

*Synthesis and characterization of oxomolybdenum(VI) complexes with  
aroyl hydrazones of benzil and diacetyl monooxime*

*A Dissertation*

*Submitted in partial fulfillment*

**FOR THE DEGREE OF  
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**NATIONAL INSTITUTE OF TECHNOLOGY,  
ROURKELA-769008**

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**NATIONAL INSTITUTE OF TECHNOLOGY  
ROURKELA**

**CERTIFICATE**

This is to certify that the dissertation entitled “Synthesis and characterization of oxomolybdenum(VI) complexes with aroyl hydrazones of benzil and diacetyl monooxime” submitted by Saswati of the Department of Chemistry, National Institute of Technology, Rourkela for the degree of Master of Science in Chemistry is based on the result obtained in the bona fide project work carried out by her under my guidance and supervision. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

I further certify that to the best of my knowledge Saswati bears a good moral character.

Date: 05/05/2010

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Date: 05/05/10

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## 1. INTRODUCTION

Molybdenum is a hard, silver-white metal discovered by Swedish chemist Carl Wilhelm Scheele in 1778. Scheele had been researching a mineral called molybdenite, which many suspected of containing lead (the Greek word *molybdos* means "lead"). He instead found that it contained a new element which he named "molybdenum" after the mineral.

Molybdenum is a transition metal in Group 6 of the Periodic Table between chromium and tungsten. Its properties are very different from those of the typical heavy metals like mercury, thallium and lead. Its low toxicity makes molybdenum an attractive substitute than more toxic materials. Molybdenum-based catalysts have a number of important applications in the petroleum and plastics industries. A major use is in the hydrodesulfurisation (HDS) of petroleum, petrochemicals and coal-derived liquids. Molybdenum also contributes to a safer environment through lower sulfur emissions. Molybdenum is an essential trace element for plants and animals. It is an essential component of the enzyme nitrogenase which catalyses the conversion of atmospheric nitrogen to ammonia. Accordingly molybdate is applied in fertilizer formulations.

Transition metal complexes of hydrazone ( $R-NH-N=C<$ ), azine ( $>C=N-N=C<$ ) and aroyl hydrazone ( $Ph-C(=O)-NH-N=C<$ ) ligands, has become a field of great interest because of the realization, that these metal complexes can be used as supramolecular building blocks, with controllable molecular architecture and tunable properties. Thus J. –M. Lehn<sup>[1]</sup> has established that suitably substituted hydrazones are capable of coordinating metals to give multimetallic square grid complexes, whose optical, photophysical and magnetic properties can be modulated by degree of protonation of the ligands.

Preparation of novel dendritic mixed valence ruthenium complexes has been reported by Wang et. al <sup>[2]</sup>, which can act as variable optical attenuator for control of optical signals.

The hydrazone ligands are known to have variety of applications, such as hole transporting agents in organic layer photo conductors, in pharmaceutical industry as drugs for treatment of cancer, schizophrenia, leprosy etc., in synthetic and industrial chemistry as plasticizers, polymer stabilizers, antioxidants, polymerization inhibitors; in analytical chemistry for the detection of carbonyl groups; as herbicides, insecticides and plant stimulants.

The coordination chemistry of aroyl hydrazones are quite interesting as it presents a combination of donor sites such as protonated / deprotonated amide oxygen, an imine nitrogen of hydrazone moiety and additional donor site (usually N or O) provided from the aldehyde or ketone forming the Schiff base .

Mo (VI) complexes of some selected ONO donor ligands may mimic the active sites of some oxotransfer molybdoenzyme and hence it is of great interest in bio inorganic chemistry.

I have been studying the chemistry of transition metal complexes with O-N containing donor environments since one year. In this dissertation I have reported the synthesis and characterization of several O-N donors Schiff base hydrazone ligands and their corresponding oxomolybdenum complexes. All the synthesized ligands and corresponding Mo(VI) complexes has been characterized by several spectroscopic technique and redox properties were explored by cyclic voltammetry. The X-ray studies of few synthesized Mo complexes are under process.

## 2. Experimental:

### 2.1. Materials:

Chemicals were procured from renowned company like Aldrich E. Merck, and used without further purification. HPLC grade DMF was used for spectroscopic and electrochemical studies and ethanol, methanol were used for synthesis of ligands and metal complexes.  $\text{MoO}_2(\text{acac})_2$  has been synthesized following a published<sup>[3]</sup> method.

### 2.2. Physical Measurements:

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyzer. IR spectra were recorded on a Perkin-Elmer Spectrum RXL. Electronic spectra were recorded on a Perkin-Elmer Lambda 25 UV/VIS spectrophotometer.

### 2.3. Synthesis of Acid hydrazide:

All the four acid hydrazides are prepared by known method<sup>[4]</sup> which are schematically shown below:

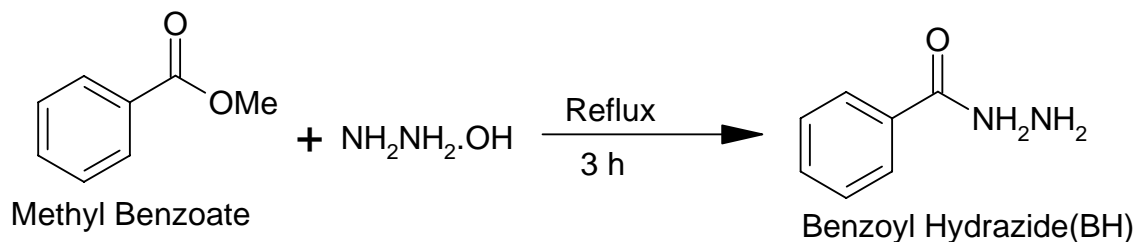
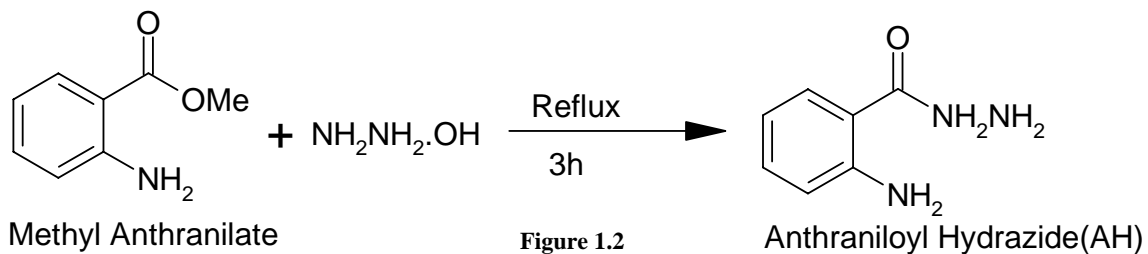


Figure 1.1

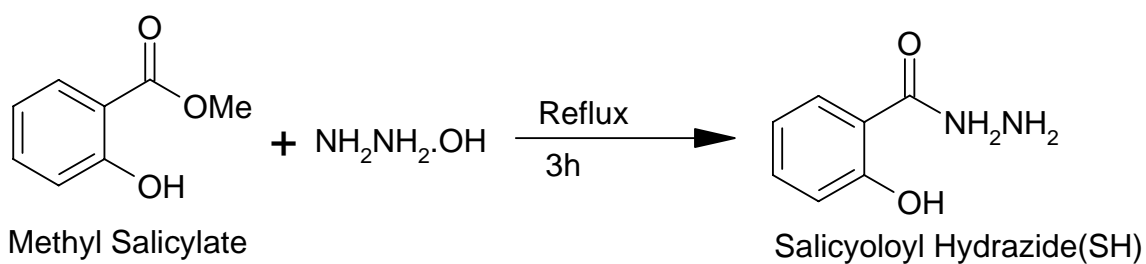
Found (calc. for  $\text{C}_7\text{H}_8\text{N}_2\text{O}$ ): C 63.21 (61.71), H 6.54 (5.92), N 22.76 (20.58). m.p.  $138^\circ\text{C}$ .

Yield: 76 %



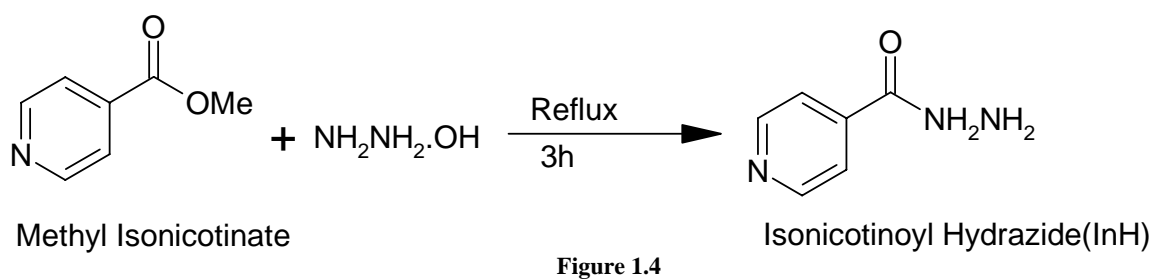
Found (calc. for  $C_7H_9N_3O$ ): C 60.21 (55.62), H 7.24 (6.00), N 29.76 (27.81). m.p. 142° C.

Yield: 75 %



Found (calc. for  $C_7H_8N_2O_2$ ): C 60.21 (55.26), H 6.24 (5.26), N 20.76 (18.42). m.p. 149° C.

Yield: 74 %



Found (calc. for  $C_7H_8N_2O_2$ ): C 57.21 (52.17), H 6.39 (5.79), N 27.76 (30.43). m.p. 172° C.

Yield: 74 %

## 2.4. Synthesis of Schiff base ligands:

### A. Benzoyl hydrazone of diacetyl monooxime (DAMOBH<sub>2</sub>):

All the four Schiff base ligands using DAMO are prepared by known method [5] which are schematically shown below:

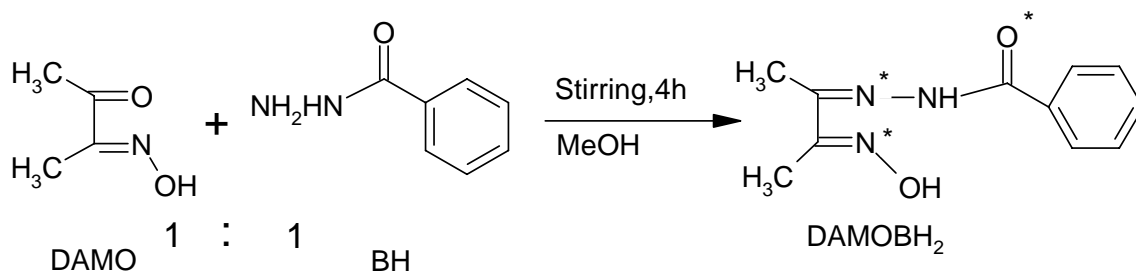


Figure 2.1

### Salicyloyl hydrazone of diacetyl monooxime (DAMOSH<sub>2</sub>):

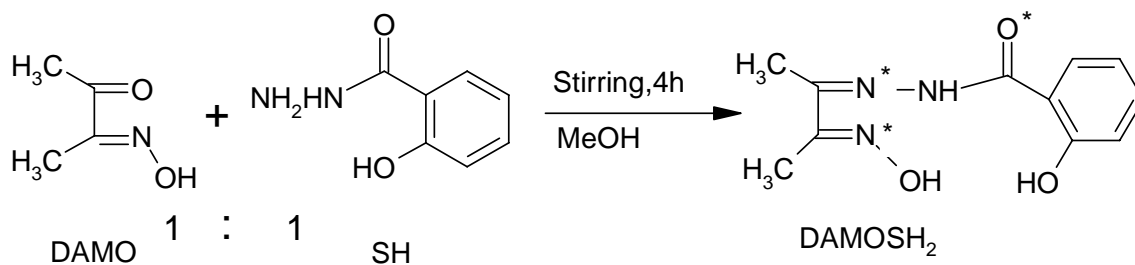


Figure 2.2

### Anthraniloyl hydrazone of diacetyl monooxime (DAMOAH<sub>2</sub>):

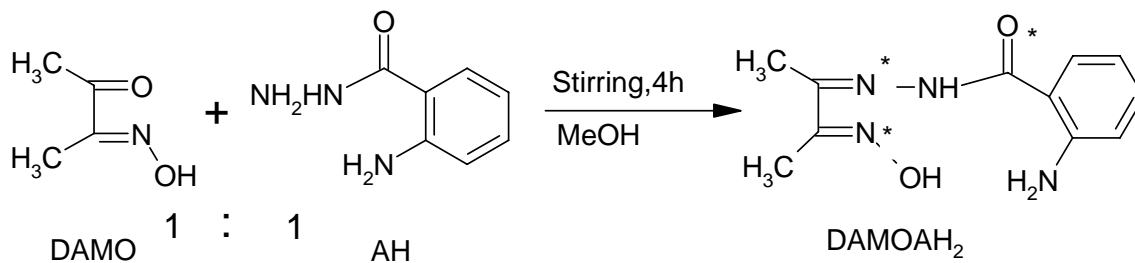


Figure 2.3



*Isonicotinoyl hydrazone of diacetyl monooxime (DAMOInH<sub>2</sub>):*

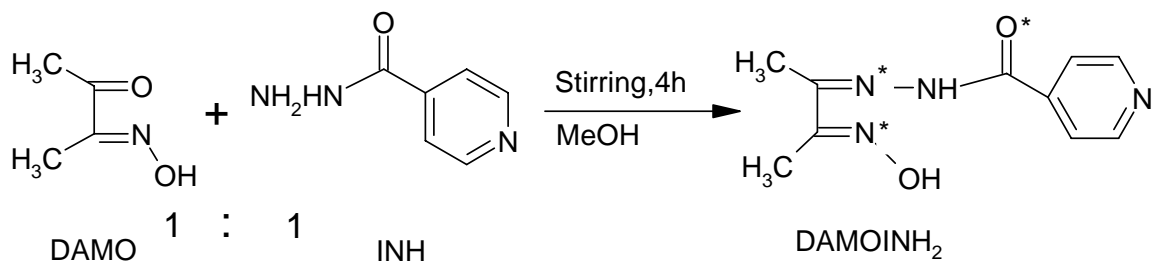
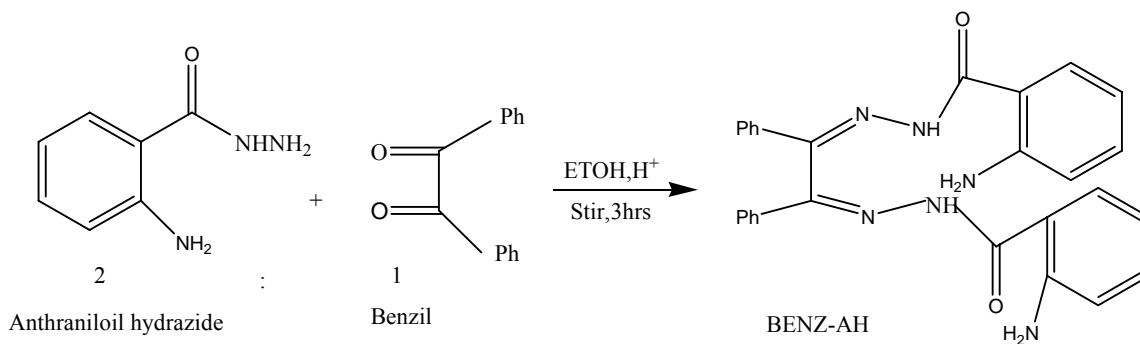


Figure 2.4

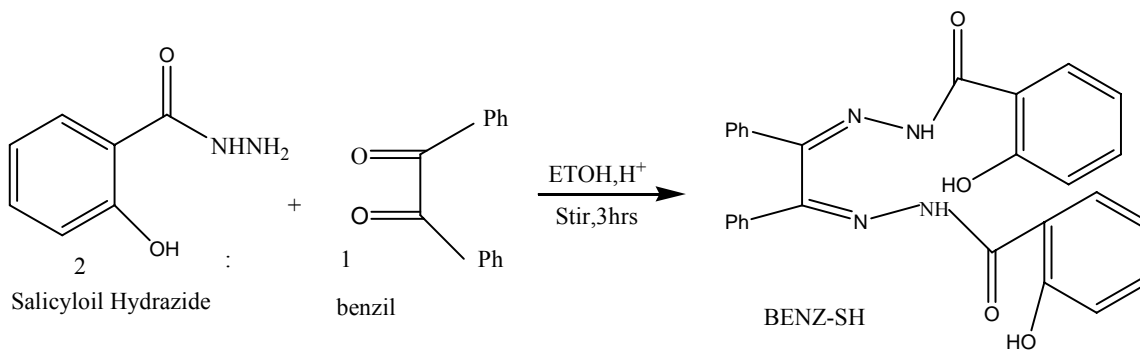
*B. Benzilhydrazone of Anthraniloil hydrazide ligand (BENZA<sub>H</sub>2)*

All the four *Schiff base ligands* using benzil are prepared by known method [6] which are schematically shown below:

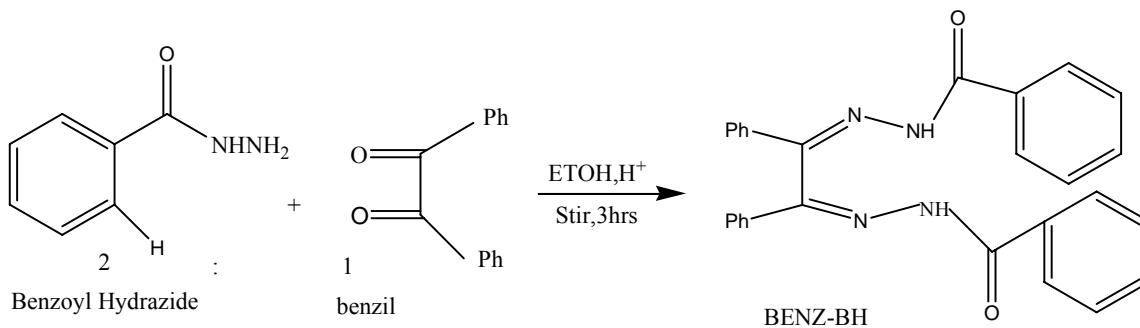


**Figure 3.1**

*Benzilhydrazone of Salicyloil hydrazide ligand (BENZSH<sub>2</sub>)*

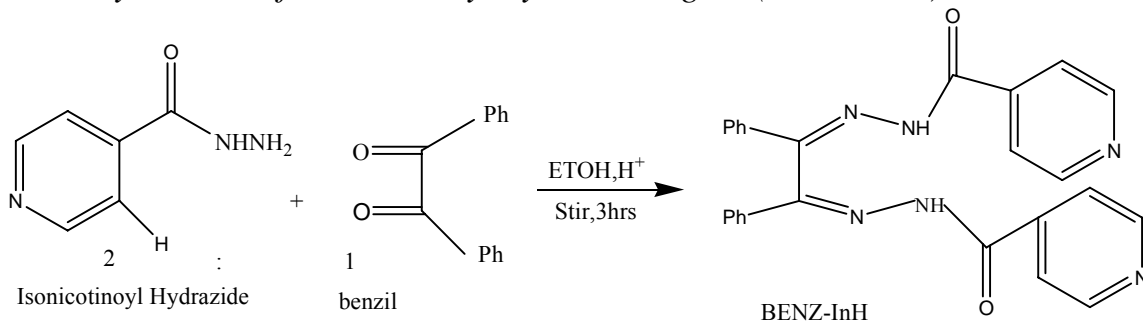


**Figure 3.2**



**Figure 3.3**

*Benzilhydrazone of Isonicotinoyl hydrazide ligand (BENZInH<sub>2</sub>)*



**Figure 3.4**

## 2.5 Synthesis of metal complexes

### A. With diacetyl monooxime containing hydrazones

All the complexes were prepared following a similar method of mixing the methanolic solutions of the metal precursor and ligand in 1:1 ratios. Preparations of the metal complexes are described below.

Complex I,  $[\text{MoO}_2(\text{DAMOBH})(\text{OMe})]$ :

A solution of  $\text{MoO}_2(\text{acac})_2$  in methanol (5 mL) was added to a suspension of the  $\text{DAMOBH}_2$  in methanol (10 mL) under stirring condition. After 10 minutes of stirring the solution became clear. Then the mixture was stirred for 3 hours. The wine red colored complex was then filtered off. After few days brown colored crystals were isolated from the filtrate. Crystal structure determination is under progress.

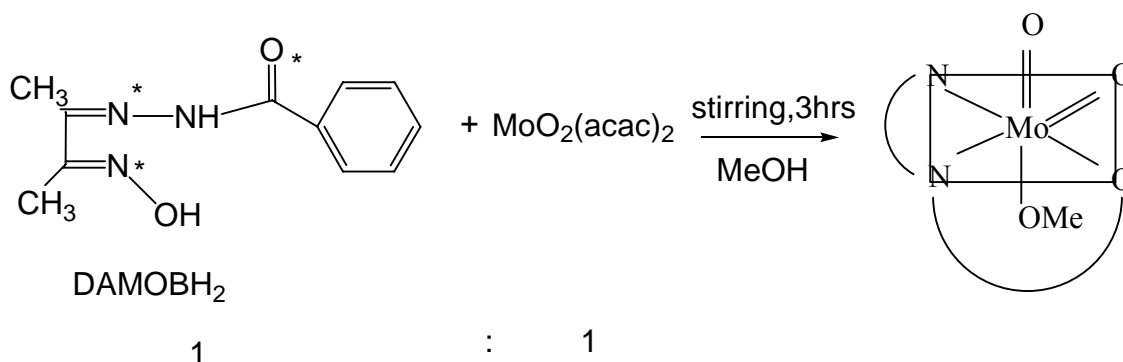


Figure 4.1

Complex II, [MoO<sub>2</sub>(DAMOAH)(OMe)]:

Complex II is prepared following the same method like Complex I above.

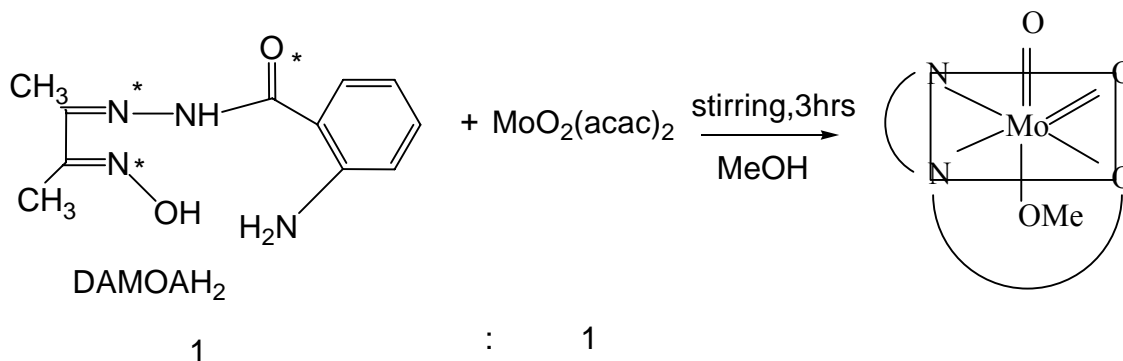


Figure 4.2

Complex III, [MoO<sub>2</sub>(DAMOSH)(OMe)]:

Complex III is prepared following the same method like Complex I above.

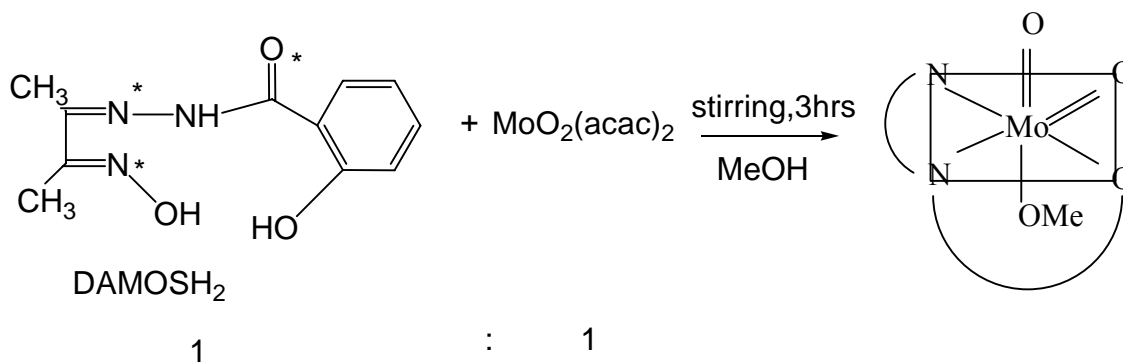


Figure 4.3

Complex IV, [MoO<sub>2</sub>(DAMOInH)(OMe)]:

Complex IV is prepared following the same method like Complex I above.

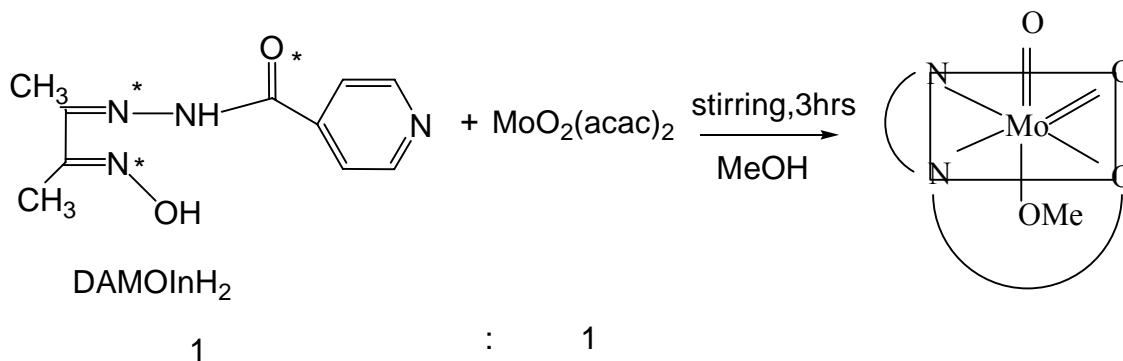


Figure 4.4

### B. With benzil containing hydrazones

Complex V, [MoO<sub>2</sub>(BENZBH<sub>2</sub>)]:

A solution of MoO<sub>2</sub>(acac)<sub>2</sub> in ethanol (5 mL) was added to a suspension of the BENZBH<sub>2</sub> in ethanol (10 mL) under stirring condition. After 10 minutes the solution became clear. Then the mixture was stirred for 3 hours. The orange colored complex was then filtered off and dried over fused CaCl<sub>2</sub>.

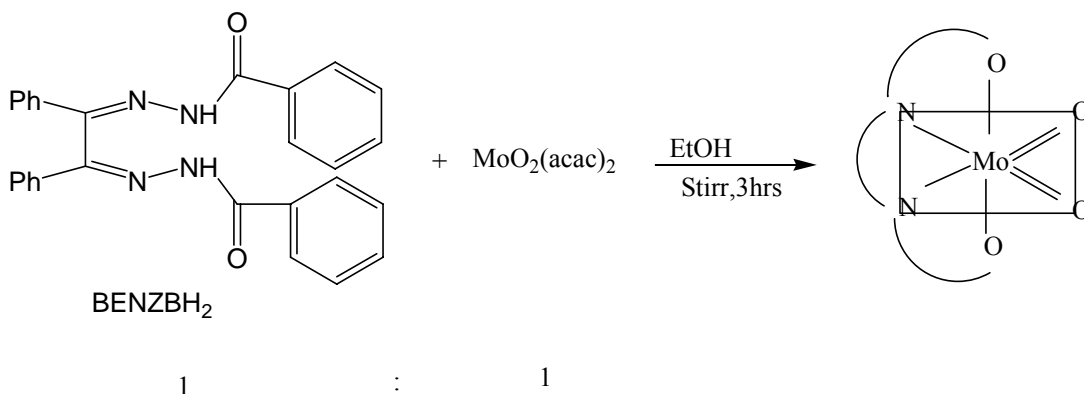


Figure 5.1

Complex VI, [MoO<sub>2</sub>(BENZAHA)] :

Complex VI is prepared following the same method like Complex V above.

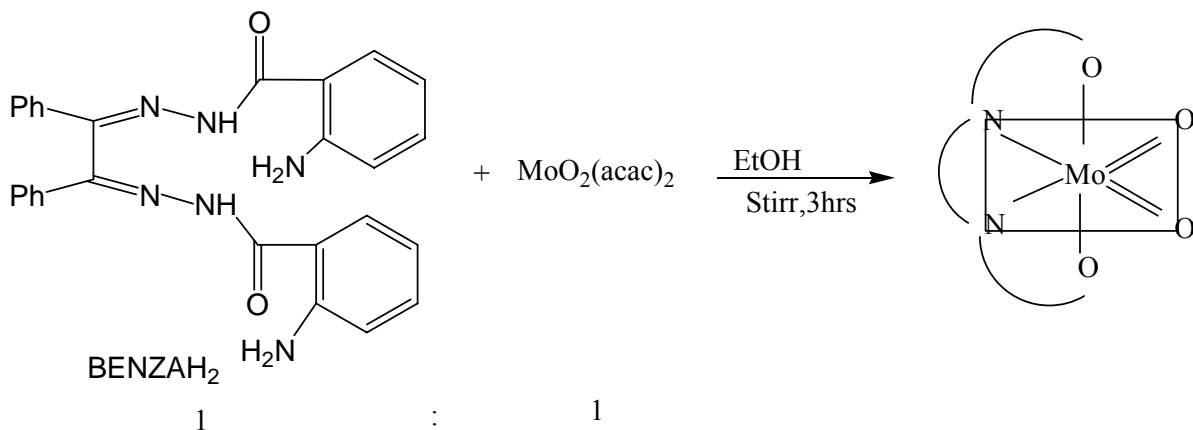


Figure 5.2

Complex VII, [MoO<sub>2</sub>(BENZSH)] :

Complex VII is prepared following the same method like Complex V above.

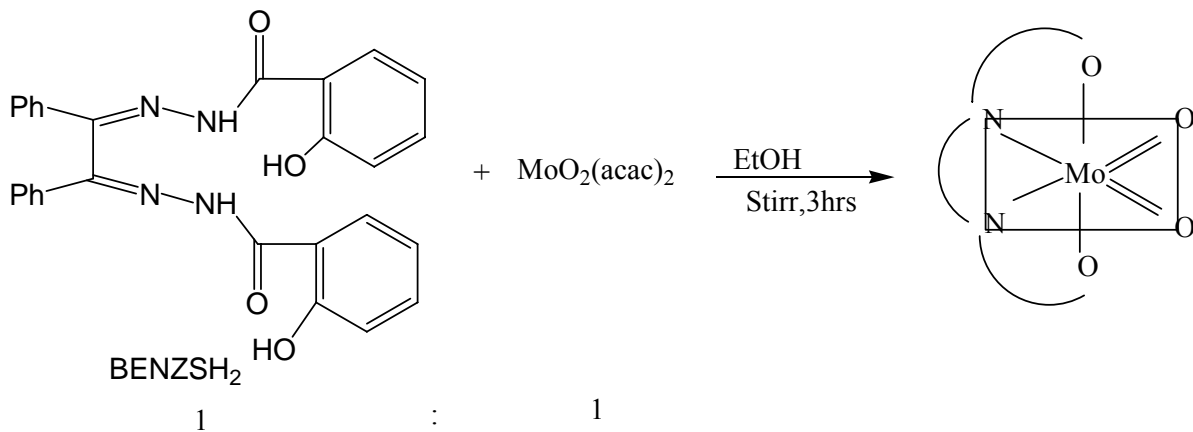


Figure 5.3

Complex VIII,  $[\text{MoO}_2(\text{BENZInH})]$  :

Complex VIII is prepared following the same method like Complex V above.

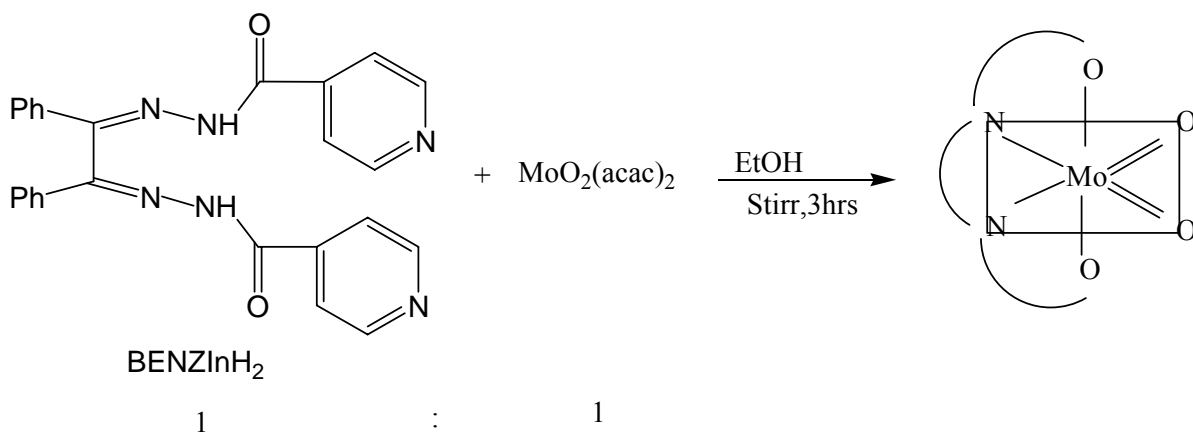


Figure 5.4



### 3. RESULT AND DISSCUSION:

#### 3.1. Stereo electronic nature of the ligand:

The DAMO-hydrazone ligands can undergo deprotonation from enolised amide oxygen as well as from the oxime oxygen. When these are reacted with a Mo(VI) metal precursor the ligands get deprotonated from the hydrazone amide moiety and the a Mo(VI) complex is formed.

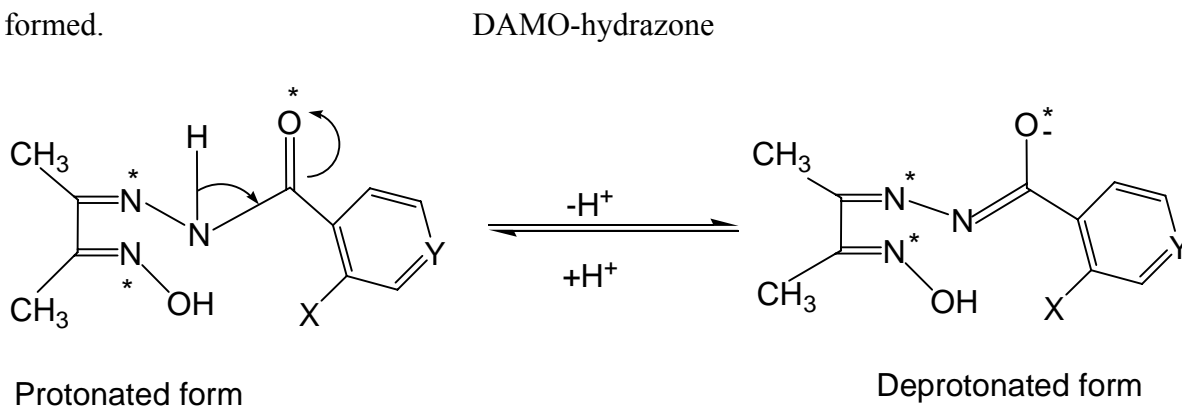


Figure 6.1

When the BENZ-hydrazones are reacted with a Mo(VI) metal precursor the ligands get deprotonated from the two hydrazone amide moiety and the a Mo(VI) complex is formed.

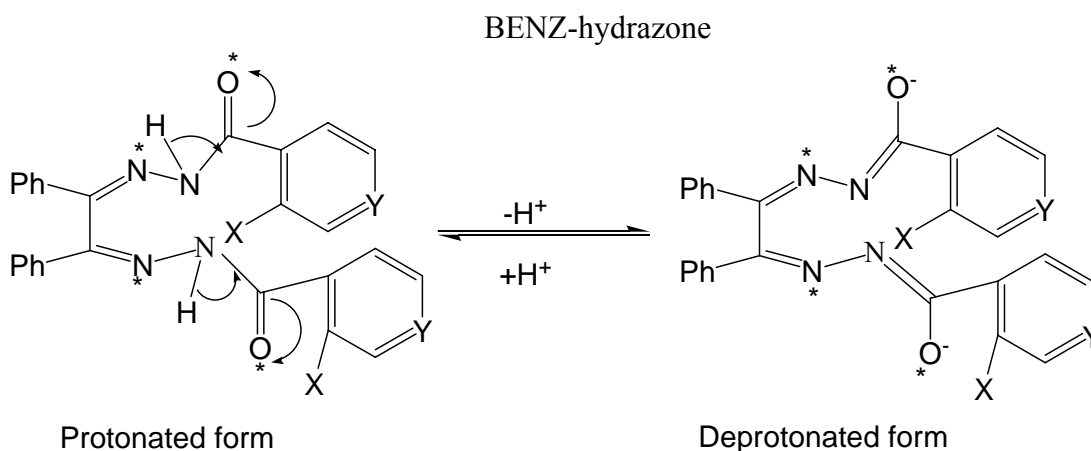


Figure 6.2

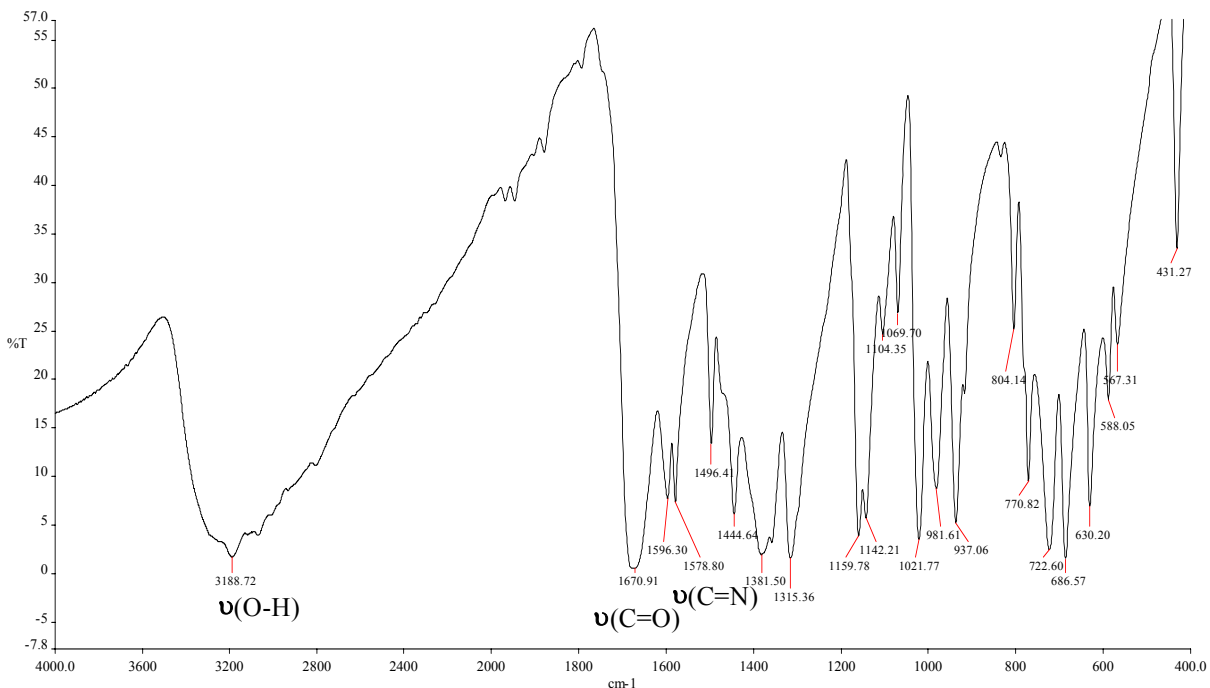
Thus the DAMO-hydrazone ligands are tridentate uni-negative, whereas BENZ-hydrazone ligands are tetradentate bi-negative.

### 3.2. Spectral Characteristics:

#### IR spectra

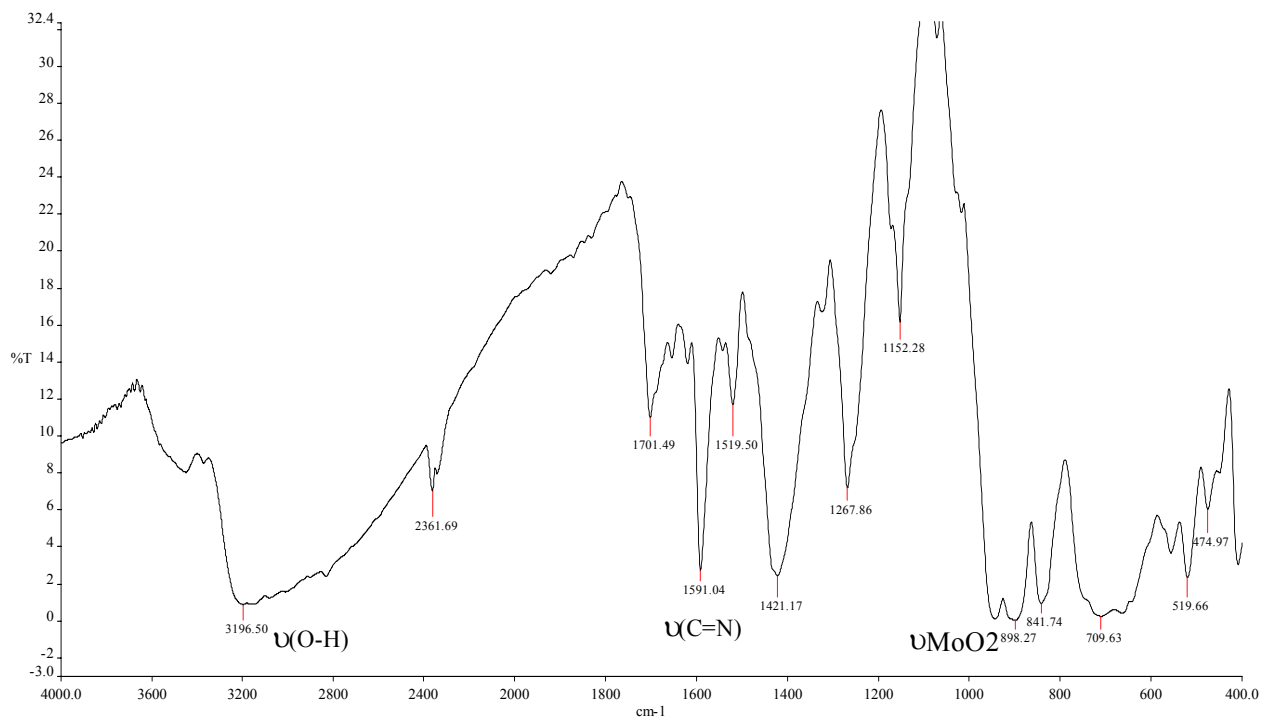
The IR spectra of all the ligands contains characteristic bands at around  $3155\text{ cm}^{-1}$ ,  $1670\text{ cm}^{-1}$  and  $1578\text{ cm}^{-1}$  due to  $\nu(\text{OH})$ ,  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}=\text{N})$  respectively. In the IR spectra of the corresponding metal complexes band at around  $1670\text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{O})$  disappears as the ligand coordinates as deprotonated enol and the band at around  $1578\text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  shifts to around  $1591\text{ cm}^{-1}$  as the N of  $\text{C}=\text{N}$  coordinates to the metal, and we obtained characteristic bands for  $\nu(\text{MoO}_2)$  at around  $841$  to  $950\text{ cm}^{-1}$  region<sup>[7-8]</sup>. Representative IR spectra of one ligands and it's corresponding Mo complex has given in **Figure 7.1 & 7.2** respectively below.

IR of benzoyl hydrazone of diacetylmonooxime(DAMO-BH<sub>2</sub>)



**Figure 7.1**

IR of **Complex I**, [MoO<sub>2</sub>(DAMOBH)(OMe)]:



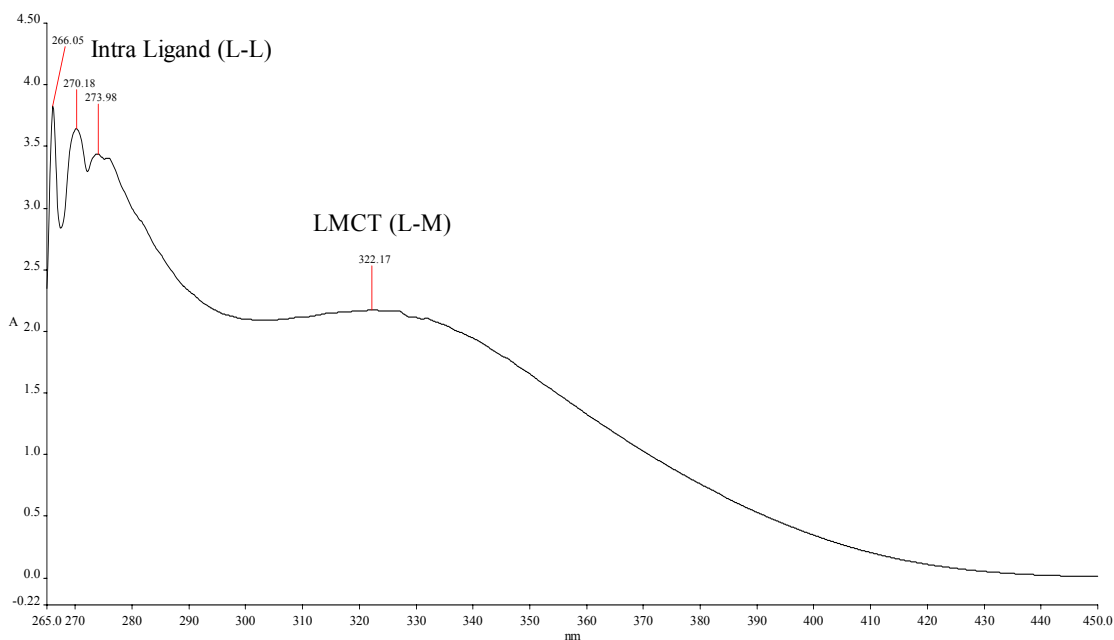
**Figure 7.2**

## UV-VIS SPECTRA

The electronic absorption spectra (in DMF) of all the complexes (**I–VIII**) display a shoulder in 322- 424 nm region and two strong absorptions are located in the 265– 270 nm range, which are assignable to L–Mo( $d\pi$ ) LMCT and intraligand transitions respectively<sup>[9-10]</sup>.

Representative UV-VIS spectra of one dioxomolybdenum(VI) complex has given in **Figure 8.1** below.

UV-Vis of **Complex II**, [MoO<sub>2</sub>(DAMOAH)(OMe)]:

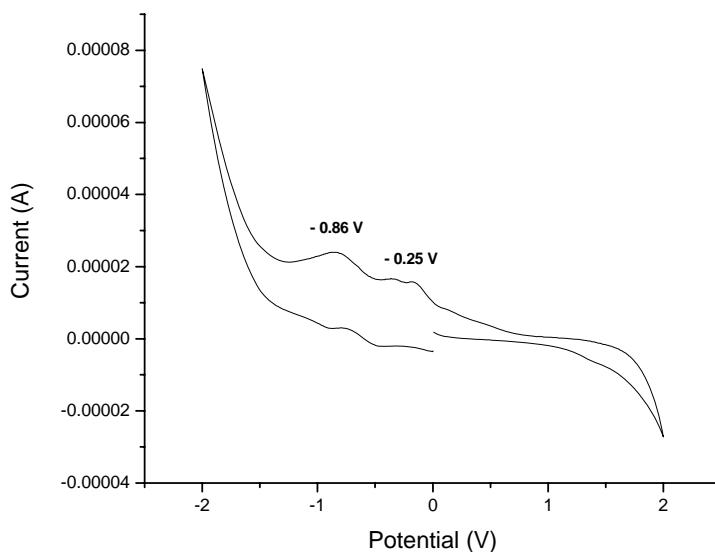


**Figure 8.1**

### 3.3. Electrochemical properties

The electrochemical behavior of all Mo<sup>VI</sup>O<sub>2</sub> complexes (**I-VIII**) has been examined in DMF solution using cyclic voltammetry at a platinum electrode with TEAP as supporting electrolyte. The representative CV traces of one complex (**I**) is given in **Figure 9.1**. When only the reduction pathway is scanned the CV trace of all the complexes display two irreversible reductive responses <sup>[11-12]</sup> within the potential window - 0.04 to - 0.96 V which are assigned to Mo(VI)/Mo(V) <sup>[13, 14]</sup> and Mo(V)/Mo(IV) processes, respectively. The ligands are redox inactive within this potential window. On scanning the oxidation half an irreversible oxidation wave for few complexes is located in the + 1.47 to + 1.60 V range. As the Mo(VI) complex cannot undergo a metal-centered oxidation, this is attributed to a ligand-centered process.

Cyclic Voltammogram of **Complex I**, [MoO<sub>2</sub>(DAMOBH)(OMe)]:



**Figure -9.1**

#### *4. Conclusion*

In this dissertation several hydrazone ligands and their corresponding dioxomolybdenum(VI) complexes has been synthesized and the ligands and their metal complexes has been characterized by IR, UV vis spectroscopy and redox properties by cyclic voltammetry. Full characterization of all complexes could not possible to report due to shortage of time. The preliminary characterization data of these complexes have failed to indicate any definite coordination mode of ligands in them. To find out the binding mode(s) of ligands in these complexes, as well as their stereochemistries, x-ray structures of the corresponding complex is required. The x-ray quality crystals of some syntesised complexes have been sent for structure determination using single crystal X-ray crystallography.

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