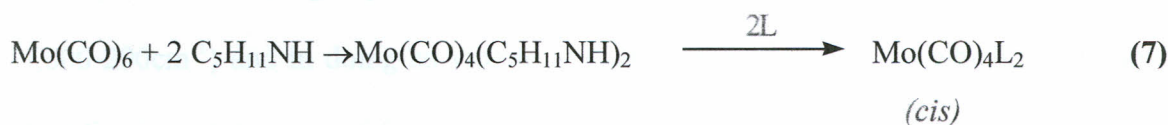


**Fig. 2: The Structure of Molybdenum Hexacarbonyl**

Lewis bases and in particular tertiary phosphorus, arsenic and antimony donors can substitute carbon monoxide in the metal carbonyl<sup>68</sup>. A sequential replacement of carbon monoxide in octahedral carbonyl Mo(CO)<sub>6</sub> occurs mainly by a series of dissociative substitution. When one carbonyl ligand is replaced by a ligand that is poorer  $\pi$ -bonding than carbon monoxide, the Mo-CO bond *trans* to it will have a greater share of  $d_{\pi}$  electrons density. As a result, the Mo-CO bond *trans* to these ligands will be strengthened relative to the *cis* carbonyl group<sup>69</sup>. This makes *cis* carbonyl groups to be readily substituted by a second and third ligand giving *cis* isomer Mo(CO)<sub>4</sub>L<sub>2</sub> (L = poor  $\pi$ -bonding ligands) and *fac*-isomer of Mo(CO)<sub>3</sub>L<sub>3</sub>, respectively. Facile substitution ends

at tricarbonyl stage because all the remaining carbonyl groups are *trans* to poorer  $\pi$ -bonding ligands.

Further substitution is possible but only under severe conditions or with ligands that are either chelating or good  $\pi$ -acceptors<sup>70</sup>. Ligands with P, As, or S donor atoms do not exert any stereospecific labilising effects on carbonyl ligand so that mixture of isomers are often obtained in direct reaction with the hexacarbonyl. They do, however, readily displace ligands such as CH<sub>3</sub>CN, piperidine or tetrahydrofuran from their complexes without any rearrangement. Stereospecific synthesis of *cis* and *fac*-isomers can be carried out in two stages in each case as follows.



In 1962, Tate, Knipple and Augl<sup>71</sup> published a seminar paper on the synthesis of the important starting material *fac*-M(CO)<sub>3</sub>(NCMe)<sub>3</sub> (M= Cr, Mo, or W) by refluxing M(CO)<sub>6</sub> in acetonitrile for various periods of time. These zerovalent tris (acetonitrile) complexes, Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub> have been used as a starting material for preparation of a wide range of organotransition-metal complexes. They are also used as reactive source of Mo(CO)<sub>3</sub> fragments since the nitrile can be displaced at lower temperature than the original carbonyl ligands.

Muriithi and Westland<sup>34</sup>, in their study aimed at finding out the maximum substitution possible when the halocarbonyls  $[\text{Mo}(\text{CO})_4\text{X}_2]_2$  are treated with large excess of poor  $\pi$ -bonding ligands, showed that complexes of the type,  $\text{Mo}(\text{CO})_{6-n}\text{L}_n$  ( $n = 0,1,2$ ) could be prepared through disproportionation of the halocarbonyl,  $[\text{Mo}(\text{CO})_4\text{X}_2]_2$ .

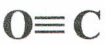

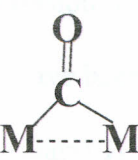
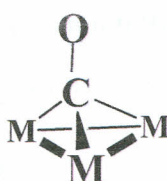
### 2.3 Identification of Molybdenum Carbonyl by Infrared Spectroscopy

Physical techniques are widely used to obtain structural information at a molecular level in inorganic chemistry<sup>72, 73, 74</sup>. A quick and convenient bench-top spectroscopic analysis of a sample will often allow chemists insight into a structural problem without recourse to single crystal x-ray diffraction study. Vibrational spectroscopy is one such spectroscopic technique. Functional groups within a molecule absorb radiation in the spectral range ( $4,000\text{-}200\text{cm}^{-1}$ ) and in doing so vibrate at characteristic frequencies which allow rapid identification of the type of functional groups present in a molecule. Mononuclear metal carbonyl complexes are well suited to study by IR spectroscopy since intense absorption due to the CO oscillations usually occur in the range  $2100\text{-}1850\text{cm}^{-1}$ . Furthermore, this region is also generally free from absorption interference from other functional groups.

The IR spectra provide information not only on the nature of metal-carbon and metal-ligand bonding, but also on the structure of the compound. One of the common applications of IR spectra is that of detecting the presence of both terminal and bridging CO groups: As one goes from a terminal CO-bonding mode to  $\mu_2$ -bridging and finally  $\mu_3$ -bridging, there is a relatively dramatic drop in the CO stretching frequency seen in the IR.



**Table 2: CO-bonding Modes**

				
	free CO	terminal mode	$\mu_2$ -bridging	$\mu_3$ -bridging
$\nu_{\text{CO}}$ IR ( $\text{CM}^{-1}$ )	2143	2120 - 1850	1850 - 1720	1730 - 1500

The position of the carbonyl bands in the IR depends mainly on the bonding mode of the CO (terminal, bridging) and the amount of electron density on the metal being  $\pi$ -back-bonded to the CO.

Separable geometrical isomers of complexes are common in ligand substituted mononuclear metal carbonyl chemistry. Group theory can be used to predict the number of IR active CO absorption band to be expected for any particular isomer, so that if the structural formula of the metal carbonyl complex is known it is often possible to identify the isomer correctly by examining the CO stretching region of its IR spectrum.

$\text{Mo}(\text{CO})_6$  has  $\text{A}_{1g}$ ,  $\text{E}_g$  and  $\text{T}_{1u}$  stretching modes. Only the modes that have the symmetry property of Cartesian coordinates  $x$ ,  $y$  and  $z$  are active in the IR. Thus the IR spectrum of  $\text{Mo}(\text{CO})_6$  displays a single  $\text{T}_{1u}$  carbonyl stretch. Appendix 2 lists expected IR-active bands in the carbonyl region for several common geometries. In the present study, the complexes were prepared according to convenient literature methods and identified mainly using micro elemental analysis and by examining the CO stretching region of their IR spectra.

## 2.4 Chemistry of Halocarbonyls of Molybdenum(II)

The first substituted halocarbonyl complex of molybdenum(II) namely  $\text{Mo}(\text{CO})_2(\text{diars})\text{I}_2$  (diars =  $\text{C}_6\text{H}_4(\text{AsMe}_2)_2$ ) was prepared by Nigam and Nyhom in 1957<sup>68</sup> (equation 9), since then, many such six and seven-coordinate complexes have been reported<sup>24, 34</sup>.



The three commonly used routes to these halocarbonyl complexes are:

- (i) The oxidation of complexes of molybdenum(0) containing strong-field ligands.
- (ii) Reaction of the reactive tetrahalooctacarbonyldimolybdenum(II).
- (iii) Halogen oxidation of  $\text{Mo}(\text{CO})_3(\text{NCMe})_3$  in acetonitrile.

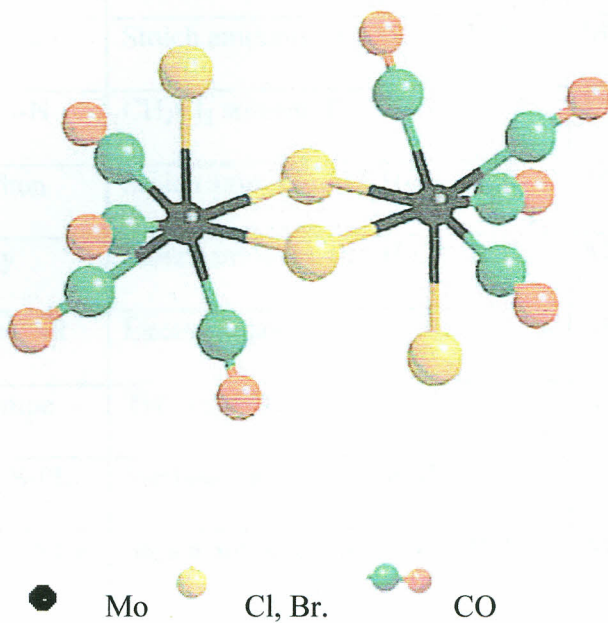
An early example of type (i) is given in reaction (9)

During the period, 1966 to 1971 Colton et al<sup>28, 75 76 77 78</sup> investigated the chemistry of  $[\text{Mo}(\text{CO})_4\text{X}_2]_2$  (M=Mo, W; X = Cl, Br, I) (fig 3) with strong-field ligands and obtained a wide range of six and seven coordinate complexes of molybdenum(II) (table 3). Similar complexes were prepared by Baker et al in 1984 through halogen oxidation of  $\text{Mo}(\text{CO})_3(\text{NCMe})_3$  in acetonitrile<sup>25</sup>.



Ten years later the same workers<sup>26</sup> developed a better route to the dibromo-complexes  $\text{Mo}(\text{CO})_3(\text{NCMe})_2\text{Br}_2$ , by carrying out the reaction of *fac*-  $\text{Mo}(\text{CO})_3(\text{NCMe})_3$  with  $\text{Br}_2$  at  $-78^\circ\text{C}$ . In the period between 1986 and 1998, these researchers have been able to prepare over 1900 new compounds using complexes of the type  $\text{M}(\text{CO})_3(\text{NCMe})_2\text{XY}$  (M=Mo, W; X=Cl, Y=I; X=Br, Y=I; X=Cl, Y= $\text{GeCl}_3$ ; X=Cl, Y= $\text{SnCl}_3$ ) as a precursor which in

turn have been prepared by oxidation of *fac*-  $\text{Mo}(\text{CO})_3(\text{NCMe})_3$  with a range of other oxidizing agents XY (XY=ICl, IBr,  $\text{GeCl}_4$ ,  $\text{SnCl}_4$ )<sup>79</sup>.



**Fig.3:** Structure of Halocarbonyls,  $[\text{Mo}(\text{CO})_4\text{X}_2]_2$

**Table 3: Some Complexes of Molybdenum(II) Prepared Using the Halocarbonyl as the Starting Material**

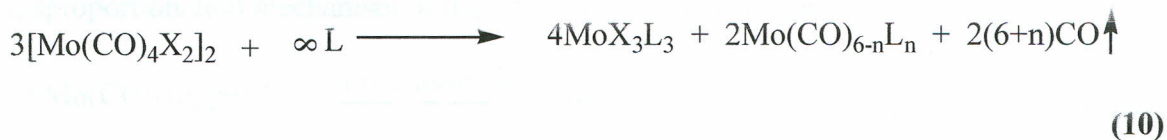
Reactants	Conditions	Product	Ref
$[\text{Mo}(\text{CO})_4\text{Br}_2]_2 + 2\text{AsPh}_3$	Stoich amounts in $\text{Me}_2\text{CO}$ R.T.	$\text{Mo}(\text{CO})_3(\text{AsPh}_3)_2\text{Br}_2$	75
$[\text{Mo}(\text{CO})_4\text{Br}_2]_2 + 2\text{SbPh}_3$	Stoich amounts in $\text{Me}_2\text{CO}$ R.T.	$\text{Mo}(\text{CO})_3(\text{Sbph}_3)_2\text{Br}_2$	75
$[\text{Mo}(\text{CO})_4\text{Cl}_2]_2 + 2\text{PPh}_3$	Stoich amounts in $\text{CH}_2\text{Cl}_2$ R.T.	$\text{Mo}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}_2$	76
$[\text{Mo}(\text{CO})_4\text{Cl}_2]_2 + 2\text{dam}$	Stoich amounts in $\text{CH}_2\text{Cl}_2$ R.T.	$\text{Mo}(\text{CO})_3(\text{dam})_2\text{Cl}_2$	77
$[\text{Mo}(\text{CO})_4\text{Cl}_2]_2 + \text{As-N}$	$\text{CH}_2\text{Cl}_2$ solvent R. T.	$\text{Mo}(\text{CO})_3(\text{As-N})\text{Cl}_2$	78
$[\text{Mo}(\text{CO})_4\text{Cl}_2]_2 + \text{Phen}$	Stoich amounts in $\text{CH}_2\text{Cl}_2$ R.T.	$\text{Mo}(\text{CO})_3(\text{Phen})\text{Cl}_2$	80
$[\text{Mo}(\text{CO})_4\text{Cl}_2]_2 + \text{py}$	Stoich amounts in $\text{CH}_2\text{Cl}_2$ R.T.	$\text{Mo}(\text{CO})_3(\text{py})_2\text{Cl}_2$	80
$[\text{Mo}(\text{CO})_4\text{Cl}_2]_2 + \infty\text{CNR}$	Excess ligand R. T.	$\text{Mo}(\text{CNR})_5\text{Cl}_2$	81
$[\text{Mo}(\text{CO})_4\text{Cl}_2]_2 + \text{dmpe}$	THF as solvent	$\text{Mo}(\text{dmpe})_2\text{Cl}_2$	82
$[\text{Mo}(\text{CO})_4\text{Cl}_2]_2 + \text{H}_2\text{S}_2\text{Ph}_2$	Methanol as solvent at R. T.	$\text{Mo}(\text{CO})_3(\text{S}_2\text{PPh}_3)_2\text{Cl}_2$	83
$[\text{Mo}(\text{CO})_4\text{X}_2]_2 + \text{NCR}$ (x=Cl, Br)	Stoich amounts in $\text{CH}_2\text{Cl}_2$ R.T.	$\text{Mo}(\text{CO})_3(\text{NCR})_2\text{X}_2$	84
$[\text{Mo}(\text{CO})_4\text{X}_2]_2 + \text{btp}$ (x=Cl, Br)	Stoich amount EtOH, R. T.	$\text{Mo}(\text{CO})_3(\text{btp})_2\text{X}_2$	85

KEY: stoich  $\equiv$  stoichiometric. R.T  $\equiv$  room temperature.

btp  $\equiv$  N-n butylthiopicolinamide.

## 2.5 Disproportionation Reaction of the Halocarbonyl $[\text{Mo}(\text{CO})_4\text{X}_2]_2$ ( $\text{X}=\text{Cl}, \text{Br}$ )

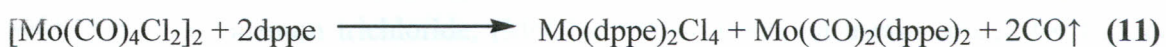
The halocarbonyls,  $[\text{Mo}(\text{CO})_4\text{X}_2]_2$  ( $\text{x}=\text{Cl}, \text{Br}$ ), react with stoichiometric amounts of poor  $\pi$ -bonding ligands such as nitriles  $\text{NCR}$  ( $\text{R}=\text{alkyl}$  or  $\text{aryl}$  radical) to give unstable substituted halocarbonyls of the type  $\text{Mo}(\text{CO})_3(\text{NCR})_2\text{X}_2$ <sup>32</sup> as is the case when halocarbonyl reacts with neutral Lewis bases (electron donor) such as phosphines or isocyanide. In 1972, a study by Westland and Muriithi<sup>34</sup> showed that the molybdenum halocarbonyls,  $[\text{Mo}(\text{CO})_4\text{X}_2]_2$ , ( $\text{X} = \text{Cl}, \text{Br}$ ) react with excess ligands of poor  $\pi$ -bonding ability such as nitriles, ether, thioethers and even pyridine at room temperature to give both  $\text{Mo}(\text{III})$  and  $\text{Mo}(0)$  species. One of the zerovalent molybdenum species was clearly shown to be molybdenum hexacarbonyl,  $\text{Mo}(\text{CO})_6$ . The mechanism proposed for a general disproportionation reaction is:-



This proposed mechanism was tested by preparing a partially substituted halocarbonyl,  $\text{Mo}(\text{CO})_3\text{L}_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{L} = \text{nitrile}$ ), which was then mixed with a large excess of the nitrile and refluxed for twelve hours. The reaction products contained both  $\text{MoX}_3\text{L}_3$  and  $\text{Mo}(\text{CO})_6$ . The disproportionation reaction was confirmed by use of  $\text{Mo}(\text{CO})_2\text{py}_2\text{Cl}_2$  and  $\text{Mo}(\text{CO})_3(\text{NCCH}_3)\text{Cl}_2$  both of which contained neither trivalent nor zerovalent molybdenum. When they were dissolved in pyridine and acetonitrile respectively, molybdenum(III) complexes and molybdenum hexacarbonyl were recovered. Molybdenum hexacarbonyl was recovered from the filtrate in the reaction of  $\text{Mo}(\text{CO})_2\text{py}_2\text{Cl}_2$  with pyridine by acidifying the filtrate with sulphuric acid. This ruled out

the possibility that the molybdenum hexacarbonyl,  $\text{Mo}(\text{CO})_6$  was an impurity in the starting material <sup>32</sup>.

Muriithi and Nthumbi<sup>82</sup> in their attempt to prepare complexes of the type  $\text{Mo}(\text{CO})_2(\text{diphos})_2\text{X}_2$  by reacting  $[\text{Mo}(\text{CO})_4\text{X}_2]_2$  with bis(diphenylphosphino)ethane under forcing conditions of high temperature, obtained  $\text{Mo}(\text{dppe})_2\text{Cl}_4$  which was a molybdenum(IV) complex. This was a disproportionation reaction of the form:



However no zero-valent complex was isolated. This reaction was later confirmed by Changamu and Muriithi, after reacting halocarbonyl  $[\text{Mo}(\text{CO})_4\text{Br}_2]_2$  with the same ligand under similar conditions to form  $\text{Mo}(\text{dppe})_2\text{Br}_4$  and  $\text{Mo}(\text{CO})_2(\text{dppe})_2$  <sup>27</sup>. A disproportionation mechanism of the type shown below was proposed.



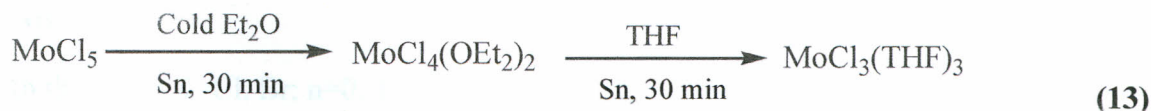
Hence, the disproportionation reaction gave Mo(IV) and Mo(0) species.

Cotton and Poli<sup>86</sup> used the THF as a solvent and some monodentate phosphine ligands and reported that molybdenum(II) disproportionates to molybdenum(III) and molybdenum(0). In the same paper it was reported that when toluene was used as the solvent some molybdenum(III) complexes were also isolated. Whereas ligands of poor  $\pi$ -bonding ability such as tetrahydrofuran are known to cause disproportionation of molybdenum(II)<sup>34,35</sup>, it was not at all clear whether this was the case in Cotton's work or whether the disproportionation was caused by the phosphine ligand.

## 2.6 Chemistry of Molybdenum (III)

All the trihalides  $\text{MoX}_3$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) are known. These trihalides except  $\text{MoI}_3$  are prepared by reduction of the higher member of the series with molybdenum metal, hydrogen or a hydrocarbon<sup>83</sup>. Reduction of  $\text{MoF}_5$  with either molybdenum metal or  $\text{SbF}_3$  gives the trifluoride which can be removed from the starting material by distillation. The trichloride is best obtained by reduction of molybdenum pentachloride with molybdenum metal, hydrogen<sup>84</sup> or with hydrocarbon. Electrolytic reduction of  $\text{Mo(VI)}$  in hydrochloric acid gives molybdenum trichloride,  $(\text{MoCl}_6)^{3-}$  in solution, a useful source for further reaction as the solid halide is not soluble in acids<sup>21</sup>.

A large number of neutral complexes of the type  $\text{MoX}_3\text{L}_3$  ( $\text{X} = \text{halide}$ ;  $\text{L} = \text{neutral ligands}$ ) are known. These are easily prepared by direct reaction between excess  $\text{L}$  and  $(\text{MoX}_6)^{3-}$  species. As noted earlier, these can also be prepared via the disproportionation reaction of the corresponding  $\text{Mo(II)}$  complexes  $[\text{Mo}(\text{CO})_4\text{X}_2]_2$  with excess neutral ligand acting as the solvent<sup>32</sup>. This reaction has been used to prepare  $\text{MoCl}_3(\text{THF})_3$  in high yield which is useful starting material for the synthesis of other  $\text{Mo(III)}$  compounds. A few examples of such compounds are given in the table 3. Trichloro-tris(tetrahydrofuran)molybdenum(III) has also been prepared by reduction of  $\text{MoCl}_5$  with tin powder in a cold dry and degassed  $\text{Et}_2\text{O}$  followed by addition of dry and degassed tetrahydrofuran<sup>85</sup>.



**Table 4: Complexes of the type  $\text{MoX}_3\text{L}_3$  Made Through Disproportionation of Molybdenum(II) <sup>32</sup>.**

Reactants	Products
$[\text{Mo}(\text{CO})_4\text{X}_2]_2 + \text{CH}_3(\text{CH}_2)_3\text{CN}$ (neat)	$\text{MoX}_3(\text{NC}(\text{CH}_2)_3\text{CH}_3)_3$ + $\text{Mo}(\text{CO})_{6-n}(\text{NC}(\text{CH}_2)_3\text{CH}_3)_n$
$[\text{Mo}(\text{CO})_4\text{X}_2]_2 + (\text{CH}_3)_2\text{CHCN}$ (neat)	$\text{MoX}_3(\text{NCCH}(\text{CH}_3)_2)_3$ + $\text{Mo}(\text{CO})_{6-n}(\text{NCCH}(\text{CH}_3)_2)_n$
$[\text{Mo}(\text{CO})_4\text{X}_2]_2 + \text{py}$ (neat)	$\text{MoX}_3\text{py}_3 + \text{Mo}(\text{CO})_{6-n}(\text{py})_n$
$[\text{Mo}(\text{CO})_4\text{X}_2]_2 + \text{CH}_3\text{CH}_2\text{CN}$ (neat)	$\text{MoX}_3(\text{NCCHCH}_3)_3$ + $\text{Mo}(\text{CO})_{6-n}(\text{NCCHCH}_3)_n$
$[\text{Mo}(\text{CO})_4\text{X}_2]_2 + \text{C}_4\text{H}_8\text{S}$ (neat)	$\text{MoX}_3(\text{C}_4\text{H}_8\text{S})_3 + \text{Mo}(\text{CO})_{6-n}(\text{C}_4\text{H}_8\text{S})_n$
$[\text{Mo}(\text{CO})_4\text{X}_2]_2 + \text{PhCN}$ (neat)	$\text{MoX}_3(\text{NPh})_3 + \text{Mo}(\text{CO})_{6-n}(\text{NPh})_n$
$[\text{Mo}(\text{CO})_4\text{X}_2]_2 + \text{C}_4\text{H}_8\text{O}$ (neat)	$\text{MoX}_3(\text{C}_4\text{H}_8\text{O})_3 + \text{Mo}(\text{CO})_{6-n}(\text{C}_4\text{H}_8\text{O})_n$

**NB.**

In this table  $\text{X}=\text{Cl}, \text{Br}$ ;  $n=0, 1, 2$



Neutral complexes of the type  $\text{MoCl}_3 \cdot 3\text{NCR}$  were made by Smith and Wedd by treatment of molybdenum(III) chloride with appropriate nitrile at room temperature<sup>87</sup>. Similar complexes were reported by Fowles and Coworkers after reacting  $\text{MoBr}_3$  with alkyl nitrile in a sealed tube<sup>88</sup>. Complexes of the type  $\text{MoX}_3\text{py}_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ) have been prepared by refluxing  $\text{K}_3\text{MoCl}_6$  with pyridine at  $115 - 117^\circ\text{C}$  or by heating molybdenum(III) chloride and pyridine in a sealed tube at  $270^\circ\text{C}$ <sup>89</sup>.

In 1957 Steele reported that  $(\text{NH}_4)_3\text{MoCl}_6$  reacted with 1,10 phenanthroline or 2,2'-bipyridyl in dilute hydrochloric acid/ethanol mixture to give  $\text{Mo}(\text{Phen})_3\text{Cl}_3$  and  $\text{Mo}(\text{bipy})_3\text{Cl}_3$ , respectively<sup>90</sup>. Steele claimed further that, the Bromo complexes,  $\text{Mo}(\text{Phen})_3\text{Br}_3$  were obtained from the reaction of  $\text{K}_3\text{MoBr}_6$  with the ligand. These claims were shown by other workers to be incorrect<sup>32</sup>, substitution of the three halides in  $(\text{MoX}_9)^{-3}$  by neutral ligands gives complexes of the type  $\text{Mo}_2\text{X}_6\text{L}_3$  ( $\text{L} =$  neutral ligand,  $\text{X} = \text{Cl}, \text{Br}$ ). These are dimeric complexes in which halide-bridge is retained. One example is  $(\text{Mo}_2\text{Cl}_6(\text{THF}))_3$  which is formed from monomeric  $(\text{MoCl}_3(\text{THF}))_3$  in solution<sup>70</sup>.

## CHAPTER THREE

### 3.0 EXPERIMENTAL

#### 3.1 Introduction

In this chapter, experimental techniques such as: - Cleaning of apparatus, Purification of organic solvents and reagents, Generation of oxygen-free nitrogen, Filtration and storage of air sensitive compounds, Analytical techniques and Physical measurements are discussed. The procedures for preparation of the halocarbonyls,  $[\text{Mo}(\text{CO})_4\text{X}_2]_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ), trivalent molybdenum complexes of the type  $\text{MoX}_3(\text{THF})_3$  and their reduction by zinc dust in the presence of carbon monoxide are also described.

#### 3.2 EXPERIMENTAL TECHNIQUES

##### 3.2.1 Cleaning of Apparatus

###### (i) Glassware

###### Glassware without grease

The glassware without grease was cleaned with liquid detergent and tap water, then filled with chromic acid (prepared by dissolving potassium dichromate in concentrated sulphuric acid) and kept overnight. The acid was removed, the glassware washed with tap water, rinsed several times with distilled water and dried at  $130^\circ\text{C}$  in an electric oven for at least two hours.

###### Glassware with Grease

Glassware with impurities which could not dissolve in water such as grease were washed with halogenated organic solvents such as dichloromethane or chloroform. The glassware

was then filled with freshly prepared chromic acid or immersed in it and kept overnight. The acid was removed and the glassware treated as explained in section 3.2.1 (i) above.

### **(ii) Sintered Glass Filter Crucibles**

Sintered glass filter crucibles of porosity No. 4 were used. Each crucible was cleaned from surface contamination using liquid detergent and tap water, rinsed with a lot of distilled water and then placed on a crucible holder in a suction flask. With gentle suction, several small 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 at 120 – 130 °C for one to two hours. The hot crucibles were transferred into the dessicator with clean crucible tongs and cooled for 30 to 40 minutes, then weighed accurately. After analysis the crucibles were cleaned as follows: the cake of the analyzed sample was removed and the crucible placed in a beaker. About 6 ml of concentrated ammonia solution was put in each crucible and the beaker covered with a watch glass. After 10 to 15 minutes the crucibles were transferred to the crucible holder in a suction flask and washed with several portions of distilled water. If the filter plate was dark after washing, it was treated in same way with a few milliliters of concentrated nitric acid and then washed well.

### **(iii) IR Cells**

These were washed with suitable distilled organic solvents such as acetone.

### 3.2.2 PURIFICATION OF ORGANIC SOLVENTS AND REAGENTS

#### Organic Solvents

Moisture-free solvents were essential in a number of reactions where the products or the intermediates were moisture-sensitive. The methods of removal of moisture were dependent on the degree of purity required. The methods described below produced solvents sufficiently dry for the preparations described in this thesis. The set-up shown in figure 4 was used for all distillation under nitrogen, while the set-up shown in figure 5 was used for all refluxing.

#### (i) Tetrahydrofuran

This was first treated with anhydrous magnesium sulphate and shaken vigorously to remove the bulk of water present. The solvent was distilled from fresh phosphorous pentoxide (100-200 g. per litre of solvent) and middle portion used.

#### (ii) Dichloromethane

This was soaked in anhydrous magnesium sulphate overnight, after which it was refluxed for 40 minutes over phosphorous pentoxide, and then distilled in an atmosphere of dry oxygen-free nitrogen.

#### (iii) Diethyleneglycoldimethylether (diglyme)

The diethyleneglycoldimethylether was left in contact with sodium metal for 24 hours. The metal was removed and the solvent treated with fresh sodium. This was repeated until the solvent no longer corroded the fresh sodium metal. The solvent was then distilled over the sodium metal in an atmosphere of dry oxygen-free nitrogen, and the

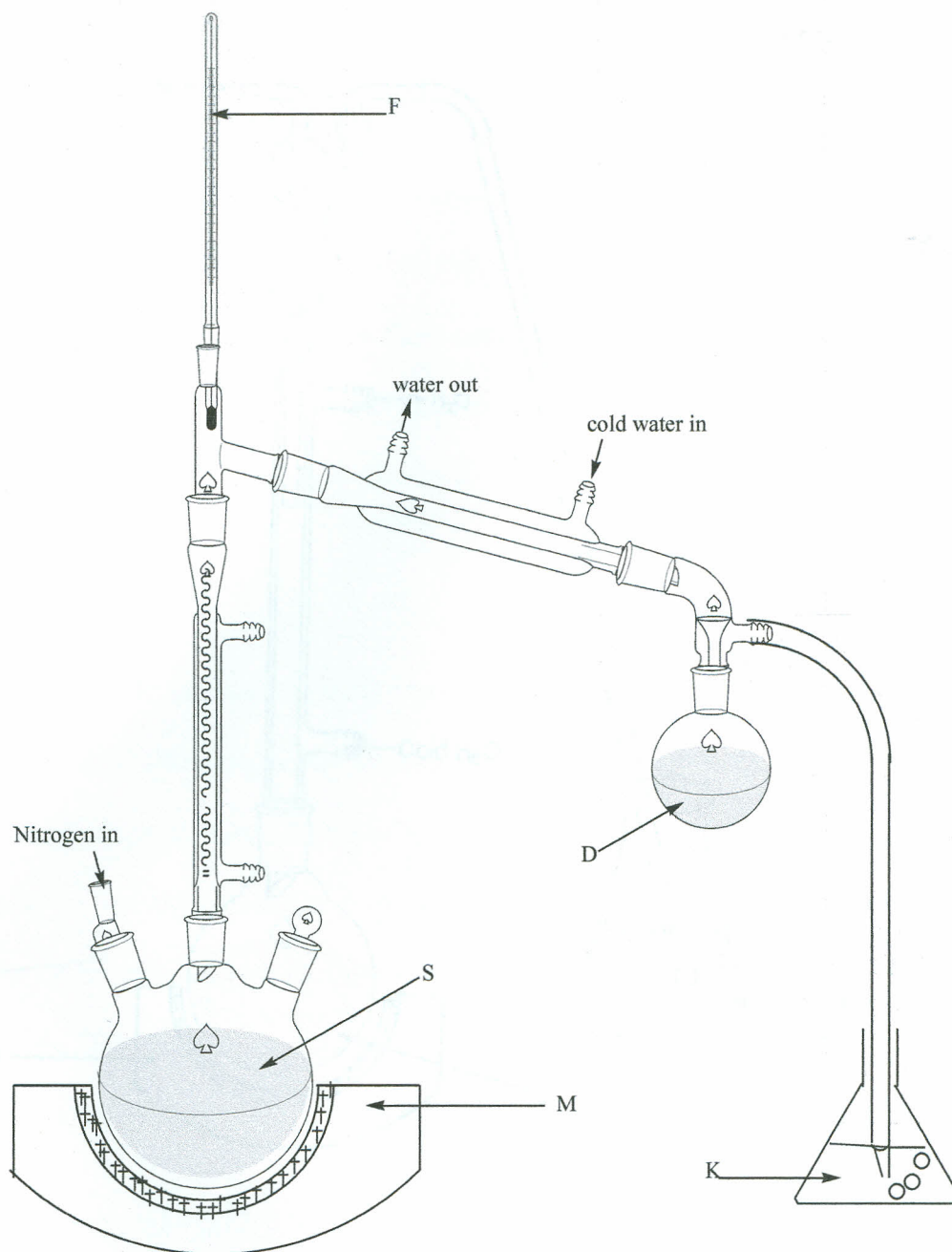
distillate mixed with naphthalene plus some freshly cut sodium metal. When sodium metal dissolved, it formed deep blue solution of sodium naphthalide

(iv) Ethanol

About 300 cm<sup>3</sup> of 95% ethanol were measured into two-neck round bottom flask containing anhydrous magnesium sulphate. The mixture was refluxed for one hour and then distilled off. The middle fraction was collected in dry 250 cm<sup>3</sup> flask. 5 gm of magnesium turnings and a few crystals of iodine were added to the distillate. The mixture was refluxed for one hour and ethanol recovered by distillation under a nitrogen atmosphere.

(v) Diethyl ether

Diethyl ether was first treated with anhydrous magnesium sulphate to remove the bulk of moisture. This mixture was then refluxed for 40 minutes over sodium metal and distilled in an atmosphere of dry oxygen-free nitrogen.



F = Thermometer

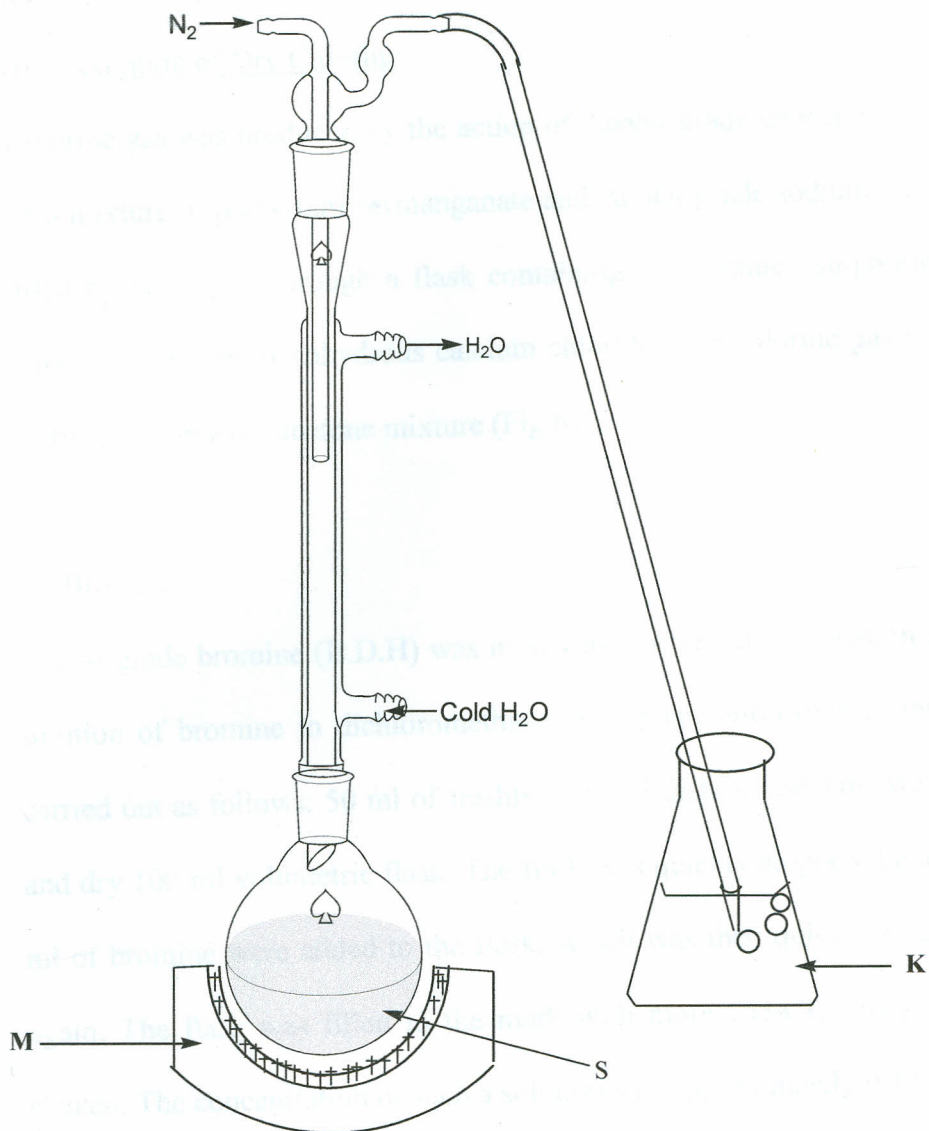
D = dry oxygen-free organic solvent (distillate)

S = Organic solvent

K = Liquid paraffin

M = Electromantle

**Fig.4: Apparatus for Distilling Organic Solvents.**



M = Electro mantle

S = organic solvent / reaction mixture

K = Liquid paraffin

**Fig.5: Apparatus for Refluxing under Nitrogen**

## Reagents

### (i) Preparation of Dry Chlorine

Chlorine gas was produced by the action of Analar grade concentrated hydrochloric acid on a mixture of potassium permanganate and Analar grade sodium chloride. The gas was dried by passing it through a flask containing concentrated sulphuric acid, and finally through a column of anhydrous calcium chloride. The chlorine gas was liquefied at  $-78^{\circ}\text{C}$  by use of dry ice-acetone mixture (Fig 6).

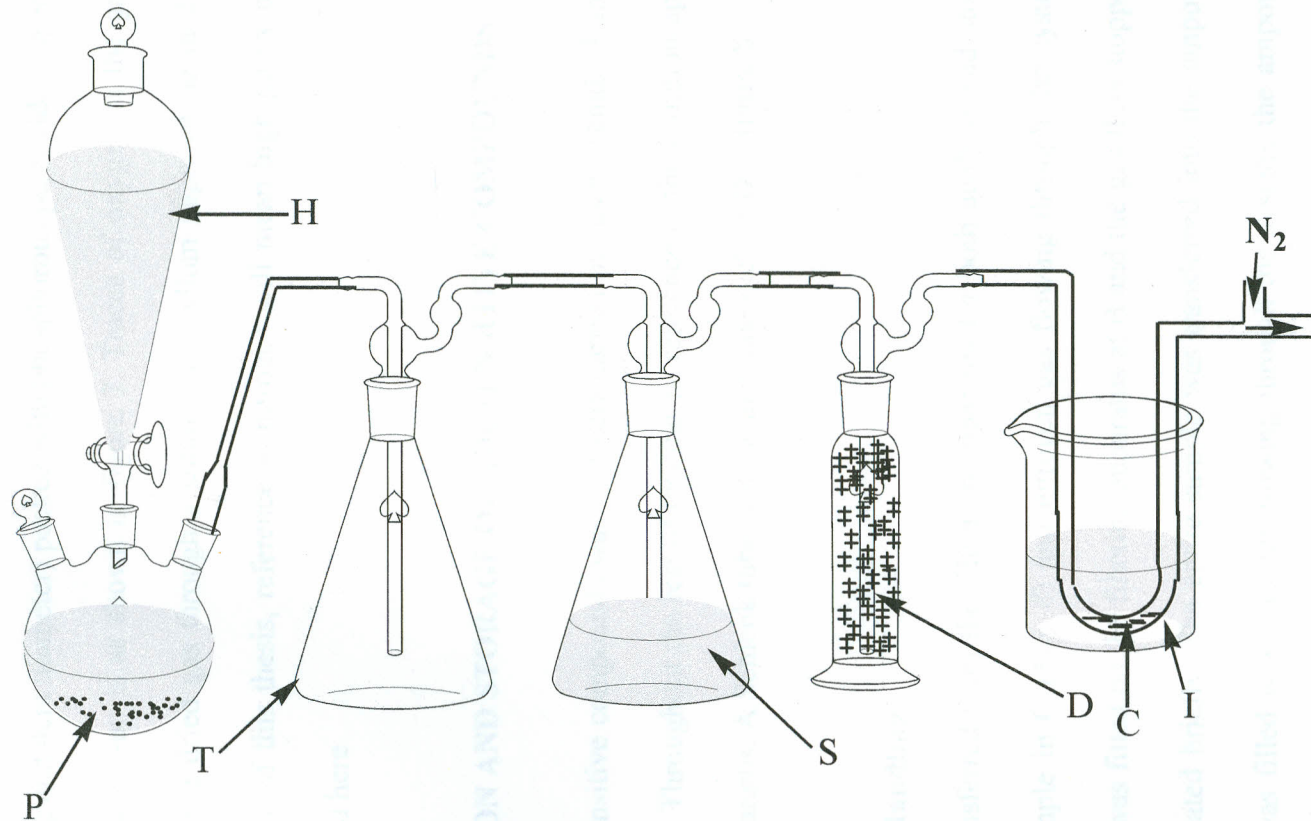
### (ii) Bromine

Analar grade bromine (B.D.H) was used with no further purification to prepare standard solution of bromine in dichloromethane. The preparation of the standard solution was carried out as follows: 50 ml of freshly distilled dichloromethane were placed in a clean and dry 100-ml volumetric flask. The flask was quickly stoppered and weighed. About 9 ml of bromine were added to the flask, which was then quickly stoppered and weighed again. The flask was filled to the mark with more  $\text{CH}_2\text{Cl}_2$ , stoppered and thoroughly shaken. The concentration of such a solution was approximately 0.32 g/ml.

### (iii) Hydrochloric acid, Molybdenum(VI) Oxide and Sodium Molybdate

These reagents were obtained from Kobian Kenya Limited and used without further purification.





H = Concentrated hydrochloric acid.

D = Phosphorous pentoxide or anhydrous calcium chloride.

P = Potassium permanganate

S = Concentrated sulphuric acid.

I = Dry ice / acetone

C = Liquid chlorine

T = Trap

N<sub>2</sub> = Oxygen-free nitrogen.

**Fig. 6: Apparatus for Generating Dry Chlorine Gas.**

### 3.2.3 GENERATION OF DRY OXYGEN-FREE NITROGEN.

Dry oxygen-free nitrogen was obtained by further purification of high purity nitrogen gas obtained from B.O.C Kenya Limited. The gas was dried by passing it through a glass column (92cm long and 4cm diameter) packed with phosphorous pentoxide suspended on pumice stones. The set-up is as shown in figure 7. Traces of oxygen in the gas were removed by bubbling dried gas through a solution of sodium naphthalene in diglyme. Throughout the rest of this thesis, reference to nitrogen will mean high purity nitrogen treated as described here

### 3.2.4 FILTRATION AND STORAGE OF AIR-SENSITIVE COMPOUNDS

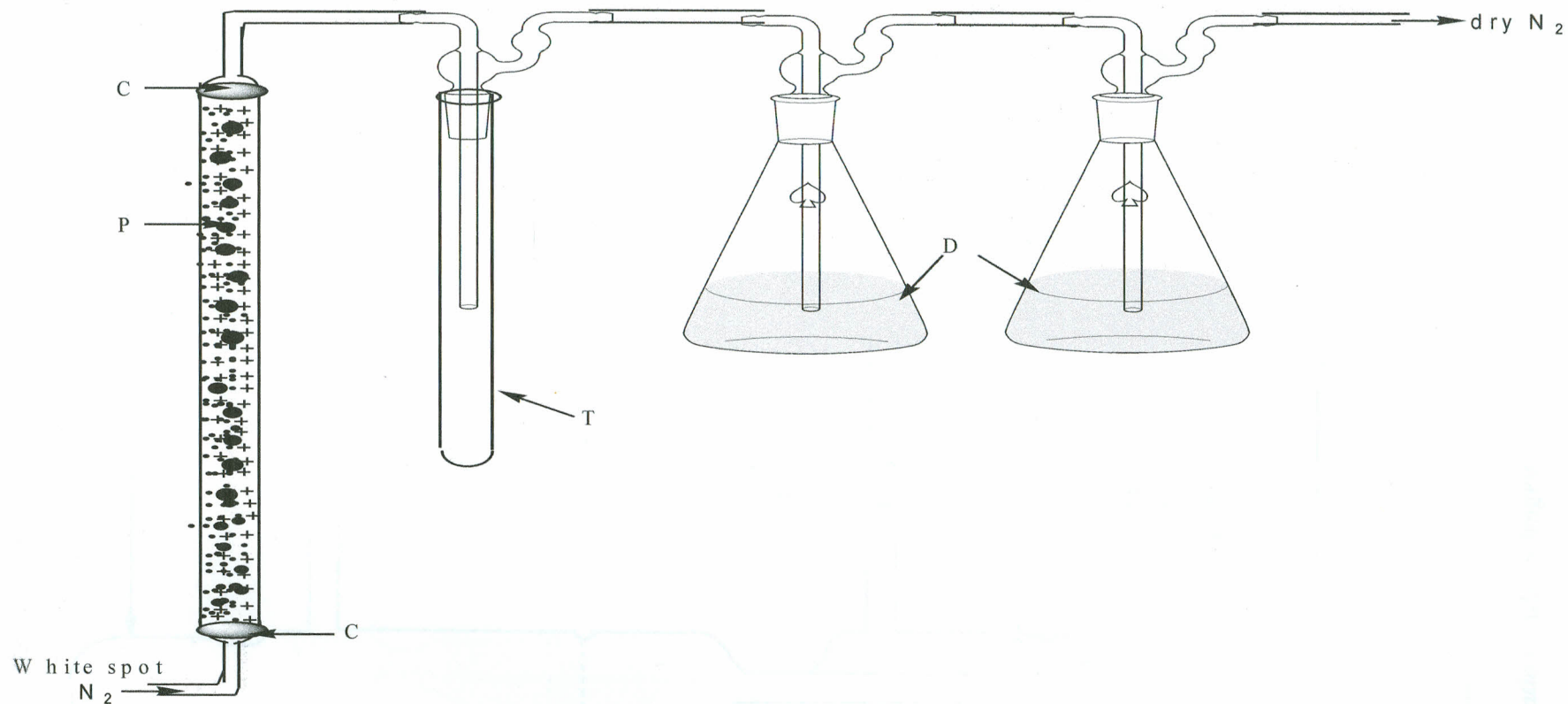
#### **Filtration**

Filtration of air-sensitive compounds was routinely carried out using standard apparatus shown in figure 8. Throughout the rest of this thesis, reference to the filtration apparatus will mean this apparatus. A Schlenk tube will mean a tube such as D in figure 8.

#### **Storage and Handling.**

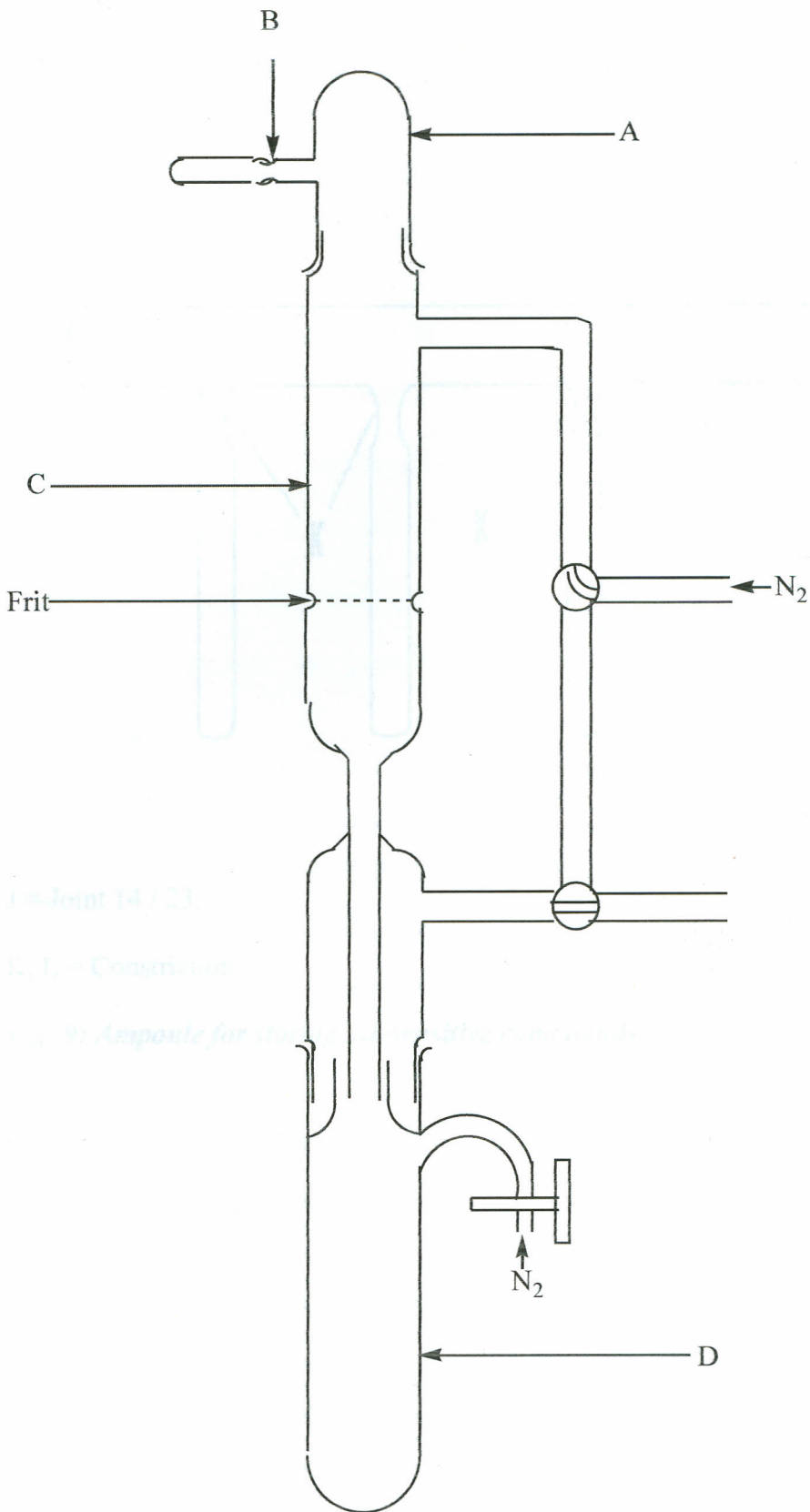
Samples were transferred from the filtration apparatus for both analysis and storage as follows: With sample in C (*Fig. 8*) and nitrogen gas flowing through the system, the ampoule (*Fig. 9*) was fitted on the filtering apparatus at B and the gas flow stopped. The system was evacuated briefly. The entire sample was transferred into the ampoule and then the system was filled with nitrogen flowing through the system, the ampoule was either quickly detached and cocked or sealed with a blow torch at the constriction labeled L. To recover samples from the sealed ampoules, the desired amount of substance was transferred to one of the side arms. The tube was dipped in dry-ice acetone slush bath in a

dewar flask, the side arm with the sample cut off with a blow torch at the constriction labeled K and used either for elemental analysis or physical measurements. Such sample tubes were normally broken open while inside a 1 ½ m x 1 m polythene bag that served as a glove box, while nitrogen was being passed through the bag.

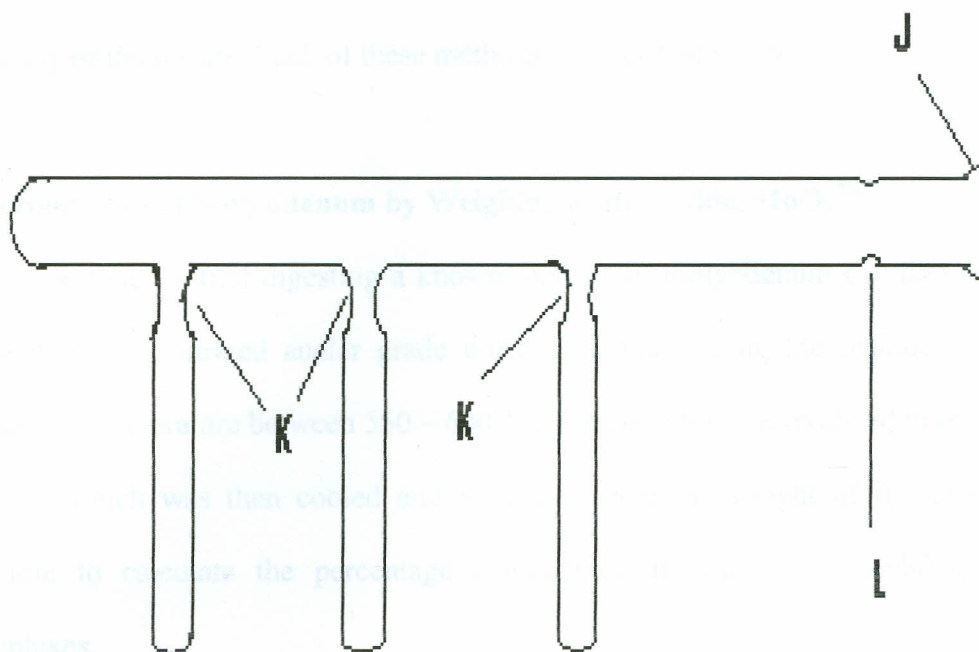


- C = cotton wool  
 D = Sodium naphthalide dispersed in diglyme  
 P = Phosphorous pentoxide supported on pumice stones  
 T = Trap

**Fig.7: Apparatus for generation of dry oxygen-free nitrogen.**



*Fig. 8: Apparatus for filtration under nitrogen*



J = Joint 14 / 23.

K, L = Constriction.

**Fig. 9: Ampoule for storing air-sensitive compounds**

### 3.2.5 ANALYTICAL TECHNIQUES

#### Determination of Molybdenum

Molybdenum was determined gravimetrically using two different methods to compare accuracy of the results. Each of these methods is described below.

#### **Determination of Molybdenum by Weighing as the Oxide, MoO<sub>3</sub><sup>91</sup>**

This was done by first digesting a known amount of molybdenum complex using little amount of concentrated analar grade nitric acid and heating the residue in a marble furnace at temperature between 550 – 600 °C. The complex was oxidized to molybdenum trioxide which was then cooled and weighed. From the weight of the oxide, it was possible to calculate the percentage composition by mass of molybdenum in the complexes.

#### **Determination of Molybdenum by Weighing as Molybdenyl Oxinate,**



8-hydroxyquinoline precipitates many metals. However, its use is made selective by proper pH control and addition of appropriate complexing agents to mask unwanted ions which otherwise interfere with the desired metal precipitate. A quantitative precipitation of molybdenum is achieved in the pH range 3.3-7.6. A pH of 5, achieved with acetic acid-ammonium acetate buffer was employed. The presence of EDTA prevents the interference from Pd, Bi, Hg(II), Cd, Cu(II), Fe(III), Al, Cr(III), Be, Co, Zn, Mn(II), and Ni, when present<sup>91</sup>. During the present work, it was not necessary to add EDTA because there were no interfering ions.

### Preparation of Buffer Solution (pH 5)

30 gm of ammonium acetate,  $\text{CH}_3\text{COONH}_4$  was dissolved in 15 ml glacial acetic acid,  $\text{CH}_3\text{COOH}$ , and diluted to 100 ml.

### Preparation of 3% 8-hydroxyquinoline mixture.

30 gm of 8-hydroxyquinoline was dissolved in 25 ml of glacial acetic acid in 1000 ml beaker. 400 ml of distilled water were added followed by dropwise addition of 4 M ammonium hydroxide,  $\text{NH}_4\text{OH}$ , solution until cloudiness appeared. To this 4 M  $\text{CH}_3\text{COOH}$  was added dropwise until the solution was clear and then diluted to 1000 ml total volume with distilled water.

### Determination of the Molybdenum Content

0.2-0.4 gm of the samples were digested with a few drops of concentrated nitric acid (analar grade) and diluted with 100 ml distilled water. This was filtered into 250-ml volumetric flask and filled to the mark with distilled water. 50 ml of the solution were put into a 250-ml beaker and the pH adjusted to 5 by adding either 1 M  $\text{H}_2\text{SO}_4$  or 1 M  $\text{NaOH}$ . 15 ml of 5% (w/v) EDTA solution were added followed by 5 ml acetic acid-ammonium acetate buffer were added. This solution mixture was diluted with distilled water to approximately 80 ml and heated gently to boiling. A 3% (w/v) 8-hydroxyquinoline was added slowly, and then a few extra drops added until no further precipitation occurred. More oxine was added until the supernatant was slightly yellow in color. The precipitate was digested at boiling temperature for 2-3 minutes, filtered through a porosity No. 4 sintered glass crucible which was cleaned and dried as described in section 2.1(ii). The residue was washed with several portions of hot distilled water until the washings were



colorless indicating that there was no free 8-hydroxyquinoline in the sample. The precipitate,  $\text{MoO}_2(\text{C}_9\text{H}_6\text{ON})_2$ , was dried in an electric oven at 130-135 °C for one hour, cooled and weighed. The process of heating and cooling was repeated until constant weight was attained. The determination was done in duplicate and from the weight the percentage mass of molybdenum in the complex was calculated.

### **Gravimetric Determination of Chloride and Bromide as AgX (X=Cl, Br) <sup>91</sup>**

A known amount of the sample containing either bromide or chloride was first digested using 5 ml of Analar grade concentrated nitric acid and about 100 ml of distilled water added. To this solution, about 2 gm of zinc powder was added a little at a time to reduce chlorate,  $\text{ClO}_3^-$  to chloride,  $\text{Cl}^-$  and bromate,  $\text{BrO}_3^-$  to bromide,  $\text{Br}^-$ . The solution was allowed to cool and then filled into another 250 ml volumetric flask, and the solution made to the mark. 50 ml of this solution was measured and put into a 250 ml beaker, into which about 40 ml of 0.1 M  $\text{AgNO}_3$  was added from the burette. The beaker was then covered with a watch glass and sealed off with aluminum foil to prevent photodecomposition of the silver halide precipitate. The precipitate was warmed up gently on a hot plate to coagulate for about 30 minutes. A few drops of 0.1 M  $\text{AgNO}_3$  were added and when no turbidity was seen, the beaker was kept in dark cupboard for two hours and the precipitate separated by filtration using a pre-weighed G4 sintered glass crucible. It was washed several times with very dilute nitric acid until it gave no turbidity with 0.1 M hydrochloric acid. The precipitate was dried at 140 °C in an electric oven, cooled in a dessicator containing phosphorus pentoxide and weighed. The process of heating and cooling was repeated until there was no significant change in weight.

These determinations were carried out in duplicate to compare the accuracy of the analysis results.

### 3.2.6 PHYSICAL MEASUREMENTS

#### **Infrared Spectra.**

FTIR spectra were recorded in the range  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  on an FTIR-8400 Shimadzu spectrophotometer. Air-stable samples were dissolved in tetrahydrofuran, which was also a reference solvent and measured in rock salt cells. Of particular interest was the region between  $2100$  and  $1800\text{ cm}^{-1}$ . This is because the terminal inorganic  $\nu(\text{CO})$  stretching absorption bands are expected in this spectral range. Details of the sampling techniques carried out are given below.

#### **Liquids**

Liquid samples were held between two KBr cells as a thin film.

#### **Solids**

The following two techniques were employed:

- a) KBr discs: KBr discs were prepared by grinding the samples (0.1-2.0% by weight) with KBr into very fine particles. This was then compressed into a transparent wafer or disc, and spectra recorded.
- b) Mulls: mulls or pastes were prepared by grinding the sample with a drop of mulling agent (liquid paraffin herein referred to as nujol); the mull was then squeezed between transparent windows as for liquid samples and the spectra recorded. The grinding was done with agate mortar and pestle.

## Elemental Analyses

Carbon and hydrogen content were determined at the school of Pure and Applied Chemistry, University of Kwa-zulu Natal on a Perkin Elmer 2400 series II CHNS analyzer.

## Chromatography

Analytical thin layer chromatography (TLC) was conducted on Kreselgel 60 F<sub>24</sub> (Merck) silica gel pre-coated aluminium plate with fluorescent indicator UV<sub>254</sub>. Column chromatography was carried out on neutral alumina (particle size 0.063 – 0.2 mm, 70 – 230 mesh, Aldrich).

## 3.3 PREPARATIVE WORK

### 3.3.1 Preparation of Tetrachlorooctacarbonyldimolybdenum(II), [Mo(CO)<sub>4</sub>Cl<sub>2</sub>]<sub>2</sub>

This halocarbonyl halide was prepared according to the literature method<sup>76</sup> as follows:-

#### Procedure

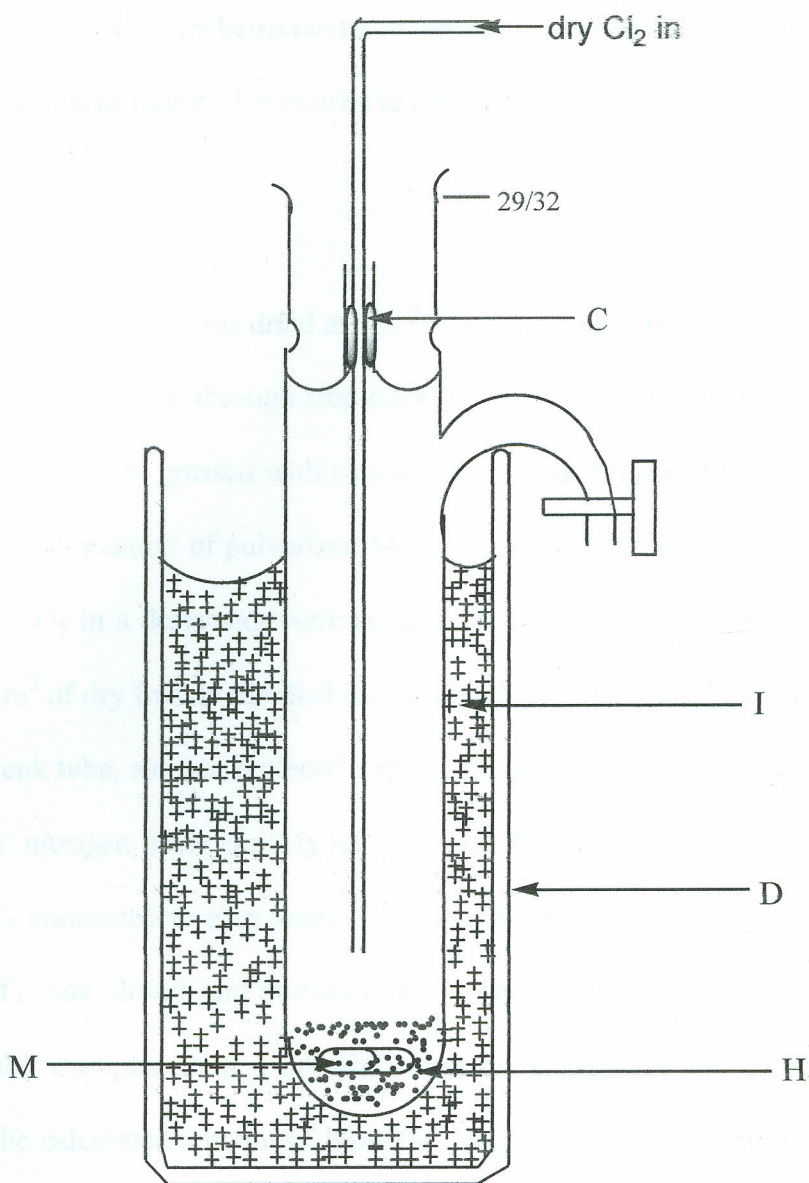
2-6 gm of well-powdered and dried hexacarbonylmolybdenum[0], Mo(CO)<sub>6</sub> were put in dry Schlenk tube which had been evacuated and filled with dry oxygen-free nitrogen (figure 10). The tube was cooled to -78 °C, and Chlorine condensed on the hexacarbonyl until excess liquid chlorine was visible. The tube was removed from the cold bath and allowed to warm up slowly. A vigorous reaction took place with gas evolution and formation of an orange solid. The excess chlorine was allowed to evaporate and last traces removed by flushing the product with nitrogen. The sample was taken immediately for analysis or for preparative work. The elemental analysis of this sample gave the following results:

	Mo	Cl
Found %	34.79	24.80
Calculated % for $C_4Cl_2MoO_4$	34.29	25.41



- Cotton wool
- Wash bottle
- Down flask
- Beaker
- (20% / Cl)

Moisture content for prep...  
NaCO<sub>3</sub> / ...



C = Cotton wool.

I = dry ice / acetone mixture.

D = Dewar flask.

M = Bar magnet.

H =  $\text{Mo}(\text{CO})_6 / \text{Cl}_2 (\text{l})$ .

**Fig.10: Apparatus for preparation of tetrachlorooctacarbonyldimolybdenum(II),  $[\text{Mo}(\text{CO})_4\text{Cl}_2]_2$ .**

### 3.3.2 Preparation of Tetrabromo-octacarbonylmolybdenum(II), $[\text{Mo}(\text{CO})_4\text{Br}_2]_2$

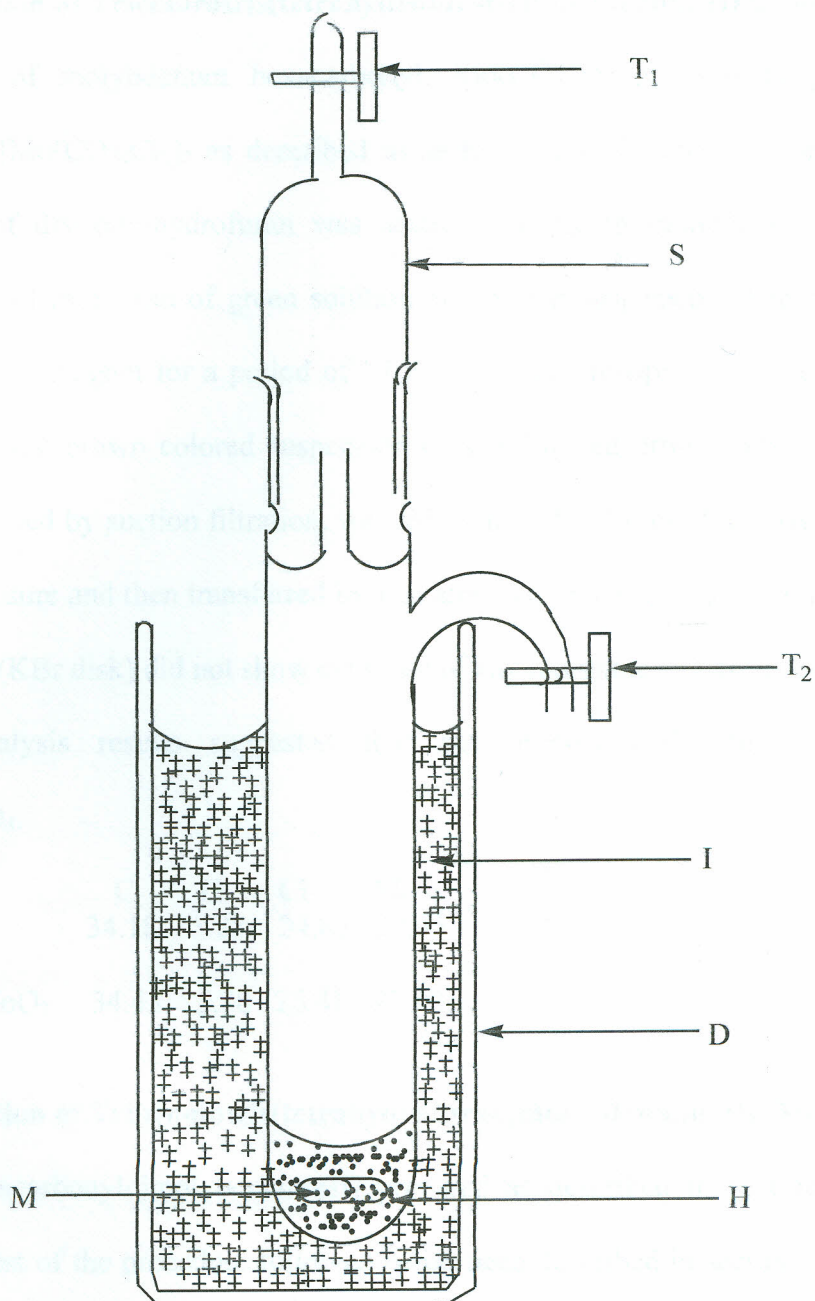
The set-up shown in figure 11 was used to prepare  $[\text{Mo}(\text{CO})_4\text{Br}_2]_2$

#### Procedure

A modified Schlenk tube was dried at  $120^\circ\text{C}$  for one hour then cooled by flushing it with dry oxygen-free nitrogen through stop-cock  $\text{T}_2$ . The joints of the cool Schlenk tube and stopper  $\text{S}$  were lightly greased with silicone grease. As nitrogen was passing through the system, suitable quantity of pulverized  $\text{Mo}(\text{CO})_6$  which had been dried over phosphorous pentoxide,  $\text{P}_2\text{O}_5$  in a desiccator were accurately weighed and put into the Schlenk tube. About  $30\text{ cm}^3$  of dry freshly distilled dichloromethane were added. A bar magnet was put in the Schlenk tube, stopper replaced and the mixture stirred. Stopcocks  $\text{T}_2$  and  $\text{T}_1$  were closed, the nitrogen flow quickly closed, and the mixture pumped off by opening stopcock  $\text{T}_1$  connected to a vacuum. The evacuation was done only for a few seconds. Stopcock  $\text{T}_1$  was closed and stopcock  $\text{T}_2$  opened to fill the tube with nitrogen. The Schlenk tube was placed in a dry ice / acetone slush bath and cooled for about 30 minutes. The calculated amount of bromine was accurately measured with an all plastic syringe and dissolved in about  $10\text{ cm}^3$  of dry freshly distilled dichloromethane. The bromine solution was added onto the cold suspension of the  $\text{Mo}(\text{CO})_6$ . While nitrogen was being passed through stopcock  $\text{T}_2$ , the stopper was quickly replaced and the Schlenk tube removed from the dry-ice / acetone slush bath. The mixture was stirred vigorously as the tube was allowed to warm-up slowly. A vigorous reaction took place with evolution of colorless gas giving an orange product. The solvent was pumped off and a sample of the solid left analyzed. Its empirical formula was found to be:  $\text{Mo}(\text{CO})_4\text{Br}_2$ ,

	Mo	Br
Found %	25.82	42.98
Calculated for $C_4Br_2MoO_4$	26.09	43.45

The molecular formula for this complex is known to be  $[Mo(CO)_4Br_2]_2$  or as  $Mo_2(CO)_8Br_4$ <sup>70</sup>



$T_1, T_2$  = Stopcocks

M = Bar magnet.

I = dry ice / acetone mixture.

H =  $\text{Mo}(\text{CO})_6 / \text{Br}_2(\text{l})$ .

D = Dewar flask.

**Fig. 11: Apparatus for the preparation of tetrabromo-octacarbonyldimolybdenum(II),  $[\text{Mo}(\text{CO})_4\text{Br}_2]_2$ .**



### 3.3.3 Preparation of Trichlorotris(tetrahydrofuran)molybdenum(III), $\text{MoCl}_3(\text{THF})_3$

About 3 gm of molybdenum hexacarbonyl,  $\text{Mo}(\text{CO})_6$  were used to prepare the halocarbonyl,  $[\text{Mo}(\text{CO})_4\text{Cl}_2]_2$  as described in section 3.3.1. To this solid in a Schlenk tube, excess of dry tetrahydrofuran was added resulting in immediate evolution of colorless gas and formation of green solution and brown suspension. The mixture was stirred with a bar magnet for a period of 17 hours in an atmosphere of nitrogen within which the original brown colored suspension changed to red brown. The resulting red solid was collected by suction filtration, washed with 4 x 20 ml of diethyl ether, dried in reduced pressure and then transferred into an ampoule under nitrogen. An IR spectrum of the product (KBr disk) did not show evidence of any inorganic CO group (spectrum 1). Elemental analysis results suggested that the product had empirical formula,  $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{MoO}_3$ .

	C	H	Cl	Mo
Found %	34.18	5.28	24.82	22.95
Calculated % of $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{MoO}_3$	34.43	5.78	25.41	22.92

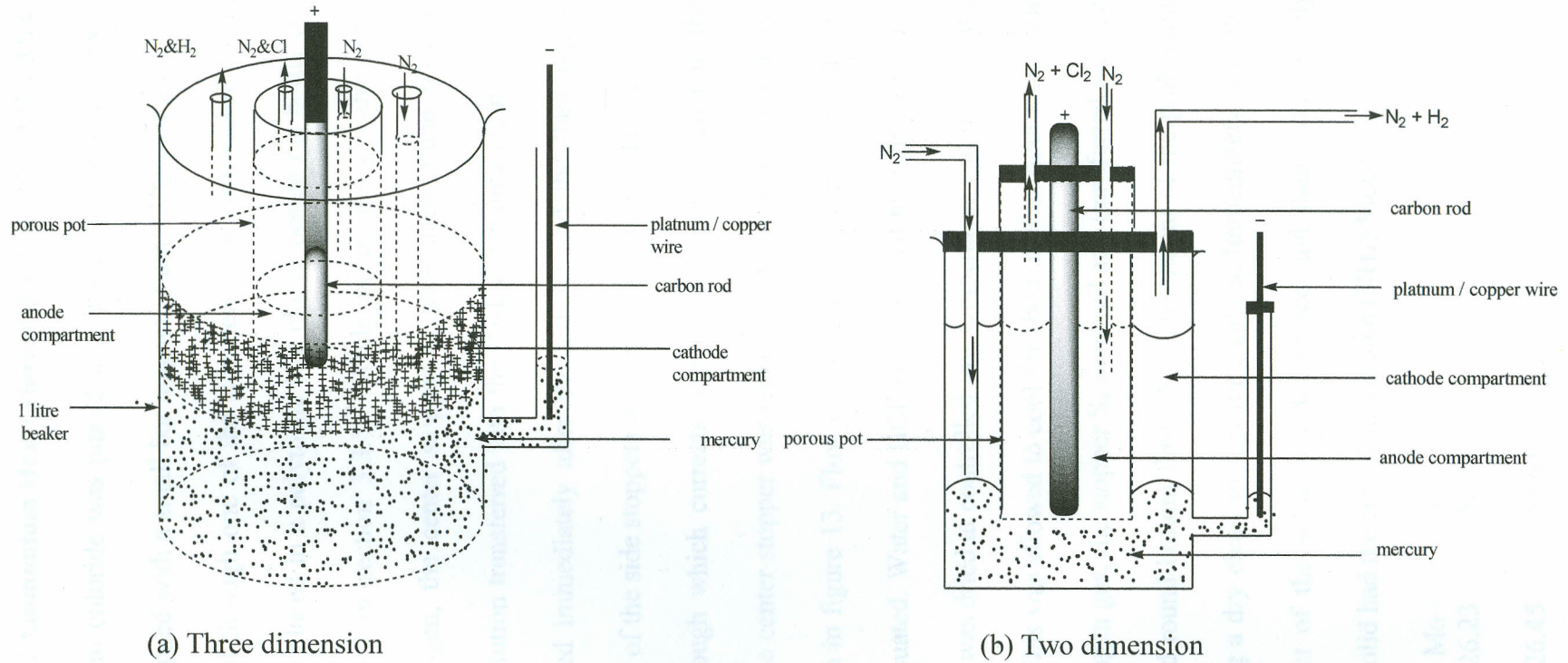
### 3.3.4 Preparation of Tribromotris(tetrahydrofuran)molybdenum(III), $\text{Mo}(\text{THF})_3\text{Br}_3$

Tetrabromooctacarbonyldimolybdenum(II) prepared as described in section 3.3.2 was used and the rest of the procedure followed is has been described in section 3.3.3 above. An infrared spectrum of the solid run in THF (spectrum 2) did not show evidence of any inorganic CO group. The elemental analysis of the sample gave the following results:

	C	H	Br	Mo
Found %	25.74	4.08	42.79	17.15
Calculated % of $\text{C}_{12}\text{H}_{24}\text{Br}_3\text{MoO}_3$	26.11	4.38	43.43	17.38

### 3.3.5 Preparation of Chloro Species, $\text{MoCl}_6^{3-}$ by Electrolytic Reduction of Molybdate in Hydrochloric Acid

10 gm of sodium molybdate,  $\text{Na}_2\text{MoO}_4\cdot\text{H}_2\text{O}$  were warmed with 175 ml of 12 M HCl until dissolution was almost complete. This mixture was transferred to the cathode compartment of the cell shown in the figure 12. The anode chamber was filled with 6 M HCl to the same level as the cathode compartment. Electrolysis was performed by passing a current of about 1.5 amperes at 4 volts with streams of nitrogen passed slowly through the electrolyte to expel chlorine and hydrogen gas from the anode and cathode compartment respectively. The color of the solution changed on introduction of the direct current, from light green to deep green to brown and finally to deep red. This change took place within a period of 18 hours. In a flow of nitrogen, the porous pot was removed and immediately the mouth of the beaker covered with cling foil. This was then placed in a polythene bag filled with nitrogen. The cling foil was removed in a nitrogen atmosphere and the deep red solution decanted carefully into a dry clean bottle which was well flushed with nitrogen. The bottle was then stoppered and left in a polythene bag whose all outlets were covered. As expected, the chloro complex,  $\text{MoCl}_6^{3-}$ , did not show evidence of any CO groups (spectrum 3).



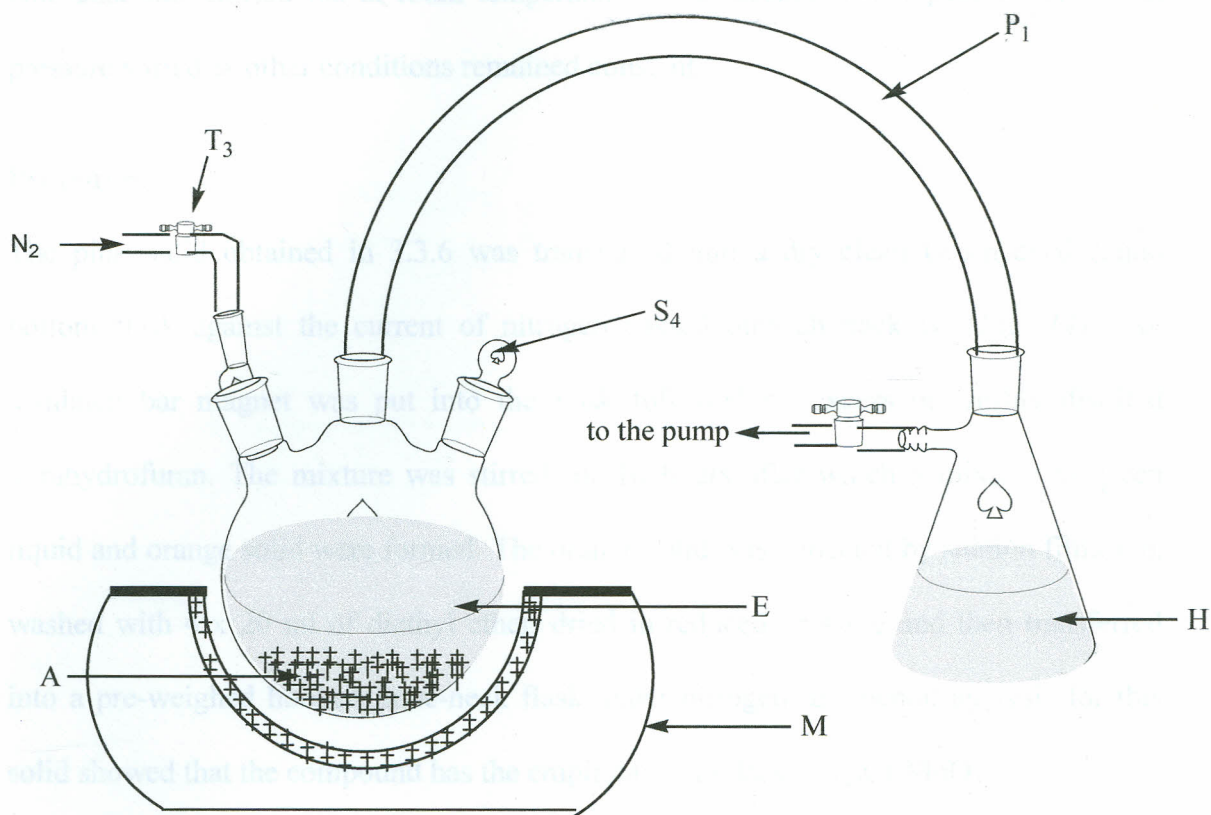
**Fig. 12: electrolytic cell for reduction of  $\text{MoO}_4^{2-}$  to  $\text{MoCl}_6^{3-}$**

### 3.3.6 Preparation of Ammonium Hexachloromolybdate(III), $(\text{NH}_4)_3\text{MoCl}_6$

10 gm of ammonium chloride was placed in a dry clean 250-cm<sup>3</sup> three-necked round bottomed flask equipped with a small bar magnet (3 cm). The centre neck was stoppered and nitrogen flushed through one of the side necks for 10 minutes and then all necks stoppered. This was placed in a polythene bag placed beside the bottle containing deep red solution obtained in section 3.3.5. While inside the polythene bag and in an atmosphere of nitrogen, the center stopper of three-neck round bottomed flask was removed and the solution transferred into the flask containing ammonium chloride. The stopper was replaced immediately after the transfer and the flask removed from the polythene bag. One of the side stoppers was replaced with a male joint (14/23) connected to stopcock  $T_3$  through which currents of nitrogen were passed into the flask. With nitrogen flowing, the center stopper was replaced with male joint (24/40) and connected to pipe  $P_1$  as shown in figure 13. Flow of nitrogen was stopped by closing stopcock  $T_3$  and the system evacuated. Water and HCl were removed by evaporation in vacuum. The resulting pink solid was dried at controlled low temperature and reduced pressure until it was a dry powder. This was allowed to cool for about half an hour after which the system was filled with nitrogen gas, the stopper  $S_4$  removed and transferred into a dry clean pre-weighed two-necked round bottom flask. A small amount of the pink solid scooped out from the flask using a dry clean spatula for analysis. Immediately after the stopper was replaced, the weight of the solid was determined and then stored safely for further reaction. The pink solid had the empirical formula  $(\text{NH}_4)_3\text{MoCl}_6$

	Mo	Cl
Found %	26.23	58.45
Calculated % for $\text{N}_3\text{H}_{12}\text{Cl}_6\text{Mo}$	26.45	58.64

Infrared spectra of this solid in both nujol (spectrum 4) and KBr (spectrum 5) confirmed the absence of carbonyl impurities.



$T_3$  = Stopcock

E = Red  $\text{MoCl}_6^{3-}$  solution

$\text{N}_2$  = Nitrogen

M = Electro mantle

A = Ammonium chloride

$P_1$  = Cubed glass tube

$S_4$  = Stopper

H = Hydrochloric acid

**Fig. 13: Apparatus for preparation of ammonium hexachloromolybdate.**

### 3.3.6.1 Reaction of Ammonium Hexachloromolybdate(III), $(\text{NH}_4)_3\text{MoCl}_6$ with Tetrahydrofuran Saturated with Carbon Monoxide and in Presence of Zinc Dust.

Reaction of  $(\text{NH}_4)_3\text{MoCl}_6$  with carbon monoxide in tetrahydrofuran and in presence of zinc dust was carried out at room temperature. This reaction was repeated twice with pressure varied as other conditions remained constant.

#### Procedure

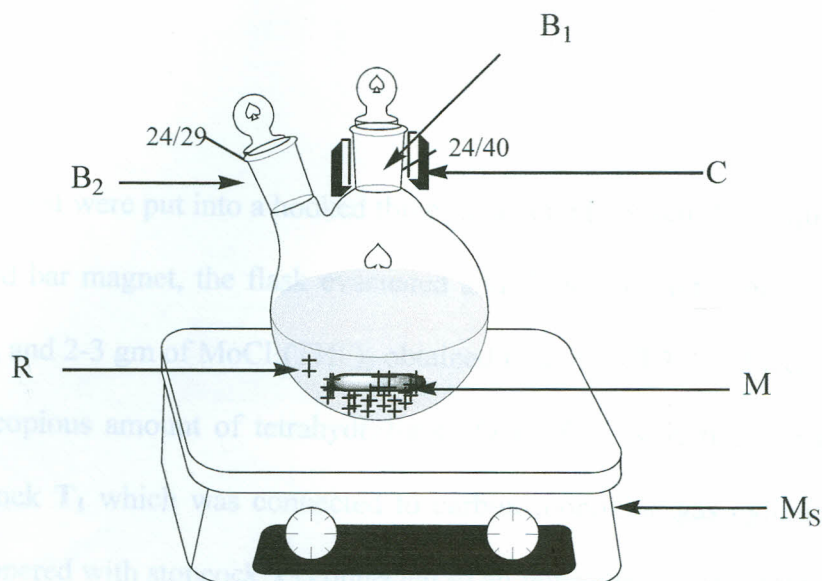
The pink solid obtained in 3.3.6 was transferred into a dry clean two-necked round bottom flask against the current of nitrogen passed through neck B<sub>1</sub> (Fig. 14). An insulated bar magnet was put into the flask followed by excess of freshly distilled tetrahydrofuran. The mixture was stirred for 16 hours after which a mixture of green liquid and orange solid were formed. The orange solid was collected by suction filtration, washed with 4 x 20 ml of diethyl ether, dried in reduced pressure and then transferred into a pre-weighed hooked three-neck flask under nitrogen. Elemental analysis for this solid showed that the compound has the empirical formula,  $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{MoO}_3$

	C	H	Cl	Mo
Found %	34.28	5.28	24.92	22.85
Calculated % for $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{MoO}_3$	34.43	5.78	25.41	22.92

The mass of the solid was determined and found to be 13.5 g, representing a 96% yield.

Against the current of carbon monoxide, 3cm insulated bar magnet was put and 10 gm of zinc dust were added followed by copious amount of dry tetrahydrofuran. The system was stoppered tightly and the mixture stirred with a bar magnet for 20 hours in an atmosphere of carbon monoxide at atmospheric a pressure of (760 - 1190 mm Hg). An

infrared spectrum of the solution (spectrum 6) was obtained. The reaction was repeated at 1520 mm Hg. The infrared spectrum of resulting crude product was recorded (spectrum 7). Chromatographic separation gave white crystalline halogen-free solid (spectrum 8).



B<sub>1</sub>, B<sub>2</sub> = Necks

C = Clamps

R = Reaction mixture

M = Bar magnet

M<sub>S</sub> = Magnetic stirrer

**Fig. 14: Apparatus for reacting  $(\text{NH}_4)_3\text{MoCl}_6$  with THF.**

### 3.3.7 Reduction of Trichlorotris(tetrahydrofuran)molybdenum(III), $\text{MoCl}_3(\text{THF})_3$ With Zinc in Anhydrous Tetrahydrofuran Saturated With Carbon Monoxide.

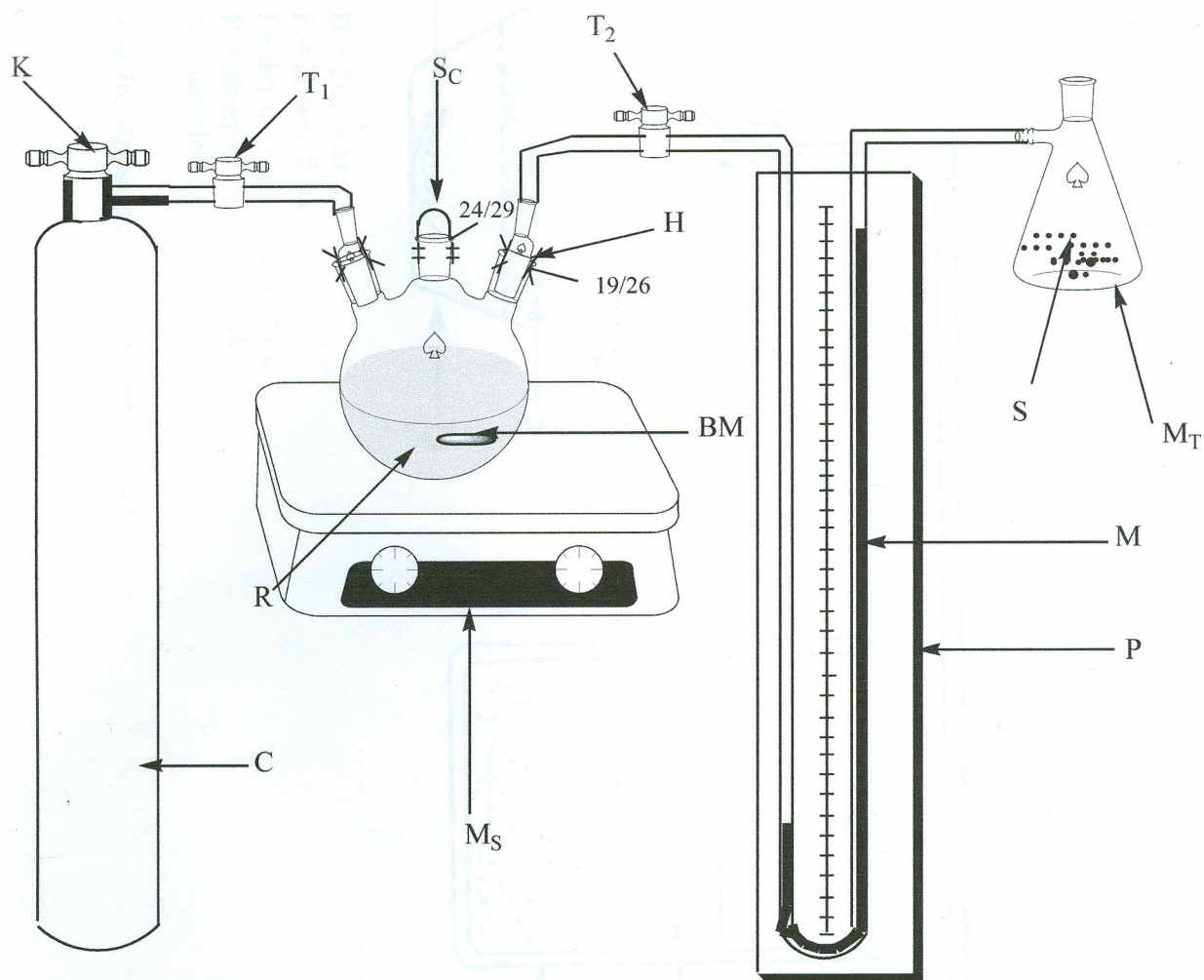
The reaction of  $\text{MoCl}_3(\text{THF})_3$  with carbon monoxide in dry tetrahydrofuran was carried out at 2 atmospheres pressure and room temperature in presence of zinc dust, using the set-up shown in figure 15.

#### Procedure

15 gm of zinc dust were put into a hooked three-neck round bottom flask equipped with a 3 cm insulated bar magnet, the flask evacuated and filled with nitrogen. It was purged with nitrogen, and 2-3 gm of  $\text{MoCl}_3(\text{THF})_3$  obtained in section 3.3.3, added into the flask followed by copious amount of tetrahydrofuran. One of the side necks was stoppered using a stopcock  $T_1$  which was connected to carbon monoxide gas cylinder while the other was stoppered with stopcock  $T_2$  connected to an improvised manometer. The center neck was tightly stoppered and then carbon monoxide allowed into the system by opening stopcocks  $T_1$  and  $T_2$ . The pressure of carbon monoxide was carefully adjusted from cylinder knob, K. The mixture was stirred with a bar magnet under constant CO pressure (2 atmospheres) for 36 hours after which the flow was stopped and center stopper,  $S_C$  removed carefully. The resulting crude product was separated by filtration on ashless filter paper mounted on filter funnel, residue washed with 5 x 20 ml of tetrahydrofuran and the filtrate obtained concentrated in a desiccator under reduced pressure to a small volume of about 10 ml. The set-up shown in the figure 16 was used. An infrared spectrum of the concentrate was recorded (spectrum 9), separated on a



neutral alumina column and eluted isocratically using tetrahydrofuran as described in section 3.3.7.1.



BM = Insulated bar magnet

M<sub>T</sub> = Mercury trapper

C = Carbon Monoxide Cylinder

P = Manometer

H = Hooks

R = Reaction mixture

K = Knob

S = Sulfur powder

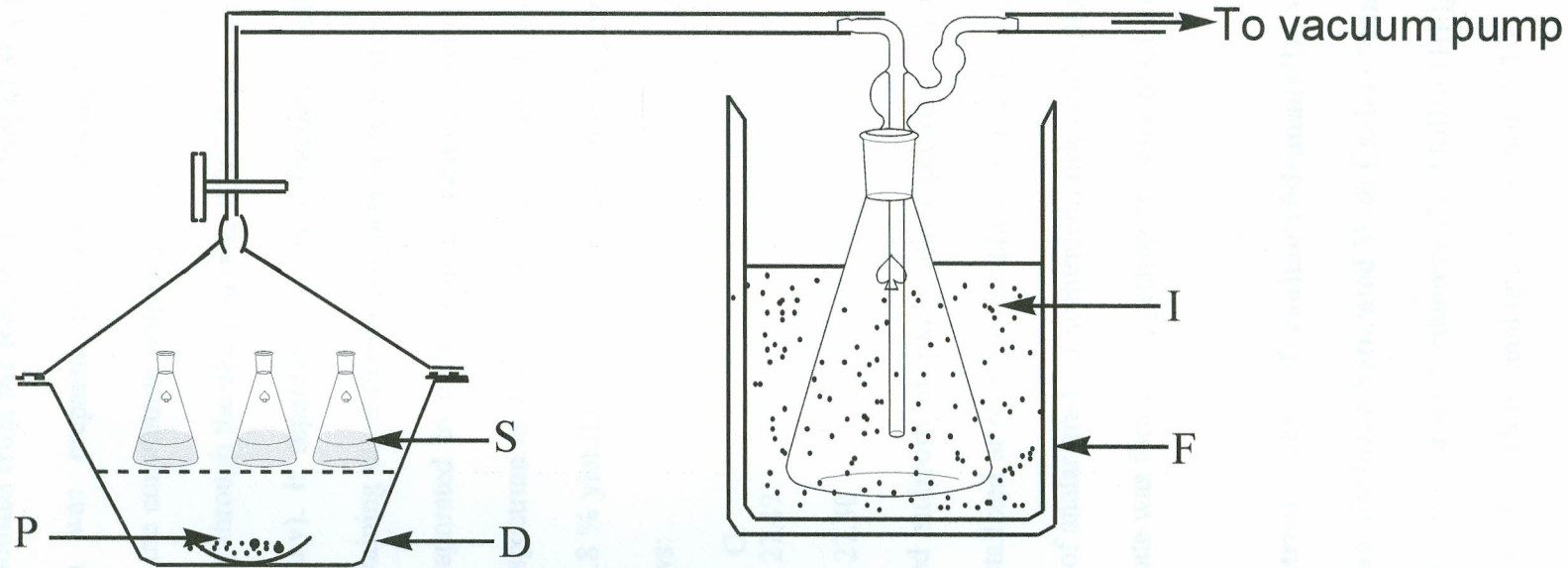
M = Mercury

S<sub>C</sub> = Center stopper

M<sub>S</sub> = Magnetic stirrer

T<sub>1</sub>, T<sub>2</sub> = Stopcocks

**Fig. 15: Apparatus for reductive carbonylation**



- D = Dessicator.  
 F = Dewar flask  
 I = dry ice / acetone mixture.  
 P = phosphorous pentoxide.  
 S = samples

**Fig.16: Apparatus for Vacuum Drying.**

### 3.3.7.1 Isolation of the Compounds from the Reduced Product of $\text{Mo}(\text{THF})_3\text{Cl}_3$

A neutral alumina column was prepared following standard method<sup>94</sup>. Using tetrahydrofuran as the eluent, the concentrate obtained in section 3.3.7 was poured into the column and allowed to flow through the alumina (size 0.063-0.200 mm, 70-230 mesh obtained from Merck Company). It separated into two fractions; yellow-green and orange-brown. The elutes containing the different products were treated as follows: the yellow-green fraction was evaporated to dryness in a vacuum leaving behind white needle-like crystals whose IR spectrum as THF solution (spectrum 10) showed evidence of carbonyl group. 1.6 gm (18.8 % yield) of this was isolated and its elemental analysis result was found to be as follows:

	Mo	C
Found %	36.57	27.47
Calculated % for		
$\text{C}_6\text{MoO}_6$	36.34	27.30

The red-brown fraction formed stubborn oil-like liquid (spectrum 11) which neither evaporated to dryness nor crystallized at room temperature after a duration of 21 days. On treating it with a few drops of analar grade concentrated nitric acid followed by 10 ml of 1 M  $\text{AgNO}_3$ , a white precipitate was formed suggesting presence of  $\text{Cl}^-$  ions.

### 3.3.8 Reduction of Tribromotris(tetrahydrofuran)molybdenum(III), $\text{MoBr}_3(\text{THF})_3$ With Zinc in Anhydrous Tetrahydrofuran Saturated With Carbon Monoxide.

Reduction of tribromotris(tetrahydrofuran)molybdenum(III),  $\text{MoBr}_3(\text{THF})_3$  was carried out in exactly the same way as the chloro analogue in section 3.3.7. The infrared spectrum (spectrum 12) was recorded as THF solution after reduction.

As for the chloro analogue (Section 3.3.7.1), the concentrate separated into two fractions; yellow-green and red-brown. On vacuo evaporation, the yellow-green fraction again gave needle like crystals with a physical appearance similar to those obtained in 3.3.7.1, while red-brown fraction formed oil-like liquid similar to that of chloro analogue. The infrared spectrum of the white crystalline solid is given in spectrum 13. 1.5 gm (17.6 % yield) of this was isolated and its elemental analysis result was found to be as follows:

	Mo	C
Found %	35.97	27.70
Calculated % for $C_6MoO_6$	36.34	27.30

## CHAPTER FOUR

### 4.0 RESULTS AND DISCUSSION.

#### 4.1 Introduction

This chapter discusses the significance of the research findings got during this study. On the basis of these results, suggestions for further research are given.

#### 4.2 Preparation of the Tervalent Complexes of Molybdenum Used as Starting Materials.

In this study, tervalent molybdenum complexes of the type,  $\text{MoX}_3(\text{THF})_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ), were prepared as described in section 3.3.3, 3.3.4, and 3.3.6. Whereas these complexes are not expected to have any carbonyl groups, experimental confirmation was mandatory because, the primary objective of the study was to find out whether carbonyl complexes, with particular reference to molybdenum hexacarbonyl, could be obtained by reducing molybdenum(III) species with zinc dust using moderately low pressure at room temperature.

The elemental analysis data (table 5) show that these complexes are relatively pure. Furthermore, the infrared data (spectra 1, 2 and 4) show beyond any reasonable doubt that, they were free of any inorganic carbonyl groups.

**Table 5: Elemental Analysis of Tervalent Complexes of Molybdenum Used as Starting Materials**

COMPLEX		C	H	X	Mo
$C_{12}H_{24}Cl_3MoO_3$	Calculated %	34.43	5.78	25.41 (X = Cl)	22.92
	Found %	34.18	5.28	24.82 (X = Cl)	22.95
$C_{12}H_{24}Br_3MoO_3$	Calculated %	26.11	4.58	43.43 (X = Br)	17.38
	Found %	25.74	4.08	42.79 (X = Br)	17.15
$N_3H_{12}Cl_6Mo$	Calculated %	-	-	58.64 (X = Cl)	26.45
	Found %	-	-	58.45 (X = Cl)	26.23

### 4.3 Reduction of $MoX_3(THF)_3$ (X = Cl, Br) With Zinc Dust in Presence of Carbon Monoxide

When tervalent complexes,  $MoX_3(THF)_3$  (X = Cl, Br) obtained from the reactions of neat tetrahydrofuran with either tetrahalooctacarbonyldimolybdenum(II),  $[Mo(CO)_4X_2]_2$  or  $(NH_4)_3MoCl_6$ , were reduced with zinc dust in presence of carbon monoxide at pressure of 1 - 2 atmospheres, inorganic carbonyl species were obtained (spectra 7, 9 and 12). Spectrum 7 showed a peak at  $1982.7\text{ cm}^{-1}$  with a shoulder at  $2018.4\text{ cm}^{-1}$  while spectra 9 and 12 showed a weak peak at  $1976.9\text{ cm}^{-1}$  and a medium peak at  $1980.9\text{ cm}^{-1}$ , respectively. This is the region where terminal carbonyl stretches are expected. Chromatographic separation of these species gave only one component in sufficient quantity for elemental analysis. This was a white solid, with an IR peaks at  $1979.8\text{ cm}^{-1}$  in THF solution. This peak is identical to that of authentic  $Mo(CO)_6$  in the same solvent

(table 6). The peak observed around  $592\text{ cm}^{-1}$  is believed to be due to Mo-C-O bending mode.

**Table 6: Summary of Infrared Data of the White Crystalline Solid**

Sample	CO stretch	MoCO bending	Medium	Spectra
I	$1979.8\text{ cm}^{-1}$	$591.1\text{ cm}^{-1}$	THF	10
II	$1979.8\text{ cm}^{-1}$	$592.1\text{ cm}^{-1}$	THF	13
III	$1979.8\text{ cm}^{-1}$	$592.1\text{ cm}^{-1}$	THF	8
IV	$1979.8\text{ cm}^{-1}$	$593.1\text{ cm}^{-1}$	THF	14

**KEY:** I – white solid obtained by reductive carbonylation of  $\text{MoCl}_3(\text{THF})_3$  (section 3.3.7)

II - white solid obtained by reductive carbonylation of  $\text{MoBr}_3(\text{THF})_3$

(section 3.3.8)

III - white solid obtained by reductive carbonylation of  $\text{MoCl}_3(\text{THF})_3$  which was prepared by reaction of  $(\text{NH}_4)_3\text{MoCl}_6$  with THF. (Section 3.3.6.1)

IV - Authentic molybdenum hexacarbonyl obtained from Aldrich Company

Elemental analysis data (table 7) gave further support that this solid is molybdenum hexacarbonyl.

**Table 7: Elemental Analysis of the White Crystalline Solid Isolated from the Reduced Mixtures**

Sample	Mo %	C %
I	36.57	27.47
II	35.97	27.70
III	36.10	27.36
*	36.34	27.30

KEY: \* calculated percentage for  $C_6MoO_6$

As can be seen from the data on both table 6 and 7, it is immaterial whether bromo or chloro complexes of Mo(III) were used for the reduction. It is noteworthy, however, that chloro complexes gave better yields.

It was found that, the quantity of the white solid was higher the higher the pressure. When the reaction was carried out in pressure range of 760 - 1190 mmHg, a mixture with distinct peaks at 1995, 1912 and  $1834.2\text{ cm}^{-1}$  (spectrum 6) was formed. However, when these mixtures were separated on neutral alumina column, no molybdenum hexacarbonyl was isolated. Instead a brown solid which was not sufficient for elemental analysis was obtained. When this solid was spotted and developed on thin layer chromatography, it gave a single spot. These observations suggest that a trans isomer of  $Mo(CO)_3(THF)_3$  was formed at carbon monoxide pressure of 760 - 1190 mmHg.



When the reaction was carried out at a pressure approaching 2 atm. (1520 mm Hg), one of the carbonyl species isolated chromatographically was a white halogen-free crystalline solid substance whose infrared data (table 6) and elemental analysis data (table 7) show that it was actually molybdenum hexacarbonyl,  $\text{Mo}(\text{CO})_6$

Furthermore, just like the authentic molybdenum hexacarbonyl, the white crystalline solid obtained did not have a definite melting point and on heating in a test tube, it decomposed into silver mirror-like substance.

#### **4.4 Percentage Yield of Molybdenum Hexacarbonyl Obtained.**

When 10 g of sodium molybdate,  $\text{Na}_2\text{MoO}_4\cdot\text{H}_2\text{O}$  was used 12.14 g (75% yield) of ammonium hexachloromolybdate,  $(\text{NH}_4)_3\text{MoCl}_6$  was obtained. When this mass of ammonium hexachloromolybdate was reacted with neat THF, 13.5 g (96% yield) of trichlorotris(tetrahydrofuran)molybdenum(III) was recovered which in turn gave 1.6 g (18.8% yield) of molybdenum hexacarbonyl.

## 5.0 CONCLUSION

The main objective of this study was to find out whether molybdenum hexacarbonyl can be prepared by the reduction of trivalent molybdenum complexes. The study has shown that this is actually possible at 18 °C – 28 °C and carbon monoxide pressure of 2 atmospheres using a very mild reducing agent namely, zinc metal. At pressure below 1190 mmHg an intermediate  $\text{Mo}(\text{CO})_3(\text{THF})_3$  is formed which at higher pressure is carbonylated to molybdenum hexacarbonyl. Thus, results presented in this study show that the objectives of the research were obtained.

## 6.0 RECOMMENDATIONS

The percentage yield of molybdenum hexacarbonyl obtained is low (18.8%). Therefore, further research is needed to investigate whether the yield can be improved by slightly elevating pressure to about 5 to 10 atm.

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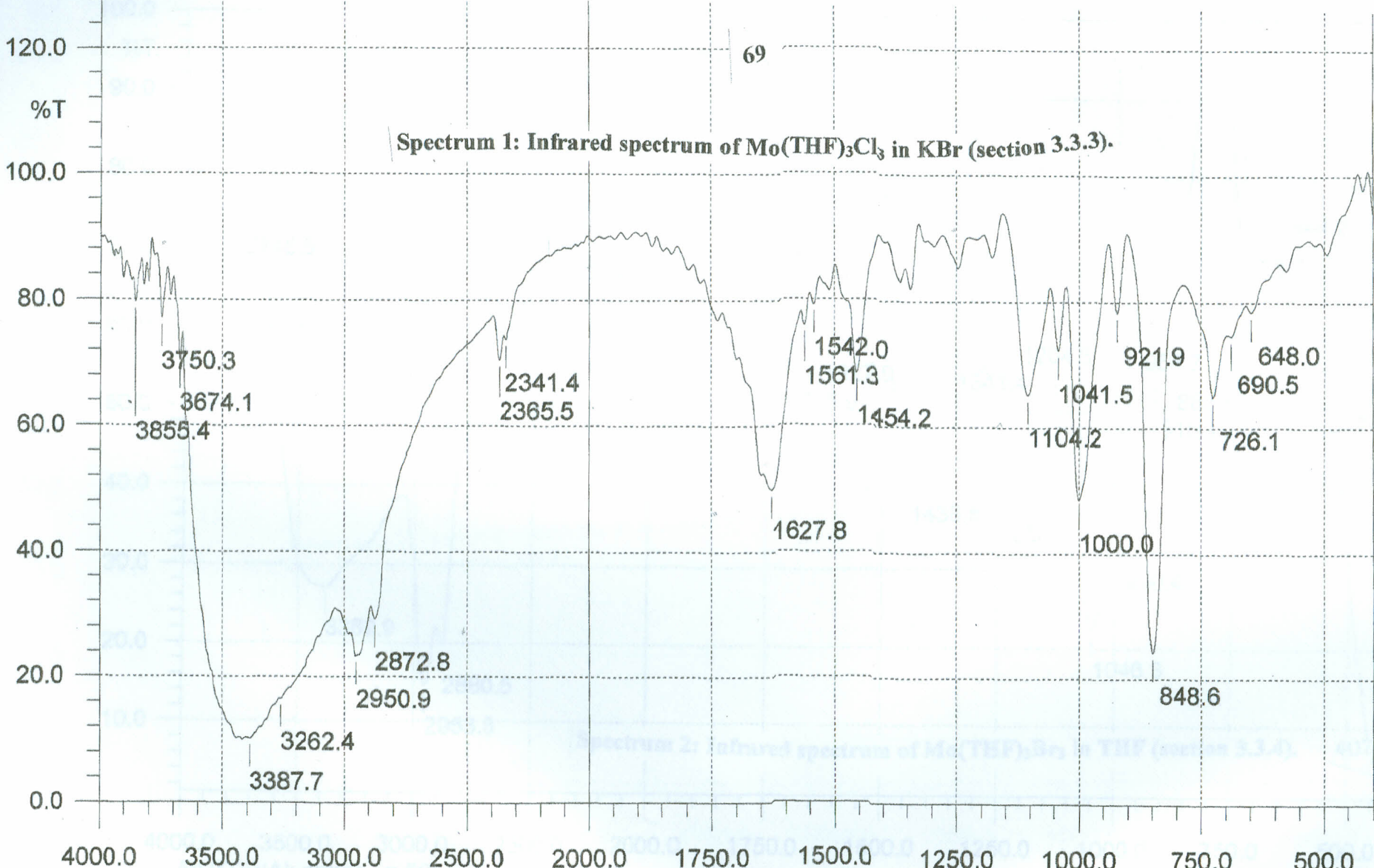
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APPENDICES

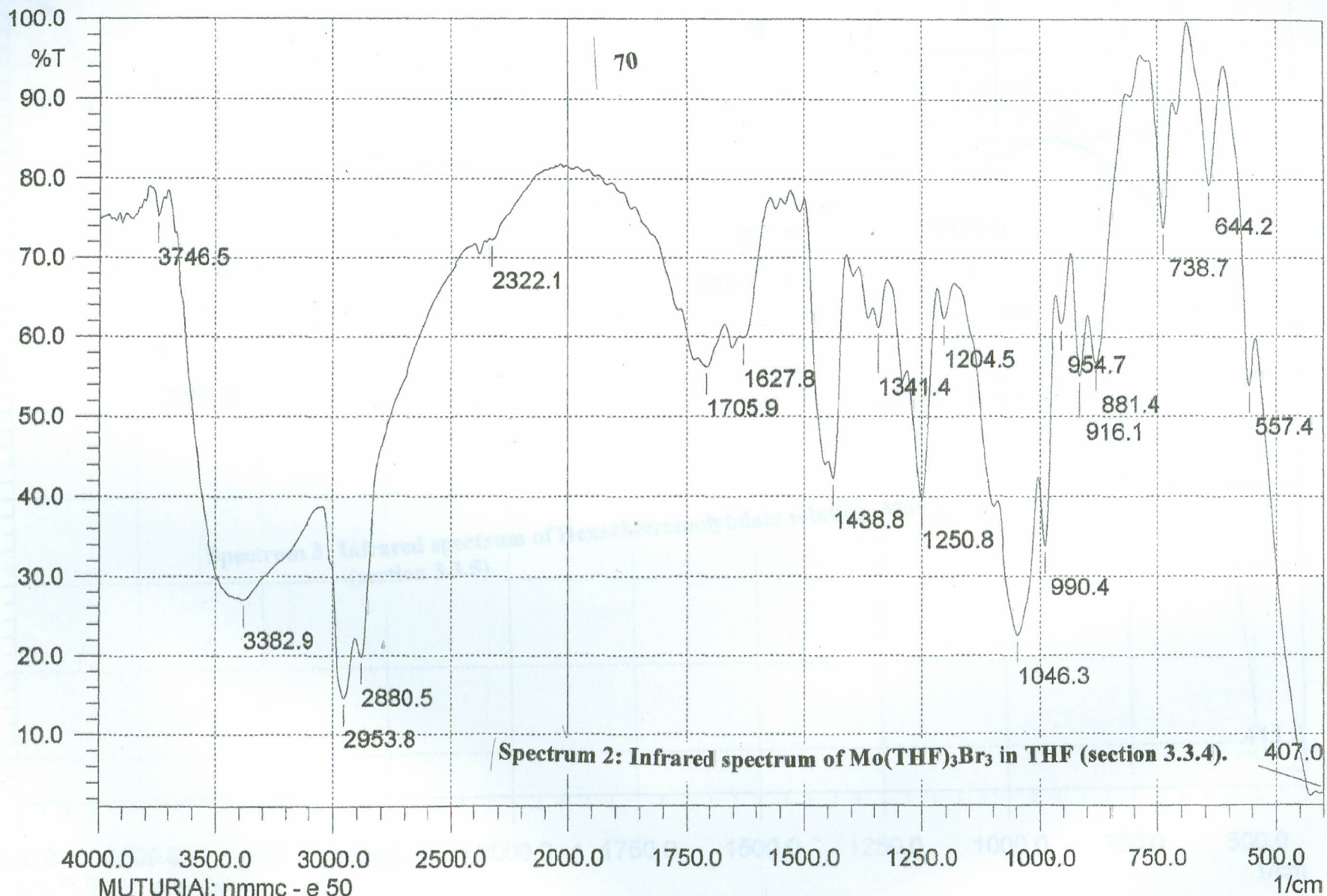


Spectrum 1: Infrared spectrum of Mo(THF)<sub>3</sub>Cl<sub>3</sub> in KBr (section 3.3.3).



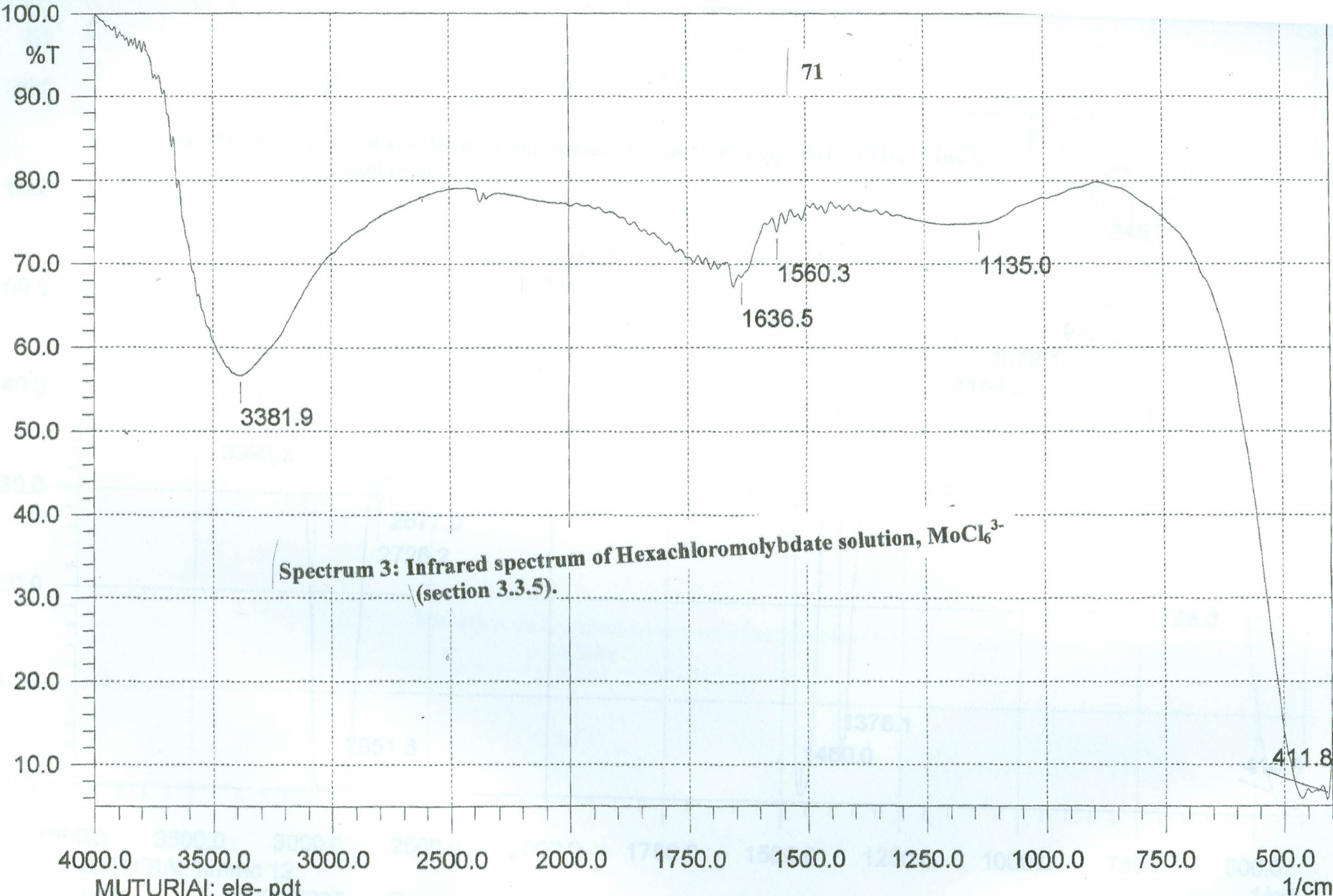
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Min: 400.20 Max: 3999.12 Range: 1/cm  
Ndp: 3733 Data Interval: 0.96434 Resolution: 2.0  
Mirror Speed: 2.8 (low)





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Gain:	auto	Aperture:	auto	Mirror Speed:	2.8(low)



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Date: 04/29/2005

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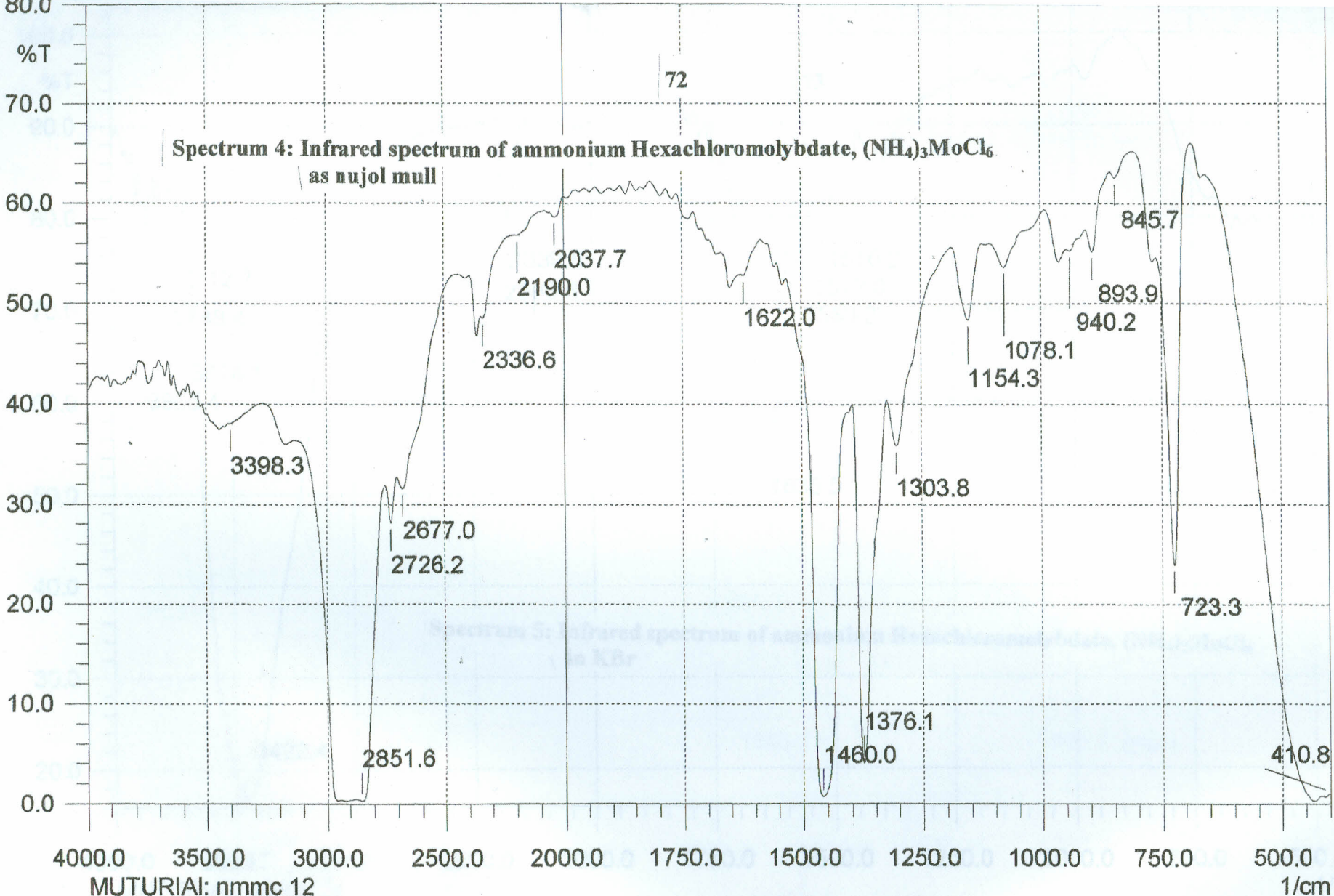
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Resolution: 2.0

Mirror Speed: 2.8(low)



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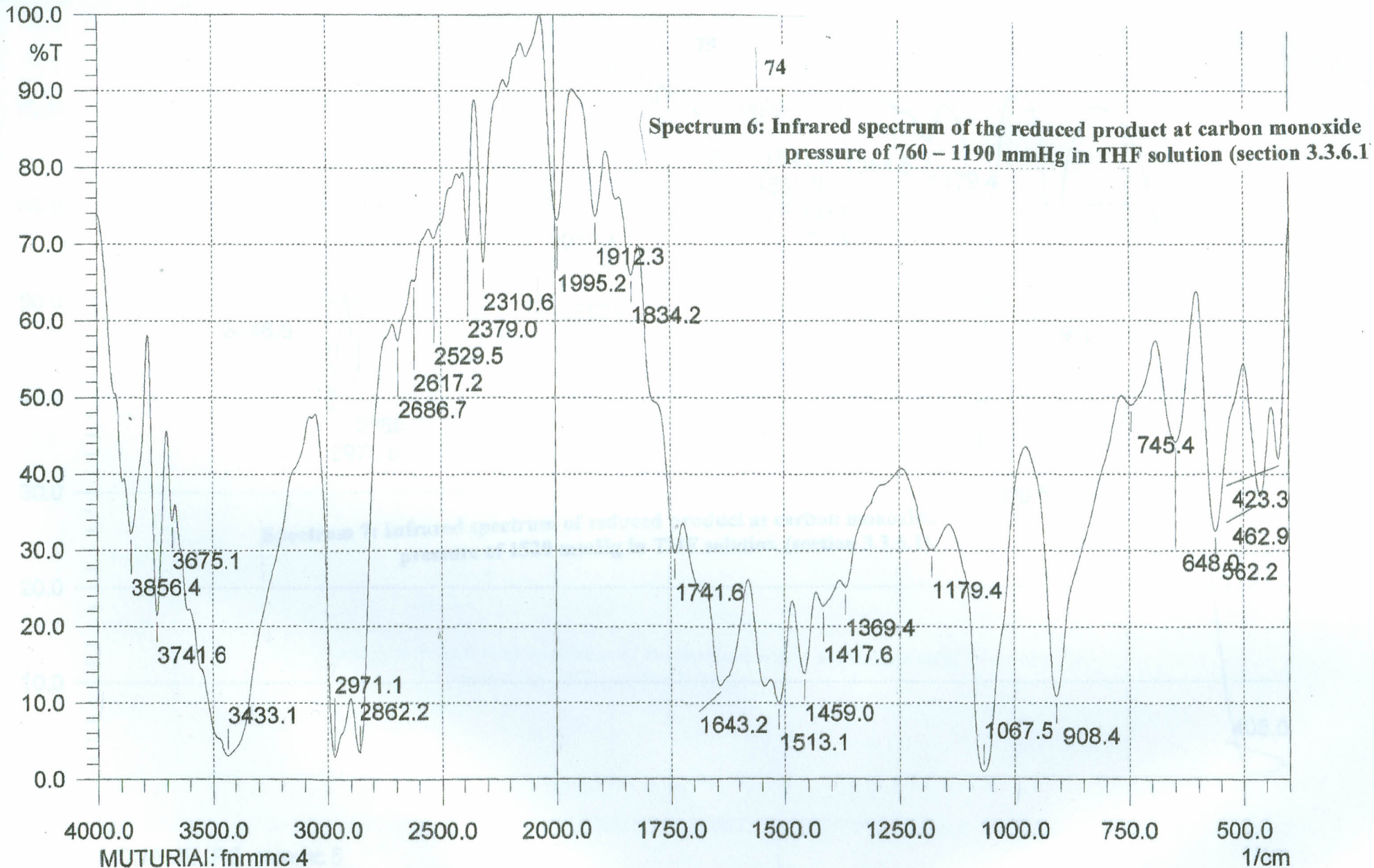
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Aperture: auto

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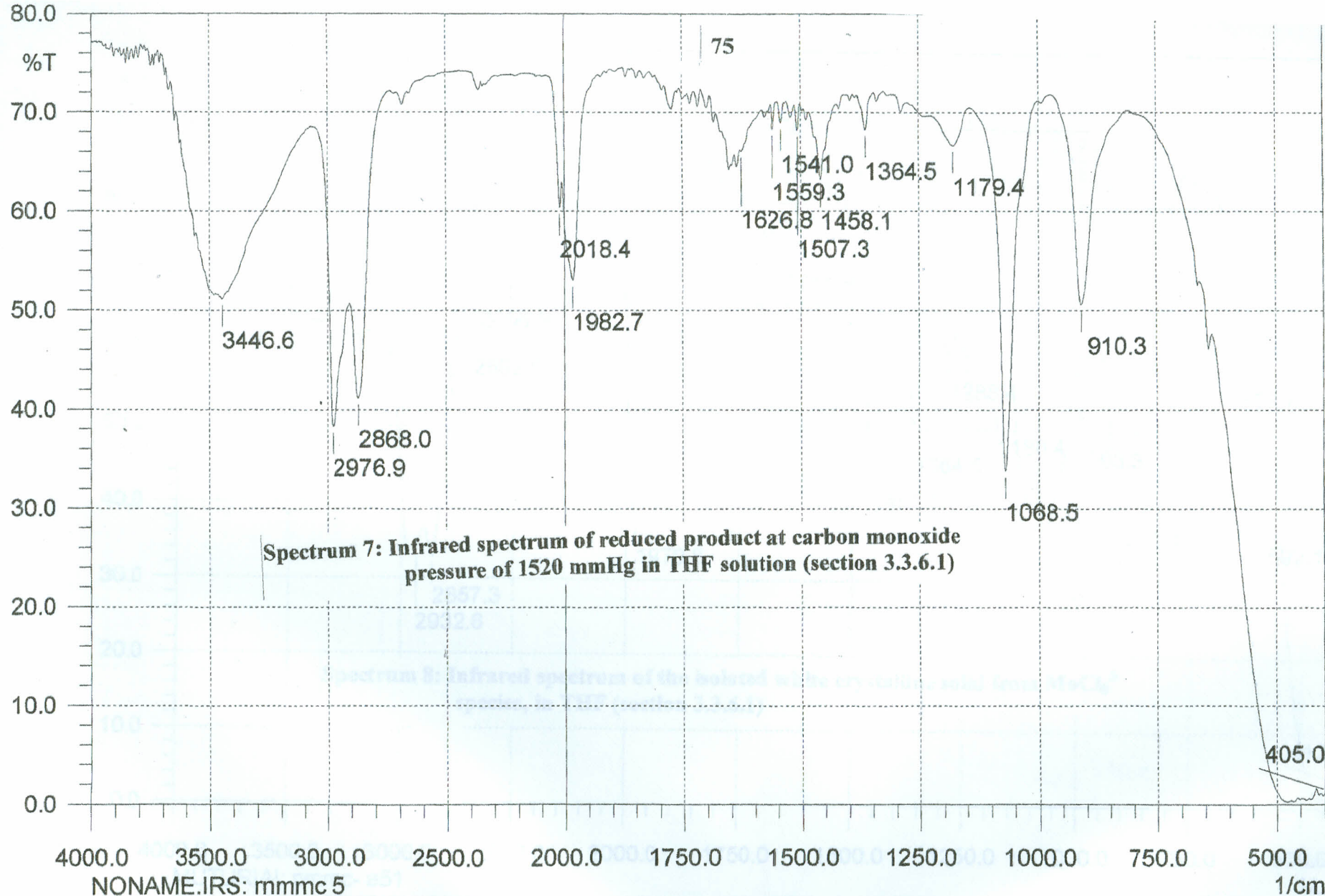
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Apodization: Happ

Range: 1/cm

Resolution: 2.0

Mirror Speed: 2.8(low)



NONAME.IRS: mmmc 5

Date: 04/29/2005

Type: HYPER IR

Abscissa: 1/cm

Min: 400.20

Ndp: 3733

Gain: auto

Time: 11:00:27

User: CHEMRE

Ordinate: %T

Max: 3999.12

Data Interval: 0.96434

Aperture: auto

NScans: 20

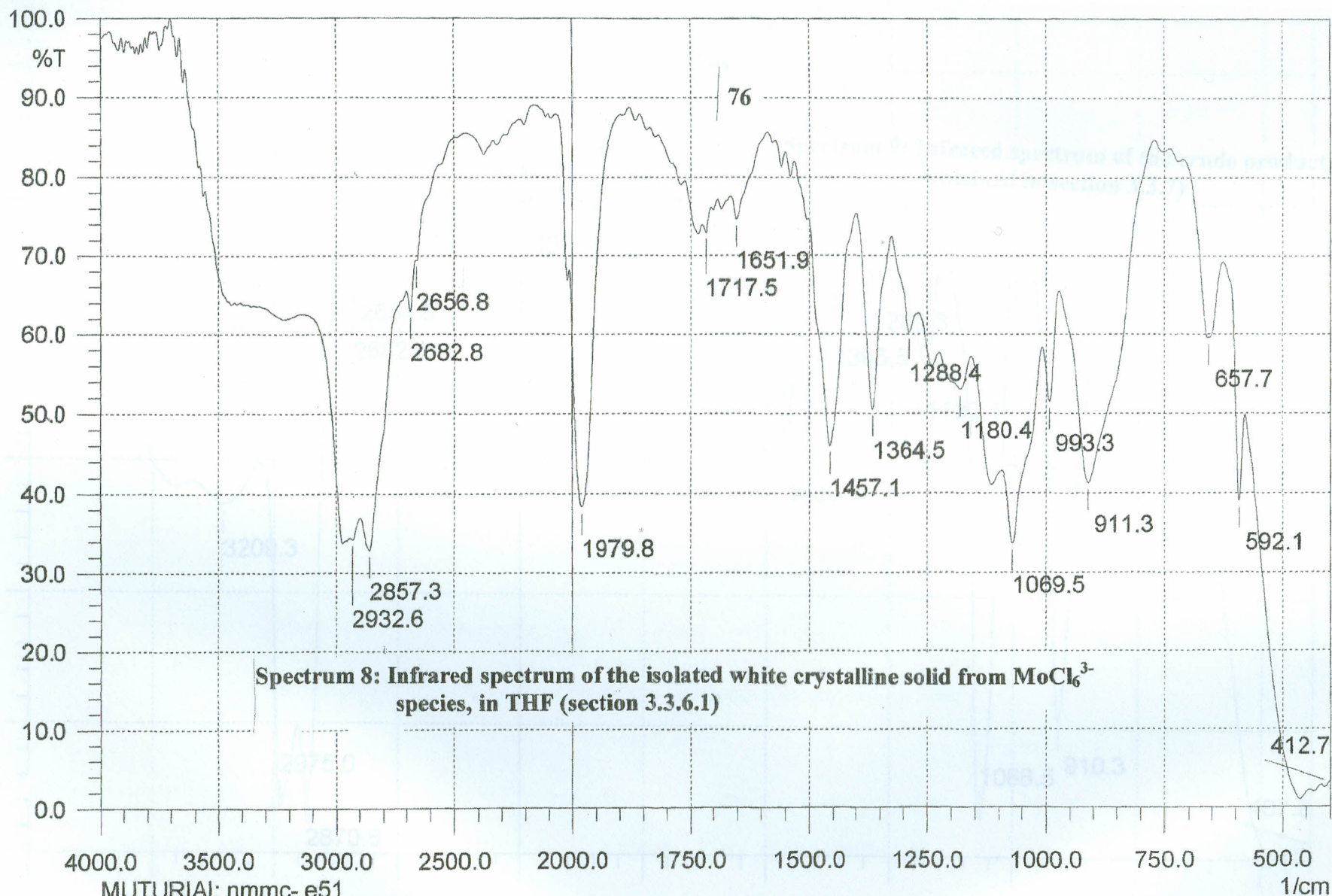
Detector: standard

Apodization: Happ

Range: 1/cm

Resolution: 2.0

Mirror Speed: 2.8(low)

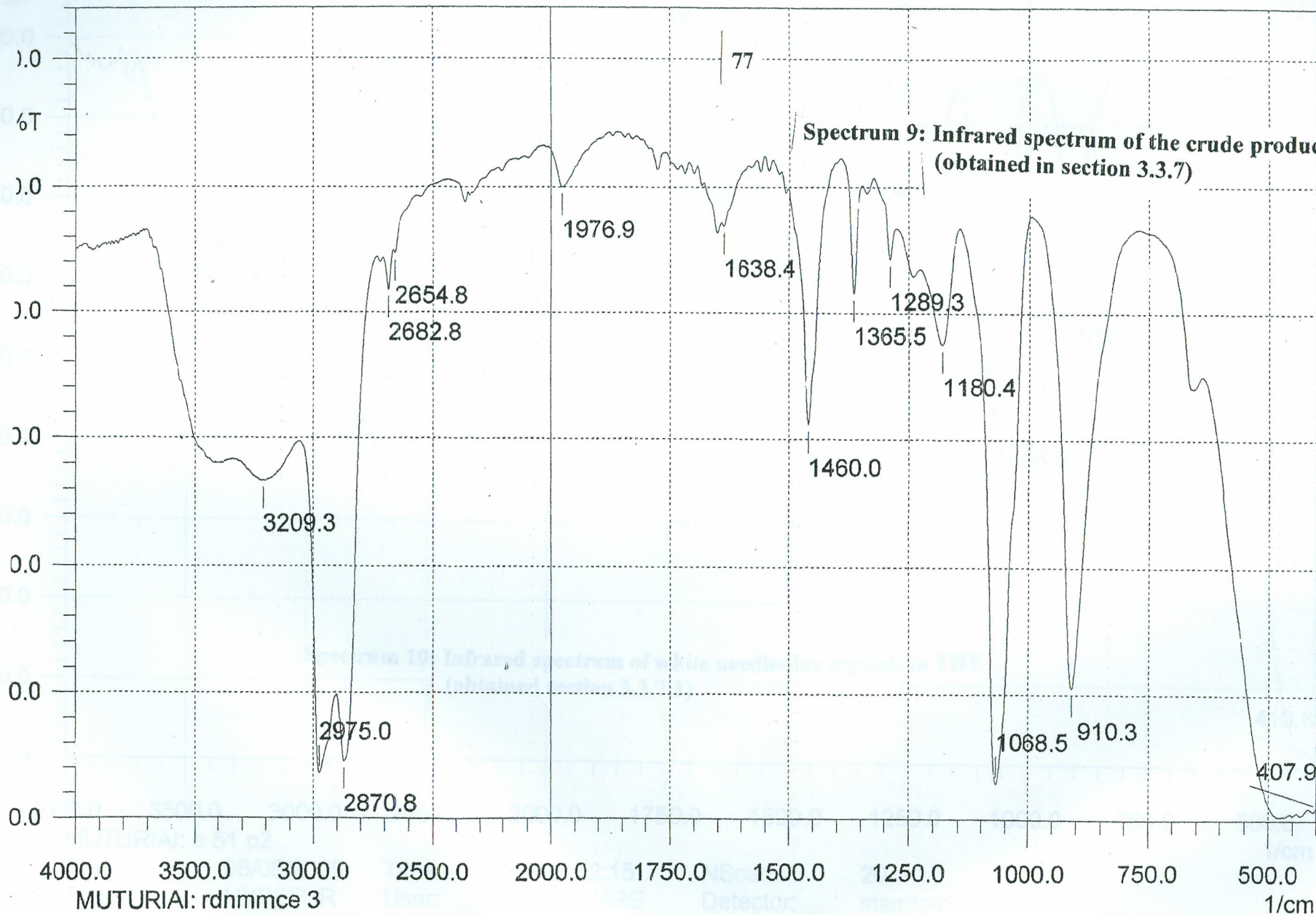


MUTURIAL: nmmc- e51

Date: 07/27/2005  
 Type: HYPER IR  
 Abscissa: 1/cm  
 Min: 400.20  
 Ndp: 3733  
 Gain: auto

Time: 13:15:18  
 User: CHEMRE  
 Ordinate: %T  
 Max: 3999.12  
 Data Interval: 0.96434  
 Aperture: auto

NScans: 20  
 Detector: standard  
 Apodization: Happ  
 Range: 1/cm  
 Resolution: 2.0  
 Mirror Speed: 2.8(low)



MUTURAI: rdnmce 3

Date: 07/12/2005

Type: HYPER IR

Abscissa: 1/cm

Min: 400.20

Ndp: 3733

Time: 11:30:58

User: CHEMRE

Ordinate: %T

Max: 3999.12

Data Interval: 0.96434

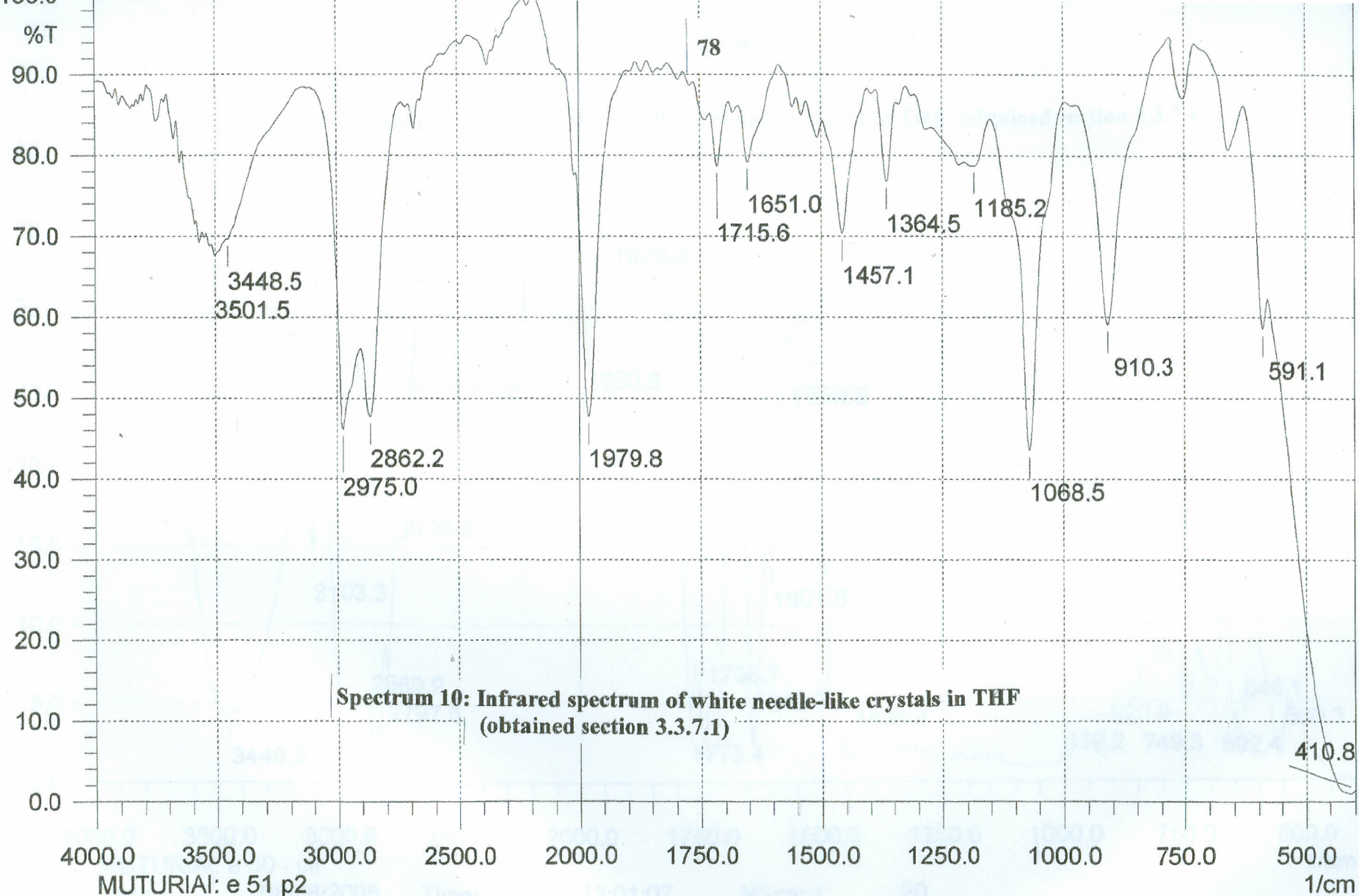
NScans: 20

Detector: standard

Apodization: Happ

Range: 1/cm

Resolution: 2.0



MUTURIAL: e 51 p2

Date: 08/08/2005

Type: HYPER IR

Abscissa: 1/cm

Min: 400.20

Ndp: 3733

Gain: auto

Time: 12:52:15

User: CHEMRE

Ordinate: %T

Max: 3999.12

Data Interval: 0.96434

Aperture: auto

NScans: 20

Detector: standard

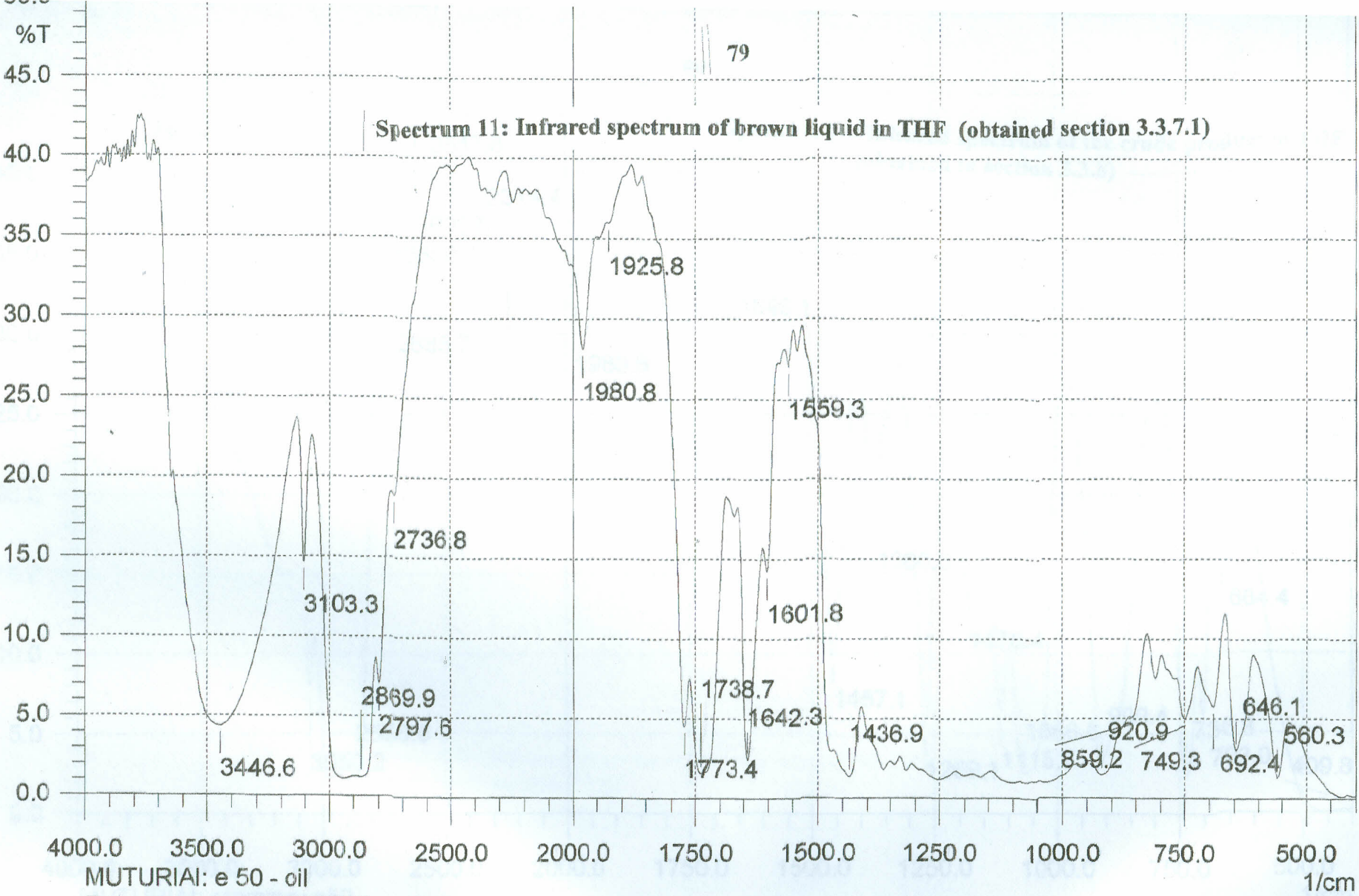
Apodization: Happ

Range: 1/cm

Resolution: 2.0

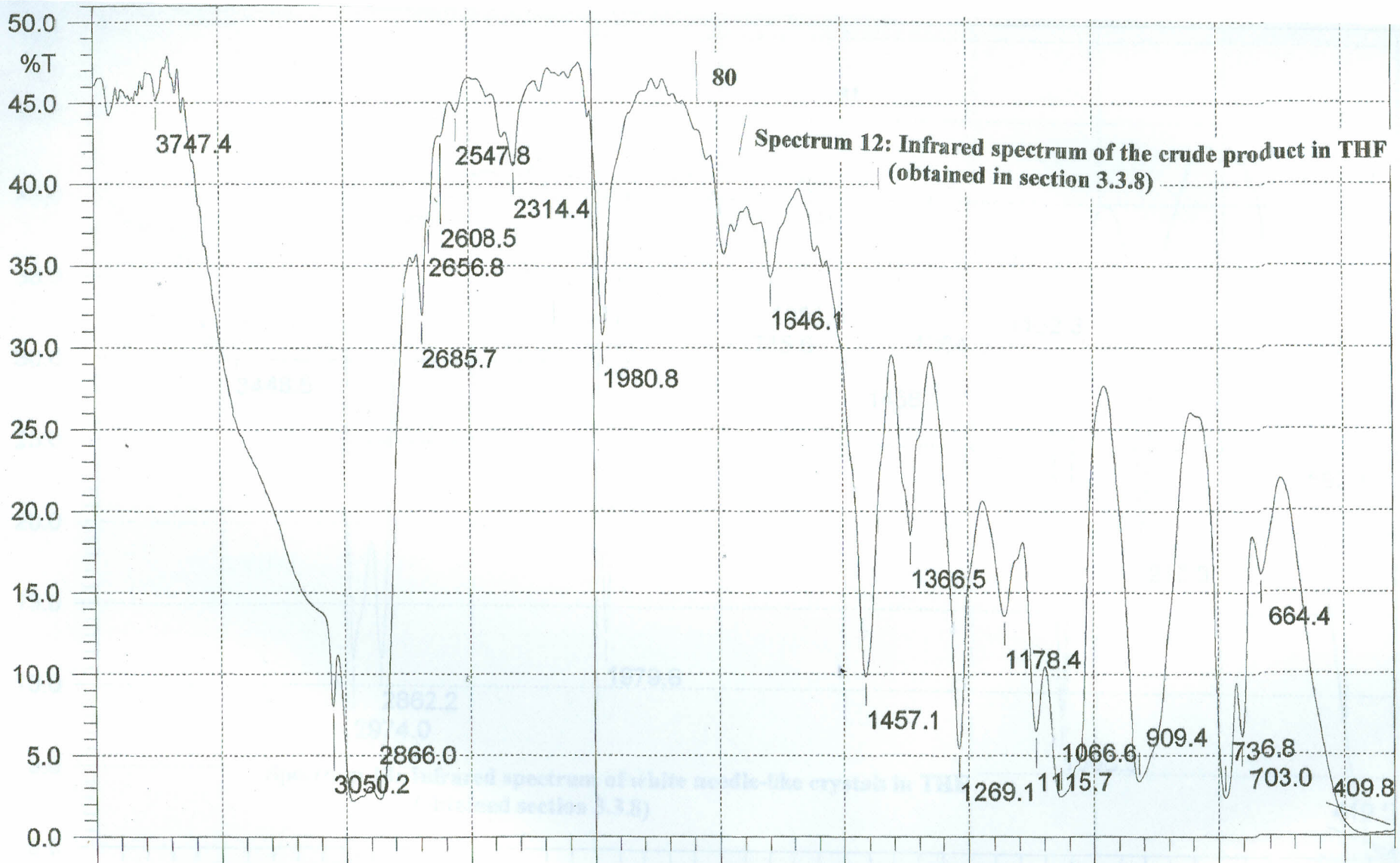
Mirror Speed: 2.8(low)



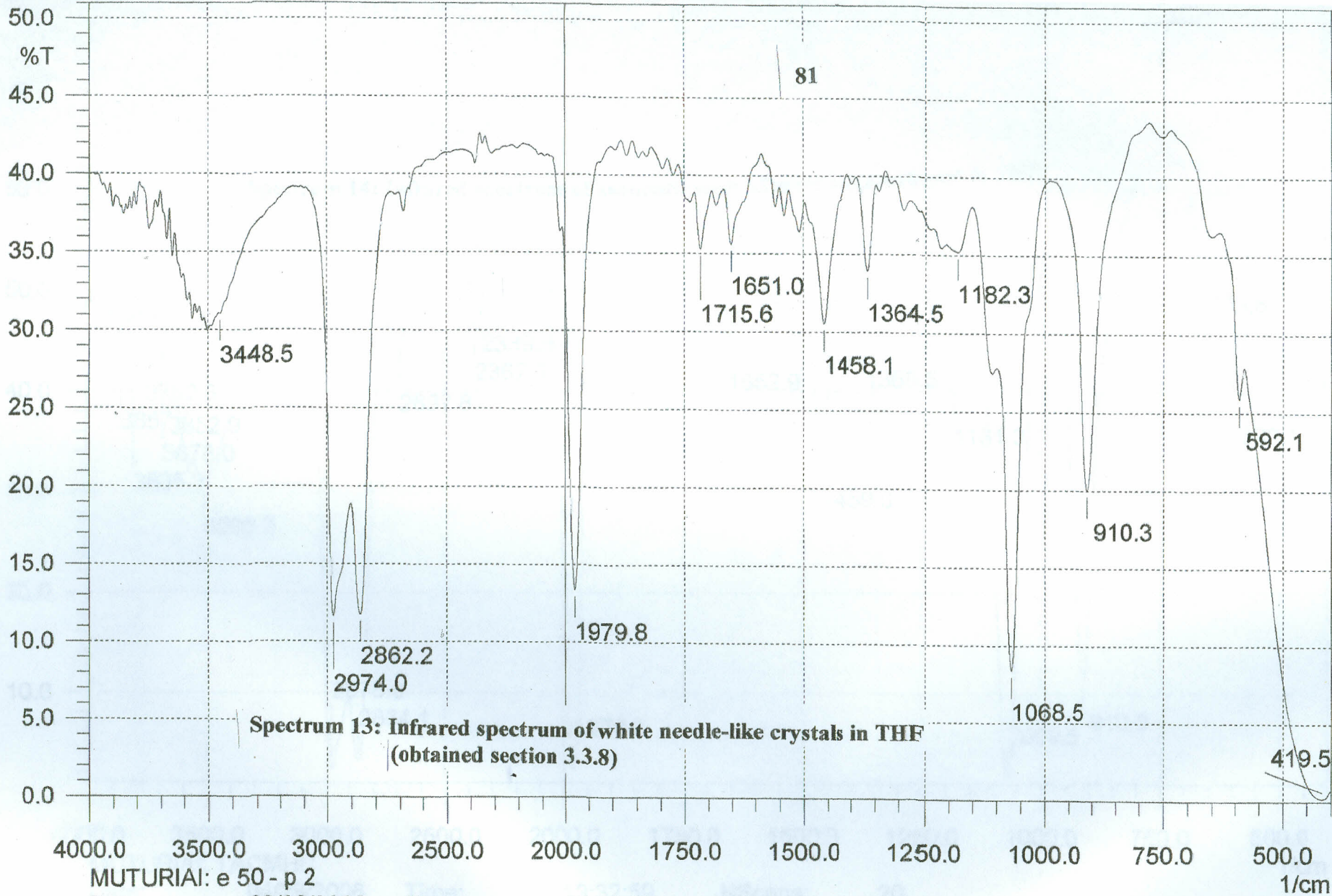


MUTURIAL: e 50 - oil

Date:	08/08/2005	Time:	13:01:07	NScans:	20
Type:	HYPER IR	User:	CHEMRE	Detector:	standard
Abscissa:	1/cm	Ordinate:	%T	Apodization:	Happ
Min:	400.20	Max:	3999.12	Range:	1/cm
Ndp:	3733	Data Interval:	0.96434	Resolution:	2.0
Gain:	auto	Aperture:	auto	Mirror Speed:	2.8(low)



MUTURIAL: rdnmmc- e50	Date: 07/27/2005	Time: 13:09:53	NScans: 20
Type: HYPER IR	User: CHEMRE	Detector: standard	Apodization: Happ
Abscissa: 1/cm	Ordinate: %T	Range: 1/cm	Resolution: 2.0
Min: 400.20	Max: 3999.12	Mirror Speed: 2.8(low)	
Ndp: 3733	Data Interval: 0.96434		
Gain: auto	Aperture: auto		



MUTURIAL: e 50 - p 2

Date: 08/08/2005

Type: HYPER IR

Abscissa: 1/cm

Min: 400.20

Ndp: 3733

Gain: auto

Time: 13:06:27

User: CHEMRE

Ordinate: %T

Max: 3999.12

Data Interval: 0.96434

Aperture: auto

NScans: 20

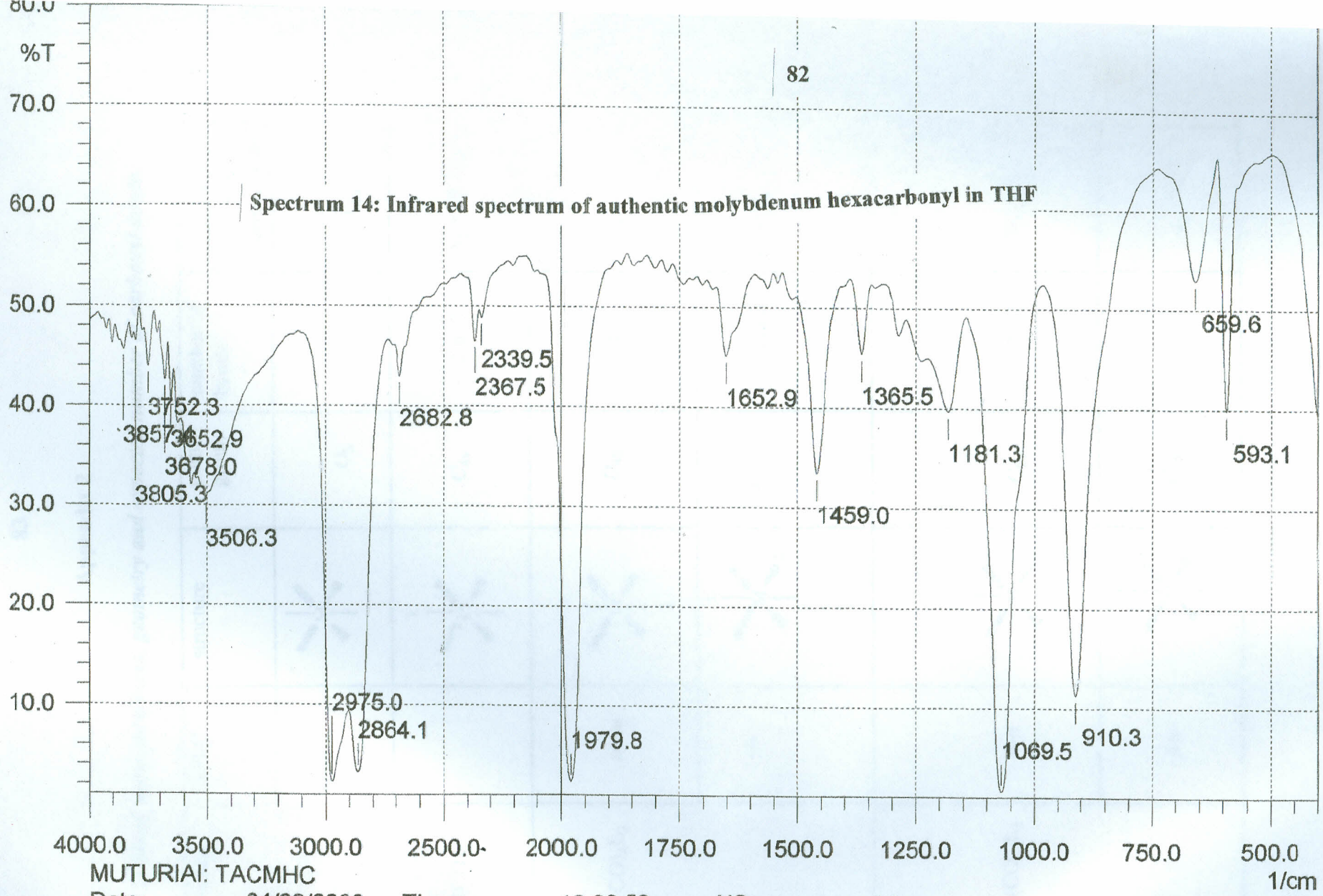
Detector: standard

Apodization: Happ

Range: 1/cm

Resolution: 2.0

Mirror Speed: 2.8(low)


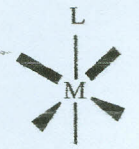

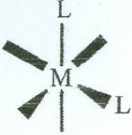
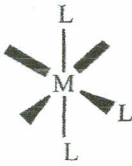
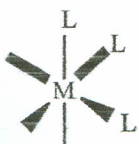


MUTURIAI: TACMHC

Date:	04/28/2006	Time:	13:32:59	NScans:	20
Type:	HYPER IR	User:	CHEMRE	Detector:	standard
Abscissa:	1/cm	Ordinate:	%T	Apodization:	Happ
Min:	400.20	Max:	3999.12	Range:	1/cm
Ndp:	3733	Data Interval:	0.96434	Resolution:	2.0
Gain:	auto	Aperture:	auto	Mirror Speed:	2.8(low)

## Appendix 2

Table of some complexes, geometry and expected number of carbonyl bonds.

complex	isomer	structure	point group	number of bands	symmetry of IR-active CO normal mode
$M(CO)_6$			$O_h$	1	$T_{1u}$
$M(CO)_5L$			$C_{4v}$	2 or 3	$A_1 + E(+ A_1)$
$M(CO)_4L_2$	<i>trans</i>		$D_{4h}$	1	$E_u$
	<i>cis</i>		$C_{2v}$	3 or 4	$A_1 + B_2 (+ A_1)$
$M(CO)_3L_3$	<i>mer</i>		$C_{2v}$	3	$2A_1 + B_2$
	<i>fac</i>		$C_{3v}$	2	$A_1 + E$