

**SYNTHESIS AND CHARACTERIZATION OXO-IMIDO
[TRIS (3,5 – DIMETHYL – PYRAZOL) BORATE]
MOLYBDENUM COMPLEXES**

**A Thesis Submitted to
the Graduate School of Engineering and Sciences of
İzmir Institute of Technology
In Partial Fulfillment of the Requirements for the Degree of**

MASTER OF SCIENCE

In Chemistry

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ACKNOWLEDGEMENT

I would like to thank to my advisor Assoc. Prof. Dr. Işıl Topalođlu Sözüer for her support and guidance in the completion of my research program.

I would like to thank to Research Foundation of İzmir Institute of Technology and TUBITAK for providing financial support for the project.

Finally, I'm grateful to my family for their understanding and support during my study.

ABSTRACT

In this study two new reactions related to oxo-Molybdenum(V)trispirazoly chemistry were investigated. The reactions between $[\text{MoTp}^*(\text{O})\text{Cl}_2]$ with *o*-substituted anilines, $\text{H}_2\text{NC}_6\text{H}_4\text{X-}o$ ($\text{X} = \text{Cl}, \text{Br}$) in the presence of triethylamine in toluene carried out to prepare dinuclear oxo-imido Mo(V) complexes of the type $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{X-}o)]$. Surprisingly, the previously reported compound, $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$, was obtained as the major product of both reactions.

The compound $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$ was characterized by $^1\text{H-NMR}$; IR, UV-visible spectroscopy techniques.

ÖZ

Bu çalışmada okso-molibden (v) trispirazolil kimyası ile ilgili iki yeni reaksiyon incelenmiştir. $[\text{MoTp}^*(\text{O})\text{Cl}_2]$ kompleksi *o*-fonksiyonel $\text{H}_2\text{NC}_6\text{H}_4\text{X-}o$ ($\text{X} = \text{Cl}, \text{Br}$) anilinlerle toluen çözeltisinde ,trietilamin varlığında, reaksiyona sokulmuş ve dimerik okso-imido molibden kompleksi elde edilmiştir , $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$.Her iki reaksiyonda da elde edilen ana ürünün literatürde varođlan dimerik okso-imido molibden kompleksi , $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$, olması beklenmedik bir durum olarak ortaya çıkmıştır.

Elde edilen dimerik okso-imido molibden (v) kompleksinin , $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$, yapısı $^1\text{H-NMR}$, IR, UV-visible spektrumlarıyla aydınlatılmış.

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ABBREVIATIONS

Tp : Trispyrazolyborate

Tp* : Tris (3,5 – dimethylpyrazolyl) borate

Cp : Cyclopentadienyl

Cp* : Pentamethylcyclopentadienyl

KTP* : Potassium hydrotris (3,5 – dimethylpyrazolyl) borate

Et₃N : Triethylamine

Me : Methyl

Et : Ethyl

Pr : Propyl

FT-IR : Fourier Transform Infrared

UV-VIS : Ultraviolet – Visible

TLC : Thin Layer Chromotography

CH₂CL₂ : Dichloromethane

P : Para

M : Meta

O : Ortho

δ : Chemical Shift

CHAPTER 1

INTRODUCTION

The work described in this thesis is concerned with oxo molybdenum (V) chemistry. In this chapter, some background information on this field is presented.

1.1 Oxo Molybdenum Trispyrazolylborate Chemistry

Molybdenum is considered as a trace element, presents several oxidation states, and therefore may change easily its coordination number and to form mono and binuclear oxo complexes which is of great importance from basic as well as applied points of view. The propensity of oxo-molybdenum species in higher oxidation states to form di, tri and polynuclear complexes is well known [1]. Molybdenum is a relevant element for the synthesis of many homogeneous and heterogeneous catalysts. The element is also essential in several enzymatic systems. One of the characteristics of the molybdenum chemistry is related to the easy conversion between its oxidation states and to the changes of coordination number, observed particularly between Mo(III), Mo(IV), Mo(V) and Mo(VI). The chemistry of oxo Mo(V) complexes is of importance especially in industrial and biochemical catalysis [2].

In the 1960s and 1970s coordination chemists were intrigued by the rôle which molybdenum might play in the enzyme nitrogenase. Before high resolution crystallographic information was available about the active site of the enzyme, and in particular the structure of the Mo-containing cofactor, many models were developed to mimic the conversion of dinitrogen to ammonia and hydrazines. Many of these models were unrealistic in terms of their biological relevance but they illuminated an area of dinitrogen chemistry which, until then, had been little explored. Notwithstanding the relevance or otherwise of the model systems, the challenge of trying to unravel the mechanism of how N₂ could be converted under mild conditions to NH₃ led to the development of very exciting, interesting and unexpected coordination and organometallic chemistry of both molybdenum and tungsten. Early developments involved the syntheses of a variety of low-valent tertiary phosphine complexes, and led to the discovery of novel dinitrogen, diazenido, hydrazido and imido compounds. Once

the structure of the cofactor, which contained a complex cluster composed of two Fe₃Mo cores bound together by sulphide ions, became clear research moved away from phosphine chemistry towards sulphide-stabilised cubane-like systems bound by more 'conventional' N/O/S ligands.

Parallel to these developments had been the steady search for appropriate molybdenum or tungsten-based models for a variety of O-atom transfer enzymes, including oxidases (xanthine, CO, aldehyde, sulphite) and reductases (formate dehydrogenase, nitrate), all of which seemingly involve interconversion of the MoO^{2+/3+} and MoO₂²⁺ groups.³ This work has blossomed with the discovery of dithiolene-like metal binding groups in several enzymes and their characterisation, *inter alia*, by EXAFS and related structural techniques.⁴²

During this period, nitrosyl chemistry of molybdenum and tungsten also developed, although it has not yet been identified with any particular enzymatic process. Most of the early interest was fundamental and although some catalytic potential was detected, most research concentrated on η^5 -cyclopentadienyl complexes. Some of these provided unusual hydrazido(1-) and (2-) compounds of potential relevance to the mechanism of N₂-fixation, and the first proof of η^2 -binding of hydrazines to transition metals. This 'Comment' focuses on more recent work with the {Mo(NO)} group which has led to unexpected and potentially applicable chemistry, particularly in the area of linear and non-linear optics, and also draws out some of the remarkable parallels between the chemical and physical properties of particular complexes containing the {Mo(NO)}^{1+,2+,3+} and {Mo(O)}^{2+,3+,4+} cores stabilised by the tris(3,5-dimethylpyrazolyl)borato ligand, Tp*.⁵ A number of factors combine to make the two metal fragments {Mo(NO)Tp*Cl} and {Mo(O)Tp*Cl} particularly useful for studying electronic and magnetic interactions between metal centres across bridging ligands. First, they are relatively easily attached to a range of difunctionalised ligands whose length, conformation and topology can be varied extensively and systematically. Second, both fragments are redox active, permitting the study of electronic interactions by voltammetry and spectroelectrochemistry. Third, they can be made paramagnetic (*S* = 1/2), enabling the study of magnetic exchange interactions by epr spectroscopy and susceptibility measurements. Fourth, the Mo–NO and Mo=O groups provide easily identifiable and strong or moderately strong IR absorptions which are very convenient

spectroscopic probes for monitoring changes in electronic density at the metal centres; a feature which may also be exploited spectroelectrochemically.

1.1.1 The Polypyrazolylborates

The polypyrazolylborate ligands $[BR_n(Pz)_{4-n}]^-$ were first synthesized by Trofimenko in 1966 [3], and the coordination chemistry of these ligands has been, and still is a vigorous research area [4]. It has been shown that there are strong analogies between the behaviour of metal complexes containing trispyrazolborato anions, and those containing η^5 -cyclopentadienyl ligand [5]. This ligand system have widely been used in inorganic and organometallic chemistry especially with d and f transition elements [6]. It was known that tris(pyrazolyl)borate ligands have had a significant impact on the modelling of active centre of Mo enzymes [7]. Also these ligands exhibit dynamic behaviour on the NMR timescale [8]. The sterically encumbering nature of the Tp^* (hydrotris(3,5-dimethylpyrazol-1-yl)borate) ligand compared with Cp^* (pentamethyl cyclopentadienyl) is widely known and explored in high activity for catalyst systems [9,10].

1.1.2 The Comparison of Tp and Cp

Tris(pyrazolyl)borate (Tp , $[HB(pz)_3]^-$), tris(3, 5-dimethyl-pyrazol)borato (Tp^* , $[HB(3,5-Me_2pz)_3]^-$) (Figure 1.1) can be compared to the ligands cyclopentadienyl (Cp , C_5H_5) and pentamethylcyclopentadienyl (Cp^* , C_5Me_5) respectively [11], in that they are monoanionic, formally six electron donors which can occupy three facial coordination sites on a metal ion.

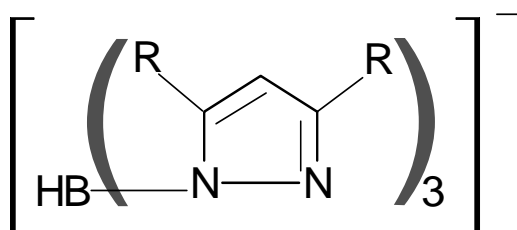


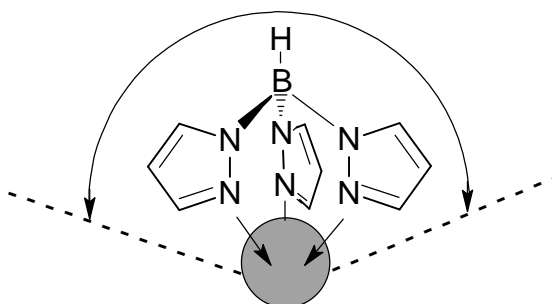
Figure 1.1. Hydrotris(1-pyrazolyl) borate ion (Tp : $R = H$), (Tp^* : $R = Me$).

However there are some important differences. Firstly, the trispyrazolylborates are tripodal with C_{3v} symmetry, whereas the cyclopentadienyl ligands are pentagonal with D_{5h} [12]. Secondly, the Tp ligands act as strong σ -donor and weak π -acceptors in contrast to the Cp ligands which act as π -donors and π -acceptors [13].

Trispyrazolylborates are better donors and comparable acceptors than cyclopentadienyl. There is evidence to show that the trispyrazolylborate ligand forms stronger bonds to metals than cyclopentadienyl. Combined with the extra steric protection afforded this means that metal complexes of the trispyrazolylborate anions are generally more thermodynamically stable. Thus stable trispyrazolylborate complexes have become more abundant than their counterparts containing cyclopentadienyl. The Tp* is an extremely bulky ligand and the methyl group in the 3-position help to envelop the metal in its coordination compounds. This can be seen from the Tolman cone angles for trispyrazolylborate, tris(3,5-dimethyl-pyrazol)borato, cyclopentadienyl and pentamethylcyclopentadienyl ligands which are 180° , 225° , 136° and 165° , respectively. It is the steric and electronic properties of this tris(3,5-dimethyl-pyrazol)borato ligand that brings about stabilisation of formally coordinatively unsaturated complexes or, in many cases compounds which are otherwise air and moisture sensitive[14].

Molybdenum trispyrazolylborates are mainly six coordinate in contrast to the predominately seven coordinate species found in the analogous molybdenum-cyclopentadienyl chemistry. This is partially due to the steric effects of trispyrazolylborates, but also to the electronic influences of these ligands. The highly directional σ -orbitals on the nitrogens help to hybridise the metal into an octahedrally coordinate structure. The highly diffuse π -orbitals of cyclopentadienyl have no such influence on the metal [15].

Cone angle = 180°



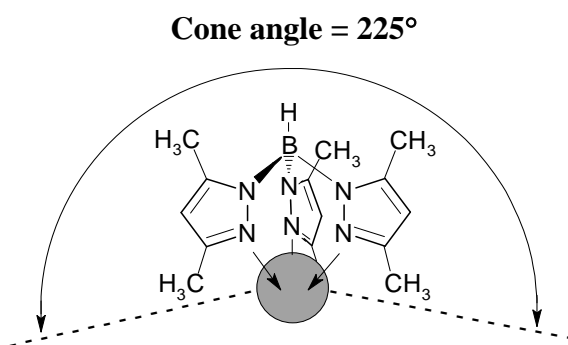


Figure 1.2. Comparison of trispyrazolylborate and tris(3,5-dimethylpyrazol)borate showing cone angles.

1.2 Oxo Molybdenum(V) Trispyrazolborate Compounds

1.2.1 Monomeric Oxo-Molybdenum(V) Complexes

$[\text{MoTp}^*(\text{O})\text{Cl}_2]$ was first obtained, a number of years ago, by Trofimenko by alumina treatment of the uncharacterized red solution that be obtained from reaction of $[\text{MoTp}^*(\text{CO})_3]^-$ with thionyl chloride [16]. The red solution has since been characterized as containing $[\text{MoTp}^*\text{Cl}_3]$, [17] and it was found that the oxidation of this compound with dioxygen gave a good yield of the yellow-green crystalline complex $[\text{MoTp}^*(\text{O})\text{Cl}_2]$, $[\text{MoTp}(\text{O})\text{Cl}_2]$ was made in an analogous manner. These monomers are paramagnetic, as expected for a d^1 system [18].

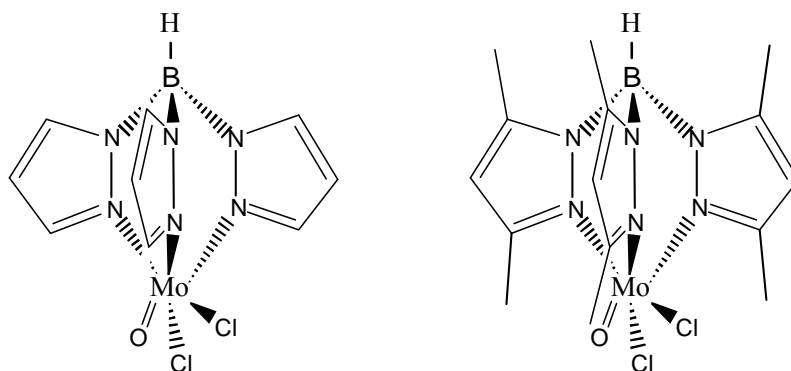


Figure 1.3. The structures of $[\text{MoTp}(\text{O})\text{Cl}_2]$, (4) and $[\text{MoTp}^*(\text{O})\text{Cl}_2]$, (1)

However, Enemark's group have developed a more convenient preparation for [MoTp(O)Cl₂]. Reaction of MoCl₅ with tetrahydrofuran (THF) under anaerobic conditions yields the known MoOCl₃(THF)₂,

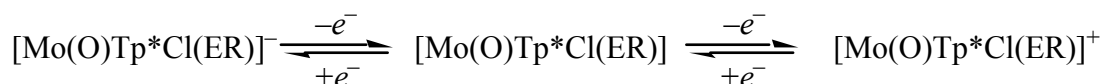


Presumably by abstraction of an oxygen atom from the solvent addition of KTp* to the reaction mixture and moderate heating affords [MoTp*OCl₂] as a green precipitate, which can be recrystallised from hot dichloromethane or 1,2-dichloroethane as bright green crystals. Typical yields are 50–70% [19].

[MoTp*(O)Cl₂] is stable in air indefinitely is stable to water and is unchanged at 200 °C. There is no evidence for ligand substitution reactions of [MoTp*OCl₂] at room temperature. Ligand-exchange reactions of [MoTp*OCl₂] probably proceed by dissociation of chloride and subsequent coordination of the new ligand [19]. [MoTp*(O)Cl]⁺ fragment is very attractive to work with, because: (i) it is electronically simple (d¹), (ii) it is redox active and paramagnetic, (iii) it is synthetically easy to use, and (iv) the coordination chemistry and bioinorganic chemistry of oxo-molybdenum (V) complexes is generally well studied, so their spectroscopic properties are fairly thoroughly understood [20].

Enemark and his coworkers have prepared a variety of derivatives from [MoTp*OCl₂], [MoTp*OCl(OR)], [MoTp*OCl(SR)] [21,22,23].

In these species the metal is in oxidation state V (d¹ configuration), and this species can be oxidised and reduced to Mo^{VI} and Mo^{IV} species, respectively. Although fewer compounds in this group have been studied electrochemically, the trends are largely similar to the nitrosyls. The electron transfer behaviour is summarised as:



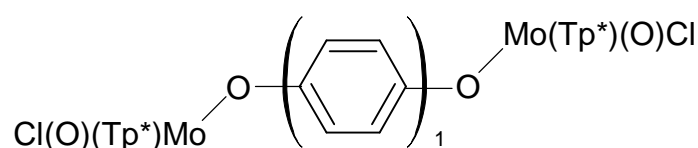
Reduction potentials for the reduction of [Mo(O)Tp*Cl(ER)] become progressively negative in the order ER = Cl < SPh < OPh < OMe [10] and with [Mo(O)Tp*(OR)₂], the reduction potentials are, on average, 470 mV more negative than their monoalkoxide analogues [8]. In contrast to the nitrosyl series, no oxidation state ambiguities exist with the oxomolybdenum complexes. The formal oxidation state of

the metal in $[\text{Mo}(\text{O})\text{Tp}^*\text{Cl}(\text{OR})]$ is V (d^1), and one-electron reduction and oxidation leads to Mo^{IV} (d^2) and Mo^{VI} (d^0), respectively. Only a few well-characterised Mo^{IV} complexes have so far been reported: $[\text{Mo}(\text{O})\text{Tp}^*\text{Cl}(\text{py})]$ and $[\text{Mo}(\text{O})\text{Tp}^*(\text{SR})(\text{py})]$ (R = Ph, alkyl), obtained by reduction of $[\text{Mo}(\text{O})_2\text{Tp}^*\text{X}]$ (X = Cl or SPh) in pyridine solution [15]. They may be oxidised reversibly to Mo^{V} species.

In order to understand the chemistry of oxo $\text{Mo}(\text{V})$ compound, it is necessary to inspect the frontier orbitals for $[\text{Mo}(\text{O})\text{Tp}^*\text{Cl}_2]$. In the $\{\text{Mo}(\text{O})\text{Tp}^*\text{Cl}\}^+$ fragment, the oxo ligand is a strong π -donor, the filled oxygen p_x and p_y orbitals overlapping with the metal d_{xz} and d_{yz} orbitals, raising them but again leaving the d_{xy} orbital unchanged. The Mo^{V} electronic configuration is therefore $d_{xy}^1 d_{xz}^0 d_{yz}^0$.

1.2.2 Dimeric Oxo-Molybdenum Complexes.

McCleverty et. al. investigated the chemistry of dinuclear oxo complexes of molybdenum of the type $[\text{Mo}(\text{O})\text{Tp}^*\{\text{E}(\text{CH}_2)_n\text{E}\}]$ (E = O or S) for several years [5]. These complexes have been of interest because of their remarkable magnetic and optical properties, which has led us recently to report systems containing the $\{\text{Mo}(\text{O})\}^{n+}$ moieties which exhibit redox-switchable magnetic, non-linear optic [4,12] or NIR electrochromic behaviour [13]. A number of factors combine to make this metal fragment particularly useful for studying electronic and magnetic interactions between metal centres across a range of bridging ligands designed to allow investigation of the effects of ligand length, conformation and topology. It is (i) redox active, permitting the study of electronic interactions by voltammetry, and (ii) paramagnetic, enabling the study of magnetic exchange interactions by epr spectroscopy and magnetic susceptibility measurements. Furthermore, Mo=O group provides easily identifiable and strong or moderately strong IR absorptions which are very convenient spectroscopic probes for monitoring changes in electronic density at the metal centres.



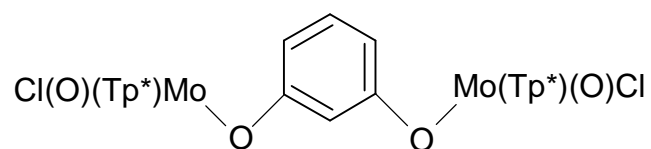


Figure 1.4. The structural formulas of complexes containing diphenolate bridging ligands.

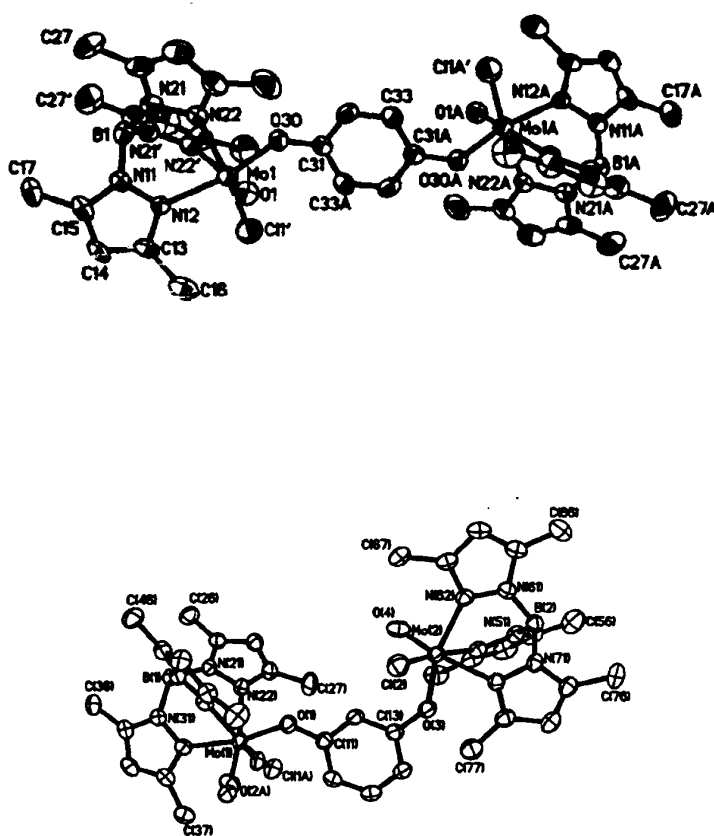


Figure 1.5. The crystal structures of the complexes containing diphenolate bridging ligands.

Hydrolysis of the Mo(V) complex $[\text{MoTp}(\text{O})\text{Cl}_2]$, leads to two geometrical isomers of formula $[\text{MoTp}(\text{O})\text{Cl}_2](\mu\text{-O})$, (cis isomer) , 10 % yield and (trans isomer) , % 60 yield (Scheme 1.1.) . The X-ray structures of and were also reported [24].

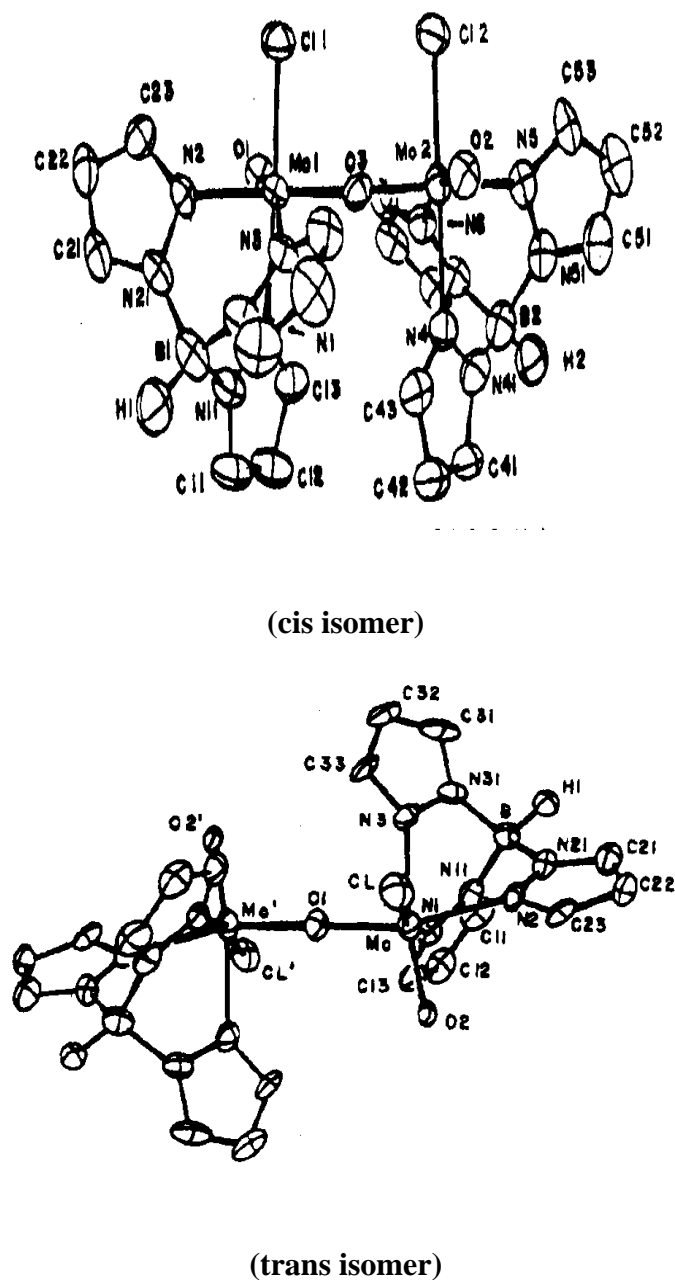


Figure 1.6. The crystal structures of $[\text{MoTp}(\text{O})\text{Cl}_2](\mu\text{-O})$, (cis isomer) and (trans isomer)

Crystal structures showed them to be linear μ -oxo bridged Mo-O-Mo complexes. A detailed FTIR and Raman experiments have been carried out related to symmetry dependence of bands associated with the Mo-O-Mo bridge [15].

$[\text{Mo}_2\text{O}_4(\text{Tp})_2]$, was the major product obtained from the reaction of $\text{KHB}(\text{pz})_3$ with solutions of $[\text{Mo}(\text{O})\text{Cl}_5]^{2-}$ in aqueous HCl solution (pH=2) according to a modification of a synthetic procedure developed by Melby for similar $\text{Mo}_2\text{O}_4^{2+}$ complexes.

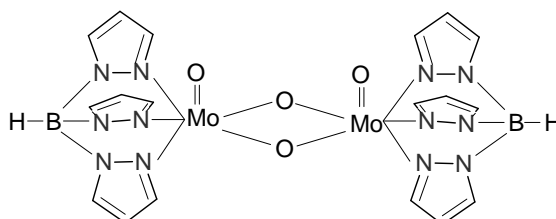
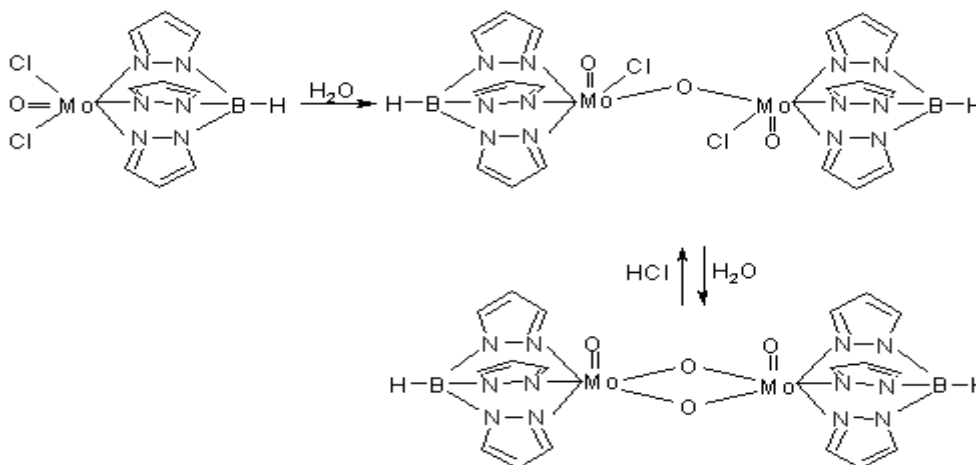


Figure 1.7. The structure of $[\text{Mo}_2\text{O}_4(\text{Tp})_2]$.

Compound $[\text{Mo}_2\text{O}_4(\text{Tp})_2]$ was reported [18,25] to be converted to the mono μ -oxo bridged species $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$ with HCl (Scheme 1.1.), which was a characteristic reaction of $\text{Mo}_2\text{O}_4^{2+}$ complexes.



Scheme 1.1. Preparation of Mo-O-Mo bridged complexes.

McCleverty et. al. [26] prepared the compound $[\text{MoTp}^*(\text{O})\text{Cl}]_2(\mu\text{-O})$ by the reaction of $[\text{MoTp}^*\text{O}_2\text{Cl}]$ and PPh_3 in wet toluene containing approximately 0.03% water. Millar et.al. [27] prepared the same compound by treatment of 1,3-dimethoxy-

para-tert-butylcalix(4)arene and $[\text{MoTp}^*(\text{O})\text{Cl}_2]$ in toluene with reflux. The synthesis was successful in the absence of calixarene as well and it was suggested that the complex was formed due to the presence of adventitious water. The crystal structure of $[\text{MoTp}^*(\text{O})\text{Cl}_2](\mu\text{-O})$ is shown in Figure 1.8.

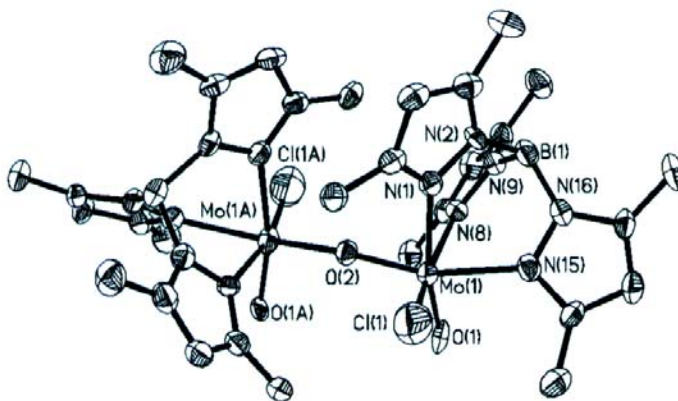


Figure 1.8. The crystal structure of $[\text{MoTp}^*(\text{O})\text{Cl}_2](\mu\text{-O})$.

1.2.3 Mixed-Valance Molybdenum ($\mu\text{-O}$) Compounds

It was reported [28] that reaction of $[\text{MoTp}^*(\text{O}_2)\text{Cl}]$ with the grignard reagent MeMgCl , MeMgI , or PhCHMgBr in tetrahydrofuran at -78 or -42°C produced a deep brown reaction mixture after rapid disappearance of an initial transient green coloration to yield orange-brown $[\text{Mo}^{(\text{V})}\text{Tp}^*(\text{O})\text{Cl}(\mu\text{-O})\text{Mo}^{(\text{VI})}\text{Tp}^*(\text{O}_2)]$. The infrared, electronic spectroscopy and X-ray diffraction structure of $[\text{Mo}^{(\text{V})}\text{Tp}^*(\text{O})\text{Cl}(\mu\text{-O})\text{Mo}^{(\text{VI})}\text{Tp}^*(\text{O}_2)]$ were reported.

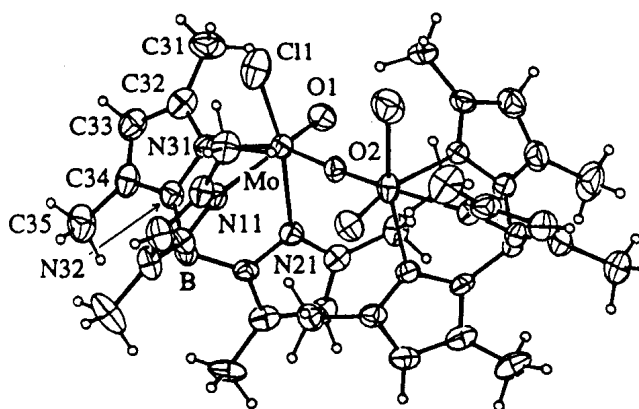
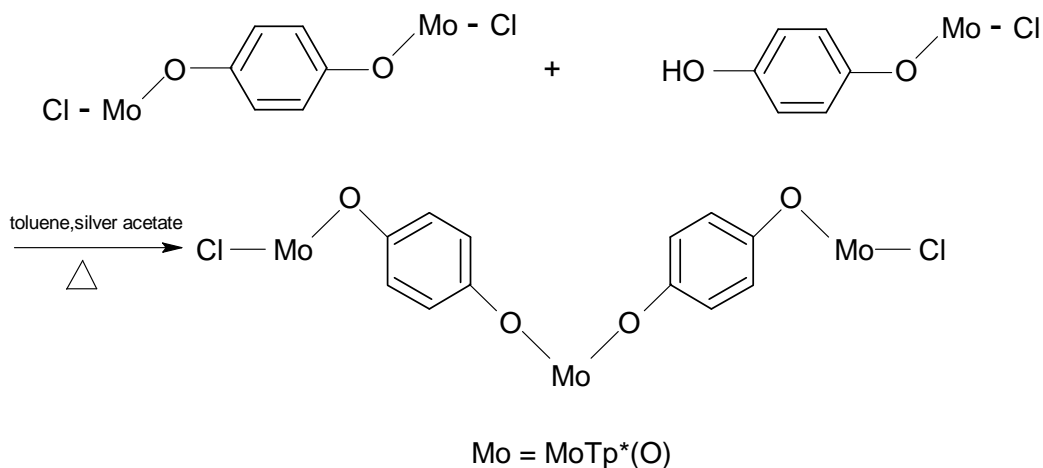


Figure 1.9. The crystal structure of $[\text{Mo}^{(\text{V})}\text{Tp}^*(\text{O})\text{Cl}(\mu\text{-O})\text{Mo}^{(\text{VI})}\text{Tp}^*(\text{O}_2)]$.

1.2.4 Trinuclear Molybdenum Compounds

The trinuclear complexes $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-1, } n\text{-C}_6\text{H}_4\text{O}_2)[\text{MoTp}^*(\text{O})](\mu\text{-1, } n\text{-C}_6\text{H}_4\text{O}_2)[\text{MoTp}^*(\text{O})\text{Cl}]$, ($n=3, 4$) have been prepared by McCleverty et al. [29], in which a chain of three paramagnetic oxo-Mo(V) fragments are linked by two 1, 4-[OC₆H₄O]²⁻ ($n=4$) (Scheme 1.2.) or 1, 3-[OC₆H₄O]²⁻ ($n=3$) bridging ligands.



Scheme 1.2. Synthesis of complex 1,4-[OC₆H₄O]²⁻ ($n=4$).

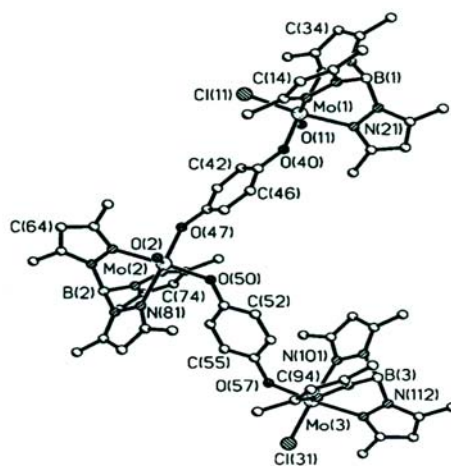
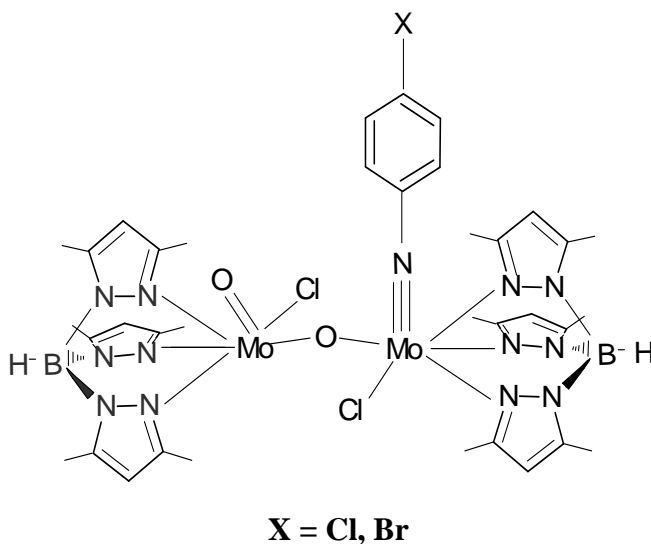
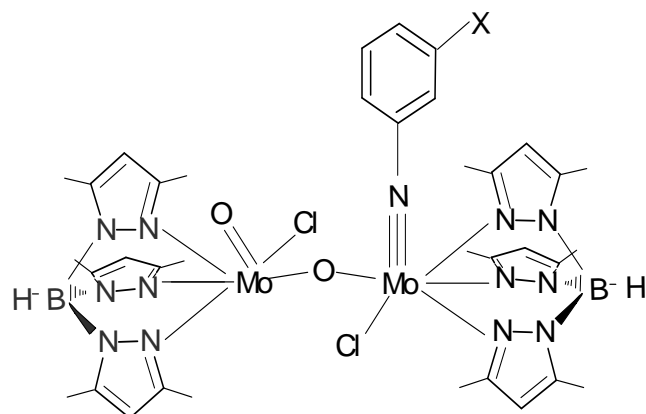


Figure 1.10. The crystal structure of $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-1, } 4\text{-C}_6\text{H}_4\text{O}_2)[\text{MoTp}^*(\text{O})](\mu\text{-1, } 4\text{-C}_6\text{H}_4\text{O}_2)[\text{MoTp}^*(\text{O})\text{Cl}]$.

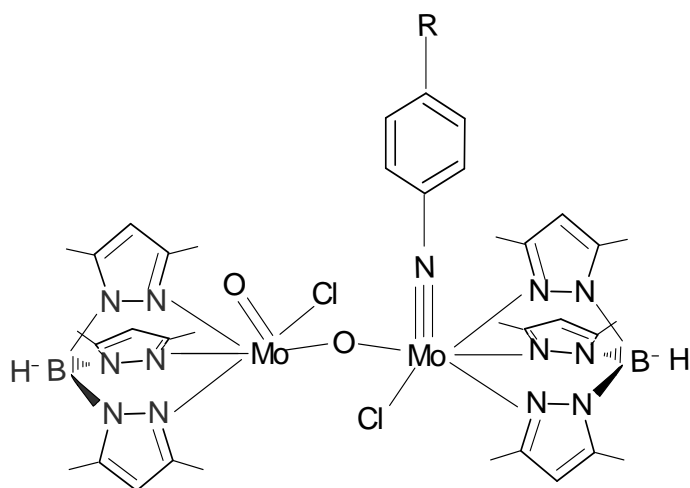
1.3 Oxo-Bridged (Haloarylimido)[tris(3,5-dimethylpyrazolyl)borato] molybdenum(V) Complexes

$[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{R-}p)]$ ($\text{R} = \text{OMe}, \text{OEt}, \text{OPr}, \text{NO}_2$), $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{X-}p)]$ ($\text{X} = \text{Cl}, \text{Br}$) and $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{X-}m)]$ ($\text{X} = \text{F}, \text{I}$) were synthesized by the reaction of $[\text{MoTp}^*(\text{O})\text{Cl}_2]$ with the appropriate aniline in the presence of triethylamine in toluene under reflux. These species are soluble in chlorinated solvents and stable in air. They can easily be separated from the reaction mixture by crystallisation from a dichloromethane/hexane mixture (1:4). These compounds were the first examples of molybdenum compounds, containing both aryylimido and μ -oxo group in the presence of tris(pyrazolyl)borate co-ligand. The compounds $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{Br-}p)]$ and $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{F-}m)]$ were obtained as two geometric isomers (cis and trans according to the position of the chloro ligand).





X = F, I



R = OMe, OEt, OPr, NO₂

Figure 1.11 Structures of the Oxo-imido Mo(V) Compounds

The single crystal X-ray crystallographic determination of $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{OMe-}p)]$, $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{F-}p)]$, $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{I-}m)]$ and $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{Br-}p)]$ revealed that there was a Mo-O-Mo bridge and a near linear arylimido group in these species. [24,30]

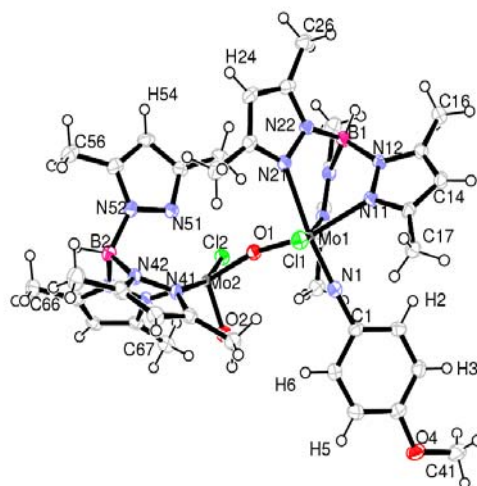


Figure 1.12. Molecular Structure of $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{OMe-}p)]$

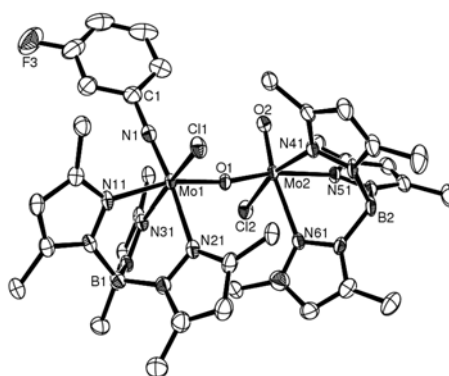


Figure 1.13. Molecular Structure of $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{F-}m)]$

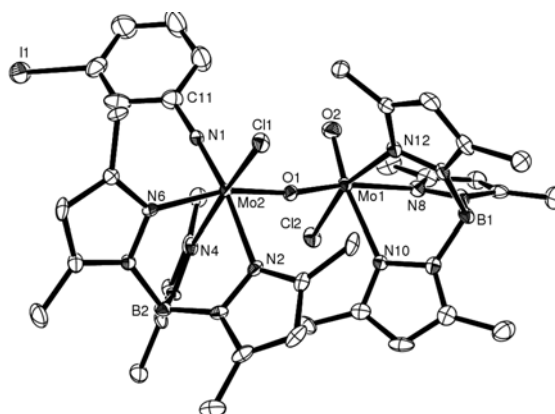


Figure 1.14. Molecular Structure of $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{I-}m)]$

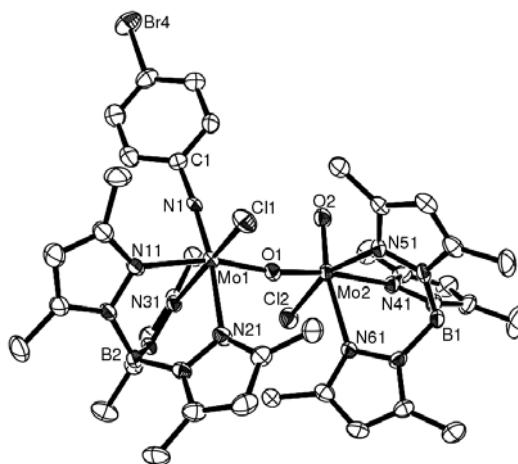


Figure 1.15. Molecular Structure of $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{Br-}p)]$

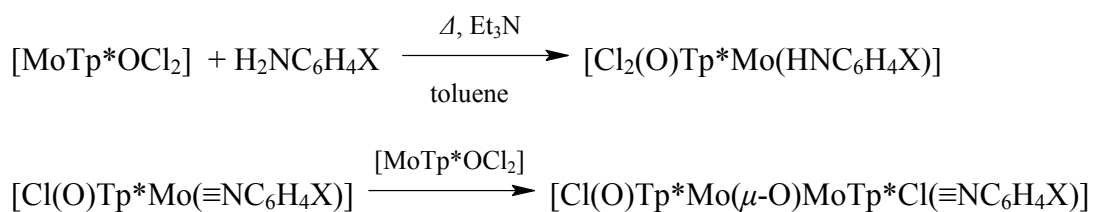
In these structures binuclear complexes are comprised of two unidentical MoTp^*Cl unit connected by a single oxo bridge, there are two pseudo-octahedral metal centers. The first metal centers is coordinated by facial Tp^* , terminal oxo, terminal chloro and bridging oxo ligand whereas the second is coordinated by facial Tp^* , terminal chloro, aryl imido and bridging oxo ligands. It was seen that two Cl atoms were trans to each other. The structures of the geometric isomers of $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{Br-}p)]$ and $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{F-}m)]$ were also determined to reveal two chlorine atoms bonded in a cis fashion. The Mo-N-C bond angles are indicative of a linear Mo-N-C(aryl) unit which supports the existence of a triple bond between Mo and nitrogen. Molybdenum nitrogen multiple bond could either be a double bond with Mo-N-C angle of 120° or a triple bond with Mo-N-C angle of 180° .



Figure 1.16. Linear (a) and bent (b) imido linkages.

In the case of **(a)** the imido group acts as a six electron donor with no lone pair in the case of **(b)** it behaves as a four electron donor.

There are a number of synthetic methods known for introducing imido functionality into coordination compounds. The preparation of the oxo-imido Mo(V) compounds was accomplished by double deprotonation of the *p*-substituted haloanilines. Despite the steric barrier provided by the 3-methyl groups of the Tp* ligand, the formation of the Mo-O-Mo linkage in these Mo(V) dimers is interesting. It was suggested that these compounds were formed by treating [MoTp*OCl₂] with *p*-substituted anilines, each of which undergoes double deprotonation to yield the mononuclear species [MoTp*OCl(H₂NC₆H₄X)] (or R), [MoTp*OCl(HNC₆H₄X)] and [MoTp*OCl(≡NC₆H₄X)] (X = F, C, I, Br) as a sequence of intermediates. The mononuclear imido species, [MoTp*OCl(≡NC₆H₄X)], further reacts with unreacted starting material to form the oxo-bridged dimetallic (haloaryl) imido molybdenum(V) compounds [MoTp*(O)Cl](μ-O)[MoTp*(Cl)(≡NC₆H₄X)]



(X = Br, **1a**, *cis*; **1b**, *trans*; Cl, **2**)

Scheme 1.3. Synthesis of complexes

Oxo and imido ligands form commonly multiple bonds when attached to transition metal centers. There has been significant interest in the chemistry of the corresponding complexes. Of particular importance are the high-valent organo-imido and -oxo molybdenum derivatives which have been widely studied. Both the imido and oxo groups lead to stabilization of high formal oxidation states. A large number of imido compounds are known for the majority of the transition metals in various oxidation states, although high-valent centres in which the metal has a d^0 - d^2 electronic configuration are particularly stable [27]. For the design of π -conjugated systems this type of ligation is desirable because strong interactions occur between the metal *d* orbitals and the *p* orbitals on nitrogen. Changing the electronic and steric characteristics of the organic group bonded to nitrogen allows the modification of the properties of the resulting metal complexes [31].

CHAPTER 2

EXPERIMENTAL STUDY

2.1 Experimental Techniques for Handling Air-Sensitive Compounds

All reactions carried out in this study are air and moisture sensitive therefore Vacuum-Line and Schlenk Technique is used for all experiments.

2.2 The Vacuum-Line Technique

2.2.1 The Double Manifold

If you wish to carry out reactions under dry and inert conditions, a double manifold is an extremely useful piece of apparatus (Figure 2.1.) [32].

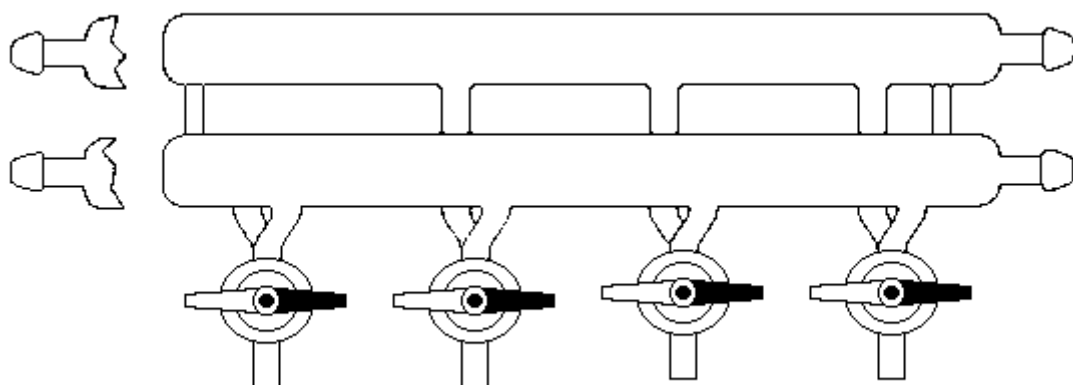
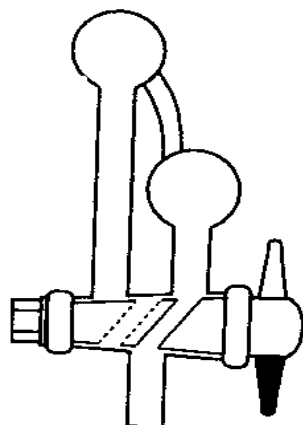
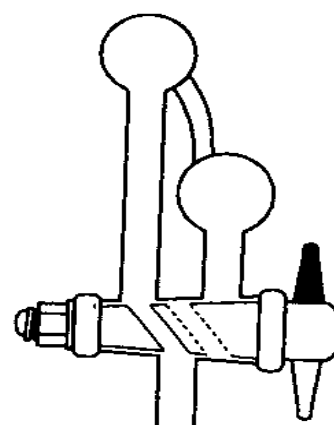


Figure 2.1. The double manifold.

The manifold consists of two glass barrel. One barrel of the manifold is connected to a high vacuum pump another to dry inert gas (Figure 2.2.). Thus, at the turn of the tap, equipment connected to the manifold can be alternately evacuated or filled with inert gas.



Tap switched to vacuum



Tap switched to inert gas

Figure 2.2. Cross section through a double oblique tap.

2.2.2 The Schlenk Technique

To use a schlenk glassware provides facility during the reactions under N_2 , with the schlenk tube one can transfer a solid or liquid in an atmosphere of an inert gas, such as nitrogen or argon [33,34].

The basic and simplest schlenk tube is shown in Figure 3.3. The schlenk tube is stoppered and evacuated by pumping through D. By introducing the inert gas through A the tube is filled with the inert gas. The tap is turned through 90° to let gas pass through the tail part and then is turned through 90° to allow gas into the flask.

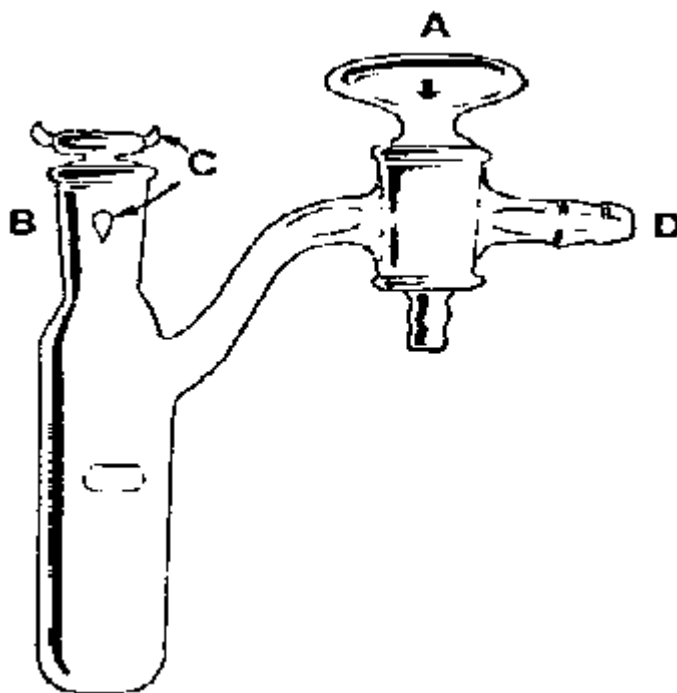


Figure 2.3. The schlenk tube.

2.3 Purification of Solvents

The solvents used are purified, dried under nitrogen by distillation system. A solvent still is used for this purpose [33,35]. This system provides removing the small amount of impurities and any water from the solvent. An example of a solvent still is shown in Figure 2.4.

It consist of a large distillation flask, connected to a reflux condenser via a piece of glassware which can simply be a pressure equalizing funnel modified by the inclusion of a second stopcock. Since the production of very dry solvents usually requires the exclusion of air from the apparatus, the still is fitted so that it can be operated under an inert atmosphere . Firstly, drying agent and solvent are added to the distillation flask under N_2 . With the stopcock A open, the solvent simply refluxes over the drying agent. When the stopcock A is closed, the solvent vapor passes up the narrow tube and dry solvent collects in the central piece of the apparatus. When the required volume of the solvent has been collected, it can be run off through the stopcock B. The solvents were prepared for the use as described below.

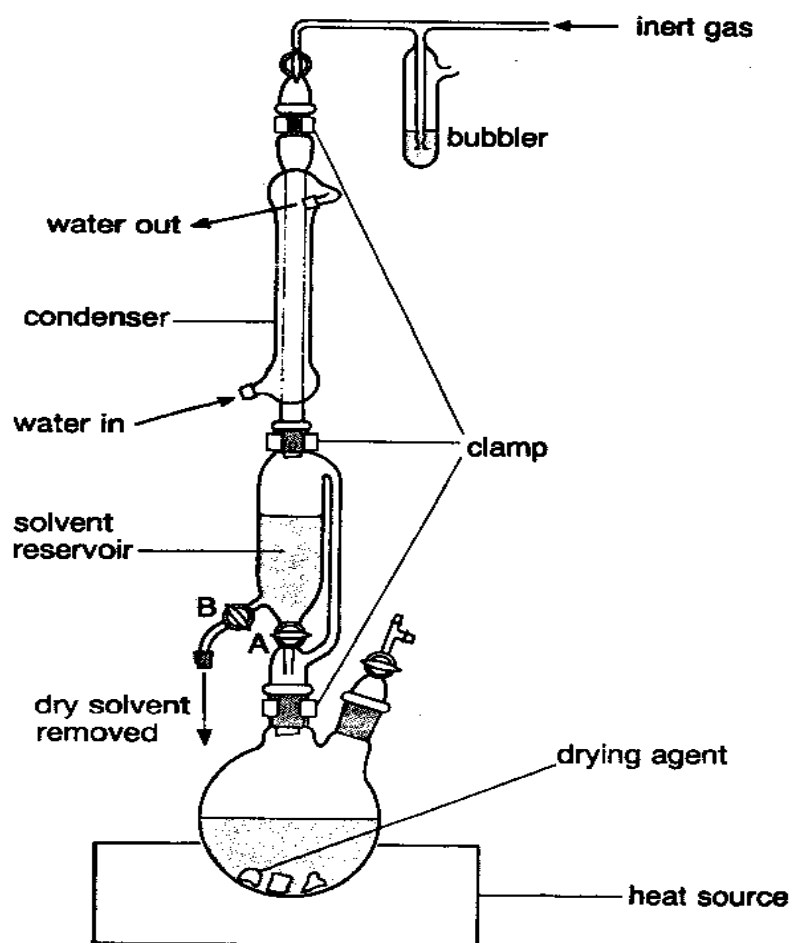


Figure 2.4. Solvent still.

2.4 Materials and Methots

All preparations and manipulations were carried out with schlenk techniques under an oxygen free nitrogen atmosphere. All glassware was oven dried at 120 °C. Solvents were dried by standart procedures, distilled and kept under nitrogen over 4A° molecular sieves.

The starting materials [MoTp*(O)Cl₂] and KTp* were prepered according to the literature procedures [45] .

The products obtained from the new reactions were characterized by IR and ¹H-NMR spectroscopy. Infrared spectra were recorded on a Magna IR spectrophotometer includedifuse reflectance accessory. ¹H-NMR spectra were recorded in CDCl₃ on varion AS 400 Mercury Plus at Ege University.

2.5 Syntheses

2.5.1 Reaction of [MoTp*(O)Cl₂] with H₂NC₆H₄Cl-o

A mixture of [MoTp*(O)Cl₂] (0.4 g, 0.83 mmol), 2-chloro aniline (0.21 g, 1.64 mmol) and dry Et₃N (0.6 cm³) in dry toluene (20 cm³) was heated to reflux with stirring under N₂ for 15 h. Reaction were monitored by thin layer chromatography (TLC). During which time the solution became dark red-brown in colour. The mixture was cooled, filtered and evaporated to dryness.The residue was dissolved in dichloromethane and chromatographed on silica gel using CH₂Cl₂/n-hexane (1:1, v/v) as eluant. Red-brown fractions were collected , crystallised from CH₂Cl₂/n-hexane and identified, as [MoTp*(O)Cl]₂(μ-O).

2.5.2 Reaction of [MoTp*(O)Cl₂] with H₂NC₆H₄Br-o

A mixture of [MoTp*(O)Cl₂] (0.4 g, 0.83 mmol), 2-bromo aniline (0.28 g, 1.66 mmol) and dry Et₃N (0.6 cm³) in dry toluene (20 cm³) was heated to reflux with stirring under N₂ for 15 h. The reaction was fallowed by tlc using the procedure described above for (2.5.1), red-brown bands identified,as [MoTp*(O)Cl]₂(μ-O).

CHAPTER 3

RESULT AND DISCUSSION

3.1 Synthetic Studies

Reaction of $[\text{MoTp}^*(\text{O})\text{Cl}_2]$ with *o*-substituted anilines, $\text{H}_2\text{NC}_6\text{H}_4\text{X-}o$ ($\text{X} = \text{Cl}, \text{Br}$) in the presence of triethylamine in toluene produced oxo Mo(V) compound, $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$ as the major product. This is such an unexpected result as the previously reported related reactions between $[\text{MoTp}^*(\text{O})\text{Cl}_2]$ with *p*- and *m*-substituted anilines, $\text{H}_2\text{NC}_6\text{H}_4\text{X-}p$ ($\text{X} = \text{Cl}, \text{Br}$), $\text{H}_2\text{NC}_6\text{H}_4\text{X-}m$ ($\text{X} = \text{F}, \text{I}$) and $\text{H}_2\text{NC}_6\text{H}_4\text{R-}p$ ($\text{R} = \text{OMe}, \text{OEt}, \text{OPr}, \text{NO}_2$) resulted in the formation of oxo-imido Mo(V) compounds, $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{X-}p)]$, $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{X-}m)]$ and $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{R-}p)]$ in moderate yields. These compounds were the first examples of molybdenum compounds containing both arylimido and oxo-Mo(V) group in the presence of hydrotris(3,5-dimethyl-1-pyrazolyl)borate) co-ligand. They could easily be separated from the reaction mixture by crystallisation from a dichloromethane/hexane mixture (1:4).

In the view of these early studies it was aimed to prepare dimeric oxo-imido Mo(V) compounds in which *o*-substituted aryl ring is attached to one of the molybdenum atoms to investigate the effect of the halide group attached to the C_6H_4 ring. Although a wide range of synthetic approaches [36] to transition metal imido complexes have been established, use of amines as the imido source is most appealing because they have almost unlimited potential for imido functionalisation. The formation of the previously prepared oxo molybdenum(V) compounds was accomplished by double protonation of aniline which is a well-known [32,36] synthetic methodology for the preparation of organoimido complexes of Mo(V) and Mo(VI). Here, organic compounds are used as the imido transfer reagent. It was also expected for *o*-substituted anilines, $\text{H}_2\text{NC}_6\text{H}_4\text{X-}o$, to behave as explained to yield the desired products, $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{X-}o)]$ ($\text{X} = \text{Cl}, \text{Br}$), but no traces of any imido moiety was detected.

Indeed, the formation of a Mo-O-Mo linkage despite the steric barrier provided by the 3-methyl groups of Tp* ligand is of interest. Lincoln and Koch [18] prepared compounds having Mo-O-Mo linkage and tris(pyrazolylborate) co-ligand by completely different methods. The syntheses of geometric isomers of $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$ (Tp = hydrotris pyrazolborate) were accomplished in aqueous media: The cis (C_2) isomer of $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$ was prepared by the reaction of $\text{KHB}(\text{pz})_3$ with MoOCl_5^{2-} and the related trans (C_i) isomer was obtained by the treatment of $\text{HB}(\text{pz})_3\text{MoCl}_3$ with $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ mixture[18].

A number of dinuclear oxo-bridged Mo(V) compounds with tris(pyrazolborate) co-ligand were reported previously by various combinations of oxygen atom transfer, comproportionation, aquation and hydrolysis reactions at Mo(VI) or Mo(V). For example; McCleverty et. al.[26] prepared the compound $[\text{MoTp}^*(\text{O})\text{Cl}]_2(\mu\text{-O})$ by the reaction of $[\text{MoTp}^*\text{O}_2\text{Cl}]$ and PPh_3 in wet toluene containing approximately 0.03% water. Millar et.al.[27] prepared the same compound by treatment of 1,3-dimethoxy-para-tert-butylcalix(4)arene and $[\text{MoTp}^*(\text{O})\text{Cl}_2]$ in toluene with reflux. The synthesis was successful in the absence of calixarene as well and it was suggested that the complex was formed due to the presence of adventitious water, probably sourced from triethylamine. This is likely what happened in the reactions of $[\text{MoTp}^*(\text{O})\text{Cl}_2]$ and *o*-substituted anilines, $\text{H}_2\text{NC}_6\text{H}_4\text{X-}o$ (X= Cl, Br). As it was pointed out before, the reactions were performed under same conditions with the previously related reactions between oxo-Mo(V) dimer and *p*- and *m*- substituted anilines. Surprisingly, only one major product, $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$, was obtained although some unidentified bands were observed in the column chromatography which could not be characterized. The compound, $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$ was separated by column chromatography and purified by recrystallisation from $\text{CH}_2\text{Cl}_2/\text{Hexane}$ (1:5) mixture.

3.2 Spectroscopic Studies

Both of the $^1\text{H-NMR}$ spectra for the products obtained from the reactions of $[\text{MoTp}^*(\text{O})\text{Cl}_2]$ with $\text{H}_2\text{NC}_6\text{H}_4\text{Cl-}o$ and $\text{H}_2\text{NC}_6\text{H}_4\text{Br-}o$ displayed no peaks due to the $\text{H}_2\text{NC}_6\text{H}_4\text{X-}o$ (X = Cl and Br) group, but are consistent with those of a dimeric Mo-O-Mo bridged species having two Tp* ligands.

In both IR spectra a strong band at 960 cm^{-1} with range characteristic of oxo-Mo(V) groups and a medium intensity band at 754 cm^{-1} assigned to the stretching mode of a bridging Mo-O-Mo unit. The presence of Tp* was indicated by a weak $\nu(\text{BH})$ at 2545 cm^{-1} as well as characteristic bands in the “fingerprint” region [24,30].

The $^1\text{H-NMR}$ spectra obtained from both reactions revealed the presence of six methyl and three C(4) proton resonances consistent with C_2 or C_i symmetry. The $^1\text{H-NMR}$ spectra obtained The signals attributable to Tp* appear as two groups of singlets in the regions δ 5.5 - 5.9 ppm, assigned to the pyrazolyl C-H protons, and δ 2.3 - 3.2 ppm assigned to the methyl protons. Owing to the low symmetry of the complexes all three pyrazolyl C-H protons and all six methyl groups of the Tp* ligand are expected to be nonequivalent in the NMR spectra[24,30].

The presence of an intense UV-Vis band at 483 nm is a strong evidence for the presence of $[\text{Mo}_2\text{O}_3]^+$ core.

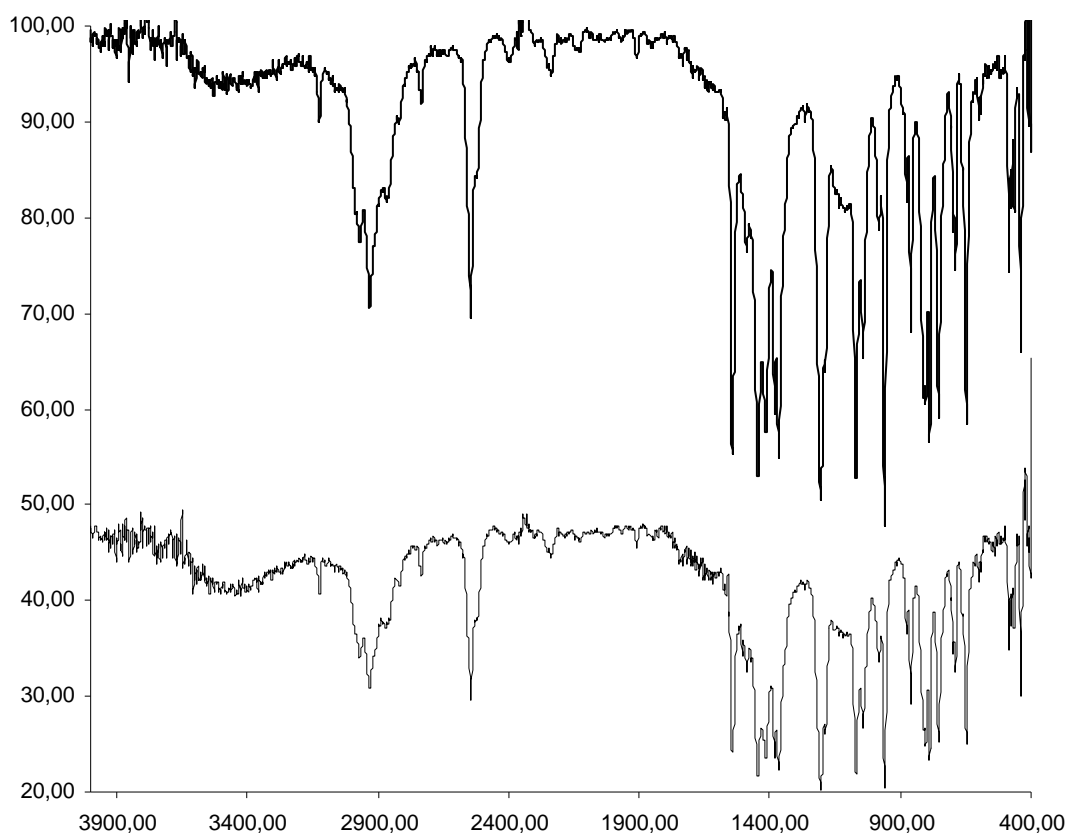


Figure 3.1. FT-IR spectrum of , $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$

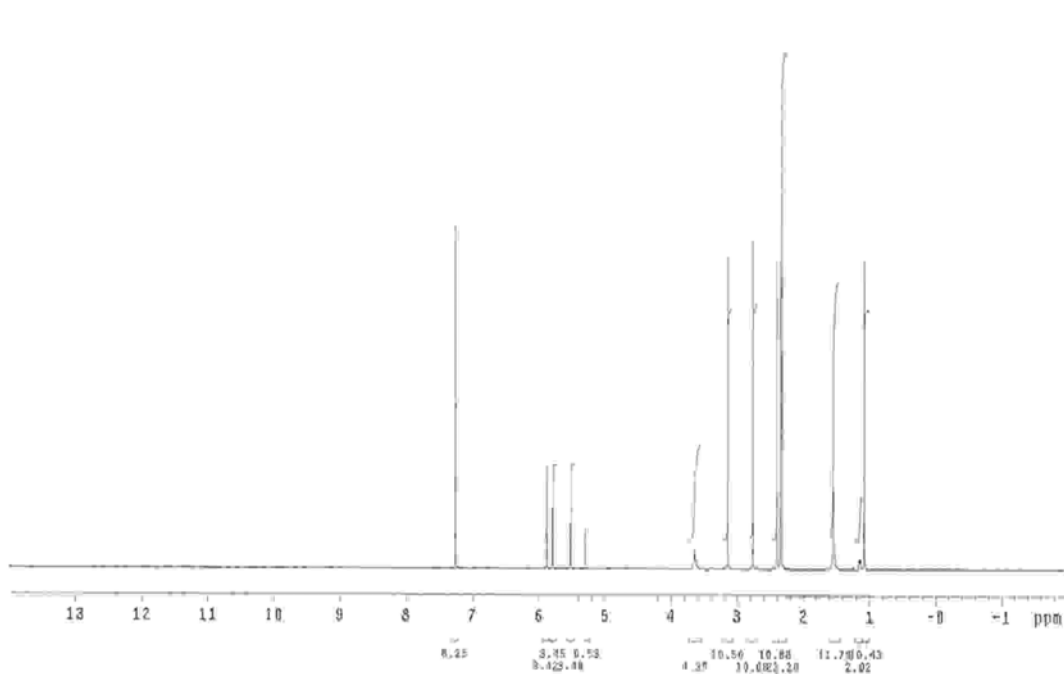
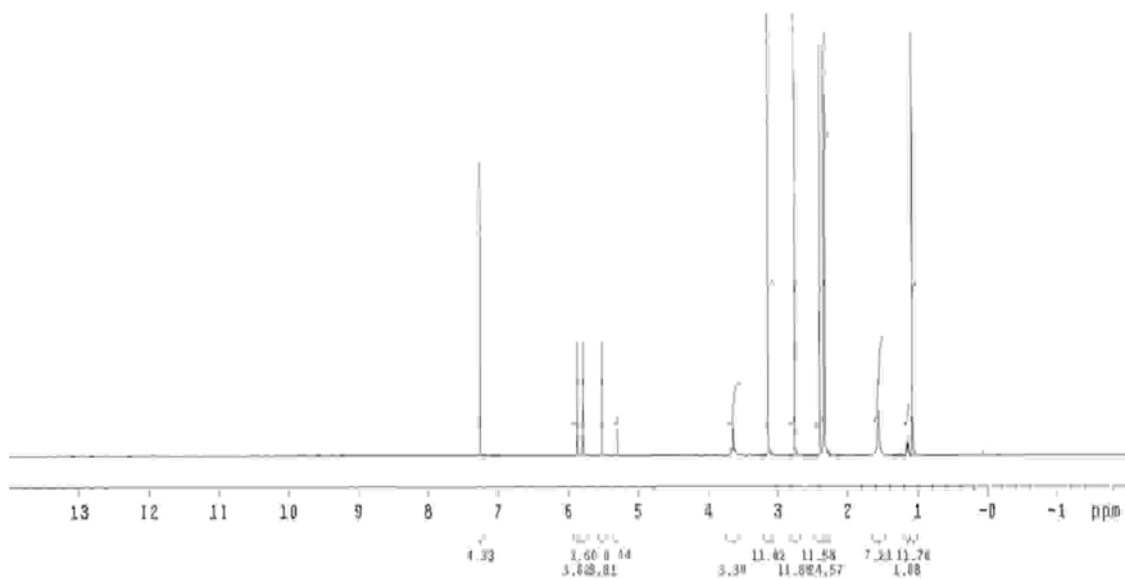


Figure 3.2. $^1\text{H-NMR}$ spectrum of $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$

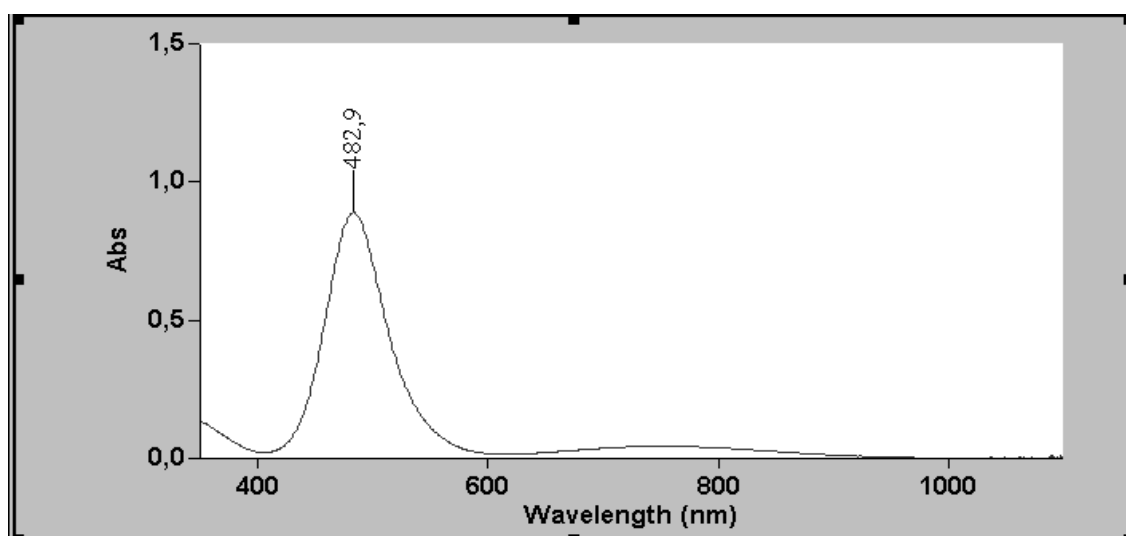
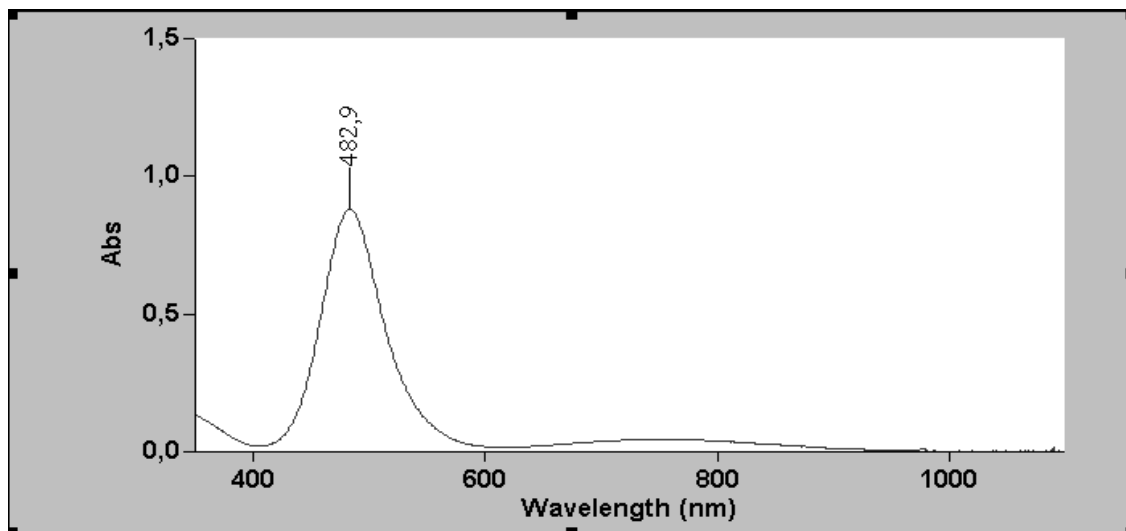


Figure 3.3. UV-Vis spectrum of $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$

CHAPTER 4

CONCLUSION

In this work, a new synthesis for the previously reported compound $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$ was discovered in the course of a work aimed at producing dimeric oxo-imido Mo(V) compounds by the reactions of $[\text{MoTp}^*(\text{O})\text{Cl}_2]$ with *o*-substituted anilines $\text{H}_2\text{NC}_6\text{H}_4\text{X-}o$ ($\text{X} = \text{Cl}, \text{Br}$). The compound $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$ is soluble in polar organic solvents and stable in air. The $^1\text{H-NMR}$, IR and UV-visible data are all in accord with the literature data.

The previously reported similar reactions between $[\text{MoTp}^*(\text{O})\text{Cl}_2]$ with *p*- and *m*- substituted anilines, $\text{H}_2\text{NC}_6\text{H}_4\text{X-}p$ ($\text{X} = \text{Cl}, \text{Br}$), $\text{H}_2\text{NC}_6\text{H}_4\text{X-}m$ ($\text{X} = \text{F}, \text{I}$) and $\text{H}_2\text{NC}_6\text{H}_4\text{R-}p$ ($\text{R} = \text{OMe}, \text{OEt}, \text{OPr}, \text{NO}_2$) yielded the oxo-imido Mo(V) compounds, $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{X-}p)]$, $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{X-}m)]$ $[\text{MoTp}^*(\text{O})\text{Cl}](\mu\text{-O})[\text{MoTp}^*(\text{Cl})(\equiv\text{NC}_6\text{H}_4\text{R-}p)]$ by double protonation reaction of the anilines. The compound $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$ was also formed as a minor product in these reactions.

Therefore, the formation of oxo Mo(V) dimer, $[\text{MoTp}(\text{O})\text{Cl}]_2(\mu\text{-O})$ as the sole product is quite surprising. Presumably it is formed due to the presence of adventitious water probably sourced from the triethylamine or toluene. Indeed, the reaction between the oxo-Mo(V) precursor $[\text{MoTp}^*(\text{O})\text{Cl}_2]$ and $\text{H}_2\text{NC}_6\text{H}_4\text{X-}o$ ($\text{X} = \text{Cl}, \text{Br}$) in (toluene + water) mixture gave the same compound spontaneously in quantitative yield. Similar observations have already been reported related to the oxo-Mo(V) chemistry as mentioned in previous sections.

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