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A MODEL COMPOUND FOR NITROGEN FIXATION STUDIES: SYNTHESIS AND SPECTROMETRIC IDENTIFICATION OF A SIX COORDINATED ORGANOIMIDO TUNGSTEN COMPLEX

Yujun Sun

A Thesis
in
The Department of
Chemistry and Biochemistry

Presented in Partial Fulfilment of the Requirements for
the degree of Master of Science at
Concordia University
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ABSTRACT

A Model Compound for Nitrogen Fixation Studies: Synthesis and Spectrometric Identification of a Six Coordinated Organoimido Tungsten Complex

Yujun Sun

In an attempt to prepare W[$(SC_6H_4)_2$Et]NMe as a potential model for nitrogen fixation studies, a tungsten (IV) imido complex W[$(SC_6H_4S)_2$Et](THF)NMe was synthesized. The tetradentate sulphur ligand $(HSC_6H_4S)_2$Et (H_2dttd) has been prepared, using an improved method, as a suitable non-participating ligand for nitrogen fixation investigations. In the presence of a reducing agent, reaction of WCl_6 with CH_3CN gave the tungsten (IV) acetonitrile compound $WCl_4(CH_3CN)_2$ which, on further reaction, gave $WCl_4(THF)_2$. The use of this complex as starting material for the coordination of dttd and imido ligand is discussed.

Elementary and spectrometric analysis were used to characterise the species produced in every stage of this synthetic procedure. The complexes of the type WCl_4L_2 were determined to have the *cis* geometric configurations from a study of IR spectra in the W-Cl stretching region. The deviation of the final complex from the target model complex was ascertained by IR., NMR., Mass spectroscopy and it is suggested to be the results of steric distortion and coordinative unsaturation in the target molecule.

ACKNOWLEDGEMENT

I wish to express my sincere thanks to my supervisor Dr. P.H. Bird for his guidance, encouragement and criticism during the course of this project, and in the preparation of this thesis. Thanks are extended to the other members of my research committee, Dr. L.D. Colebrook and Dr. J.A. Capobianco, for their helpful suggestions throughout this investigation.

I would also like to thank Dr. R.T. Rye whose help in mass spectrometric analysis was greatly valued.

Thanks are also due to the Department of Chemistry and Biochemistry for financial support.

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LIST OF ABBREVIATIONS

Ar	aryl
^{t}Bu	t-butyl
dppe	1,2-bis(diphenylphosphino)ethane $[Ph_2PCH_2CH_2PPh_2]$
dtc	dialkyldithiocarbamate $[S_2CNMe_2^-]$
Et	ethyl
IR.	infrared
L	neutral ligand
M	metal
Me	methyl
NMR.	Nuclear Magnetic Resonance
Ph	phenyl
^{n}Pr	n-propyl
Py	pyridine
R	alkyl group
THF	tetrahydrofuran

CHAPTER 1

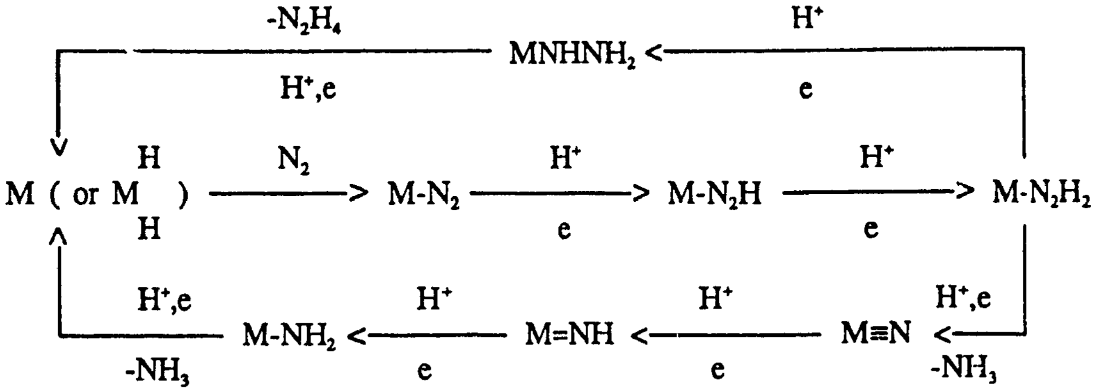
INTRODUCTION

1.1 SIGNIFICANCE AND OBJECTIVES

The provision of an adequate supply of fixed nitrogen is central to meeting of the food challenge successfully for a seemingly overexpanding human population. The fixed nitrogen needed in agriculture comes either from biological nitrogen fixation or from industrial fixation. Over the years, alternative or improved routes to industrial N-fertiliser, which is mostly made by the Haber process, has been investigated [1][2] in order to find a lower cost nitrogen fixation process, preferably operating at atmospheric pressure and ambient temperature as does the biological system.

The current phase of interest in nitrogen fixation started in the early sixties when bacterial nitrogenase was first extracted in active form, and when the first stable and well-characterized transition metal dinitrogen complex was isolated. Since then, there have been many studies, featuring two main approaches: biological and chemical. The former has concentrated on the natural nitrogen-fixing systems found in bacteria, while the latter has concentrated on attempting to model the natural systems using transition metal complexes, especially dinitrogen complexes of the transition metals. A cyclic process which has been proposed as a reasonable model for the reduction of dinitrogen at a metal centre in transition metal complexes is shown in scheme 1:

SCHEME 1



The basic assumptions of this reaction model are that reduction of dinitrogen or its derivatives (" N-ligand " will be used later on in this thesis for all of these ligands) to ammonia occurs by the protonation of the coordinated N-ligands bound at a single metal site, with either one or two protons at a time, and that concomitant electron flow into the coordinated N-ligand occurs via the metal. This mechanism will serve as the basis of the discussion. Up to now, the main research work toward this cycle has concentrated on: a) Synthesizing the dinitrogen transition metal complexes (or the intermediate types in the reaction cycle) which exhibit a variety of binding modes. b) Investigating the mechanism of reactions for coordinated N-ligands.

Although no complex has yet been found being able to complete such a nitrogen fixation cycle, a number of relatively stable transition metal complexes, e.g. molybdenum and tungsten complexes, have been found which are able to convert the bonded dinitrogen into ammonia on treatment of the compounds with protons at ordinary temperature and pressure. For example, treatment of *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M= Mo or W) with acid in methanol at 20°C results in a reduced nitrogen molecule, i.e. N_2H_4 or NH_3 [3][4]. This result gave the first definitive evidence that mononuclear metal complex of coordinated dinitrogen could indeed be involved in the reaction of nitrogenase. Although the mechanisms of these protonations are not clear, the isolation of the complexes containing diazenido (N_2H) and hydrazide(2^-) (N_2H_2) groups from such reaction systems [5][6] is firm evidence for the initial steps of the nitrogen fixation cycle described above.

However, in the research described in this thesis, there has been no attempt to investigate the reactions of nitrogen fixation: the focus is only on obtaining a potential model, from which a greater understanding of how nitrogen bonds to, and reacts at a transition metal centre may be gained. Before starting to design the model, it is necessary to look back on some prior work of considerable significance: work on the synthesis of transition metal complexes with N-ligands in nitrogen fixation studies.

1.2 PREVIOUS WORK

Transition metal complexes synthesized for nitrogen fixation studies can be classified mainly into three series depending on the different "N-ligand". The first species includes those with dinitrogen, the second those with diazenido, diazene and hydrazido(2-) ligands, and the third with imido and amido ligands.

1.2.1 DINITROGEN COMPLEXES

Dinitrogen complexes involving most of the transition metals have been isolated and intensively studied since 1965 [7][8], when the first dinitrogen complex $[Ru(NH_3)_5(N_2)]^{2+}$ was isolated by Allen and Senoff [9]. There are essentially two ways in which dinitrogen can bond to a metal centre, i.e. end-on coordination (I) and (II), and side-on coordination (III) and (IV). In the vast majority of cases dinitrogen binds end-on to metals, while the case of side-on bonding are few.

$M \leftarrow N \equiv N$

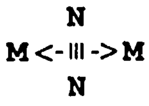
(I)

$M \leftarrow N \equiv N \rightarrow M$

(II)


$M \leftarrow \overset{N}{\underset{N}{|||}}$

(III)


$M \leftarrow \overset{N}{\underset{N}{|||}} \rightarrow M$

(IV)

Dinitrogen complexes can be prepared mainly in three routes:

The first is by direct reaction of N_2 either via substitution, or more conveniently, in an one-vessel-reduction of a suitable complex in a nitrogen atmosphere. Below are three examples:

$$MoCl_2(PR_3)_4 \xrightarrow[N_2]{Na/Hg} Mo(N_2)_2(PR_3)_4 \qquad [10]$$

$$(\eta^5\text{-}C_5H_5)_2ZrCl[CH(SiMe_3)_2] \xrightarrow[N_2]{Na/Hg,THF} (\eta^5\text{-}C_5H_5)_2ZrN_2[CH(SiMe_3)_2] \qquad [11]$$

$$Ta(CHCMe_3)Cl_3(PMe_3)_2 \xrightarrow[N_2]{Na/Hg} [Ta(CHCMe_3)(PMe_3)_2Cl]_2N_2 \qquad [12]$$

For three dinitrogen complexes above, the first one was identified to contain end-on dinitrogen, the second one was believed to contain side-on dinitrogen, while the last one was ascertained to have bridging dinitrogen.

The second route can be by indirect methods, such as the generation of the dinitrogen ligand by oxidation of a hydrazine ligand. This kind of reaction can be thought as a reverse of the protonation process described before, e.g.:

$$Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2H_4) \xrightarrow{H_2O_2/Cu^{2+}/THF} Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2) \qquad [13]$$

$$[Ru(NH_3)_6]^{3+} + NO \longrightarrow [Ru(NH_3)_5(N_2)]^{2+} \qquad [14]$$

The last route is the synthesis of new dinitrogen complexes from others by ligand exchange, e.g.:

$$ReCl(N_2)(PMe_2Ph)_4 \xrightarrow{Py} ReCl(N_2)(Py)(PMe_2Ph)_3$$

The objective of this route is that the reactivity of the ligating dinitrogen molecule is a very sensitive function of the other ligands and a simple metathesis as in above equation provides a convenient way of modifying the reactivity of the complex.

Because they are the fundamental complexes for nitrogen fixation studies, the number of known dinitrogen complexes has grown rapidly. Some of the complexes previously described have demonstrated unambiguously that the reduction of dinitrogen under ambient conditions is a chemically feasible process. But up to now, the mechanisms of the reactions in this process are still not clear mainly because of the difficulties in isolating the intermediates from this reaction system. So, in the field of synthesis, a large part of the effort, as is presented below, has been on making complexes, which are suggested to be the intermediates in the fixation process, by means other than from dinitrogen complexes. Obtaining these complexes makes it possible to investigate the mechanisms of reactions occurring in each stage of the nitrogen fixation process.

1.2.2 DIAZENIDO, DIAZENE AND HYDRAZIDO(2-) COMPLEXES

Diazenido, diazene and hydrazido(2-) complexes can be prepared from dinitrogen complexes, but in the ammonia-forming reactions of dinitrogen complexes, the only intermediate which has been identified with certainty is the hydrazido(2-) species. The number of these three species formed from dinitrogen complexes is relatively small: most of them have been synthesized indirectly.

Diazenido complexes

There are six principal routes available to prepare diazenido complexes, others are of much less general utility:

a) Reaction with diazonium salts [15]:

$$\mathrm{RuCl_2(PPh_3)_3} \;+\; \mathrm{ArN_2^+Cl^-} \xrightarrow{\text{EtOH-acetone}} \mathrm{RuCl_3(N_2Ar)(PPh_3)_2} \;+\; \mathrm{PPh_3}$$

b) Insertion of diazonium ions into metal hydride bonds [16]:

$$\mathrm{Pt(H)Cl(PEt_3)_3} \xrightarrow{\mathrm{ArN_2^+}} \mathrm{[Pt(NHNAr)Cl(PEt_3)_2]^+} \xrightarrow{\text{base}} \mathrm{Pt(N_2Ar)Cl(PEt_3)_2}$$

c) Reaction with hydrazine and substituted hydrazines [17]:

$$\mathrm{MoO_2(dtc)_2} \;+\; \mathrm{PhNHNH_2} \xrightarrow{\mathrm{Na(dtc)}} \mathrm{Mo(N_2Ph)(dtc)_3}$$

d) Reaction with diazenes [18]:

$$(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{TiCl_3} \;+\; \mathrm{Me_3SiNNPh} \longrightarrow (\eta^5\text{-}\mathrm{C_5H_5})\mathrm{TiCl_2(N_2Ph)} \;+\; \mathrm{Me_3SiCl}$$

e) Hydride or carbanion attack on diazoalkane complexes [19]:

$$\mathrm{[Mo(NN{=}CH_2)F(dppe)_2]^+} \;+\; \mathrm{LiAlH_4} \longrightarrow \mathrm{Mo(NNMe)F(dppe)_2}$$

f) Formation from dinitrogen complexes [20]:

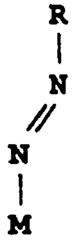
$$\textit{trans-}\ \mathrm{W(N_2)(dppe)_2} \xrightarrow[\mathrm{-N_2,\ THF}]{\mathrm{HBr}} \textit{trans-}\ \mathrm{[W(NNH_2)Br(dppe)_2]^+}$$

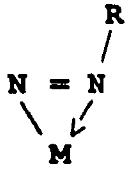
$$\xrightarrow[\mathrm{MeOH}]{\mathrm{Me_3N}} \textit{trans-}\ \mathrm{W(N_2H)Br(dppe)_2}$$

Depending upon the electronic requirements of the metals, the diazenido ligand can adopt one of the following geometries when coordinating with a single metal:


(I)


(II)


(III)


(IV)

Most of the diazenido complexes are believed to adopt the singly bent configuration (II), only a few examples of the doubly bent structure (III) are known, while the examples of linear configuration (I) and the sideways bonded form (IV) are very rare. The structure (III) is represented only in the complexes of the later transition metals, where electron-rich metals and the 18-electron rule preclude the diazenido ligand acting as a three-electron donor. As can be seen in the diazenido complexes obtained from the six synthetic routes above, only $Pt(N_2Ar)Cl(PEt_3)_2$ was assigned the structure (III); all the remaining products were identified as adopting configuration (II). The modes of bonding for bridging diazenido ligands were rarely observed [21].

Diazene complexes

There are four pathways leading to diazene complexes, they are:

a) Insertion of diazonium salts into metal hydride bonds [22].

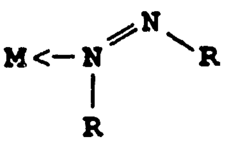
b) Reaction with hydrazines [23].

c) Reaction with diazenes [24].

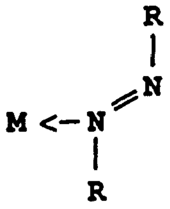
d) Reaction of dinitrogen complexes [25].

These routes are to some extent the same as those for the preparation of diazenido complexes, therefore the examples are omitted here.

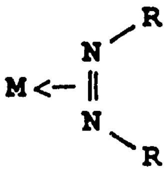
Upon coordination at a single metal site, the diazene ligand can adopt one of three potential configurations:



(I)



(II)



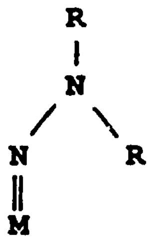
(III)

Both *cis* form (I) and side-on bonded form (III) are common whereas the *trans* structure (II) has not yet been observed. A structure with a bridging diazene has thus far been reported for only one complex [26].

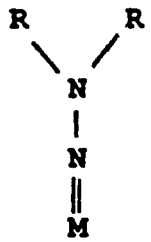
Hydrazido(2-) complexes

Despite the fact that hydrazido(2-) complexes are in general restricted to the metals of molybdenum, tungsten and rhenium, they represent an important (if not the most important) intermediate on the pathway leading to ammonia in the biological fixation of dinitrogen, so the synthesis and study of these species is of fundamental importance. Four general routes have been employed to yield this class of complexes:

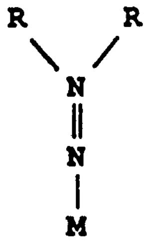
(I)



(II)

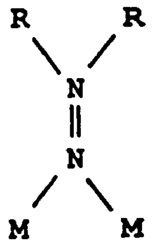


(Ia)

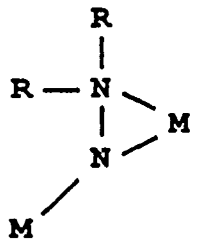


(Ib)

The structures of many hydrazido(2-) complexes have been determined, however only few have been shown to adopt the singly bent form [31]. The linear form (I) can be classified further into two species, the hydrazido(2-) form (Ia) and the iso-diazene form (Ib). However of all authenticated linear structures, only few have been shown to adopt form (Ib) [32]. As a bridging ligand the hydrazido(2-) species can be visualized as adopting two forms (III) and (IV), of which, form (III) is more common [33].



(III)



(IV)

1.2.3 IMIDO AND AMIDO COMPLEXES

As has been noted before, the reactions of dinitrogen complexes, in general, proceed only as far as the hydrazido(2-) stage, so almost all of the imido and amido complexes are prepared by an indirect route.

Imido complexes

A number of synthetic routes to imido complexes have been reported, some are very specific, whereas others are much more general. The more general routes are listed below:

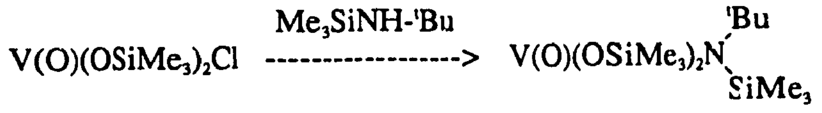
a) Deprotonation of primary amines [34]:

$$2\ \mathrm{Ti(NMe_2)_4} + 4\ {}^{n}\mathrm{PrNH_2} \text{ ------> } [\mathrm{Ti(N\text{-}{}^{n}Pr)_2}]_2 + 8\ \mathrm{Me_2NH}$$

b) Use of silylamines [35]:

$$\mathrm{L_nMX_m} + \mathrm{RN(SiMe_3)_2} \text{ ------> } \mathrm{L_nMNR} + \mathrm{(Me_3Si)_2X_m}$$

(X=O, when m=1; X=F, when m=2)



$$\mathrm{V(O)(OSiMe_3)_2Cl} \xrightarrow{\mathrm{Me_3SiNH\text{-}{}^{t}Bu}} \mathrm{V(O)(OSiMe_3)_2N}\begin{matrix}\diagup {}^{t}\mathrm{Bu} \\ \diagdown \mathrm{SiMe_3}\end{matrix}$$

$$\text{---------> } \mathrm{V(N\text{-}{}^{t}Bu)(OSiMe_3)_3}$$

c) Addition of organic azides [35]:

$$\mathrm{Mo(CO)_2(S_2CNEt_2)_2} + 2\ \mathrm{PhN_3} \text{ -----> } \mathrm{Mo(NPh)_2(S_2CNEt_2)_2} + 2\ \mathrm{CO} + 2\ \mathrm{N_2}$$

d) Alkylation (or arylation) of nitrido complexes [36]:

$$\mathrm{W(N)Br(dppe)_2} + \mathrm{EtI} \text{ ------> } [\mathrm{W(NEt)Br(dppe)_2}]\mathrm{I}$$

e) Oxo/imido exchange reactions using phosphinimines, isocyanates and sulfinylamines:

$L_nM{=}O$ + R'_3PNR ------> $L_nM(NR)$ + R'_3PO [37]

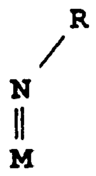
$L_nM{=}O$ + RNCO ------> $L_nM(NR)$ + CO_2 [38][39]

$L_nM{=}O$ + RNSO ------> $L_nM(NR)$ + SO_2 [40]

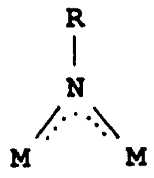
Of these three reagents, phosphinimines is the most useful because of the high affinity of phosphorus for oxygen. Isocyanates and sulfinylamines have been applied with varying degrees of success to the preparations of tungsten, molybdenum, rhenium and vanadium phenylimido complexes.

The four known modes of bonding can be summarized as below:

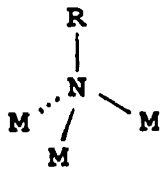
(I)



(II)



(III)



(IV)

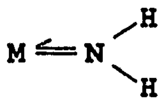
The terminal linear configuration (I) is the bonding mode most commonly observed in structures of imido complexes. The linearity is thought to reflect triple bond character in the metal-nitrogen linkage. Compounds where the metal is in a low formal oxidation state are likely in terminal bent structure (II), while the early transition metal imido complexes usually fall in the doubly bridging category (III).

The triply bridging coordination mode (IV) is only found in a number of cluster complexes of the iron triad.

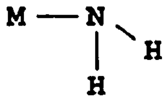
Amido complexes

The most common route used to prepare amido complexes is by deprotonation of coordinated ammonia of transition metal complexes, although some others are frequently used [41].

Normally the amido ligand binds to metals in a terminal position as (I) and (II).



(I)



(II)

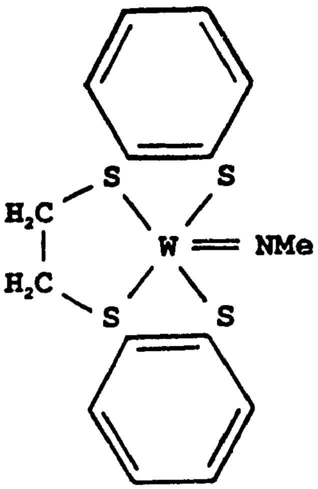
Both of them are common, while form (II) is more susceptible to protonation.

Despite the hundreds of transition metal complexes with nitrogen ligands that have already been isolated, undoubtedly, the studies on nitrogen fixation field will still remain an important impetus for searching for new synthetic routes to these complexes, and the research work in this field will continue to afford interesting new complexes and new chemistry.

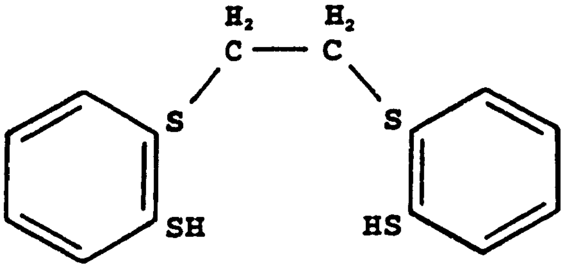
CHAPTER 2

MODEL DESIGNING

The model complex which is the target of this work is shown as below (I):



(I) W(dttd)NMe



[$(dttd)H_2$]

It is a tungsten imido complex which is one of the intermediate type outlined in fixation cycle. In this chapter, the metal centre and two ligands (dttd and imido ligand) are discussed separately and two factors, oxidation state and coordination number, are dealt with briefly in the section that follows.

2.1 THE TRANSITION METAL CENTRE

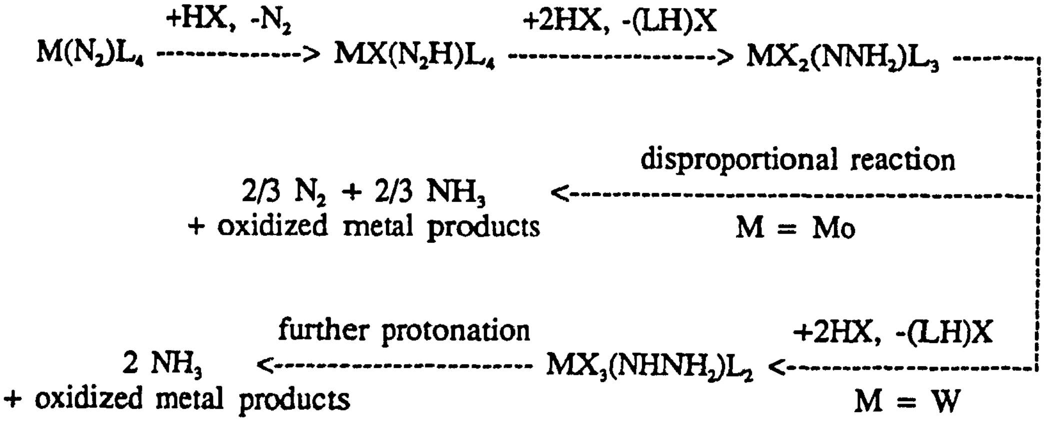
It is now evident that N-ligands will form complexes with all transition elements, but the qualities of different transition metals for binding, and more important, for activating the N-ligands to protonation are not yet defined. For various reasons, not all are convenient for nitrogen fixation investigations. For example, those of first transition period elements are rather labile hence not easy to study, while those of Ni, Pd, Pt series have attracted less interest presumably because their chemistry is not such as to lead to hydronitrogen species.

In this work, tungsten was chosen to be the metal centre of the model complex, there are two reasons for this:

a) Because of the great chemical similarity with molybdenum which was found to be essential for nitrogen fixing bacteria [42][43], tungsten complexes, like those of molybdenum, have been especially intensively studied. It was found that tungsten and molybdenum systems are the most versatile for synthesizing and isolating a whole series of dinitrogen complexes (or their derivatives) in a nitrogen fixation cycle.

b) Although molybdenum and tungsten are similar chemically, there are differences between them in certain compounds: some compounds of the same type differ noticeably in their reactivities in ways which are not easy to explain. For instance, on reaction with H_2SO_4/methanol, the complex $W(N_2)(PMe_2Ph)_4$ provides almost 98% yield of ammonia, while in the same conditions, the analogous molybdenum complex provides only about half that found with tungsten. The mechanism of this reaction may thus be illustrated by the following scheme:

SCHEME 2



This mechanism appears to diverge for the two metals at the N-NH$_2$ stage, possibly a reflection of the greater lability of molybdenum complexes and the poorer reducing power of this element as compared with tungsten in its intermediate oxidation states [44][45]. Thus, tungsten complexes are probably the better mimic of nitrogenase action.

2.2 LIGANDS

Two kinds of ligands are involved in the model complex: "participative" and "non-participative" ligands. The non-participative ligand in this thesis is dttd, it does not directly participate in the potential nitrogen fixation reaction and remains associated with the metal centre during the procedure, in other words, it does not appear among the reaction products at any step of the reaction cycle. The participative ligand here is imido ligand which is supposed to bond to, and dissociate reductively from, the metal centre repeatedly during a cyclic reaction.

2.2.1 DTTD

Although the non-participative ligand dttd does not physically contribute to the direct products of the reaction, it plays an fairly important part in determining the behaviour of our complex in a nitrogen fixation reaction.

Dttd is a tetradentate chelating ligand with both thiol and thioether donor groups, it coordinates with tungsten metal through four sulfur atoms. Two thiolate sulfur atoms covalently bond to tungsten by losing the two thiol protons while another two sulfur atoms of thioether groups coordinately bond to the metal. Two factors are involved here which explain why such kind of a ligand may be appropriate.

Why a sulfur based ligand?

There are several reasons for using a sulfur-based ligand.

Firstly, as being a fundamental ligating element in nitrogen-fixing enzymes, sulfur is used frequently in synthesis of complexes relating to nitrogen fixation. For example, molybdenum complexes with sulfur donor chelating ligands, e.g. benzene-1,2-dithiolates, or ethane-1,2-dithiolates, have received much attention.

Secondly, although N-ligands can bind to a variety of metal sites, a major focus in this area is the binding of N-ligands to a metal ***in an environment*** of sulfur atoms. Because, in comparison with some other widely used ligating elements, the sulfur atom is larger and more polarizable, therefore sulfur compounds are more powerful nucleophiles and they can stabilize a negative charge on an adjacent atom. Consequently, a metal site in an environment of sulfur was found not only to be able to bind a N-ligand, but also able to activate it toward electrophilic attack, facilitating the reduction reaction later on.

Another important reason for using S-ligands as non-participative ligands is the high stability of sulfur-metal bond. It is clear that in order only to study the mechanisms of reaction for a coordinated N-ligand, the non-participative ligand should be sufficiently robust to enable the reaction to go on and remain itself bound to the metal centre without any change.

The high affinity of metals for sulfur is clearly demonstrated by the enormous variety of metal sulfide minerals in nature. Qualitatively this might be understood using Pearson's concept of hard and soft acids and bases. It is better described, however by the covalency of the metal-sulfur bond. A high covalency is usually obtained when the metal's d valence orbital ionization potential (VOIP) (of the open shell transition metals) matches the sulfur 3p VOIP. In contrast to oxygen and nitrogen as donor atoms, sulfur has low lying, unoccupied 3d-orbital available, so it is suggested that metal-sulfur bonds involve some π back-donation from metal to sulfur whenever there are orbital of correct symmetry available for bonding. Actually, there is no unambiguous evidence available for such a bonding, so this influence should not be overstressed.

Turning now to the model of this study. Being highly polarisable, the two thiol groups of dttd can readily complex tungsten metal by losing thiol protons and forming strong bonds. The formation tendency of complexes with thioether groups is relatively low. Recent theoretical and structural studies indicate that thioethers possess two donor molecule orbitals which mix upon coordination forming two new ligand orbitals. One new orbital is approximately σ donating with respect to the metal, and the other orbital is oriented for potential π donation to the metal. When these donor orbitals are favourably directed toward the empty metal orbital, a very stable complex can be formed [46].

Why a chelating ligand?

Although there has been a good deal of argument about the origin of the chelate effect [47], the existence of this effect is well-confirmed, that is, metal chelates are inherently more stable than closely related non-chelate complexes [48]. There are several factors which influence the stability of a metal chelate, they are:

a) The size of the chelate ring: Most of the observations on the effect of ring size on stability are qualitative, being based on preparative experience.

b) The number of rings: Of two similar chelating agents, that which forms the greater number of chelate rings with a given metal forms the more stable complex.

c) The basic strength of the chelating molecule: In general, metal ions are Lewis acids, that is, electron acceptors. Therefore, for a series of closely related chelating agents, the greater the basic strength (pKa), the greater the stability of the metal chelate.

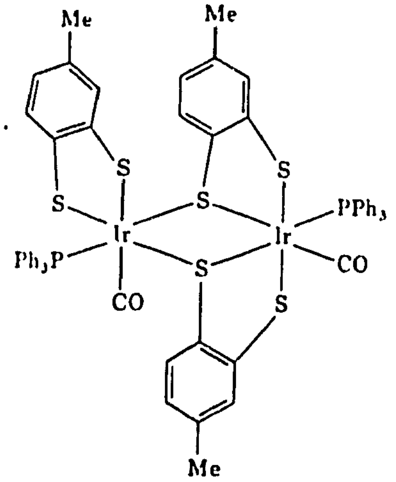
d) The effect of substitution in the chelating molecule: This may contribute to the effect of steric hindrance leading to a decrease in stability of the complexes.

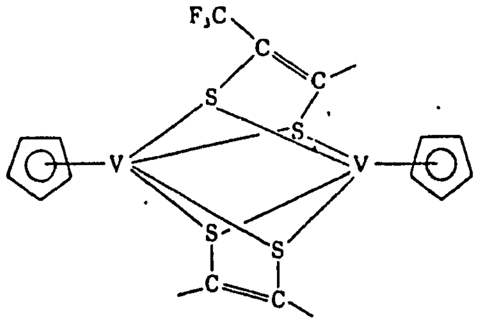
e) Nature of the donor atoms: This exerts the same stabilizing effect on both chelate and non-chelate complexes.

According to above effects, both of the factors, that the structure of three 5-member chelate rings in dttd upon coordination and the electron delocalization within the rings which extends into the rest of the ligands, favour the stability of the model complex [49][50][51].

However, another reason might be more important: In this work a single-metal model for the active site of nitrogenase is considered. Unfortunately, the chemistry of sulfur ligands is always plagued by their high tendency to bridge forming dimeric or polymeric complexes. For example, thiolate ligands show a high tendency to utilize an additional sulfur lone-pair of electrons to form dinuclear complexes with two bridging ligands [52][53], while for doubly bridging thiolate ligands, they can also 'glue' more then two metals together, forming rings [54].

In the case of this work, two benzene-1,2-dithiolate segments are joined. As mentioned above, benzene-1,2-dithiolate ligands and also ethane-1,2-dithiolate ligands have been studied extensively due to their connection to biological systems containing transition metal-to-sulfur bonds. In this field also, the sulfur bridge is the main problem which sometimes made it impossible to isolate a monomeric complex. Two examples of such kind of " sulfur-bridged " complexes with dithiolate ligands are shown as below:





The chelate structure of dttd formed by the ethyl chain linkage decreases the possibility of such kind of sulfur bridge, mainly because:

a) Two thiolate groups are converted to thioether groups upon ethyl linking. Although thioether ligands also sometimes form stable dinuclear complexes through sulfur bridges [55], it is less likely because they possess fewer lone pairs, relatively.

b) Sometimes characterizable complexes with sulfur-ligands can only be obtained with thiolates or thioethers having bulky groups to prevent bridging. The structure of two dithiolates linked by a ethyl chain in dttd itself doubles the space occupied by one coordinated ligand and, to certain extent, increases the steric crowding around the metal centre thus facilitating the isolation of a monomeric complex.

2.2.2 IMIDO LIGAND

While dinitrogen or hydrazido(2-) complexes are normally used for understanding the early stages of nitrogen fixation process, imido complexes are the potential models for investigating the last stage which leads to the production of ammonia. Although not much is known about the reactions of imido complexes, early studies have shown that surprisingly high yields (70%) of ammonia can be obtained by treatment with base (triethylamine or lithium methoxide) in methanol under ambient conditions [56][57].

2.3 OXIDATION STATE AND COORDINATION NUMBERS

Two factors which are always taken into account for a transition metal complex, are oxidation state and coordination number, which, to some extent, determine the stabilization and activation of a complex [58].

Oxidation state

Neutral tungsten element has a outermost electron structure $5d^4 6s^2$. Its oxidation states are the same as those of molybdenum ie. 2- to 6+. In this model complex, the oxidation state of tungsten centre is considered to be 4+ due to two metal-thiolate valence bonds and one metal-nitrogen double bond. The other two metal-thioether bonds are considered to be "coordinate" bonds which leave the oxidation state of the metal unchanged.

The complex was designed in its intermediate oxidation state for facilitating the protonation of N-ligand. According to the nitrogen fixation model presented in the Introduction, the protonation of a bonded N-ligand should be accompanied by the flow of electron into these N-ligands via the metal centre. In the high-oxidation-state complex, the increased partial positive charge presented on the metal strongly stabilizes the d levels and any electrons they contain become less available. This might be the reason, why in all of the nitrogen fixation systems, none of the central metal atoms has reached its highest available oxidation state prior to the protonation of N-ligands.

Coordination number

For tungsten complexes, coordination numbers between 4 and 6 are commonly encountered. Among them, coordination number 6 associated with corresponding octahedral geometry is the most common. In general, it is better for the complex to adopt its usual coordination number, 6, in order to minimize the possibility of undesired reaction, e.g. the coordination of solvent ligands during the reaction [59].

However, in our model complex, the target coordination number adopted is five, which makes it possible for us to investigate the reactions occurring only at the imido ligand site. It must be pointed out here, our model is neither coordinatively saturated nor in the least strained configuration, therefore the possibility exists, that some ligands left over from the starting tungsten complex can not be completely replaced by dttd and the imido ligand, or that some donor solvent will coordinate with the metal in the course of synthesis. Details are included in the Conclusions.

CHAPTER 3

SYNTHETIC ROUTE

This chapter describes the preparation of complexes of the type presented in the previous sections. Several convenient new methods were developed in the course of this work for the synthesis of the tungsten complexes.

3.1 MAIN REACTIONS

The preparation of dttdH$_2$

$H_2NC_6H_4SH$ + $NaOCH_2CH_3$ -----> $H_2NC_6H_4S^-Na^+$ + CH_3CH_2OH

2-Aminothiophenol

[Aromatic amine]*

(2 Na + 2 CH_3CH_2OH -----> 2 $NaOCH_2CH_3$ + H_2)

2 $H_2NC_6H_4S^-Na^+$ + $BrCH_2CH_2Br$ -----> $(H_2NC_6H_4S)_2Et$ + 2 NaBr

1,2-Di(o-aminophenylthio)ethane

[Diaromatic amine]

$(H_2NC_6H_4S)_2Et$ + 2 $NaNO_2$ + 4 HCl -----> $(Cl^-N_2^+C_6H_4S)_2Et$ + 2 NaCl + 4 H_2O

[Aryldiazonium salt]

---

* Simplified names or formulas in [ ] are used later on in the text.

$(\mathrm{Cl^-N_2^+C_6H_4S})_2\mathrm{Et}$ + 2 $\mathrm{MeOCS_2K}$ -----> $(\mathrm{MeOCS_2C_6H_4S})_2\mathrm{Et}$ + 2 $\mathrm{N_2}$ + 2 KCl

[Methylxanthate] [Aryl alkylxanthate]

(KOH + MeOH -----> KOMe + $\mathrm{H_2O}$)

(KOMe + $\mathrm{CS_2}$ -----> $\mathrm{MeOCS_2K}$)

$$(\mathrm{MeOCS_2C_6H_4S})_2\mathrm{Et} \xrightarrow{\mathrm{LiAlH_4}} (\mathrm{^-SC_6H_4S})_2\mathrm{Et} \xrightarrow{\mathrm{H^+}} (\mathrm{HSC_6H_4S})_2\mathrm{Et}$$

2,3,8,9-Dibenzo-1,4,7,10-Tetrathiadeciane

[$\mathrm{dttdH_2}$]

<u>The preparation of tungsten (IV) complexes</u>

2 $\mathrm{WCl_6}$ + $\mathrm{W(CO)_6}$ + 6 $\mathrm{CH_3CN}$ -----> 3 $\mathrm{WCl_4(CH_3CN)_2}$ + 6 CO

Bis(acetonitrile)tetrachlorotungsten(IV)

[Acetonitrile tungsten(IV)]

$\mathrm{WCl_4(CH_3CN)_2}$ + 2 THF -----> $\mathrm{WCl_4(THF)_2}$ + 2 $\mathrm{CH_3CN}$

Bis(tetrahydrofuran)tetrachlorotungsten(IV)

[Tetrahydrofuran tungsten(IV)]

<u>The formation of the model complex</u>

$\mathrm{WCl_4(THF)_2}$ + $(\mathrm{HSC_6H_4S})_2\mathrm{Et}$ -----> $\mathrm{W[(SC_6H_4S)_2Et]Cl_2}$ + 2 THF + 2 HCl

[$\mathrm{W(DTTD)Cl_2}$]

$\mathrm{W[(SC_6H_4S)_2Et]Cl_2}$ + $\mathrm{[(CH_3)_3Si]_2NMe}$ -----> $\mathrm{W[(SC_6H_4S)_2Et]NMe}$ + 2 $\mathrm{(CH_3)_3SiCl}$

[W(DTTD)NMe]

3.2 SYNTHETIC METHOD DISCUSSION

3.2.1 DTTD PREPARATION

The optimisation of the preparation of dttd is critical due to the relatively lengthy procedure and inherently poor yields. Basically, this preparation can be considered as the synthesis of a thiophenol from an aromatic amine. The synthetic method has been published elsewhere [60]. Although the behaviour of the diaromatic amine used here as starting material is somewhat different from that of simple aromatic amines, the method used here is still mainly based on well-established procedures. However, some steps were significantly modified in this special case.

The preparation of the starting material Diaromatic amine

$$H_2NC_6H_4SH + NaOEt \text{ -----> } H_2NC_6H_4S^-Na^+ + EtOH$$

$$(2\,Na + 2\,EtOH \text{ -----> } 2\,NaOEt + H_2)$$

$$2\,H_2NC_6H_4S^-Na^+ + BrCH_2CH_2Br \text{ -----> } (H_2NC_6H_4S)_2Et + 2\,NaBr$$

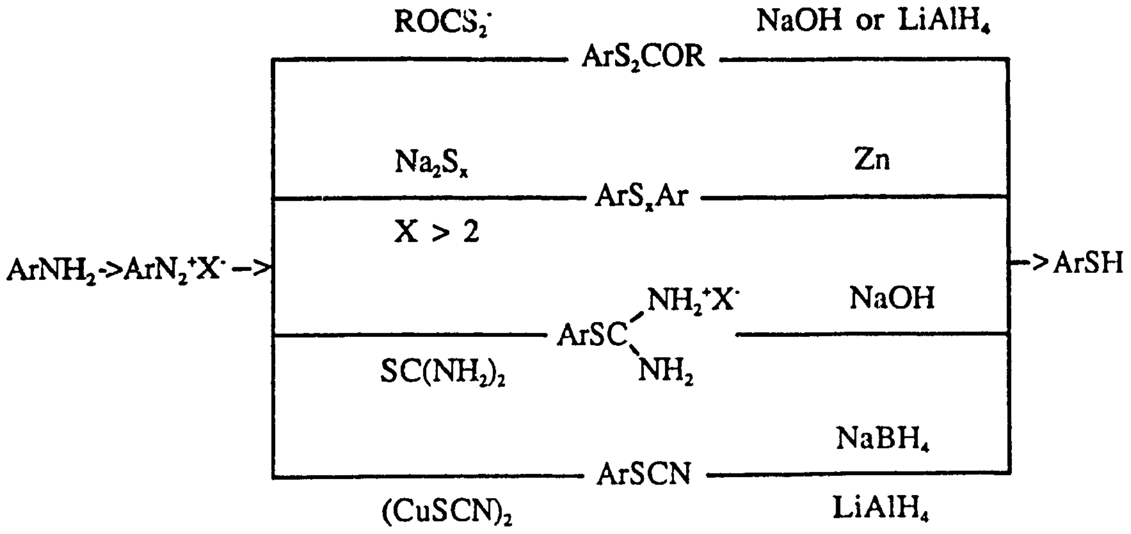
This is a typical nucleophilic reaction of thiophenol, the strong nucleophilicity of thiophenol results from the great polarizability of electrons on sulfur atom [61]. When two thiophenol molecules react with one dibromoethane in the presence of sodium ethoxide, nucleophilic attack occurs at two ends of dibromoethane molecule simultaneously, and as the result, two thiophenols became linked by the ethyl group [62].

Diazotization

$$(H_2NC_6H_4S)_2Et + 2\ NaNO_2 + 4\ HCl \text{ -----> } (Cl^-N_2^+C_6H_4S)_2Et + 2\ NaCl + 4\ H_2O$$

Diazotization of aromatic amine is included as the first step in all the possible pathways by which the primary aromatic amine can be converted to the product thiophenol. Some complete pathways are shown below [63]:

SCHEME 3



There are normally three methods for diazotization: a) In dilute aqueous mineral acid. b) In concentrated acid. c) In organic solvents.

Because of the relatively higher efficiency and higher reaction speed, commonly, diazotization of aromatic amine is carried out with nitrous acid in dilute aqueous mineral acid and usually yields the diazonium salt in solution. Since nitrous acid is an unstable compound, it is generated in the presence of the amine by reaction between sodium nitrite and a mineral acid. Despite the lower efficiency and slower rate, some weakly basic amines bearing strongly electron-attracting substituents on the aromatic nucleus are diazotized preferentially in concentrated acids, since hydrolysis of the generated diazonium compounds occurs in aqueous solutions with rising dilution. Usually, in such reactions the amine is dissolved in a concentrated acid, and diazotized with nitrosylsulphuric acid (NO^+HSO_4). Organic solvents are sometimes used in order to prepare solid diazonium salts.

As is explained later, the xanthate procedure was chosen in this work. In the literature procedure, concentrated acid was employed for diazotization in order to make a solid diazonium salt, which is suited for the base conditions required for the following xanthate reaction. However, by adjusting the acidity of diazonium salt solution before xanthate reaction and using it immediately after preparation, diazotization in dilute acid was proved, in this work, to be much faster and more efficient than in concentrated acid, normally, a complete conversion can be achieved. The final product (dttd) from dilute-acid-pathway is better, both in quality and quantity, than from concentrate-acid-pathway. The mechanism of diazotization in dilute acid is suggested to be as follows:

$$NaNO_2 + 2\,HCl \text{ ------> } H_2O + NO^+ + NaCl + Cl^-$$

$$Ar\text{-}NH_2 + NO^+ \overset{\text{slow}}{\text{------>}} Ar\text{-}NH_2^+\text{-}NO$$

$$Ar\text{-}NH_2^+\text{-}NO \overset{\text{fast}}{\text{------>}} Ar\text{-}NH\text{-}NO + H^+$$

$$Ar\text{-}NH\text{-}NO + H^+ \overset{\text{fast}}{\text{------>}} Ar\text{-}N^+{\equiv}N + H_2O$$

More than the theoretically required amount of sodium nitrite was prepared in the expectation of some loss of nitrous acid as NO and NO_2 during the reaction. Also more acid was used than the 4 equivalents per mole of amine that are required by the equation: this excess acid serves to keep the mixture strongly acidic which is necessary to prevent undesirable side reactions.

Xanthate reaction

$$(Cl^{-}N_2^{+}C_6H_4S)_2Et + 2\ MeOCS_2K \text{ -----> } (MeOCS_2C_6H_4S)_2Et + 2\ N_2 + 2\ KCl$$

$$(\ KOH + MeOH \text{ ------> } KOMe + H_2O\ )$$

$$(\ KOMe + CS_2 \text{ ------> } MeOCS_2K\ )$$

As has been seen above, several variations are possible for the step after diazotization, the most frequently used method is the xanthate reaction, but all the others listed have considerable potential. Ethylxanthate is the common reagent for xanthate method, while in this work methylxanthate was used instead because of the possible steric hindrance existing in this particular di-arylxanthate product. This was proved to be necessary by comparing the yields obtained from methyl- procedure with that of from ethyl- procedure.

In this reaction, there was found to be a danger of explosions: The explosions occurred on heating solutions of aryldiazonium salts and potassium methylxanthate. In order to avoid this, a small amount of nickel was added. Nickel acts as a catalyst in the formation of the aryl alkylxanthate and its addition circumvents heating the mixture and so makes the procedure much safer [64].

The most probable side products from the xanthate reaction in this work are the diaryl dithiocarbonate $OC(SC_6H_4S)_2Et$ and alkyl alkylxanthate $CH_3OCS_2CH_3$, and both of these side products can also be reduced to thiols by $LiAlH_4$ in succeeding reactions [65].

The cleavage of aryl alkylxanthates and formation of dttdH_2

$$(MeOCS_2C_6H_4S)_2Et \xrightarrow{LiAlH_4} (^{-}SC_6H_4S)_2Et \xrightarrow{H^+} (HSC_6H_4)_2Et$$

Two methods of cleavage of xanthate are available: a) hydrolysis under basic conditions [66] and b) reduction, particularly using Lithium aluminium hydride [67]. For aromatic compounds, hydrolysis of xanthate by sodium (or potassium) hydroxide is normally used, since most substituents are inactive to the hydroxide ion under the conditions needed for hydrolysis. But for hindered aromatic thiols, if there are no other easily reduced groups presented, like the diaromatic thiol (dttd) in this work, reduction of the xanthate by lithium aluminum hydride was proven to be a much more effective method.

Lithium aluminium hydride is a very powerful reducing agent, reducing a wide range of functional groups to their lowest oxidation state, selective reductions of functional groups are rarely possible. As the result, the reactions occurring in our system are very complex. The aryl alkylxanthate together with the side products formed in the xanthate reaction, i.e. diaryl dithiocarbonate and alkyl alkylxanthate, were all reduced. Moreover, some leaving groups cleaved in this procedure were reduced further to their lowest oxidation state. Therefore, the disadvantage of using $LiAlH_4$, to offset against the increasing yield resulting from the efficient reduction of diaryl dithiocarbonate to the desired product, is that a considerable amount of alkylthiols, e.g. CH_3SH were formed. Those remained in crude dttd, and were not easy to remove in the purification process.

DTTD purification

The crude product dttd was usually an oil-like product containing various kinds of impurities which might interfere with subsequent reactions, therefore it had to be purified before use.

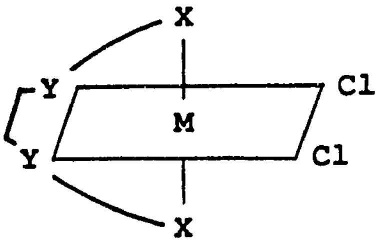
Under basic conditions, the corresponding salt of dttd is insoluble in certain organic solvents, thus we were able to isolate its salt from ether, and leave the polymeric impurities behind. The rest of the impurities were removed by filtering the aqueous salt solution and extracting the pure dttd from aqueous solution with ether after acidification. Normally after purification a solid product was obtained and, although this purified product might still contain some alkylthiols, it was useable for " metal-ligand" assembly.

3.2.2 THE PREPARATION OF STARTING TUNGSTEN (IV) COMPLEXES

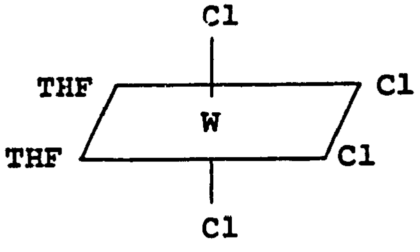
Several considerations

A tungsten(IV) complex, WCl$_4$(THF)$_2$, was synthesized by way of an intermediate complex WCl$_4$(CH$_3$CN)$_2$. WCl$_4$(THF)$_2$ served in this work as the starting tungsten complex for tungsten-ligand (dttd and imido group) complexation. The reason for using it as precursor is that it may complex these ligands by simple substitution reactions in which the oxidation state of metal centre remains constant. To predict if a compound is substitutionally labile is very difficult, even for the simplest substitution reaction. It depends upon the parameters of a) the metal ion, e.g. size, oxidation state, electronic configuration, coordination number, b) the ligands, e.g. size, dipole moment, nature of the donor atom, c) the complex, e.g. geometrical arrangement, isomerism etc. For brevity, only two facts are discussed below, they are configuration and bonding ability of both the precursor WCl$_4$(THF)$_2$ and ligands.

a) Configuration: According to the previous results [68][69], tetradentate ligands of the type (XC$_6$H$_4$Y)$_2$Et (dttd is the case when Y=S X=S$^-$) function as chelating agents upon complex formation, and, if a 6-coordinate complex is formed, e.g. MCl$_2$(chelate), the least strained configuration is that of (I):



(I)



(II)

So, a $WCl_4(THF)_2$ complex, in which two THF ligands *cis* to each other (II), should be suitable in configuration for binding dttd by replacing pairs of trans Cl and cis THF ligands with pairs of thiolate and thioether ligands.

An imido ligand might bind to a "vacant" metal site or displace a ligand (in a process which is presumably dissociative) or even, as we desired, displace two ligands. But as mentioned before, the possibility of causing an unsaturated coordination number and strained configuration makes this displacement unlikely.

b) Bonding ability: It is also necessary to compare the bonding ability of each pair of ligands which replace or are replaced in the substitution reaction.

Thiolate-Halido: Concerning each of the two thiolate groups RS^- in dttd independently, the electronic structure and reactivity are comparable to some extent to those of halido ligands, such as, for instance, a terminal monodentate RS^- ligand which can often replace or be replaced by a halido one. So, thiolate complexes are, in general, prepared by reaction of halogeno complexes with thiolate anions. In spectrochemical series, RS^- is placed between F^- and Cl^- [70].

Thioether-THF: Normally, THF can act as weak ligand and its complexes can be synthetically useful, especially in ligand exchange reactions [71]. In the spectrochemical series, it comes between H_2O and NH_3 [70]. The stability of the transition metal complexes with THF ligand and thioether ligand, like THT (tetrahydrothiophene), has been studied previously [72][73]. It was found that due to the greater polarizability, the sulfur atom in THT bonds more readily than does oxygen atom in THF with right-hand transition metal ions, e.g. Pt(II) and Au(I), which were normally thought to be among the better acceptors. This tendency decreases on going to the left in the transition series. In the case of Mo(IV) and W(IV), the adduct formation with THT is only slightly more favourable than that of with THF probably because these two transition metal ions are the type which are more or less exactly intermediate between the extremes of π-accepting and π-donating ions.

Imido-halido: Because of the strong π bonding capability of the imido ligand, the metal-imido bond is considered having triple bond character although its bond length is normally a bit longer than corresponding metal-oxo ($M\equiv O$) or metal-nitrido ($M\equiv N$) bond lengths. The imido ligand can bond to a metal site, by replacing some other ligands, forming stable imido complexes. If a silylamine is used (It is the case in this work), the great strength of Si-O and Si-X (X=F, Cl, Br) bonds will make silylamines especially effective for replacing oxo or halido ligands. Examples were shown before in section 1.2.

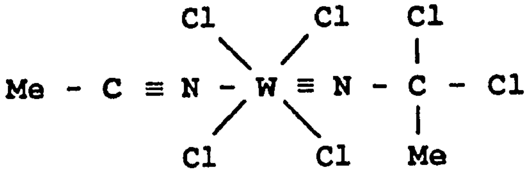
The preparation of Acetonitrile tungsten (IV) complex

$$2\ WCl_6 + W(CO)_6 + 6\ CH_3CN \text{ -----> } 3\ WCl_4(CH_3CN)_2 + 6\ CO$$

Tungsten hexachloride was employed here to prepare the complex $WCl_4(CH_3CN)_2$, although some other tungsten compounds can also be used. Tungsten halides exhibit a great tendency toward reduction. Under certain reaction conditions, W(VI) and W(V) halide can complex with various donor ligands and the products are WX_nL_{6-n}

(n= 4 or 5), while with amine or nitriles, they more commonly react to give W(IV) complexes because of the reducing properties of these ligands. Among various W(IV) complexes formed in this sort of the reaction, nitrile complexes, especially acetonitrile complexes, are employed mostly as precursors in the formation of other W(IV) complexes by replacement of the relatively labile acetonitrile groups with other ligands [74].

$WCl_4(CH_3CN)_2$ can be obtained simply by dissolving WCl_6 (or WCl_5) in neat acetonitrile and stirring for a long period. It has been suggested that this reaction goes by way of an alkylimido intermediate $[WCl_4(NCMeCl_2)]MeCN$ which then loses HCl and reacts further with acetonitrile to give $WCl_4(CH_3CN)_2$ [75][76]. The formation of the imido ligand may be taken as an addition of two Cl atoms to the C≡N group:



An infrared absorption around 1300 cm^{-1} has been attributed to the W≡N bond. However, this reaction is too slow to be convenient without a reducing agent.

In this work, a stoichiometric amount of $W(CO)_6$ was added. Although the mechanism of this reaction is not quite clear, it is obvious that the addition of $W(CO)_6$, which acts as both reactant and reducing agent, makes the rate of this reaction much higher. The product was obtained as a fine brown powder in high yield. $WCl_4(CH_3CN)_2$ is slightly soluble in acetonitrile, air sensitive in the solid state but stable under nitrogen. The *cis* configuration of this complex was confirmed by IR spectroscopy. (The discussion is in the section on analysis of IR spectra.)

The formation of tetrahydrofuran tungsten (IV) complex

$$WCl_4(CH_3CN)_2 + 2\ THF \dashrightarrow WCl_4(THF)_2 + 2\ CH_3CN$$

Compared with acetonitrile, THF is less strongly ligating, so, unlike the acetonitrile complex, $WCl_4(THF)_2$ can not be prepared directly by reacting with tungsten halide without any reducing agent.

Several methods have been published for making $WCl_4(THF)_2$, for example:

$$2\ WCl_6 + ZnEt_2 \dashrightarrow 2\ EtWCl_5 \xrightarrow{THF} 2\ WCl_4(THF)_2 \qquad [77]$$

$$[(n\text{-}C_4H_9)_4N]W(CO)_5Cl + WCl_6 \xrightarrow{THF} WCl_4(THF)_2 \qquad [78]$$

However the severe conditions needed for these reactions make these procedures difficult to control and only very low yields can be obtained.

A simple and high-yield procedure was performed in this work simply by stirring $WCl_4(CH_3CN)_2$ with excess of THF for 6-7 hours at room temperature. The product recovered is a microcrystalline orange-yellow powder which is air sensitive in the solid state and almost insoluble in THF. This complex was used immediately for subsequent synthesis because it deteriorates even under nitrogen when stored for a period of weeks. Elementary analysis confirmed its composition as $WCl_4(THF)_2$ and again, the IR spectra indicated the *cis* configuration for this complex. (Discussion is presented later in the section on IR spectral analysis.)

3.2.3 THE FORMATION OF MODEL COMPLEX

The coordination of dttd

$$\underset{}{WCl_4(THF)_2} + \underset{[\ dttdH_2\ ]}{(HSC_6H_4S)_2Et} \dashrightarrow \underset{[\ W(DTTD)Cl_2\ ]}{W[(SC_6H_4S)_2Et]Cl_2} + 2\ THF + 2\ HCl$$

This should be a simple substitution reaction in which two Cl^- and two THF ligands were replaced by one dttd ligand without change in oxidation state and coordination number. However, in fact, the result showed that more than one reaction occurred in this system: there are at least two compounds in the resulting product. Fortunately, the desired monomeric product can be isolated from THF due to its insolubility in this solvent. The compound left in THF, which became oil-like after evaporating all of the solvent, might be a dimeric or polymeric compound resulting from sulfur bridges formation or dttd ligand bridges.

As has been explained, because of the strong binding ability of the sulfur atoms and their high tendency to bridge, it is possible that one dttd ligand binds to two or more tungsten metals to form dimeric or polymeric compounds in the reaction. On the other hand, one tungsten centre binding more than one dttd ligand seems less possible because of steric crowding. According to this assumption, using excess of dttd and adding $WCl_4(THF)_2$ slowly to it so as to keep a high dttd/W ratio in the course of reaction is necessary.

The purity of dttd is another important factor that determines the success of this reaction. Some small-molecule impurities in dttd, e.g. alkylthiols, might react with tungsten(IV) compound predominantly and consume a considerable amount of $WCl_4(THF)_2$. As a result, only a very low yields, or sometimes nothing, was obtained. The composition of this complex was confirmed by elemental analysis and its IR spectrum is discussed later.

The coordination of imido ligand

$$W[(SC_6H_4)_2Et]Cl_2 + [(CH_3)_3Si]_2NMe \text{ -----> } W[(SC_6H_4S)_2Et]NMe + 2\ (CH_3)_3SiCl$$

Among tungsten-halido complexes, tungsten-fluoro complexes were used mostly with $[(CH_3)_3Si]_2NMe$ to prepare organoimido tungsten compounds, because of the great strength of Si-F bond. In the presence of certain solvents (acetonitrile, pyridine), the reactions go fast at, or even below, room temperature, while in the absence of solvent, the reactions go very slowly [79].

Since we were concerned about the relatively weak strength of Si-Cl bond, our reaction was carried out in THF solvent under reflux for 4 hours. The result was not as simple as that indicated by the equation shown above. Details are included in relevant sections later on.

CHAPTER 4

EXPERIMENTAL SECTION

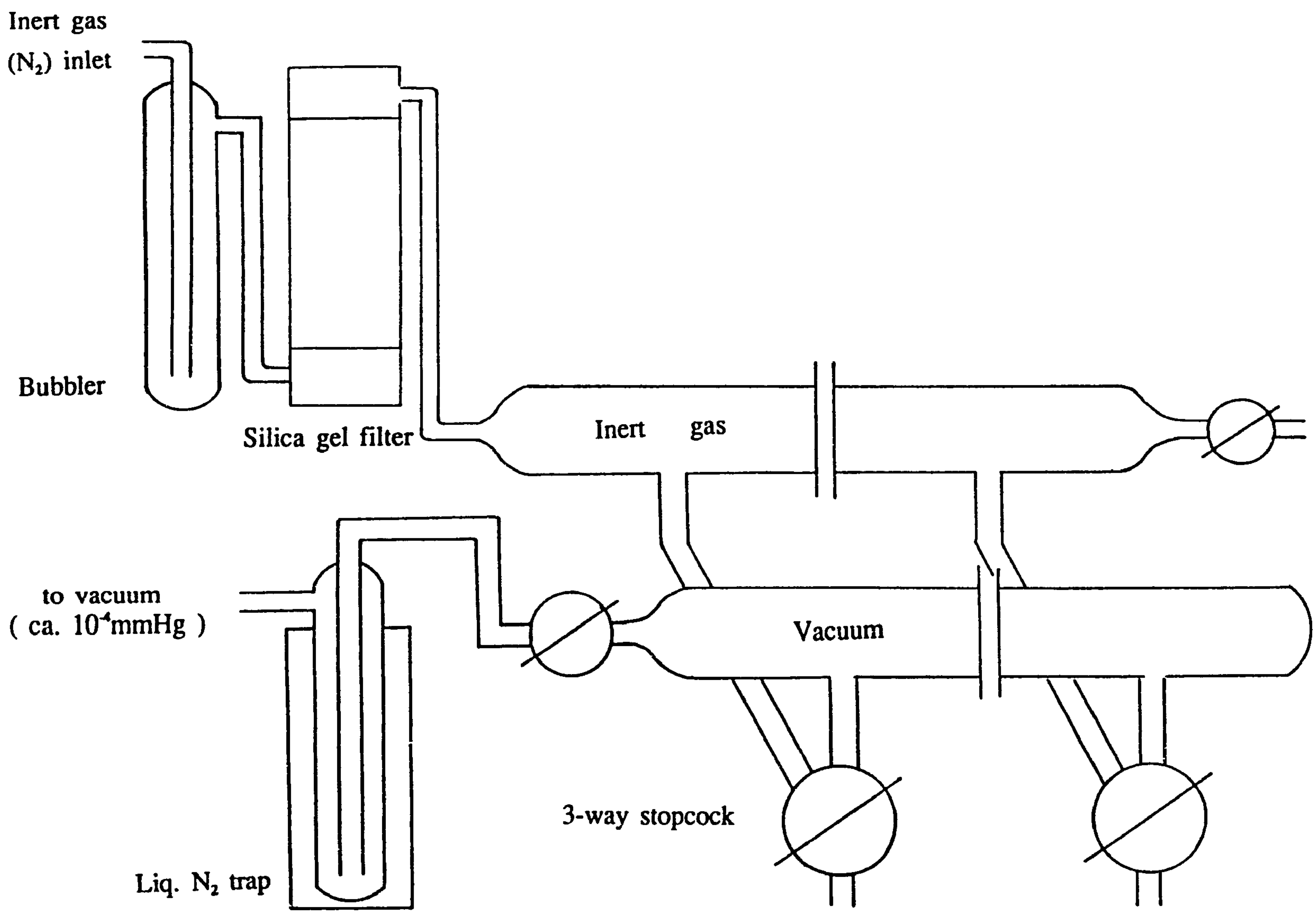
4.1 EQUIPMENT

In this work, reactions which were sensitive to air and moisture were conducted in a nitrogen filled dry-box. The dry-box supplied by the Kewanee Sci. and Eng. Co. was maintained under an nitrogen atmosphere that was recirculated routinely for removing traces of gaseous substances produced during the reaction, and any oxygen or water contamination.

An " Inert-gas-vacuum line " (simplified as " the line " later) was also used for the procedures which needed to be performed under vacuum condition or refluxed under nitrogen. Two long-glass tubes are included in the line, one is supplied with purified nitrogen which is pre-dried by passing through silica gel, another one is kept at high-vacuum with a rotary vacuum pump.

Part of the line is shown in Fig. 4.1.

Figure 4.1 Inert-gas-vacuum Line



4.2 MATERIALS

The materials listed below were used as purchased from commercial suppliers:

TABLE 4.1

COMMERCIALL PURCHASED MATERIALS

CHEMICALS	SUPPLIER
2-Aminothiophenol [$H_2NC_6H_4SH$], (99%)	a*
1,2-Dibromoethane [$BrCH_2CH_2Br$], (99+%)	a
Lithium aluminum hydride [$LiAlH_4$], (powder, 95+%)	b*
Tungsten (VI) chloride [WCl_6], (99.9+%)	c*
Heptamethyldisilazane [$(CH_3)_3SiN(CH_3)Si(CH_3)_3$], (97%)	a
Tungsten hexacarbonyl [$W(CO)_6$], (99%)	a
Sodium metal [Na], (lump, 99%)	d*
Potassium hydroxide [KOH], (flakes, 90%)	d
Sodium hydroxide [NaOH], (pellets, 99.9%)	d
Sodium nitrite [$NaNO_2$], (97+%)	d
Carbon disulfide [CS_2], (anhydrous, 99+%)	e
Hydrochloric acid [HCl], (37%)	e
Ethanol [C_2H_5OH], (99+%)	d
Methanol [CH_3OH], (99+%)	d

* a: Aldrich Chemical Co. Inc.
* b: Anachemia Chemicals Ltd.
* c: Alfa Products
* d: Fisher Scientific Co. Ltd.
* e: J.T. Baker Inc.
* f: ACP Chemicals Inc.

The materials, which were pre-purified before use, are listed in table 4.2:

TABLE 4.2

PRE-PURIFIED MATERIALS

Tetrahydrofuran (THF) [C_4H_8O], (99+%) f

Ethyl ether [$(C_2H_5)_2O$], (anhydrous, 99+%) d

These two solvents were initially dried over sodium for one week and were tested for dryness by adding benzophenone in the final stages. When dry, solvents turn dark blue due to the formation of a Na-benzophenone complex. The solvents were then distilled under nitrogen into clean dry flasks, and stored in dry-box prior to use.

Acetonitrile [CH_3CN], (99.5+%) d

It was dried over Calcium hydride (CaH_2) for one week and was distilled under nitrogen immediately before use.

Dichloromethane [CH_2Cl_2], (99.6%) b

It was dried over Linde type 4A molecular sieves, distilled under nitrogen, bubbled with nitrogen stream for 6 hours and stored in dry-box prior to use.

4.3 PREPARATION

4.3.1 THE SYNTHESIS OF DTTD

The preparation of the diaromatic amine [$(H_2NC_6H_4S)_2Et$]

This reaction was carried out in a 500-mL three-necked flask fitted with a reflux condenser, a 250-mL dropping funnel and a magnetic stirrer. The flask was charged with small pieces of clean sodium metal (9.2 g, 0.4 mole), and an excess of 170 mL ethanol (99%) was added rapidly through the dropping funnel. Then the mixture was stirred for 6 hours until all the sodium was dissolved.

2-Aminothiophenol (150 g, 0.4 mole) was added dropwise from dropping funnel over a period of 30 minutes with constant stirring. Then, to this solution, 1,2-Dibromoethane (37.6 g, 0.2 mole) was added in the course of 1 hour, and the mixture was heated under reflux for an additional 1.5 hours. The flask was cooled to room temperature and 200 mL water was poured in, causing a yellow precipitate to form. This yellow solid was collected as crude product by suction filtration and washed thoroughly with cold water.

For purification, this crude product was redissolved in 200 mL boiling ethanol. On completion of hot filtration, the filtrate was cooled to room temperature and crystallization was completed by keeping the flask in the refrigerator for 10 hours. The pure product was collected in 88-90% yield on a Buchner funnel, washed with two 50 mL portions of cold ethanol and dried in the air.

The preparation of potassium methylxanthate [$MeOCS_2K$]

Potassium hydroxide (86 g, 1.5 mole) was charged in a 500-mL three-neck flask fitted with a reflux condenser, a 250-mL dropping funnel and a magnetic stirrer. Methanol (99%, 170 mL) was added to flask rapidly through the dropping funnel and the mixture was stirred until all potassium hydroxide had dissolved. Then, CS_2 (114 g, 1.5 mole) was added dropwise into this stirred solution from the dropping funnel over a period of 1 hour. After the end of addition, the mixture was heated under reflux for 30 minutes. The orange solution was cooled to room temperature and kept in a refrigerator for 3 hours. The yellow cotton-like crystals were recovered in 55-60% yield by suction filtration, then washed with two 50 mL portions of cold methanol and dried in the air.

Diazotization

A suspension of aromatic amine (11 g, 0.04 mole) in an aqueous solution of HCl (20 mL, 0.24 mole) mixed with water (40 mL) was prepared in a 250-mL flask fitted with a 250-mL dropping funnel and a magnetic stirrer. This mixture was stirred and cooled in an ice-salt bath to a temperature between 0° and -5°. A solution of sodium nitrite was prepared by stirring 7 g (0.10 mole) of this finely divided salt in 20 mL water at 0°C for about 10 minutes. This cold sodium nitrite solution was placed in dropping funnel and then added dropwise into the stirred amine solution at such a rate that the temperature did not rise above 5°C.

(Diazotization is an exothermic reaction.)

The conversion proceeded rapidly and the end-point was determined by testing the reaction mixture with starch-potassium iodide paper - excess sodium nitrite forms nitrous acid that was not consumed by the amine and this nitrous acid, being an oxidizing agent, caused a deep blue colour of the test paper. Excess of nitrous acid was destroyed by the addition of a small amount of urea and the resulting solution was then brought to faint acidity (PH=6) with aqueous sodium carbonate. This diazonium salt solution was used immediately to avoid decomposition.

Xanthate reaction

This reaction was run in the open flask so that the nitrogen formed during the reaction could disperse rapidly to avoid danger.

Thus, methylxanthate (30 g, 0.2 mole) was dissolved in 200 mL of water in a 500-mL three-neck flask which was fitted with a dropping funnel, charged with the cold freshly made diazonium salt solution, and a magnetic stirrer. The other two necks of the flask were left open during the reaction.

Before the reaction, $NiSO_4$ (0.8 g, 0.005 mole), which served as a catalyst, was added into the xanthate solution. The mixture in the flask was then stirred in a water bath held at 10-15°C while the contents of the dropping funnel were added dropwise at a rate such that the reaction temperature did not exceed 20°C. During the course of this procedure, the evolution of nitrogen was observed and the aryl alkylxanthate appeared as brown oil on the surface of the solution. This product was then extracted with three 40 mL portions of ether in a separatory funnel, the ether extracts were then combined and dried over sodium sulfate for 24 hours.

Cleavage of aryl alkylxathates and formation of dttd

In a oven-dried 500-mL three-neck flask, fitted with a reflux condenser, a 250-mL dropping funnel and a magnetic stirrer, were placed lithium aluminum hydride (3.8 g, 0.1 mole) and 20 mL dry ether. This mixture in the flask was stirred all the time during the reaction.

The aryl alkylxanthate solution from last step was placed in dropping funnel, and was then added dropwise at a rate such that the reaction temperature was maintained to keep a mild refluxing. On completion of this addition, the mixture was heated under reflux in water bath held at 40°C for 1 hour. The water bath was then removed, the flask was allowed to cool to room temperature. 40 mL water was added dropwise from dropping funnel very carefully to destroy the unreacted $LiAlH_4$. The mixture was then acidified to a PH of about 4 by addition of approximate 15 mL of 34% hydrochloric acid.

The resulting two-phase solution was separated in a 250 mL separatory funnel. The lower aqueous phase was drawn off into a flask and was extracted with two 30 mL portions of ether. The ether extracts and the original ether phase remaining in the separatory funnel were combined and dried over sodium sulfate for 24 hours. The crude yellow oil-like dttd was obtained after evaporating the ether solvent at room temperature under reduced pressure.

DTTD purification

To the crude product was added sodium hydroxide (2 g), ethanol (80 mL) and THF (15 mL). The mixture was stirred in a 1000-mL flask for 1 hour until a clear brownish solution was obtained. Ether, (700 mL) was then poured in to precipitate the sodium salt. The yellow solid was collected on a Buchner funnel, washed with two 20 mL portions of ether and dried in the air for 10 minutes. This salt was dissolved in 30 mL water and acidified to a PH of about 4 by addition of dilute hydrochloric acid.

The pure product was extracted with three 20 mL portions of dry ether from the aqueous solution and dried over sodium sulfate for 24 hours. The ether was then removed under vacuum and a yellow, usually solid product was obtained. The yield was about 25-30%.

4.3.2 THE PREPARATION OF STARTING TUNGSTEN (IV) COMPLEXES

The preparation of acetonitrile tungsten (IV) complex $WCl_4(CH_3CN)_2$

This reaction was carried out in the dry-box. In a 100-mL flask, a stoichiometric mixture of WCl_6 (5.2 g, 0.013 mole) and $W(CO)_6$ (2.3 g, 0.0065 mole) was stirred at room temperature in an excess of 50 mL acetonitrile for 24 hours. During this procedure, evolution of CO was monitored with a mercury bubbler. The relatively insoluble brown product was recovered by suction filtration and washed repeatedly with acetonitrile to remove soluble by-products and any unreacted $W(CO)_6$. A yield of about 70-75% was obtained.

The preparation of tetrahydrofuran tungsten (IV) complex [$WCl_4(THF)_2$]

In the dry-box, a 100-mL flask was charged with $WCl_4(CH_3CN)_2$ (5 g, 0.01 mole) and THF (40 mL). The mixture was initially brown but turned bright orange after 6 hours stirring. The orange solid product was recovered in 65-70% yield by suction filtration and washed with two 20 mL portions of THF. The elemental analysis is given in table 4.3.

4.3.3 THE FORMATION OF THE MODEL COMPLEX

The coordination of dttd

In the dry-box, a stoichiometric excess of dttd (3.1 g, 0.01 mole) was dissolved in THF (10 mL) in a 100-mL flask with constant stirring. A suspension of $WCl_4(THF)_2$ (3.3 g, 0.007 mole) mixed with 10 mL of THF was then added dropwise into the stirred solution very slowly. All solid $WCl_4(THF)_2$ was dissolved and the solution turned intense violet in a period of 2 hours. The black solid product appeared gradually during the additional 2-hours of stirring and was separated by suction filtration from the dark purple solution. The product was washed by two 20 mL portions of THF and dried under nitrogen, obtaining a yield of about 60-65%. The result of elemental analysis is shown in table 4.4.

The coordination of imido ligand

In the dry-box, a suspension of $W(DTTD)Cl_2$ (1.4 g, 0.0025 mole) in 10 mL of THF was prepared in a 100-mL two-neck flask fitted with two septum caps. Then,

$[(CH_3)_3Si]_2NMe$ (0.45 g, 0.0025 mole) was added dropwise. After that the flask was taken out of the dry-box and set on the line, while one septum cap was replaced with a condenser connected with a mercury bubbler. During this procedure, a slow stream of dry N_2 was passed through the flask via the other septum cap to avoid air contact.

The flask was immersed in a water bath so that the level of the reaction mixture, which was stirred throughout the reaction, was the same as the water level of the bath. The temperature of the water bath rose to 65°C in a period of 30 minutes, while the flow of dry N_2 was maintained. After that the N_2 was shut off and reaction continued under reflux for 3 hours. The resulting mixture, which contained considerable amount of insoluble red solid, was filtered under nitrogen and vacuum dried on the line, the black solid obtained was washed repeatedly with hexane followed by ether. The red solid obtained from filtration was considered to be a by-product. (Details are included in relevant sections.)

TABLE 4.3

ELEMENTAL ANALYSIS OF $WCl_4(THF)_2$

$WCl_4C_8H_{16}O_2$ Molecular weight 469.91

	Calculated for above formula (weight %)	Found
W	39.14	35.04
Cl	30.18	26.18
C	20.45	18.93
H	3.43	3.62
O	6.81	16.23 (by difference)

* The elemental analysis in Table 4.3 and Table 4.4 were performed by Guelph Laboratories Ltd. (Ontario Canada)

TABLE 4.4

ELEMENTAL ANALYSIS OF W(DTTD)Cl_2

$WCl_2C_{14}H_{12}S_4$		Molecular weight 563.28
Calculated for above formula (weight %)		Found
W	32.65	31.64
Cl	12.59	10.80
C	29.85	31.17
H	2.15	2.54
S	22.77	24.05

CHAPTER 5

SPECTROMETRIC IDENTIFICATION AND DISCUSSION

5.1 EXPERIMENTAL CONDITIONS

Infrared

The infrared spectra were recorded on a Bomen-Michelson 102 spectrometer. NaCl or CsI windows were used depending on the different wave-number regions to be examined. Solid samples were prepared by mulling with mineral oil in the dry box and sealing the mull between windows. Solution samples were prepared by dissolving samples in CCl_4 and sealing them in cells. The peaks arising from CCl_4 have been eliminated from the spectra. All IR spectra are in units of cm^{-1} and vibrations are not assigned to symmetric or antisymmetric modes.

Nuclear Magnetic Resonance

The n.m.r. spectra were obtained on a 80 MHz, Bruker WP-80S1 instrument. The samples were dissolved in $CDCl_3$ using TMS as internal standard. The chemical shift values were expressed in ppm units from the TMS peak.

5.2 SPECTRA ANALYSIS

5.2.1 DTTD and The Diaromatic Amine

IR spectra

Searching for Table 5.1, the obvious changes between IR spectra of amine, diamine and dttd are:

a) The absence of two bands in region from 3360-3470 cm^{-1}, which were assigned as $\nu(NH_2)$, and one band at around 1305 cm^{-1}, which was assigned as ν(Ar-N), in the dttd spectrum, indicates the replacement of NH_2 group.

b) In the spectra of the diaromatic amine and dttd, two bands in region from 2914-2970 cm^{-1} arising from $\nu(CH_2)$, are due to the formation of the ethyl linkage.

c) The band at 2520 cm^{-1} can be surely designated as ν(SH). The absence of only this band in the spectrum of the diaromatic amine indicates the loss of thiol protons of the aromatic amine upon ethyl linking (on convertion to the diaromatic amine) and the replacement of NH_2 by the SH group (when converting from diaromatic amine to dttd).

All the bands designated as benzene modes show the characteristics of the type of substituted aromatic ring. The bands in the region 730-750 cm^{-1} arise typically from 1,2-disubstituted benzene derivatives.

NMR spectrum

DTTD shows a sharp ^1H n.m.r. spectrum: the absorptions fall into three classes. The ethyl group gives rise to a singlet at 3.05 ppm., another singlet at 4.26 ppm. is due to the thiol groups. A multiplet at 7.32-7.07 ppm. is typically the response of the substituted benzene ring.

The ratios of the protons in these three groups were determined approximately by measurement of relative peak areas. The result of a ratio of 2 : 4.2 : 8.3 for $H(SH_2)$: $H(CH_2)$: $H(C_6H_4)$ is close to the calculated value of 2 : 4 : 8 correspondingly.

TABLE 5.1

IR SPECTRAL RESULTS OF DTTD AND THE DIAROMATIC AMINE

Abbreviations: ν= stretch; δ= bend; β= in-plane bend; γ= out-of-plane bend; r= rock; ω= wag; vs.= very strong; s.= strong; ms.= medium strong; m.= medium; w.= weak; vw.= very weak; vbr.= very broad; br.= broad; cmbn.= combination;

$(HSC_6H_4S)_2Et$ ($dttdH_2$)	$(H_2NC_6H_4S)_2Et$ (diaromatic amine)	$H_2NC_6H_4SH$ (aromatic amine)	
	3450 s.	3470 ms.	ν(NH_2)
	3362 s.	3380 ms.	ν(NH_2)
3049 m.	3051 m.	3070 m.	ν(=CH)
2966 m.	2970 ms.		ν($-CH_2-$)
2914 ms.	2915 m.		ν($-CH_2-$)
2520 s.		2520 m.	ν(SH)
1923 w.	1935 w.	1900 w.	ν(=CH)
1686 w.	1703 w.	1665 w.	ν(=CH)
1572 s.	1607 s.	1615 s.	ν(=CH)
1477 ms.	1478 s.	1480 s.	ν(C-C)

1435 s.	1446 ms.	1455 s.	ν(C-C)
	1305 m.	1305 s.	ν(Ar-N)
1261 s.	1264 s.	1262 m.	ν(C-C)
1198 cmbn.	1157 cmbn.	1158 cmbn.	ν(C-C)
1112 ms.		1086 m.	unassigned
1041 s.	1044 ms.	1024 m.	β(=CH)
937 m. cmbn.		908 m.	unassigned
743 vs. cmbn.	733 vs. cmbn.	750 vs. cmbn	ν(Ar-S) or β(=CH)
657 m.			r(=CH)

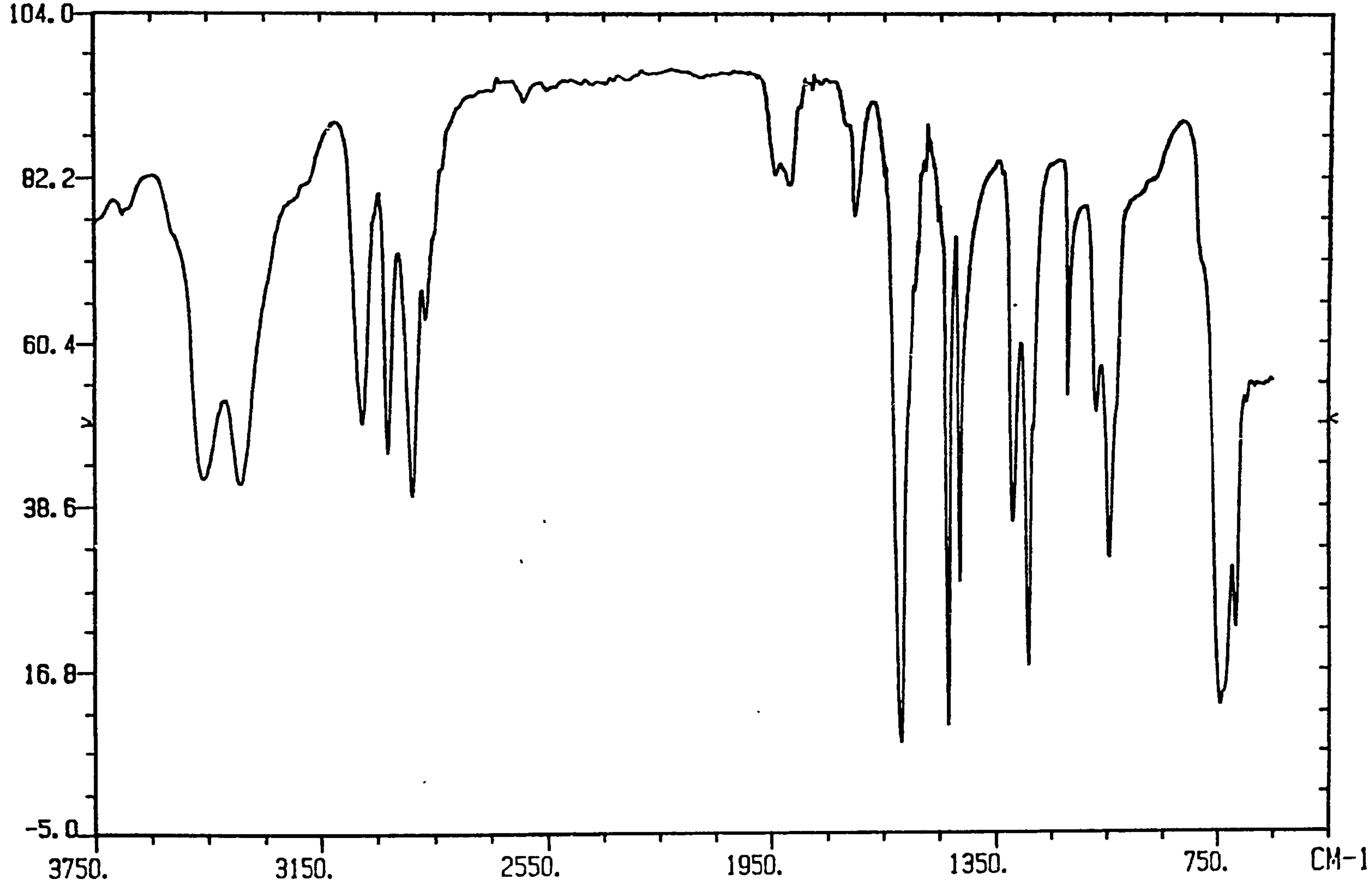


Figure 5.1 IR Spectrum of The Diaromatic Amine $(H_2NC_6H_4)_2Et$

Figure 5.2 IR Spectrum of DTTD

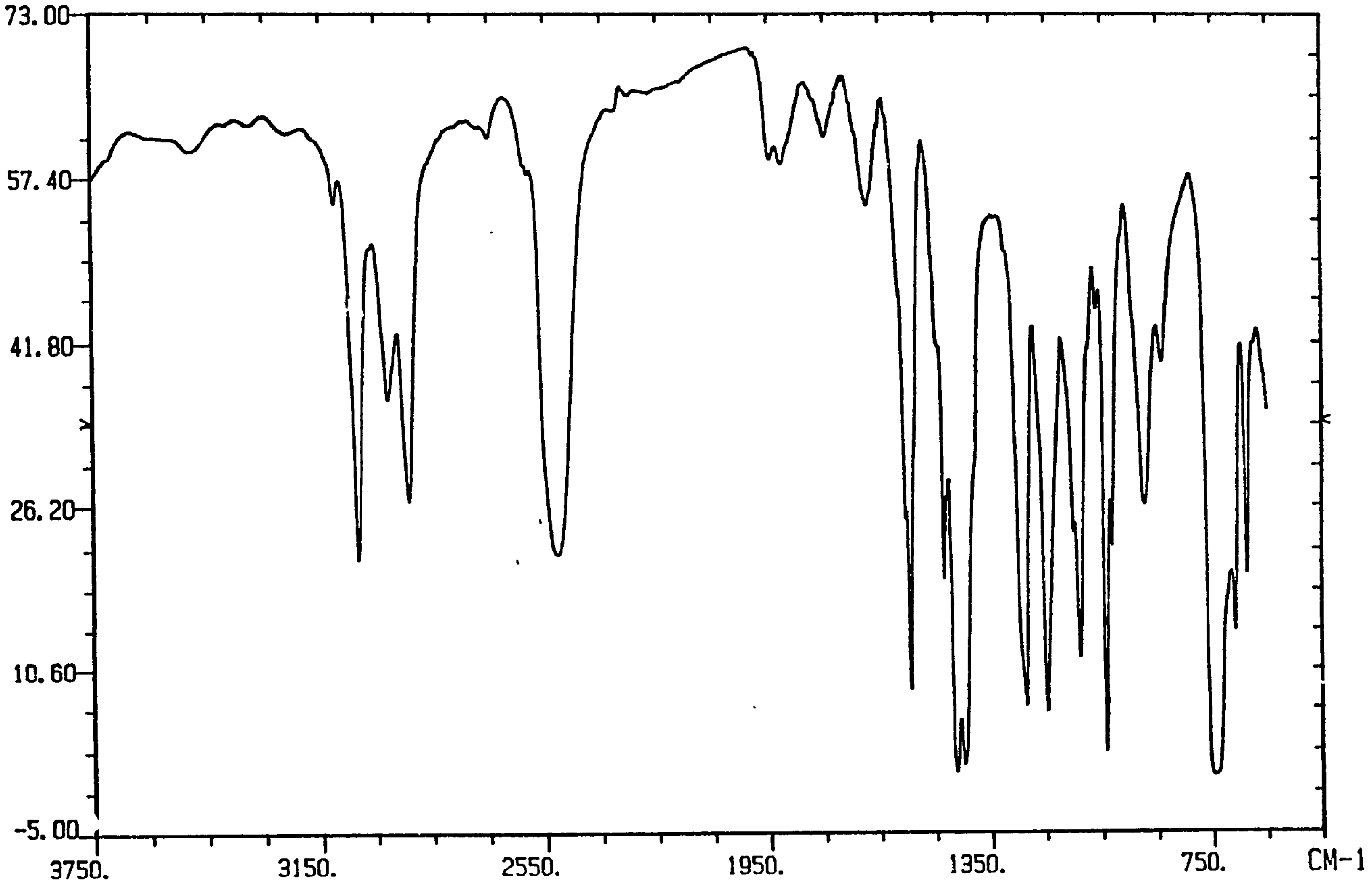
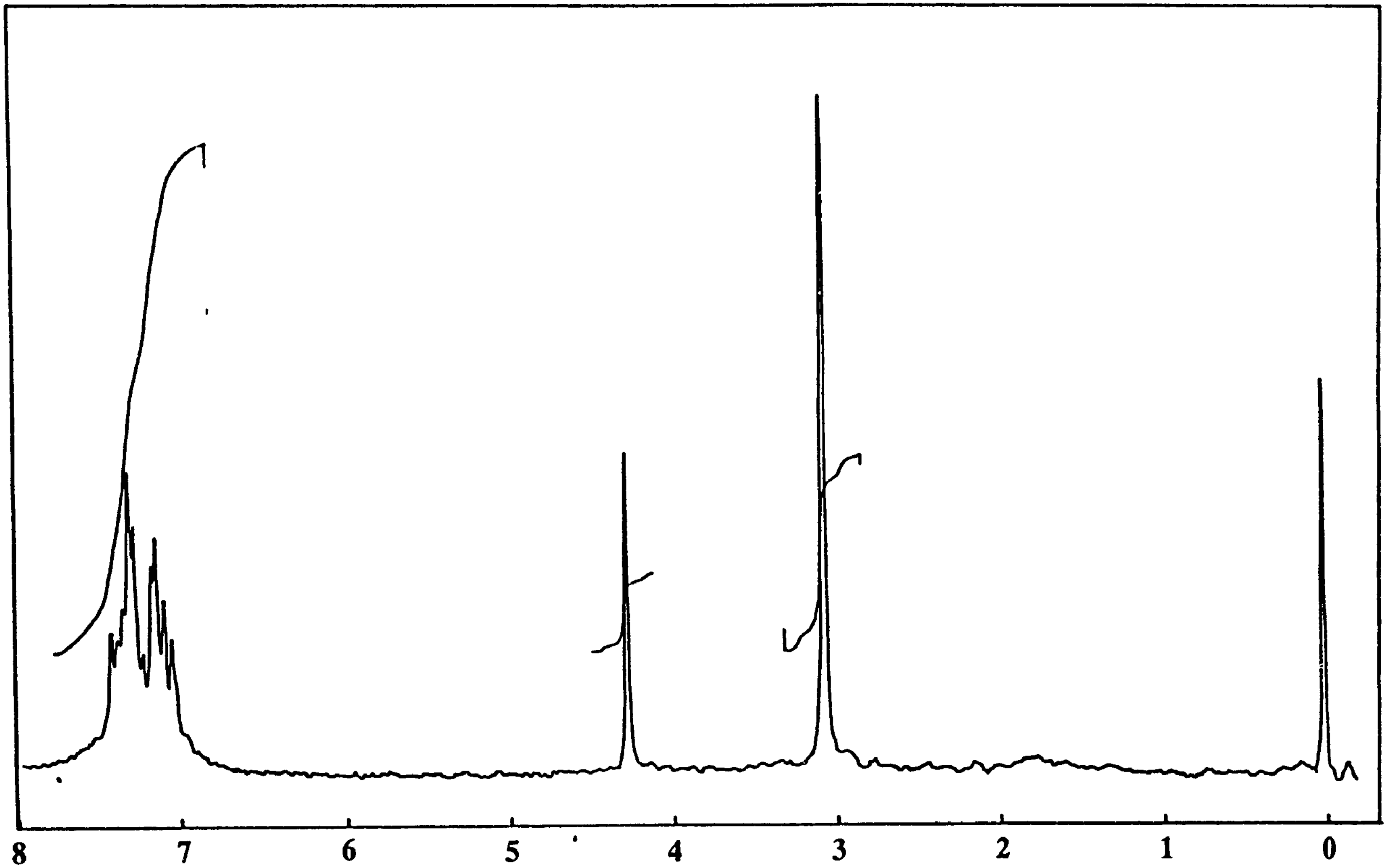


TABLE 5.2

NMR SPECTRAL RESULTS OF DTTD

CHEMICAL SHIFTS (p.p.m.)	INTEGRAL	INTENSITY	ASSIGNED
7.320	4.377	2.719	Ph
7.278	10.411	4.970	Ph
7.249	7.120	4.061	Ph
7.145	6.985	3.454	Ph
7.120	6.925	3.876	Ph
7.075	5.637	2.889	Ph
4.263	9.956	5.760	SH
3.049	21.105	10.643	CH_2

Figure 5.3 NMR Spectrum of DTTD



5.2.2 $WCl_4(CH_3CN)_2$

IR spectrum

In this spectrum, the region 500-4000 cm^{-1} is typical only of the coordinated organic ligands, and alterations to the stretching frequencies of a ligand are usually used to ascertain the formation of the "coordinate bond". It can be seen in Table 5.3 that the coordinated nitriles show the bands of ν(C≡N) at 2305 cm^{-1} and 2270 cm^{-1}, which are 30-40 cm^{-1} higher than in the free nitrile at 2266 cm^{-1} and 2235 cm^{-1} correspondly [ν(C-C) and δ(C-C≡N) also obviously increased]. This increase in magnitude of the "C≡N" stretching frequency upon adduct formation by the N lone pair of electrons of nitrile appears to be quite general [80][81]. Two mechanism might make significant contributions to this frequency increase:

a) A kinematic coupling of the CN and M-N stretching vibrations during excitation of the CN normal mode [82]: It is associated with the mechanics of the system and does not require an increase in the CN bond force constant. This effect could account only for a minor increase of the CN stretching frequency thus is less important.

b) An increase in bond force constant resulting from hybridization changes in the coordinated nitrile [83]: This fact was suggested to be the main cause for the frequency increase. In general, N (as well as C) is thought being hybridized in the CN entity and rehybridized at the nitrogen upon coordination. After measuring the contribution of the bonding electron density of each atom orbital (AO) pair of the energy of the molecule in free and coordinated CH_3CN, it was found that the N_{2s}

orbital, in overlapping with the C_{2s} and $C_{2p\sigma}$ orbital in all the MO'S, is the major cause for stabilization of the CN group following adduct formation.

The region 200-400 cm^{-1} in this spectrum includes the bands arising from tungsten-halogen (W-Cl) and tungsten-ligand (W-N) stretching modes. The bands arising from W-Cl stretching modes were used to ascertain the geometric configuration of this complex. $WCl_4(CH_3CN)_2$ is an octahedral molecule, it may be in the *cis* configuration (approximate C_{2v} symmetry) or the *trans* configuration (approximate D_{4h} symmetry). For the *cis*-isomer, four W-Cl infrared active modes ($2A_1 + B_1 + B_2$) are expected, whereas for the *trans*-isomer, only one W-Cl infrared active stretching mode (Eu) is expected. In this spectrum, two bands at 326 cm^{-1} and 281 cm^{-1} were observed, which can safely designated as W-Cl stretching modes. At high resolution, one band at 326 cm^{-1} can be resolved into two peaks at 330 cm^{-1} and 320 cm^{-1} respectively. The appearance of these three bands strongly suggests a *cis* configuration for this complex although the fourth W-Cl mode was not observed. (Which might be below the cutoff frequency for this spectrum.)

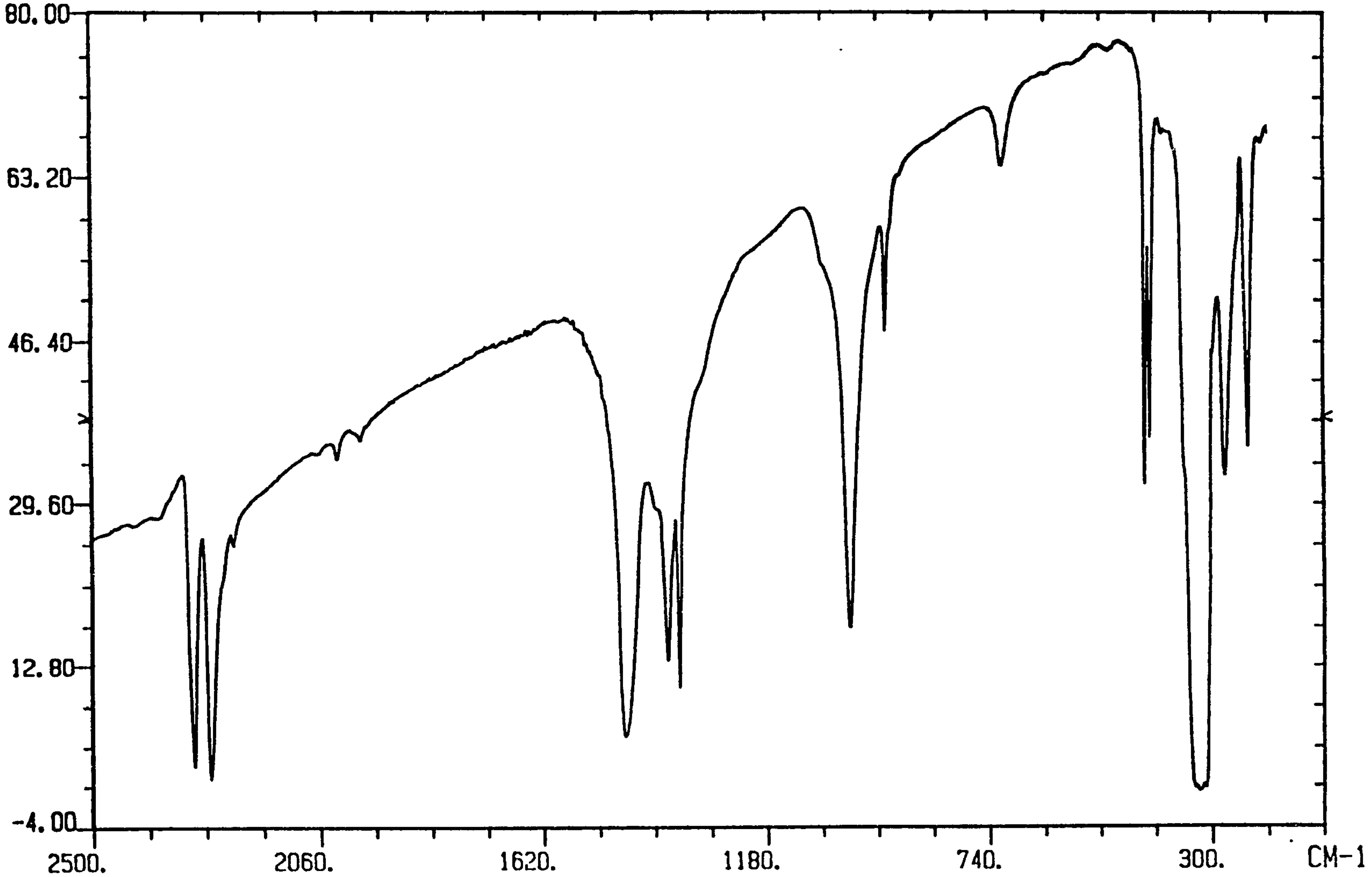
There is no evidence that the band at 233 cm^{-1} in this spectrum can be assigned to W-N stretching mode. Although the ν(M-N) bands of acetonitrile complexes are assigned in 450-160 cm^{-1} region, these stretching modes are difficult to identify because they are easily confused with other bands.

TABLE 5.3

IR SPECTRAL RESULTS OF $WCl_4(CH_3CN)_2$

$WCl4(CH_3CN)_2$	CH_3CN (neat)	
2305 m.	2266 ms.	$\nu(C\equiv N)$
2270 ms.	2235 s.	$\nu(C\equiv N)$
1456 vs. (also nujol)	1450 vs.	$\delta(CH_3)$
1375 s. (also nujol)	1372 s.	$\delta(CH_3)$
1353 ms.		nujol
1015 s.	1040 s.	$\delta(CH_3)$
945 m.	920 ms.	$\nu(C-C)$
724 w.	742 m.	unassigned
431 m.	376 m.	$\delta(C-C\equiv N)$
422 m.	361 m.	$\delta(C-C\equiv N)$
326 vs. br.		$\nu(W-Cl)$
281 m.		$\nu(W-Cl)$
233 m.		unassigned

Figure 5.4 IR spectrum of $WCl_4(CH_3CN)_2$



5.2.3 $WCl_4(THF)_2$

IR spectrum

The spectrum of coordinated THF differs from that of uncomplexed THF principally in the region 800-1100 cm^{-1}. Two strong THF bands at 1070 cm^{-1} and 910 cm^{-1} are shifted respectively to 989 cm^{-1} and 815 cm^{-1} upon coordination, these bands are apparently associated with ν(C-O-C). The decrease of these stretching frequencies is expected. THF here acts as electron donor, when coordinating with tungsten, the electron density transfer partly from oxygen to metal centre, as a result, the C-O-C bond is weaker than that of in free THF.

The band for ν(W-O) was not identified. Normally the stretching of the tungsten-oxygen multiple bond is observed at 940-970 cm^{-1}, of single bond at 300-600 cm^{-1} and of coordinated bond at 300-380 cm^{-1}. For coordination compounds, these stretching modes are always coupled with other vibrations.

Compared with that of in $WCl_4(CH_3CN)_2$ spectrum, the bands of ν(W-Cl) in this spectrum shifted from 326 cm^{-1} and 281 cm^{-1} to 316 cm^{-1} and 253 cm^{-1} respectively. This shift was reported previously [84] and was suggested to be the consequence of replacing the relatively weaker donor ligand (e.g. CH_3CN_2) with stronger donor ligand (e.g. THF).

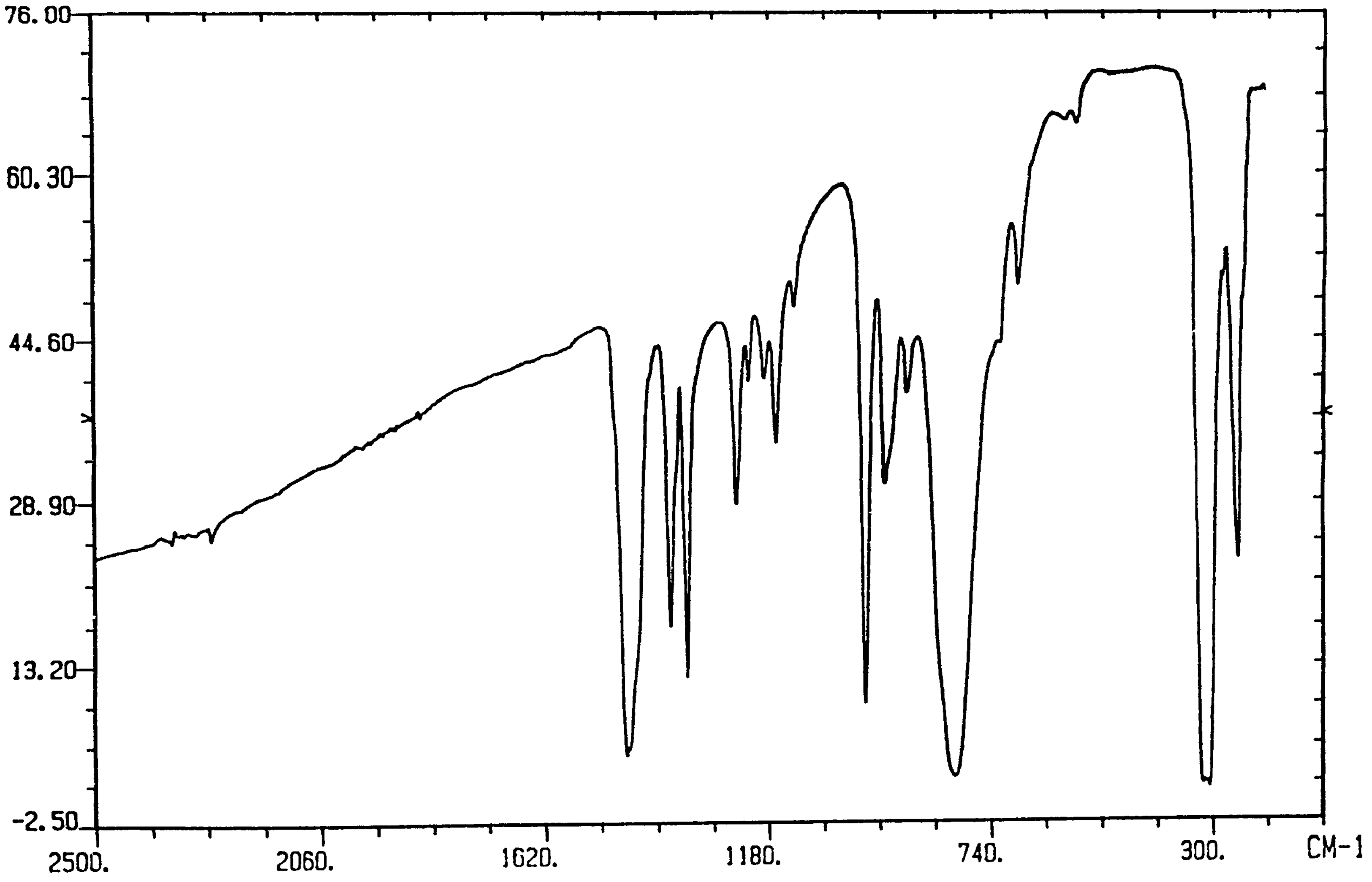
The *cis* configuration of this compound is again supported by the appearance of one single and one combined band. (The explanation is presented in the previous section.)

TABLE 5.4

IR SPECTRAL RESULTS OF $WCl_4(THF)_2$

$WCl_4(THF)_2$	THF (neat)	
1455 vs. (also nujol)	1455 m.	$\delta(CH_2)$
1376 ms. (also nujol)	1360 w.	$\omega(CH_2)$
1343 ms. (also nujol)	1330 vw.	$\omega(CH_2)$
1245 m.	1285 w.	$\omega(CH_2)$
1226 w.	1220 w. cmbn.	ν(ring)
1189 w.	1188 ms.	ν(ring)
1166 w.	1140 w.	ν(ring)
989 s.	1070 vs.	ν(C-O-C)
947 m.		unassigned
918 w.		unassigned
815 vs.	910 vs.	ν(C-O-C)
685 w.	660 w. vbr.	unassigned
316 vs.		ν(W-Cl)
253 s.		ν(W-Cl)

Figure 5.5 IR Spectrum of $WCl_4(THF)_2$



5.2.4 W(DTTD)Cl_2

IR spectrum

A strong band at 380 cm^{-1} in this spectrum can be undoubtedly assigned to W-S stretching mode arising from tungsten-thiolate bond. The stretching mode of tungsten-thioether may be assigned at 222 cm^{-1} according to the usual assignment of 350-200 cm^{-1} for metal-thioether stretching. Like some other S-bonded transition metal complexes, several bands of low intensity near 450 cm^{-1} are shown in this spectrum. Bands between 304-332 cm^{-1} are assigned to W-Cl stretching.

The vibration of coordinated dttd can be clearly seen at 743 cm^{-1}, which is typically the β(=CH) for 1,2-disubstituted aromatic compound.

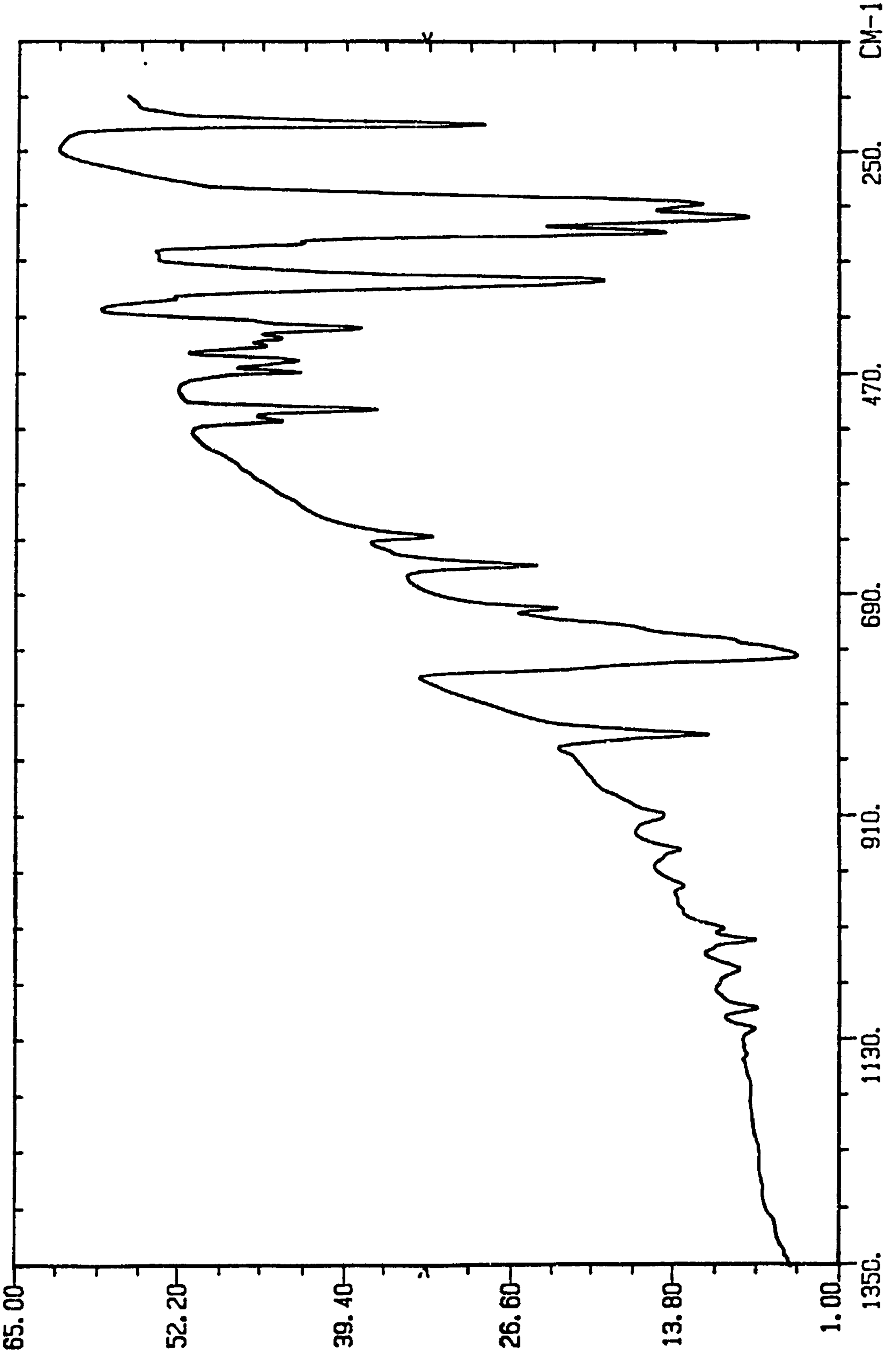
TABLE 5.5

IR SPECTRAL RESULTS OF $W(DTTD)Cl_2$

$W(DTTD)Cl_2$

829	m.	unassigned
743	s.	ν(Ar-S) and β(=CH)
660	w.	r(C=H)
506	w.	unassigned
469	w.	unassigned
457	w.	unassigned
426	w.	unassigned
380	s.	$\nu(W\text{-}S_{thiolate})$
331	vs.	ν(W-Cl)
317	vs.	ν(W-Cl)
304	vs.	ν(W-Cl)
222	ms.	$\nu(W\text{-}S_{thioether})$?

Figure 5.6 IR Spectrum of W(DTTD)Cl_2



5.2.5 W(DTTD)(THF)NMe

The final compound was identified as W(DTTD)(THF)NMe by its Mass spectrum, NMR spectrum and IR spectrum. The compound was not obtained analytically pure as small quantities of by-product, which can be seen in both IR and mass spectrum, are retained even after purification.

IR spectrum

Owing to the large metal-nitrogen bond strength and the large dipole moment of the bond, it might be presumed that IR spectroscopy would represent a useful tool for probing the structure of mononuclear organoimido complexes. However for a variety of reasons this potential has not been fully realized. The other ligands in many organoimido complexes have bands which frequently obscure those of the imido group. Coupling of the M-N vibrational modes with other metal-ligand modes and with modes of the organic substituent on imido nitrogen atom seem to further complicate the situation. However searching through table 5.6, we may still conclude:

a) Two bands at 1250 cm^{-1} and 720 cm^{-1} may be assigned the W=N-C stretching mode. It has been well established that the majority of the tungsten-imide vibrations fall in the range 1100-1300 cm^{-1} with a second associated band at 720 cm^{-1} [85][79]. Some authors have stated that these values represent the metal-nitrogen stretching frequencies, while others merely correlated these bands with the presence of the organoimido ligand.

b) By comparison with the IR spectrum of W(DTTD)Cl_2 (which has no band around 800 cm^{-1}), one strong band at 808 cm^{-1} in this spectrum may indicate the coordination of THF.

c) In this spectrum, the continued presence of β(=CH) at 740 cm^{-1}, ν(W-$S_{thiolate}$) at 386 cm^{-1} and ν(W-$S_{thioether}$) at 235 cm^{-1} demonstrates the stability of the coordination of dttd with tungsten centre.

d) The band at 437 cm^{-1} (at 426 cm^{-1} before) has become stronger, which may indicate the overlap with a new band δ(W=N-C) [79].

e) A small peak at 314 cm^{-1}, which may be due to a W-Cl stretching mode, is tentatively attributed to a by-product left in the sample. (The explanation is presented in the next section.)

NMR Spectrum

NMR spectroscopy has proven to be an effective tool for the study of organoimido derivatives which are diamagnetic and sufficiently soluble [86]. Although our final complex has a d^2 electron configuration, it may be diamagnetic as a result of the ground-state splitting of the octahedral $^3T_{1g}$ term under spin-orbit and low-symmetry perturbation [87][88]. A relatively sharp ^{1}H n.m.r. spectrum was obtained and it can be assigned by general comparison.

Compared with the n.m.r. spectrum of dttd, it is as expected that, in this spectrum, the benzyl and ethyl resonances are retained while the thiol hydrogens disappear. Two multiplets at around 1.80 ppm and 3.70 ppm clearly indicate the presence of a THF group.

The downfield chemical shift of the methyl hydrogens in NMe from 2.66 ppm for $(Me_3Si)_2NMe$ to 5.40 ppm for W(DTTD)(THF)NMe in this spectrum is a common feature of the ^1H n.m.r. of alkylimido ligands, and is comparable with the corresponding value (δ 5.50 ppm) for $[WF_5(NMe)]^-$ and (δ 5.53 ppm) for $W(NMe)F_4(MeCN)$ [85]. This downfield shift is consistent with triple-bond character in the tungsten-nitrogen bond [87].

Mass spectrum

Table 5.8 lists the most abundant W-containing fragments in the mass spectrum. Peaks due to ligand fragment ions were also observed. The presence of a molecular ion peak (m/e=604) is suggested to be due to the by-product. (The explanation is presented in next section.)

TABLE 5.6

IR SPECTRAL RESULTS OF W(DTTD)(THF)NMe

W(DTTD)(THF)NMe	
1250 s.	ν(W=N-C)
1034 w.	unassigned
940 m.	unassigned
902 m.	unassigned
838 m.	unassigned
808 ms.	ν(C-O-C)
740 vs.	ν(Ar-S) and β(=CH)
720 s.	ν(W=N-C)
661 w.	r(C=H)
517 w.	unassigned
437 w.	δ(W=N-C) ?
386 s.	ν(W-S$_{\text{thiolate}}$)
314 w.	ν(W-Cl)
235 ms.	ν(W-S$_{\text{thioether}}$) ?

Figure 5.7 IR Spectrum of W(DTTD)(THF)NMe

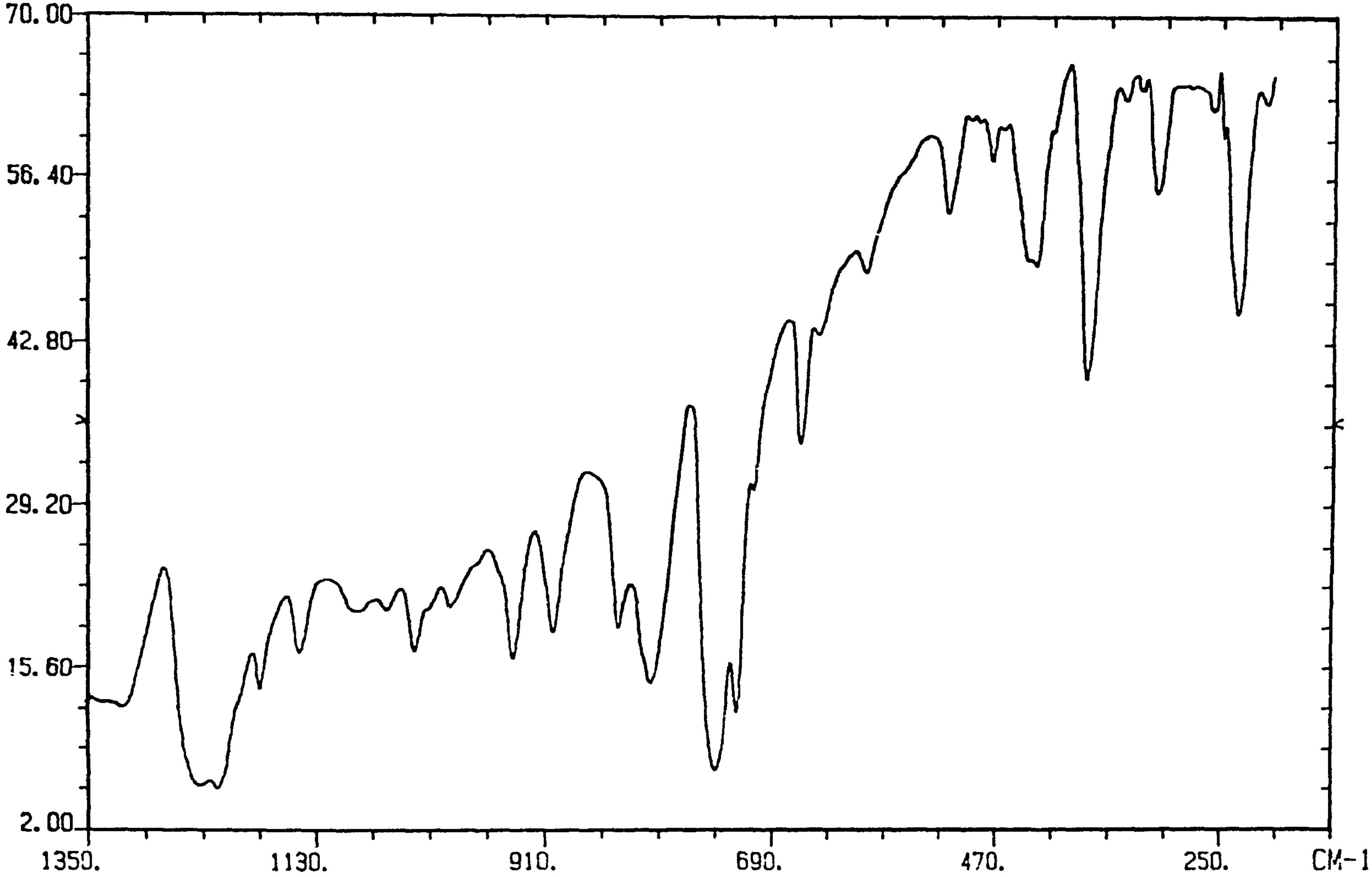


TABLE 5.7

NMR SPECTRAL RESULTS OF W(DTTD)(THF)NMe

CHEMICAL SHIFTS (p.p.m.)	ASSIGNED
7.00 - 7.40	Ph
5.37	NCH_3
3.70 (multiplet)	THF
3.03	$-CH_2-$
1.80 (multiplet)	THF

Figure 5.8 NMR Spectrum of W(DTTD)(THF)NMe

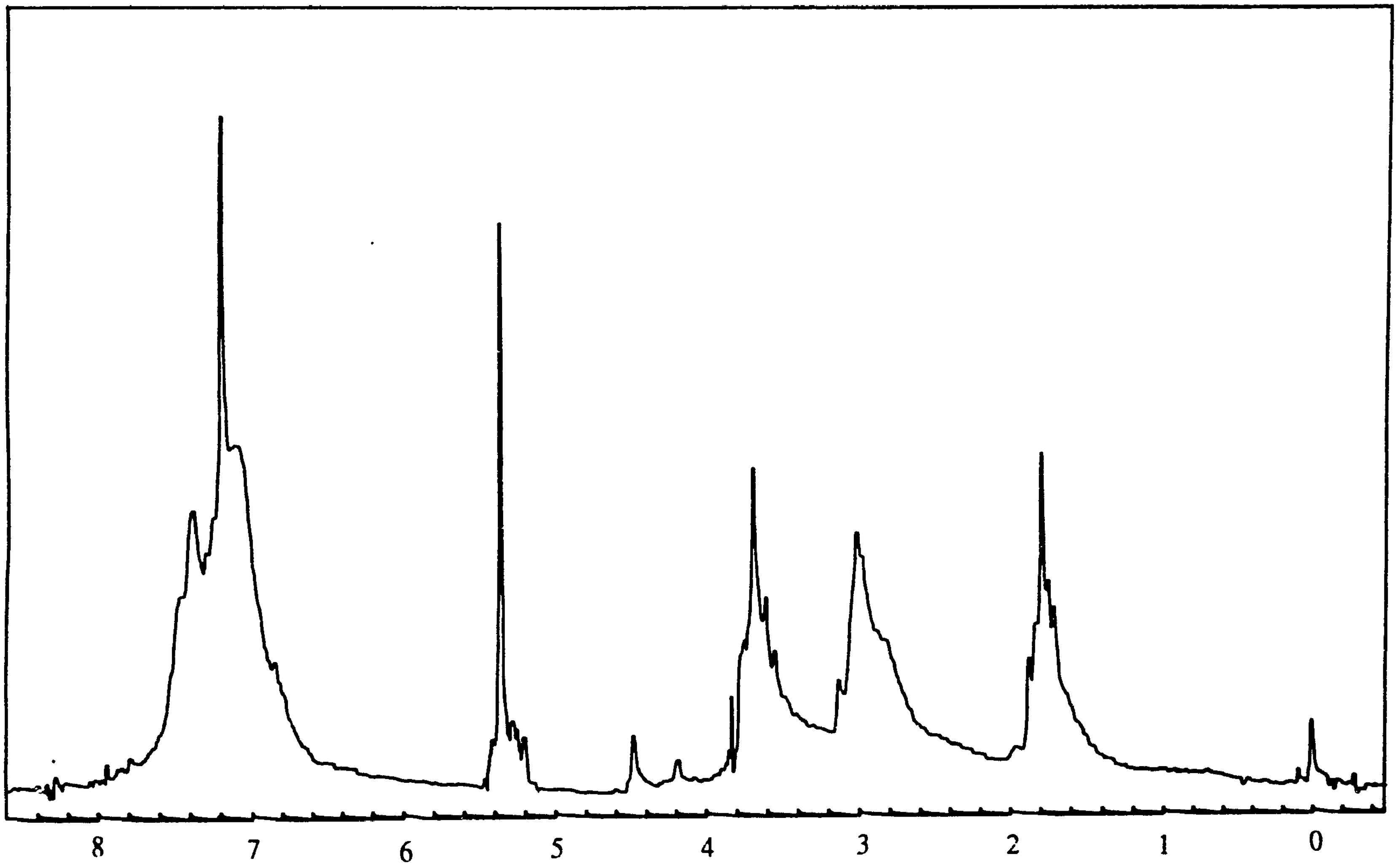


TABLE 5.8

MASS SPECTRAL RESULTS OF W(DTTD)(THF)NMe

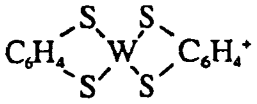
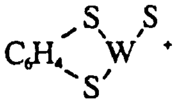
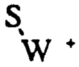
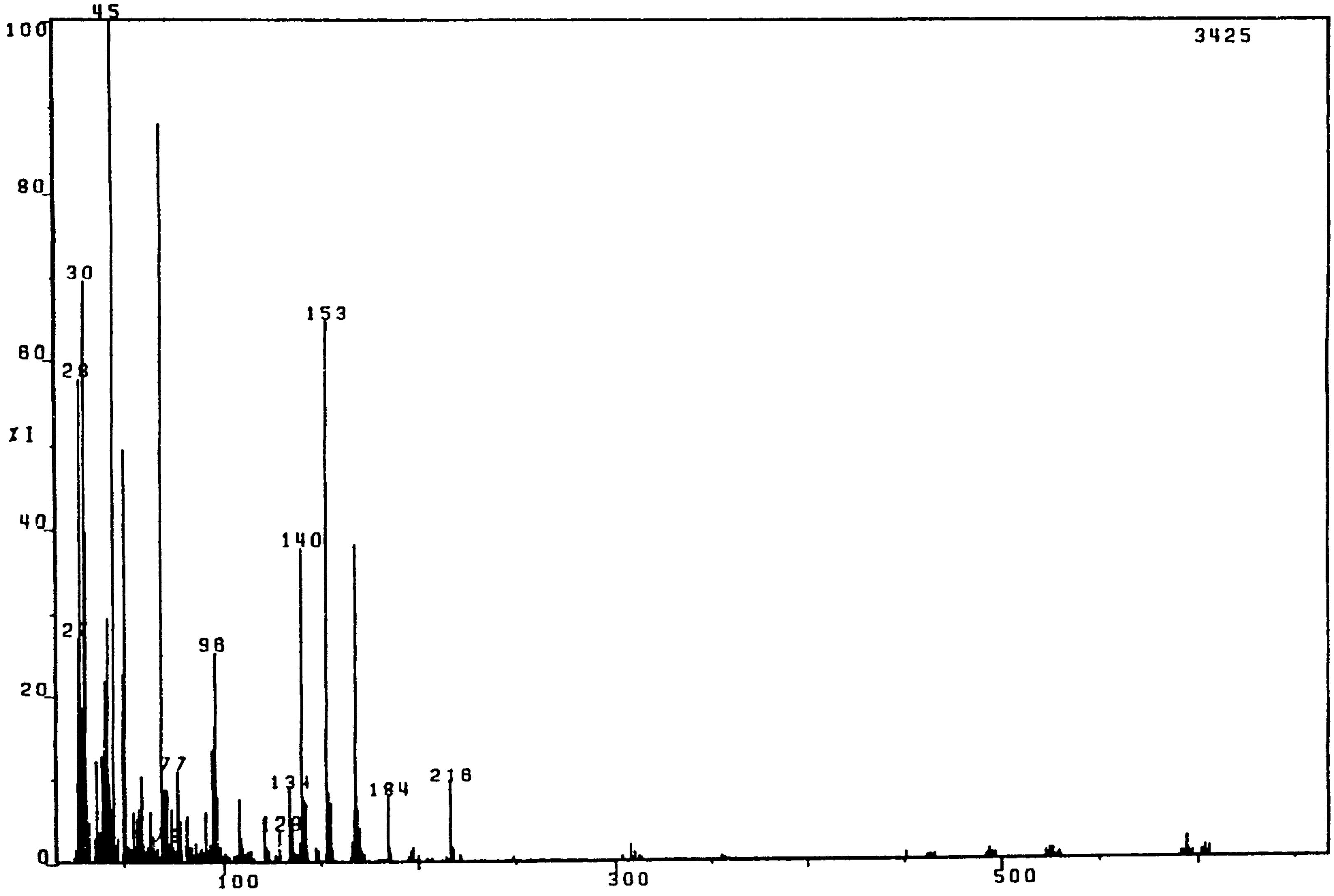
m/e	RELATIVE INTENSITY	ASSIGNMENT
593	81	W(dttd)(THF)NMe$^+$
521	100	W(dttd)NMe$^+$
492	54	W(dttd)$^+$
464	35	
356	26	
248	11	
216	244	
184	191	W$^+$

Figure 5.9 Mass Spectrum of W(DTTD)(THF)NMe



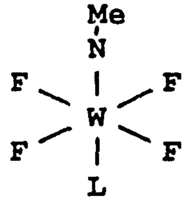
CHAPTER 6

CONCLUSIONS

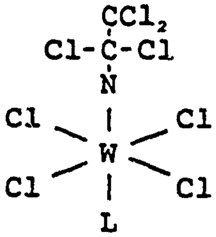
Coordination number of product

In this work, the actual reaction appears to deviate from the desired synthetic route at the last stage - the coordination of imido ligand: a six-coordinated, instead of five-coordinated, complex was obtained. As pointed out before, for tungsten-imido complexes, a coordination number of six associated with corresponding octahedral (or slightly distorted octahedral) geometry is the most common, and the majority of these complexes possess the desired electron count of 16 or 18 electrons. Some examples are shown below:

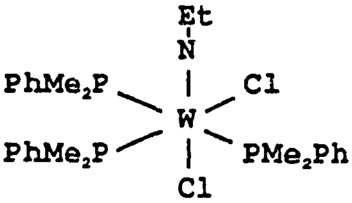
[79]



[89]



[87]



Normally, only in the absence of a solvent or in a non-coordinating solvent, can a five coordinated tungsten-imido complex be obtained. For example:

(1) $WF_6 + (Me_3Si)_2NMe \xrightarrow[\text{1 week}]{\text{without solvent}} WF_4(NMe) + 2\ FSiMe_3$ [79]

(2) $WOCl_4 + RNCO \xrightarrow[\text{24 hr}]{\text{benzene}} WCl_4(NR) + CO_2$ [87]

Commonly, when a six coordinated octahedral tungsten complex loses a ligand, one of the remaining ligands rearranges, or an additional ligand (e.g. solvent molecule) adds on, so as to fill the vacant site created and solve the coordination unsaturation. Thus, a strong tendency to produce a six-coordinated complex was found in above reactions:

a) In solvent L (L = MeCN or Py), reaction (1) gives complex $WF_4(NMe)L$ rapidly even at very low temperature (77-298K).

b) By dissolving $WCl_4(NR)$ produced in reaction (2) in THF, a six-coordinated complex $WCl_4(NR)(THF)$ can be obtained after only 15 minutes stirring.

Therefore, if our target model complex $[M(tetradentate)_1(unidentate)_1]$ was formed, a significantly distorted configuration from regular geometry (trigonal bipyramid or square pyramid) would be expected. However, the actual product, $[M(tetradentate)_1(unidentate\ A)_1(unidentate\ B)_1]$ can exist as the usual *cis* and *trans* octahedral isomers, which should be much more stable.

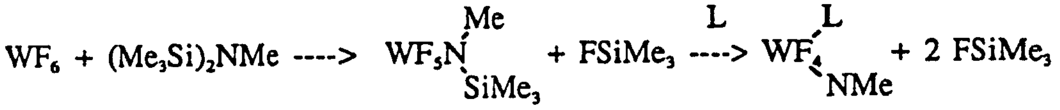
From the above facts, we may conclude that, the degree of steric distortion, as well as the ability to tolerate coordination unsaturation, might be responsible for the six-coordinated complex finally obtained in this work.

The impurities

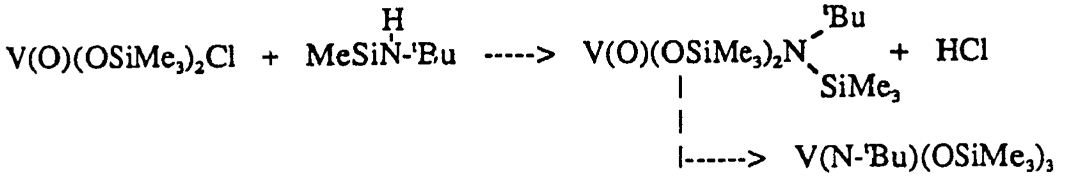
The final product was not obtained analytically pure, a small amount of an unidentified by-product was retained, which gives the peak at m/e= 604 in the mass spectrum and a W-Cl stretching band in IR spectrum. The spectral analysis results for the red solid isolated from the last reaction (refer to " the coordination of imido ligand " in chapter 4) showed a great similarity (a maximum m/e= 604 peak in mass spec., a W-Cl band in the IR), which leads us to believe that it is this by-product that is retained in our final complex.

According to previous studies, there are several possibilities for what has occurred in this reaction:

a) The organoimido tungsten compound was always synthesized by the way of an organoamido compound when using silylamines as reactant, this intermediate was not easy to remove: a trace of it might be retained in the product. Examples are:



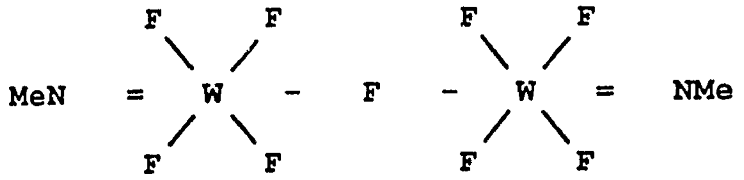
$$WF_6 + (Me_3Si)_2NMe \longrightarrow WF_5N\begin{smallmatrix}Me\\SiMe_3\end{smallmatrix} + FSiMe_3 \xrightarrow{L} WF_4\begin{smallmatrix}L\\NMe\end{smallmatrix} + 2\,FSiMe_3$$ [79]



$$V(O)(OSiMe_3)_2Cl + MeSi\overset{H}{N}\text{-}{}^tBu \longrightarrow V(O)(OSiMe_3)_2N\begin{smallmatrix}{}^tBu\\SiMe_3\end{smallmatrix} + HCl$$ [35]

$$\longrightarrow V(N\text{-}{}^tBu)(OSiMe_3)_3$$

b) In this sort of the reaction, sometimes a halogen bridged dimer was produced. For example, under different reaction conditions, WF_6 reacts with $(Me_3Si)_2NMe$ gives a di-octahedral complex:



[79][90]

However, our by-product does not seem to fit the possibilities described above.

Suggestions for further work

In synthesizing the target complex, although some other synthetic routes have been tried without much success, there are still several methods which can be investigated:

a) Using a W(VI) oxychloro compound as the starting tungsten complex. When treated with $(Me_3Si)_2NMe$, RNCO, or RNH_2 under mild conditions, the coordinated oxygen in tungsten oxychloro compounds is readily substituted by an imido ligand, giving an organoimido complex and $(Me_3Si)_2O$, CO_2 or H_2O respectively. The possibility of producing a six coordinated or dimeric complex still exists.

b) The relatively weak strength of the Si-Cl bond makes it impossible to obtain a five-coordinated complex in the absence of solvent or in a non-coordinating solvent when using $(Me_3Si)_2NMe$ in this reaction. While RNH_2 may be a good substitute. In a non-coordinating solvent, the reaction of $W(DTTD)Cl_2$ with RNH_2 may be possible with an addition of a non-coordinating base, which can consume any liberated acid, or with a lithium amide salt, LiNHR.

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