

*Synthesis and characterization of dioxidomolybdenum(VI) complexes of
azo-hydrazone ligands*

A Dissertation

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CERTIFICATE

This is to certify that the dissertation entitled “**Synthesis and characterization of dioxidomolybdenum(IV) complexes of azo-hydrazone ligands**” submitted by Usha Mishra 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 Usha Mishra bears good moral character.

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1. INTRODUCTION

Molybdenum coordination chemistry has become a fascinating area of research in recent years because of the presence of molybdenum in various metalloenzymes [1-8]. Majority of the molybdo-enzymes[7-8] have Mo(VI) as the active site and polydentate nitrogen, sulphur and oxygen ligands. Due to its ready availability in the biological systems, the coordination chemistry of Mo(VI) has fostered substantial interest in view of its biochemical significance, and several Mo(VI) complexes has been studied as models of molybdoenzymes[9-15].Also, molybdenum complexes have potential applications in catalysis and organic transformations particularly in the epoxidation of alkenes [16-19]On the other hand, Schiff bases, characterized by the azomethine group ($-RC-N-$), are known to have potential applications in biological field due to their antibacterial, antifungal and antitumor activity.[20]. Hydrazones, play a very important role in the field of analytical and medicinal chemistry. In medicinal field hydrazones act as antioxidants, anticancer, anti-inflammatory, antinociceptive, and antiplatelet drugs [21].Azo containing compounds are of growing interest because of their applications in many industries such as the dyeing of textiles, optical switching, non-linear optical properties [22], and preparation of photoactive materials [23]. Biological systems such as inhibition of DNA, RNA, and protein synthesis, carcinogenesis, and nitrogen fixation also involve azo compounds [24,25]. In addition, azo compounds and their metal chelates show good anti-bacterial activity [26-31]. Transition metal complexes of aroylhydrazones therefore constitute an interesting topic of current research due to their varied biological and catalytic acpplications [32].

To extend these observations, we have combined the aroylhydrazone Schiff bases and azo derivatives to enhance the properties of oxidomolybdenum complexes so that they can be used as better catalysts and have significant biological activities. The proposal is aimed to design some new azo- aroylhydrazone ligands and their corresponding oxidomolybdenum complexes. The ligands and their corresponding molybdenum complexes were successfully characterized by IR, UV-VIS spectroscopy.

2. EXPERIMENTAL

2.1 Materials:

[MoO₂(acac)₂] was prepared as described in literature [33]. Reagent grade solvents were dried and distilled prior to use. All other chemicals were reagent grade, available commercially and used as received. HPLC grade DMSO was used for spectroscopic and electrochemical studies and ethanol, methanol, acetonitrile were used for synthesis of ligands and metal complexes.

2.2. Physical Measurements:

IR spectra were recorded on a Perkin-Elmer Spectrum RXI spectrometer. Electronic spectra were recorded on a Lambda25, Perkin Elmer spectrophotometer.

2.3 Synthesis of ligands

5-(Arylazo) salicylaldehyde derivatives were prepared by a known method reported earlier [34]. Benzoylhydrazide, Salicylhydrazide and Isonicotinyl hydrazide were prepared from the corresponding methyl esters (**Scheme 2**) as reported in the literature [35]. The azo-arylhyazone ligands (H₂L¹⁻⁵) were prepared by refluxing the 5-(Arylazo) salicylaldehyde derivatives and the respective acid hydrazides following a standard procedure [36].

2.4 Synthesis of oxido-molybdenum complexes:

All the complexes were prepared following the same procedure. Ethanolic solution of MoO₂(acac)₂ was mixed with hot ethanolic solution of the ligand [H₂L¹⁻⁵]. The color of the solution changed to dark red. The mixture was refluxed. The orange residue was recrystallized and the dark orange crystals, suitable for X-ray crystallography were obtained.

3. RESULTS AND DISCUSSION:

3.1. Spectral Characteristics:

IR spectra

Infrared spectra of all the complexes are similar. The IR spectra of H_2L^1 and its metal complex $[\text{MoO}_2\text{L}^1(\text{EtOH})]$ (**1**) show that the ligand exhibits prominent bands due to N–H, and O–H moieties in $3321\text{--}2984\text{ cm}^{-1}$ region, however the complex do not exhibit, the N–H as well as the O–H bands. Thus it reveals that the ligands coordinate to the metal centre in the anionic forms. The characteristic bands at 937 and 913 cm^{-1} in metal complex attributes to the presence of dioxido $\nu(\text{Mo}=\text{O})$. [19]

UV-VIS spectra

The electronic absorption spectra (in DMSO) of all the complexes display a shoulder in $400\text{--}440\text{ nm}$ region and two strong absorptions are located in the $260\text{--}320\text{ nm}$ range, which are assignable to L–M($d\pi$) LMCT and intraligand transitions respectively.

3.2. Expected Structure of $[\text{MoO}_2(\text{L}^{1-5})(\text{EtOH})]$

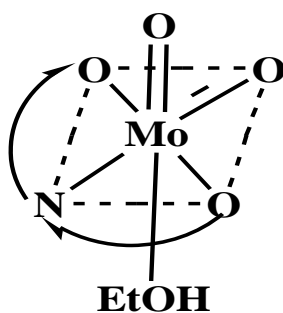


Figure 6.1

4. CONCLUSION

In this dissertation five 5-(Arylazo)-hydrazones and their corresponding Mo(VI) complexes have been synthesized. The ligands and their metal complexes have been characterized by IR, UV-VIS and NMR spectroscopy. X-ray structure of complex **1** is done using single crystal X-ray crystallography. Full characterization of all the complexes has not been possible due to shortage of time.

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