CHAPTER I

ASPECTS OF THE CHEMISTRY OF *CIS*-DIOXOMOLYBDENUM(VI)(TRIDENTATE) SYSTEMS AND THE PURPOSE OF THE PRESENT INVESTIGATION

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Abstract: In this chapter the known chemistry of *cis*-dioxomolybdenum(VI)(tridentate) systems is summerised. The scope and the purpose of the present work is also discussed.

I.1 INTRODUCTION

One area of active research work in the fundamental chemistry of transition elements in recent years is the chemistry of Molybdenum. R.H.Holm in his review[1] pointed out that three forces impelled research in molybdenum chemistry. The first force is the syntheses of different small molecules and larger cluster, where Mo-Mo bonds of different multiplicities are present[2,3]. These studies are limited to lower oxidation states of molybdenum. A second force is the area of industrial catalysis and metallurgy[4]. Molybdenum catalysts are extensively used in the purification of petroleum[5] and the gasification of coal[4]. The third one is the role of molybdenum in biology.

A. MOLYBDENUM IN BIOLOGICAL SYSTEMS

Molybdenum is an essential trace element present in two classes of enzymes *viz. nitrogenase*[6-7] and *hydroxylases*[6,8-9].

(i) *Nitrogenase* :

The enzymes *nitrogenase* is found in simple bacteria and also in plants. This type of enzymes is responsible for the reduction of N_2 to ammonia[2].

$$N_2 + 6H^+ + 6e^- \longrightarrow 2NH_3$$

Despite extensive studies, the active site of *nitrogenase* where N_2 binds and is reduced remains unknown[10-12]. But it is well established that cofactor in *nitrogenase* contains both iron and molybdenum[7]. Numerous investigations[13-14] on *nitrogenase* have shown that the molybdenum centers exhibit oxidation state of + IV or even higher.

(ii) *Hydroxylases* :

The molybdenum *hydroxylases* catalyze either substrate oxidations or reductions[2]. These include[2,8] a group of multicomponent enzymes such as *xanthine oxidase*, *xanthine dehydrogenase*, *sulfite oxidase*, *aldehyde oxidase and nitrate reductase*. These enzymes catalyze a two electron oxidation or reduction of the substrate[2].

$$X + H_2O \rightleftharpoons XO + 2H^+ + 2e^-.$$

Recent studies established that these enzymes possess a common molybdenum cofactor[6]. On the basis of EXAFS studies[15-18] and EPR spectra[19-21] obtained for the *hydroxylases*, it has been established that molybdenum center in *hydroxylases* is mononucler with oxo and sulphur ligation and it exhibits VI, V, IV oxidation states during catalytic cycle. *Xanthine oxidase* and *xanthine dehydrogenase*, contain *cis*-oxothio-Mo(VI) center coordinated by

thiolate ligands[6,15]. Terminal thio ligation is absent in *sulfite oxidase, aldehyde oxidase and nitrate reductase*. These enzymes contain *cis*-dioxo Mo(VI) center in their oxidised forms[2,15]. It is shown[8,22] that oxidised Mo fragment of rat liver *sulfite oxidase* absorbs at relatively low energy around 475 nm.

B. SYNTHETIC ANALOGUE APPROACH

Inorganic chemists take interest to synthesize molybdenum complexes that can mimic the EXAFS, EPR, spectroscopic and electrochemical properties of molybdoenzymes. Their success is limited to certain aspects of molybdoenzymes. However such attempts enrich the coordination chemistry of molybdenum in its higher oxidation state. The enthusiasm shown in the preparation of dioxomolybdenum(VI) complexes follows from the identification[6,23] of $[Mo^{VI}O_2]^{+2}$ group in fully oxidized states of a number of redox enzymes. The cofactor of such enzymes is expected to be coordinatively unsaturated, so that effective binding of the substrate may occurr. Introduction of dianionic tridentate ligand to the coordination sphere of $[Mo^{VI}O_2]^{+2}$ moiety can provide an open active site on Mo. Therefore the coordination chemistry of dioxomolybdenum(VI) complexes with dibasic tridentate ligands has received considerable attentions.

C. **WORKDONE** :

Considerable progress has been made in the preparation of dioxomolybdenum(VI) complexes with tridentate ligands. *cis*-dioxomolybdenum(VI) complexes have been prepared with dibasic tridentate ligands (LH_2) starting from bis(acetylacetonato)dioxomolybdenum(VI), $(NH_4)_6Mo_7O_{24}.4H_2O$, MoO_2(salicylaldehyde)$_2$, $Na_2MoO_4.2H_2O$ or MoO_2Cl_2. The complexes are isolated in the form of MoO_2L or $MoO_2L(A)$ (where A = monodentate neutral ligand) depending on molybdenum precursor, ligand and reaction conditions. Rajan and Chakravorty[24-25] have described the synthesis of dioxomolybdenum(VI) complexes by the use of tridentate schiff bases derived from salicylaldehyde or its substituted derivatives and *ortho*-substituted phenol. They have used bis(acetylacetonato)dioxomolybdenum(VI), bis(salicylaldehydato)dioxomolybdenum(VI) and $(NH_4)_6Mo_7O_{24}.4H_2O$ as molybdenum precursors[25]. Topich *et al.*[26] have reported the synthesis and characterization of a number of *cis*-dioxomolybdenum(VI) tridentate schiff base coordination complexes. 2,6-disubstituted pyridine ligand has been used[27] to prepare complexe $MoO_2(py(CO_2)_2)$(HMPA), where HMPA is hexamethylphosphoric triamide. Dey *et al.*[28] have described the synthesis of *cis*-dioxomolybdenum(VI) complexes by the reaction of $Na_2MoO_4.2H_2O$

with the tridentate schiff base ligands derived from salicylaldehyde, thiosalicyldehyde with *ortho*-aminoalcohols or *ortho*-aminophenols. The attractive *cis*-dioxomolybdenum(VI) complexes with flexible yet bulky tridentate ligands have been reported by Berg and Holm[29-30]. Treatment of bis(acetylacetonato)dioxomolybdenum(VI) with 2,6-bis(2,2-diphenyl-2-hydroxyethyl)pyridine [$LN(OH)_2$] in methanol give[30] $MoO_2(LNO_2)(MeOH)$ while 2,6-bis(2,2-diphenyl-2-mercaptoethyl)-pyridine [$LN(SH)_2$] give[30] $MoO_2(LNS_2)$. It is shown[31-32] that tridentate schiff base ligands obtained from salicylaldehyde, substituted salicylaldehyde and salicylhydrazide or benzoylhydrazide easily form dioxomolybdenum(VI) complexes where water molecule or THF are present in coordination sphere of Mo. The aquo complexes have been obtained[31] by reacting dilute sulphuric acid solution of $(NH_4)_2MoO_4$ with a dilute sodium hydroxide solution of schiff bases in aquous medium. The water molecule in aquocomplexes is easily replaced by tetrahydrofuran. Other hydrazide schiff base complexes of dioxomolybdenum(VI) are also known[33-35]. Dutta and Pal have reported[33] the preparation of dioxomolybdenum(VI) complexes by the reaction of bis(acetylacetonato)dioxomolybdenum(VI) and hydrazide schiff base in methanol. Dioxomolybdenum(VI) complexes of the type $Mo_2L(MeOH)$ have been reported[36] with different types of tridentate dibasic

schiff base ligands. Casella *et al.*[37] have used bis(acetylacetonato)dioxomolybdenum(VI) as molybdenum precursor to synthesis dioxomolybdenum(VI) complexes with tridentate ligands of the type N-salicylidene-L-amino acids. Tandon and coworkers[38] have prepared dioxomolybdenum(VI) complexes by the reaction of bis(acetylacetonato)dioxomolybdenum(VI) with tridentate schiff base ligands derived from condensation of 2-hydroxy-1-naphthaldehyde, 2,4-pentanedione and 2-hydroxy-acetophenone with glycine or β-alanine. Hydrotris(3,5-dimethylpyrazolyl)borate [$HB(3,5\text{-}Me_2pz)_3$] has been used[39] as tridentate ligand to isolate compounds of the type [$MoO_2X(HB(3,5\text{-}Me_2pz)_3)$], where X is a monodentate unianionic ligand. The reaction of $K[HB(3,5\text{-}Me_2pz)_3]$ with $MoO_2X_2(OPPh_3)_2$ (X = F,Cl), $MoO_2Br_2(Me_2SO)_2$ and $(NEt_4)_2[MoO_2(NCS)_4]$ yields[40] $MoO_2X[HB(3,5\text{-}Me_2pz)_3]$.

Recently tridentate ligands salicylaldehyde S-methylisothiosemicarbazone having O,N,N donor atoms have been used by Leovac and coworkers[41]. They have used bis(acetylacetonato)dioxomolybdenum(VI) as starting material to prepare Mo(VI) complexes of the type [MoO_2(ONN)S] (where S = Py, MeOH, EtOH).

MoO_2(tridentate) complexes allow the binding of various monodentate neutral molecules to the labile coordination site.

Rajan and Chakravorty have shown[25] that MoO_2L complexes react with different monodentate ligands (A) to form complexes of the type $MoO_2L(A)$. The complexes undergo substitution reaction of the type,

$$MoO_2L(A) + A' = MoO_2L(A') + A$$

(where A' = different monodentate neutral ligands). The $MoO_2L(A')$ lose A' in a single endothermic step on heating. Prabhakaran and Nair have studied[34] the spectral properties and thermal stability of different adducts of hydrazide schiff complexes of dioxomolybdenum(VI). Syamal and Kumar[32] have used H_2O, DMF, Pyridine-N-oxide, tetrahydrofuran and DMSO as monodentate neutral ligands to prepare monomeric non-electrolytic and diamagnetic *cis*-dioxomolybdenum complexes, $[MoO_2L(A)]$. It is shown[42-43] that different bidentate ligands (AA) such as ethylenediamine, trimethylenediamine, tetramethylenediamine *ortho*-phenanthroline, 2,2'-bipyridine, *ortho*-phenylenediamine and 2-aminoethylpyridine can form the seven coordinate heterochelates $[MoO_2L(AA)]$. Dash *et al.* have used[44] biologically important molecule imidazole and its derivatives to study the acceptor behaviour of MoO_2(tridentate) system.

The electron transfer charecteristics of *cis*-dioxomolybdenum(VI) complexes have been studied with the use of cyclic voltametric techniques. Irreversible behaviour has been

reported for MoO_2(tridentate) complexes[25-26]. Berg and Holm have described[30] that the dioxomolybdenum(VI) complex [$MoO_2(LNS_2)$] exhibits an irreversible reduction which approaches chemical reversibility at 250 K.

Oxo transfer behaviour of MoO_2(tridentate) system have got attention of inorganic chemists. Topich and Lyon[45] have reported the oxygen transfer reaction of $Mo^{VI}O_2$(tridentate) systems with PPh_2Et in DMF.

$$MoO_2(L) + PPh_2Et = MoOL + OPPh_2Et$$

The reactions are first order with respect to $Mo^{VI}O_2$(tridentate) system and PPh_2Et. Oxo transfer cycle has been studied in details by Berg and Holm[30]. The *cis*-dioxomolybdenum(VI) complexesof 2,6-bis(2,2-diphenyl-2-mercaptoethyl)pyridine [$MoO_2(LNS_2)$] reacts with PPh_3 in DMF to form monomeric monoxo Mo(IV) complex [$MoO(LNS_2)(DMF)$], which on reaction with Me_2SO in DMF gives back the original *cis*-dioxomolybdenum(VI) complex.

In the solid state IR spectra indicates[25,29] $Mo^{VI}O_2$(tridentate) systems attain linear polymeric structure involving Mo = O , Mo bridge between six coordinate molybdenum centres. Ziółkowski *at el.*[46] have reported a dimeric structure with an asymmetric double oxygen bridge for $Mo^{VI}O_2$(tridentate) complexes. Although a few five coordinate $Mo^{VI}O_2$(tridentate) species are known[47-48].

2,2′-dihydroxyarylazo compounds can serve as a tridentate dibasic ligands. There is a scope to employ 2,2′-dihydroxyarylazo compounds to generate *cis*-dioxomolybdenum(VI) complexes.

I.2 PURPOSE OF THE PRESENT WORK :

In nature molybdenum is found an essential component[8] in the conversion of atmospheric nitrogen to ammonia at room temperature and pressure. In this context it is worthwhile to study the binding of azo function with molybdenum.

Arylazo-molybdenum linkage is reported in a number of carbonyl and cyclopentadienyl complexes of Mo in its lower oxidation states. King and Bisnette[49] have prepared compounds $(C_5H_5)Mo(CO)_2(N{=}NAr)$, (where Ar = *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$NO_2C_6H_4$). Green *et al.*[50] have isolated complex of the form $(C_5H_5)Mo(CO)_2(N_2C_6H_5)$. The complexes of the type $[RB(pz)_3Mo(CO)_2N_2Ar]$ have been prepared by Trofimenko[51], where R = H, pz = 1-pyrazolyl, Ar = C_6H_5, *p*-FC_6H_4, *m*-FC_6H_4, *p*-$NO_2C_6H_4$ etc. Otsuka and coworkers[52-53] have described the reaction of $(C_5H_5)_2MoH_2$ with PhNNPh to prepare complex $(C_5H_5)_2Mo(PhNNPh)$. Since molybdenum centers in *nitrogenase* are suggested to exhibit

higher oxidation states and the dinitrogen fixation is believed to occur step wise through diazene and hydrazine,a number of organohydrazido(2-) molybdenum complexes have been reported in its higher oxidation states[54-57].

A systematic investigation of the interaction of arylazo compounds with Mo(VI) seems interesting. In the present work 2,2′-dihydroxyarylazo compounds have been employed to prepare MoO_2(tridentate) complexes and to study their electrochemical behaviour. The planner tridentate dibasic 2,2′-dihydroxyarylazo ligands occupy three coordination sites around the *cis*-$[MoO_2]^{2+}$ moiety leaving the sixth coordination site free. The acceptorbehaviour and reactivities of *cis*-dioxomolybdenum (VI) complexes have been studied.

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