

***Synthesis and Characterization of
Oxomolybdenum and Oxovanadium Complexes***

A Dissertation

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Affiliated to

Deemed University



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CERTIFICATE

This is to certify that the dissertation entitled “*Synthesis and Characterization of Oxomolybdenum and Oxovanadium Complexes*” submitted by Ms. Purabi Kar of the Department of Chemistry, National Institute of Technology, Rourkela for the degree of Master of Science in Chemistry is based on the result obtain 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.

Date: 05/05/10

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Date: 05. 05. 2010

Name: Purabi Kar

Introduction

Molybdenum is the metal which is placed in group 6 has atomic number 42 and atomic mass 95.94. It has chemical properties similar to those of chromium and tungsten. It has variable oxidation states which are from II to VI. It can coordinate ligands up to 8. Hence it can coordinate with a large number of ligands which may be organic or inorganic, or bridging ligands and it has a tendency to form binuclear as well as poly-nuclear complexes. Its complexes has many applications and thereby making its chemistry challenging. Molybdenum catalysts have wide range of applications in many of the fields. For example in fuel refining, conversion of coal to hydrocarbon liquids, synthesize raw materials for plastics and fibres, used in making alloys because it provides strength greater than that of steel. It is an important component of the enzyme nitrogenase that reduces atmospheric nitrogen to ammonia. Thus by exploiting its chemistry a large number of desired complexes can be synthesized. Cis dioxo complexes of molybdenum are exploited for the achiral and chiral epoxidation which is mentioned by Jin Zhao [1].

Vanadium is the element present in group V. It has atomic number 23 and atomic mass 50.94. Vanadium can form wide range of coloured compounds. It has a great biological role as it is found in some of the nitrogenase enzymes, found in vanadium chromagen proteins in sea squirts, help to control diabetes mellitus disease by controlling the body glucose level due to its insulin mimetic characteristics [2-5] and it is found in blood cell of the organisms like sea cucumber. Vanadium alloys have large number of potential applications. Due to its low neutron adsorption abilities it is used in nuclear reactors. Vanadium compounds are highly stereoselective in their catalytic activities for oxidation of allylic alcohols in presence of oxidising agents which has been reported by Hubert Mimoun [6]. Its complexes are also used as therapeutic agents. So many discoveries of the uses of the above mentioned metals have drawn attention of bio-inorganic chemists to synthesis their complexes.

There are various applications of the aroyl hydrazones which depends upon their characteristics. Derivatives of aroyl hydrazone are effective to act as inhibitor to prevent the corrosion of the copper metal in presence of nitric acid. It is due to the electron donating capacity of those hydrazone ligands [7]. The ruthenium complex of aroyl hydrazone plays an important role in controlling the microbial growth. Aryl-aryl coupling can be carried out by

the ruthenium complexes of aroyl hydrazone. They also help in oxidation of alcohols [8]. Schiff bases have application in optical sensors as they show fluorescence properties over a particular pH range [9]. Transition metal complexes (Co(II), Cu(II), Ni(II), Fe(II), Mn(II)) with Schiff's bases have wide range of catalytic activities [10]. The hydrazones complexes have several applications in biological, pharmaceutical fields also.

Several biochemical reactions are carried out in presence of enzymes, which have Mo as their cofactor [11-13]. Molybdenum complexes are used as catalysts for oxidation of organic compounds [14-15]. Nitrate reductase is a transferase enzyme which has cis-dioxo Mo moiety [16-17]. Molybdenum has greater affinity for oxygen, nitrogen, sulphur donor sites of the ligands hence form stable complexes with them. Mo Schiff's bases can act as catalyst for both homogenous and heterogeneous reactions [18].

Vanadium has a greater affinity for oxygen. There are certain vanadium dependent enzymes such as nitrogenases, haloperoxidases, phosphomutases. These contain VO^{2+} , VO_3^+ as motifs. These motifs are present in active site of the enzymes. The basicity of the donor atoms present in the ligand decides the fate of the co-ordination of these motifs. V(V) is highly stabilised due to the coordination of the enolated oxygen and an imine group (neutral moiety) of the ligand [19].

I have been engaged to synthesize some dioxomolybdenum(VI) complexes using O-N donor hydrazide ligands and to explore its chemistry as it can bind to a number of separate substrates as it has open co-ordination sites for binding of the substrates and oxotransfer properties. I have also been interested to synthesise corresponding oxovanadium(V) complexes which can be used as catalyst for several catalytic oxidation reactions. In this dissertation I have reported the synthesis and characterization of two different hydrazide and one O-N Schiff base hydrazone ligands and their corresponding dioxomolybdenum(VI) and oxovanadium(V) complexes. All the synthesized ligands and corresponding metal complexes have been characterized by several spectroscopic technique and redox properties were explored by cyclic voltammetry. The X-ray studies of few synthesized Mo & V complexes are under process.

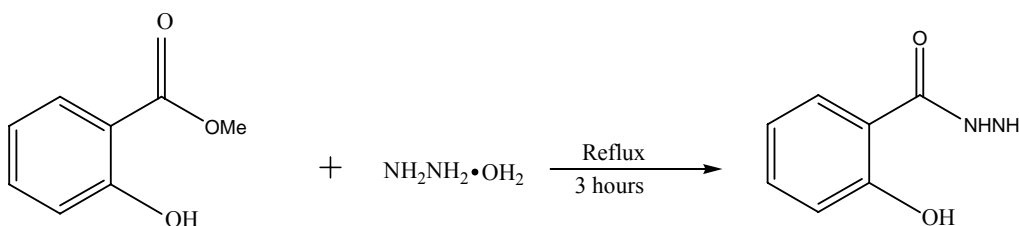
Experimental Section

Materials: Highly purified chemicals were used for the experiments. These chemicals were obtained from the chemical companies like Aldrich, E.Merck and Fluka. Solvents used were acetonitrile, chloroform, DMF, DMSO, for obtaining electronic spectra and cyclic voltamogram. The metal precursor $\text{MoO}_2(\text{acac})_2$ [20] and $\text{VO}(\text{acac})_2$ [21] were synthesized in the laboratory by following the procedure which has been described in the literature. NH_4VO_3 was obtained from the Loba Chemie.

Synthesis of ligands:

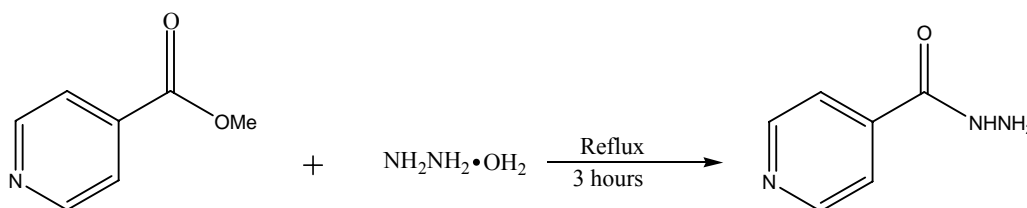
Synthesis of acid hydrazides: The two acid hydrazides are prepared following a reported procedure [22-23] which is shown diagrammatically below (**Fig 1 & 2**):

Preparation of salicyloyl hydrazide (SH):



Yield =71%, M. P: 149°C; M. F: $\text{C}_7\text{H}_8\text{O}_2\text{N}_2$; (152 M.wt); C H N values: C: 55.29(55.26); H: 5.28(5.26); N 17.82 (18.42)

Preparation of Isonicotinoyl hydrazide (InH):



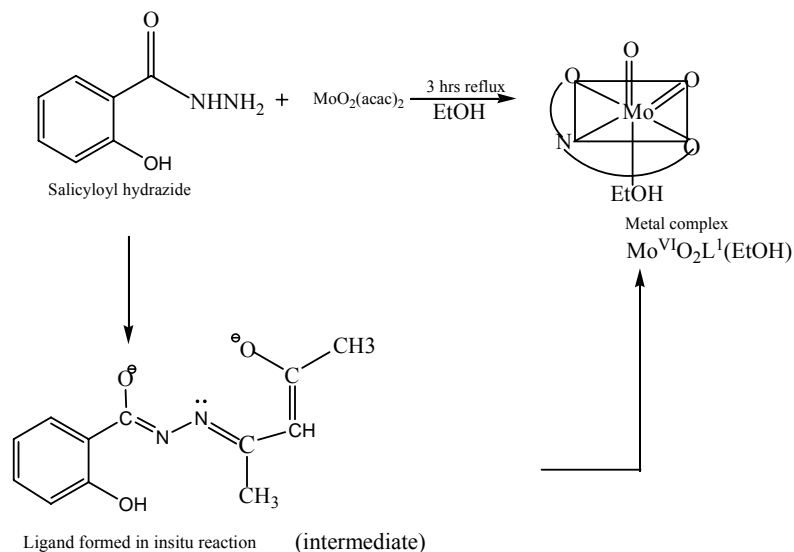
M.P.172 ° c. Yield: 70%; M. F: $\text{C}_6\text{H}_7\text{ON}_3$ (137 M. wt); C, H, N values: C: 55.58 (55.55); H: 5.08 (5.10); N: 30.71(30.65).

Synthesis of the Oxomolybdenum(VI) Complexes:

Complex 1: $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}^1(\text{EtOH})]$

The complex **1** is prepared by taking the precursor molybdenum(VI) acetyl acetonate and the prepared salicyloyl hydrazide in stirring condition at room temperature using ethanol as solvent. The details about the reaction are given in **schematic representation 1**.

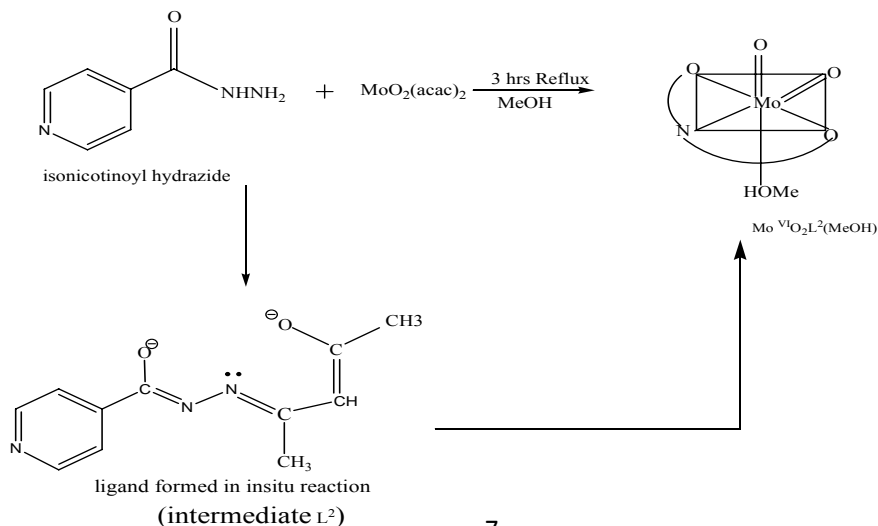
Schematic representation 1



Complex 2: $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}^2(\text{MeOH})]$

The Complex **2** is prepared following the same procedure like **1**. The details about the reaction are given in **schematic representation 2**.

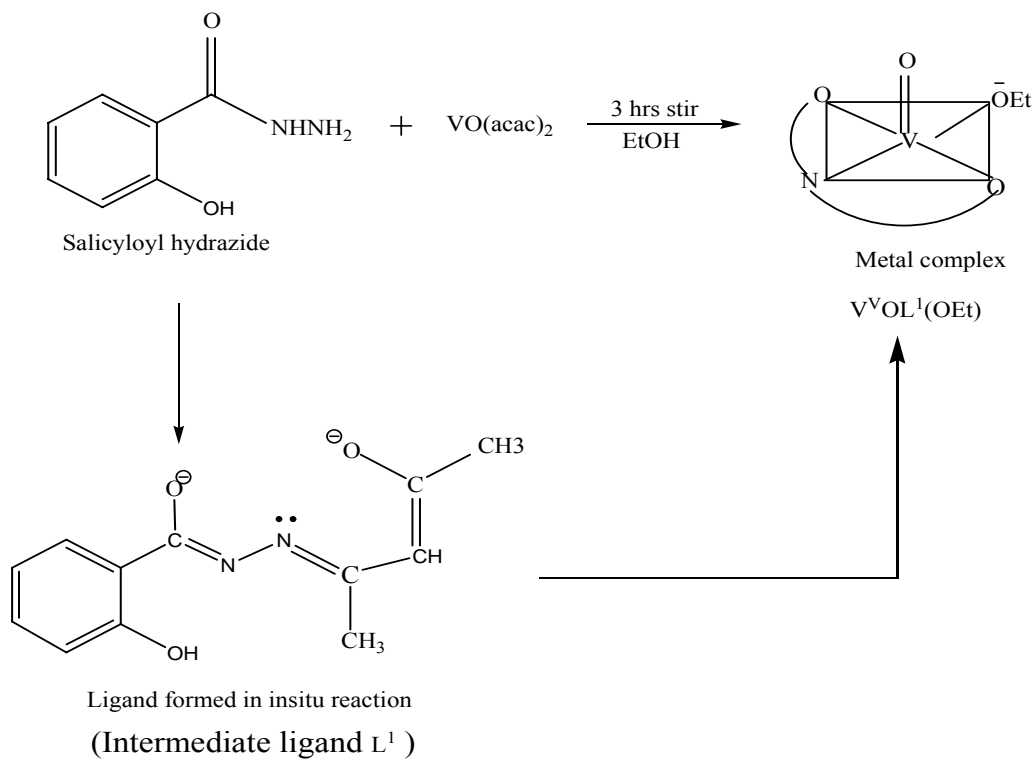
Schematic Representation 2:



Complex 3: $[V^V OL^1(OEt)]$

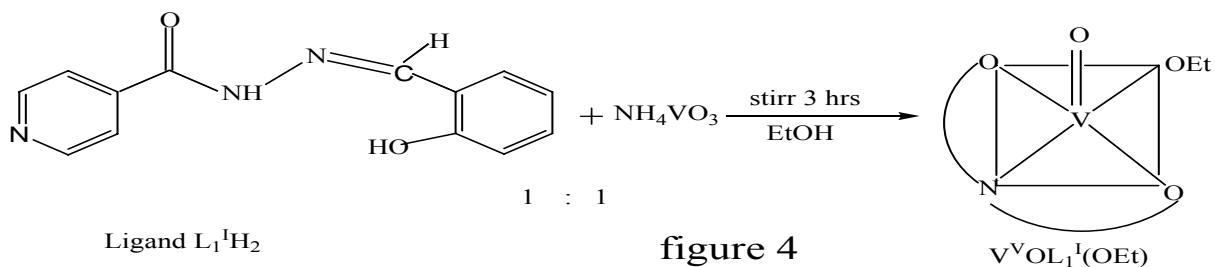
The Complex 3 is prepared following the same procedure like 1. The details about the reaction are given in **schematic representation 3**.

Schematic representation 3:



Complex 4: $[V^V O(L_1^I)OEt]$

The complex **4** is prepared by taking the precursor, NH_4VO_3 and the prepared ligand the ligand $L_1^I H_2$ in stirring condition at room temperature using ethanol as solvent. The reaction mixture was filtered and kept undisturbed for slow evaporation. After 3 days yellow colour crystals of irregular shaped were obtained. The details about the reaction are given in **figure 4**.



Physical measurements:

The IR spectra of the ligand and all four metal complexes have been recorded using Perkin Elmer spectrum RXI Spectrophotometer in KBr disc. Perkin Elmer Lambda 25 UV/Vis spectrophotometer was used for obtaining UV-Vis spectra of our complexes. In order to have C, H, N, elemental analysis Perkin Elmer 240 instrument was in great use. For examining the electrochemical properties of the samples help of PC- controlled EG and G/PAR-273A potentiostat was taken. The analysis was done with the help of the three electrodes, those are working electrode and auxiliary electrode made of platinum wire. The reference electrode was Ag/AgCl/KCl and TBAP was taken as supporting electrolyte.

Results and Discussions:

Spectral characteristics:

IR Spectra of Mo(VI) complexes (1-2)

The vibrational spectra of all the hydrazide ligands show peaks at around 3319($\nu_{\text{O-H}}$) cm^{-1} , 3270($\nu_{\text{N-H}}$) cm^{-1} , 3048($\nu_{\text{-NH}_2}$) cm^{-1} , 1647($\nu_{\text{C=O}}$) cm^{-1} and 1591($\nu_{\text{C=C}}$) cm^{-1} . These peaks are obtained due to stretching mode of vibration of the respective functional groups. On analyzing the IR spectra of corresponding metal complex it was found that the bands due to stretching of O-H, -NH₂ and N-H bonds were vanished. Missing of bands may be due to deprotonation of -OH and -N-H group and condensation of -NH₂ with keto of acetyl acetone. But some new strong bands can be located in the spectra. They are around 1602($\nu_{\text{C=N}}$) cm^{-1} due to C=N-N=C part of the complex [24]. The presence of two molybdenum oxo peaks at around 840 to 944($\nu_{\text{Mo=O}}$) cm^{-1} shows the presence of cis dioxo groups attached to molybdenum. The IR spectra of salicyoloyl hydrazide and its corresponding Mo(VI) complex are given in **figure 5 & 6** respectively below as representative one.

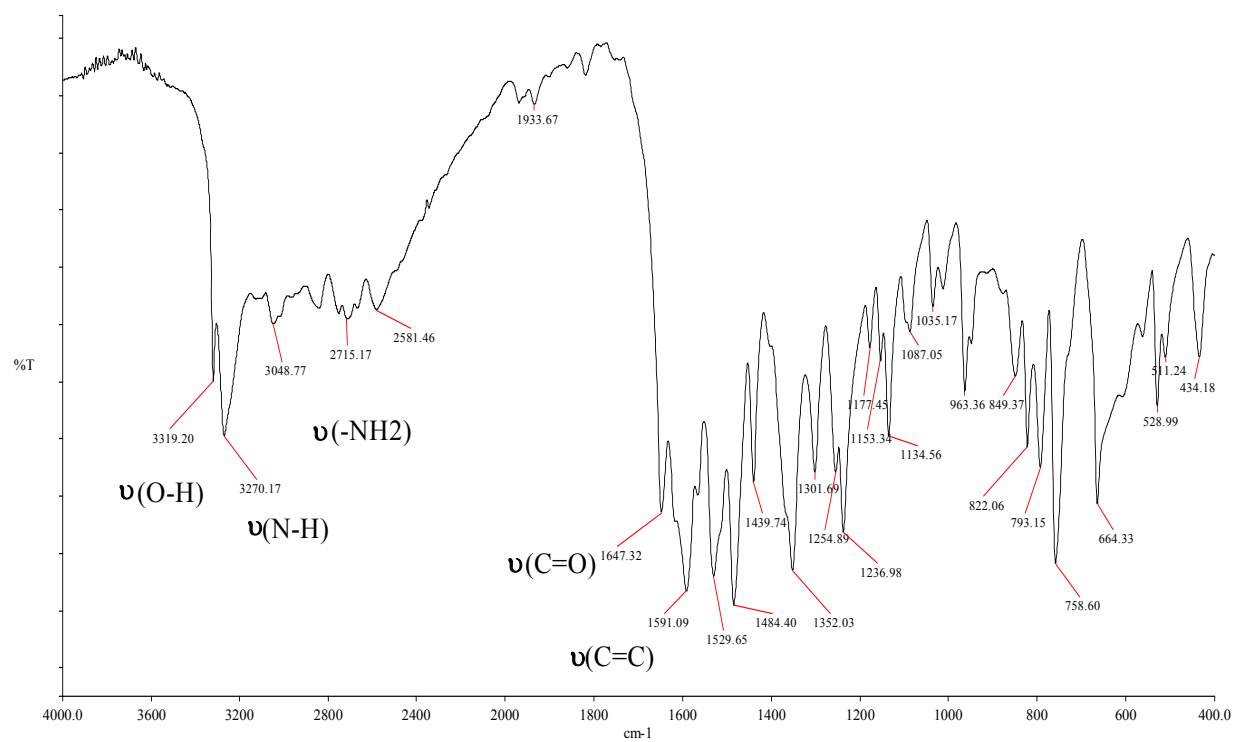


figure 5: IR spectra of salicyloyl hydrazide:

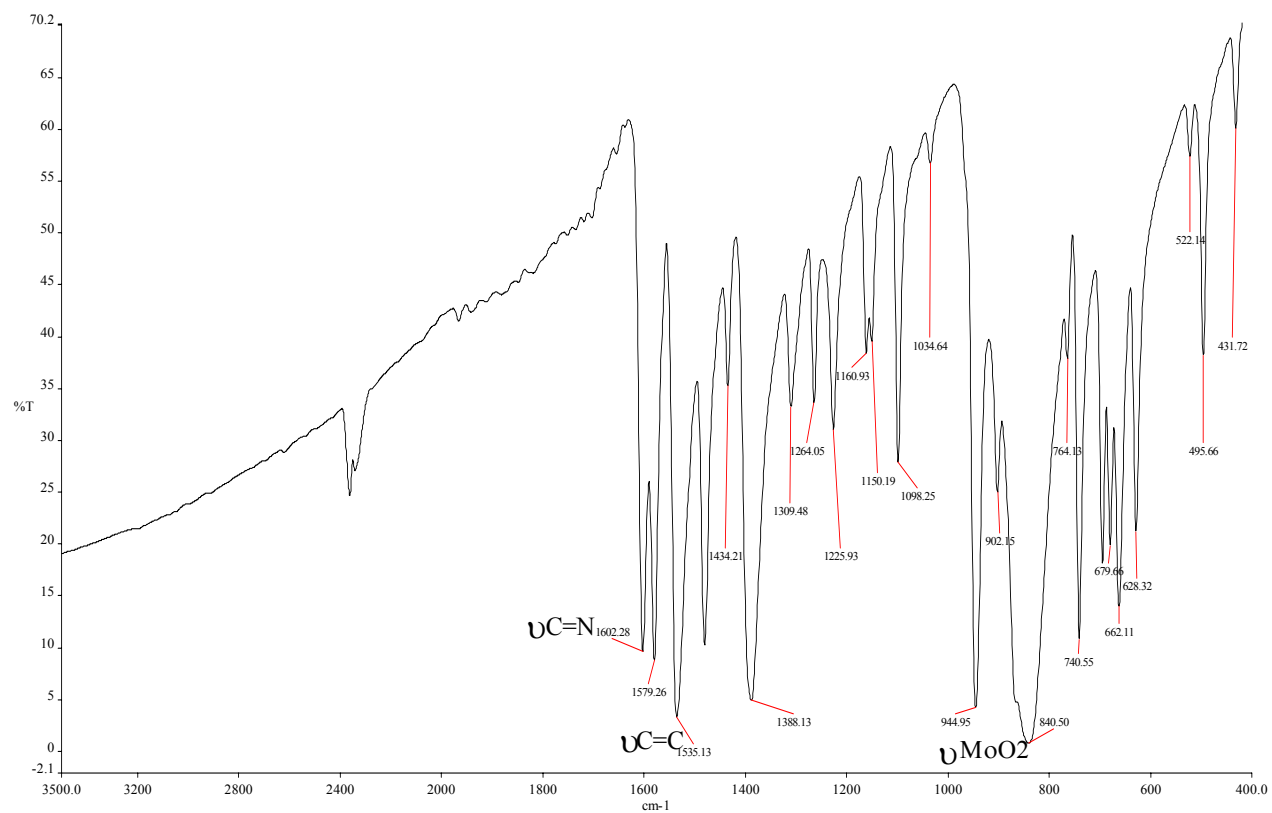


figure 6: IR spectra of complex 1 $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}^1(\text{EtOH})]$:

Redox properties

The electrochemical behavior of $\text{Mo}^{\text{VI}}\text{O}_2$ complexes, **1-2** have been examined in DMF solution using cyclic voltammetry at a platinum electrode with TBAP as supporting electrolyte. The representative CV trace of complex **1** is given in the **figure 7**. When only the reduction pathway is scanned the CV trace of the complexes display two irreversible reductive responses [25,26,27] within the potential window -0.17 to - 1.02 V which are assigned to Mo(VI)/Mo(V) [28,29] 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 these complexes is located in around + 1.43 V. As the Mo(VI) complex cannot undergo a metal-centered oxidation, this is attributed to a ligand-centered process.

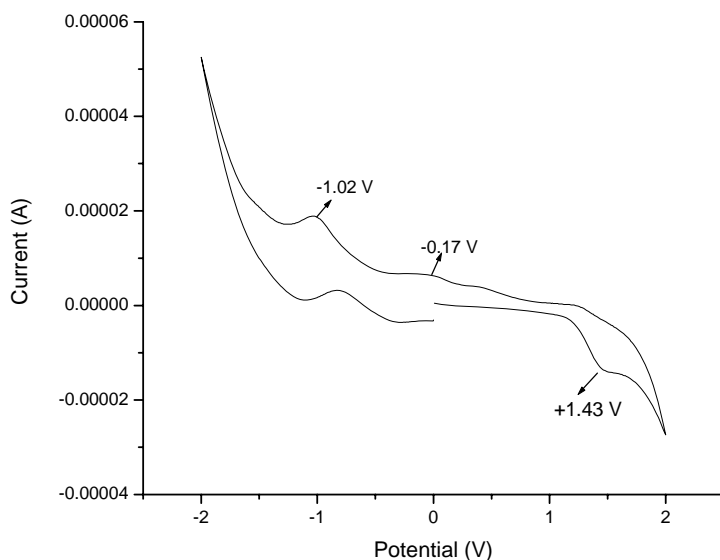


figure 7: Cyclic Voltammogram of complex 1 [$\text{Mo}^{\text{VI}}\text{O}_2\text{L}^1(\text{EtOH})$]

Electronic Spectra

The electronic spectra of these complexes were obtained at around 422 nm by which it can be predicted that metal has bound to the insitu ligand. The strong band at this position due to ligand to metal [L–Mo($d\pi$) LMCT] charge transfer. A strong absorption is also located in the region of 269 nm, which is assignable to intraligand transitions. The UV-Vis spectrum of the complexes was taken in DMF. Corresponding UV-VIS spectrum of one dioxomolybdenum(VI) (**2**) complex is given in **Figure 8** below.

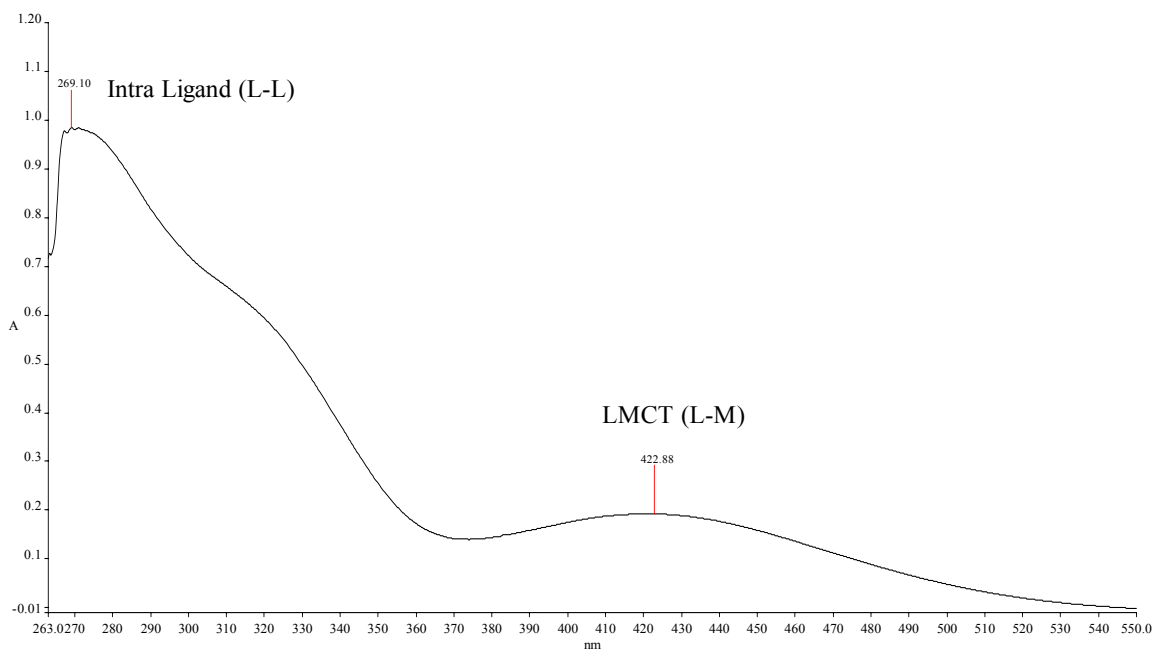


figure 8: Electronic spectra of complex 2 [$\text{Mo}^{\text{VI}}\text{O}_2\text{L}^2(\text{MeOH})$]

IR of Complex 3 [$V^V OL^1(OEt)$]:

IR spectra of the salicyloyl hydrazide have been described for the complex **1**. The prominent peaks of the salicyloyl hydrazide are present at 3319 cm^{-1} for stretching of $-OH$ group. But in the complex the peak shifted to 3235 cm^{-1} . Another prominent peak was observed at 972 cm^{-1} . This may be due to stretching of $V=O$ bond. For this complex another new prominent peak is at 1603 cm^{-1} . It may be due to $C=N$ stretching. The IR spectrum of this complex, **3** is given in **figure 9** below.

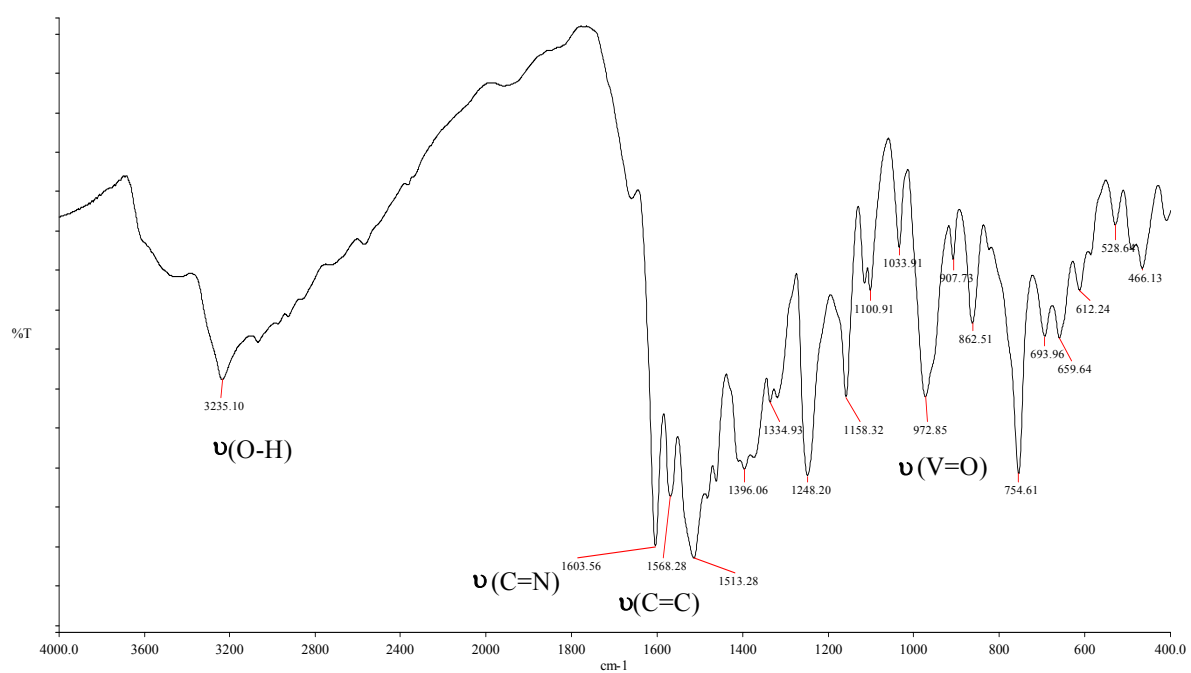


figure 9: IR spectra of the complex 3 [$V^V OL^1(OEt)$] :

Electronic Spectra of the complex 3 $[V^V OL^1(OEt)]$:

The electronic spectrum of this complex was obtained at 395 nm by which it can be predicted that metal has bound to the insitu ligand. The strong band at this position due to ligand to metal $[L-V(d\pi) LMCT]$ charge transfer. Strong absorptions are also located in the 369-345 nm, which is assignable to intra ligand transitions. The UV-Vis spectrum of the complex was taken in DMF. Corresponding UV-VIS spectrum of this oxovanadium(V) complex is given in **Figure 10** below.

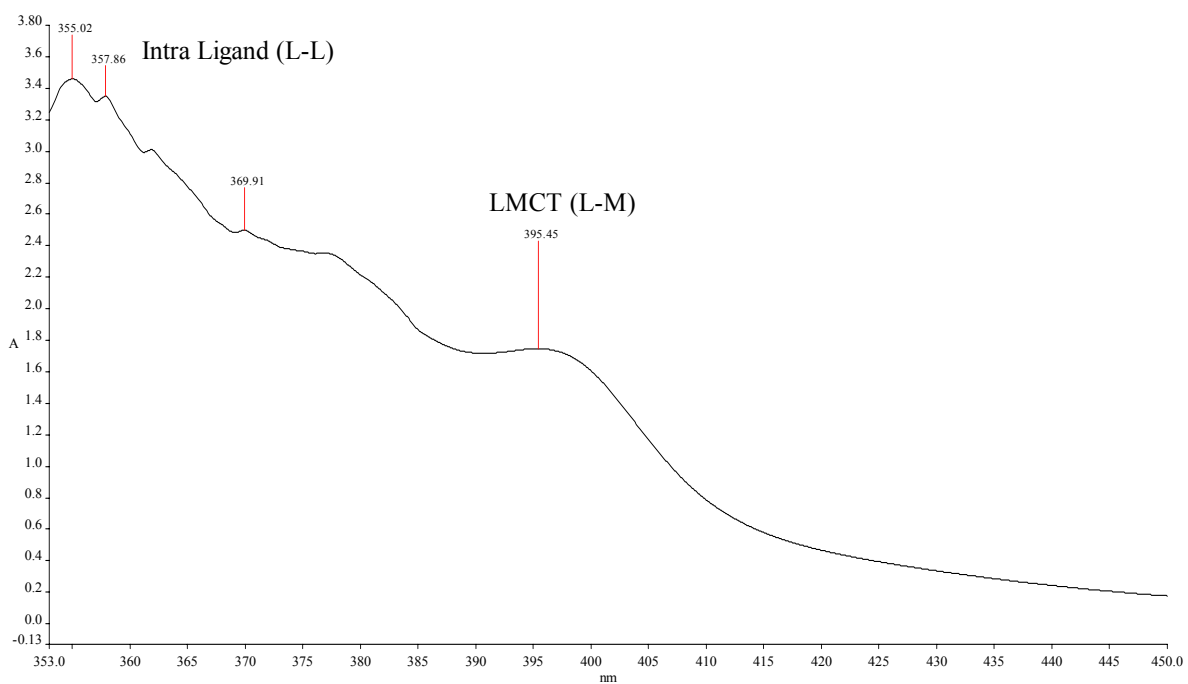


figure 10: UV spectra of $[V^V OL^1(OEt)]$

Conclusion:

The hydrazides were prepared successfully with good yield. The yield was about 70-71%. These hydrazides were characterized by IR spectroscopy and by C, H, N, analysis. I have used hydrazides directly for metallation with metal precursors having acetyl acetate groups. One of the acetyl acetate groups get separated from the metal precursor and carbonyl group of that acetyl acetate group undergoes condensation with hydrazide forming insitu hydrazone ligand. The complexes (1-4) formed were also successfully characterized by IR, UV, C, H, N analysis and cyclic voltammetry. 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 stereochemistry, x-ray structures of the corresponding complexes are required. The x-ray quality crystals of some synthesised complexes have been sent for structure determination using single crystal X-ray crystallography.

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