CHAPTER I

INTRODUCTION
The field of coordination chemistry has been growing steadily since Alfred Werner put forth his theory. In recent times coordination chemistry is one of the active areas of research in inorganic chemistry.

Earlier coordination chemistry was limited only to synthesis and stereochemistry. But now coordination compounds have occupied many branches of science such as analytical chemistry, metallurgy and industrial chemistry. After the invention of the fact that, metal chelates are responsible for many enzymatic activities, coordination chemistry has leaped into a new area referred as bio-inorganic chemistry. Apart from bio-inorganic chemistry the coordination chemists have sustained interest in stereochemical, thermodynamic, kinetic, spectral and magnetic properties of coordination compounds. This area of research still offers many interesting problems to be resolved.

The aim of present work was to select a variety of potentially biologically active ligands, synthesis and investigate the chemistry of their complexes with molybdenum (V) and molybdenum (VI).

The biological importance of molybdenum, and the challenge to reproduce the spectroscopic properties and the reactions of the molybdenum centres of the molybdoenzymes, have been considerable stimuli for the development of the
coordination chemistry of this element. Molybdenum is one of the few elements which currently has its own series of international conferences. It has attracted interest chiefly because of its role in biological processes and also because it shows a great variety of oxidation states and coordination numbers.

Molybdenum is the only element in the second and third transition series which appears to have a major role as a trace metal in enzymes. The existence of a biological role for molybdenum was first recognised in 1930. Since then, an increasing volume of evidence has accumulated which shows that molybdenum is essential for significant number of biological processes. Molybdenum is known to be present in large number of enzymes viz., xanthine oxidase, nitrogenase etc. Molybdenum is required both for nitrogen fixation and nitrate reduction, and its participation in some animal hydroxylase enzymes and several bacterial and fungal enzymes is now firmly established. The molybdoenzymes are reasonably large proteins the functions of which involve the molybdenum centres undergoing redox reactions in concert with other redox active constituents. Molybdoenzymes other than nitrogenases are usually termed oxomolybdoenzymes. The redox states of molybdenum, involved in the normal catalytic cycle of these enzymes are Mo$^{VI}$, Mo$^{V}$ and Mo$^{IV}$ and the EPR characteristics of the Mo$^{V}$ centres, and hence the Mo$^{VI}$ and Mo$^{IV}$
states. are mononuclear in molybdenum and coordinated to sulphur\(^8\).

There is an extensive literature of the coordination chemistry of molybdenum.

Molybdenum has vast aqueous solution chemistry\(^9\) for oxidation states II through VI. It is unique in having aqua / oxo ions for all five states in acidic solution (pH \(<2\)).

Molybdenum displays a remarkable propensity to form metal-metal bonds\(^{10-13}\), in all of its oxidation states. This tendency to form metal-metal bonds can be rationalized in terms of the effective covalent overlap that can be achieved using the 4d orbitals, especially for the metal in its lower oxidation states.

Lower oxidation states of molybdenum, (C), (I) and (II) have an extensive literature of arene, alkene alkyne and other organometallic complexes which are studied under organometallic chemistry\(^{14}\). Coordination chemistry of molybdenum (0), (I) and (II) consists of mainly carbonyls, nitrosyls, cyanides, isocyanides, carbonyl-isocyanides. etc\(^{15}\).

Molybdenum (III) is relatively a rare oxidation state and is easily oxidized to more stable states by air and other mild oxidants. However recent work has shown the existence of many Mo(III) compounds in aqueous and nonaqueous systems.
Also Mo(III) may be involved in catalytic and biological reactions of molybdenum, such as dinitrogen reduction.

Monomeric complexes of Mo(III) with halides, oxygen and sulphur donor ligands like dithiocarbamates and dithiophosphates and nitrogen donor ligands like thiocyanate, selenocyanate and cyanide are known\textsuperscript{16}. All the monomeric Mo(III) complexes are paramagnetic. For six-coordinate compounds the values lie between 3.53 and 3.86 BM as predicted for octahedral d\textsuperscript{3} complexes\textsuperscript{17}. EPR spectroscopy has been used to examine molybdenum (III) complexes with Cl, O, S and N donor ligands\textsuperscript{18}. At temperatures between 5 and 80\textdegree{}K, these compounds show broad axial or rhombic signals centered at g=2 and 4. Electronic absorption spectra of Mo(III) species with octahedral symmetry consist of three spin allowed transitions corresponding to \(4\ T_{2g} \leftarrow 4\ A_{2g} \) (19400-20000 cm\textsuperscript{-1}), \(4\ T_{1g}(F) \leftarrow 4\ A_{2g}\) and \(4\ T_{1g}(P) \leftarrow 4\ A_{2g}\) (24200 - 25500 cm\textsuperscript{-1}). Bands due to spin-forbidden transitions like \(2\ E_g \leftarrow 4\ A_{2g}, 2\ T_{1g} \leftarrow 4\ A_{2g} \) (8800-9500 cm\textsuperscript{-1}) and \(2\ T_{2g} \leftarrow 4\ A_{2g}\) can also be detected because of spin orbit coupling.

The best characterized Mo(III) dimers are those with Mo-Mo triple bond alone between the metal atoms or bridged by halides, as in [Mo\textsubscript{2} X\textsubscript{9}]\textsuperscript{3-}. \textit{O}x\textit{o} bridged dimers having Mo\textsubscript{2}O\textsubscript{3}, Mo\textsubscript{2}O\textsubscript{2}\textsuperscript{2+} and Mo\textsubscript{2}O\textsubscript{4}\textsuperscript{4+} species have been prepared and character-
ized\textsuperscript{16,19,20}. Low magnetic moments of these complexes between 0.4 and 0.6 BM provide clear evidence for spin-pairing between the metal centres. Mo(III) complexes dimerized by hydroxide bridges\textsuperscript{21} and the ligand itself\textsuperscript{22} are also known.

The coordination chemistry of Mo(IV) is diverse and involves an extensive range, of monomeric and trimeric systems\textsuperscript{16}. The coordination sphere of molybdenum in the oxomolybdenum enzymes is believed to contain oxo and sulphur ligands\textsuperscript{23} and therefore interest has been focussed on oxo complexes of Mo (IV) with S-donor ligands as possible models for the reduced state of these systems. [MoO(S\textsubscript{2}CNR\textsubscript{2})\textsubscript{2}] and a selection of other Mo (IV) complexes are special in respect of participating in reversible oxygen atom transfer, MoO\textsuperscript{2+} + XO $\rightarrow$ MoO\textsubscript{2}\textsuperscript{2+} + X, which have particular relevance to the catalyses effected at the molybdenum centres of oxomolybdoenzymes such as xanthine oxidase, sulfite oxidase or nitrate reductase\textsuperscript{23}.

Mo(IV) complexes containing the monooxo MoO\textsuperscript{2+} and the trans-dioxomolybdenum (IV) MoO\textsubscript{2} cores have been characterized\textsuperscript{23,24,25}. The vibrational spectra of oxomolybdenum (IV) complexes all show a band due to Mo=O stretching at around 900-1000 cm\textsuperscript{-1}. The magnetic moment values of six-coordinate Mo(IV) complexes range between 1.9 and 2.8 BM. In the case of seven coordinate complexes the values are slightly less due to spin-orbit coupling. Most of the four and eight coordinate
complexes are diamagnetic.

Electronic spectra have been recorded for a number of complexes, but in addition to d-d transition, there is possibility of two electron excitations, charge transfer bands and splitting of degenerate energy levels due to low symmetry. These factors make it difficult to interpret or even to compare the spectra.

Molybdenum (IV) forms a variety of dimeric and polymeric complexes having oxide, halide or other ligand bridges. The oxo bridged mixed oxidation state Mo (IV), Mo (V) compounds have been prepared. These compounds are found to have low magnetic moments due to the presence of metal-metal interaction.

Chemistry of molybdenum (V) is dominated by oxo complexes, many of these exist as dimers, but monomeric species can be isolated from strongly acidic solutions or under nonaqueous conditions. Non-oxo compounds are known, both as monomers and as dimers or polymers with halide or sulphur bridges.

Molybdenum (V) forms many mononuclear complexes containing one oxo group but no analogues of the cis-dioxomolybdenum (VI) or trans-dioxomolybdenum (IV) species have been reported. A large number of compounds are known containing
the anions \([\text{MoOX}_5]^{2-}\) (X=F, Cl, Br). These complexes are stable in acidic solution, but magnetic measurements show that as the pH is increased towards neutrality the magnetic moment decreases. This is indicative of dimer formation, which allows an antiferromagnetic metal-metal interaction\(^{26}\). Complexes of the form \([\text{LH}_2]\) \([\text{MoOX}_5]\) (L=bidentate N donor ligand; X=Cl, Br) can be isolated from the reaction between MoO₃ in hot HX and HI followed by addition of L. These compounds lose HCl when dissolved in dry solvents, yielding \([\text{MoOX}_3\text{L}]\). Molybdenum halides and oxyhalides, including \([\text{Mo}_2\text{Cl}_{10}]\), \([\text{Mo}_2\text{O}_2\text{Cl}_6]\) and \([\text{NH}_4]_2[\text{MoOCl}_5]\) are useful starting materials for the preparation of monomeric Mo\(^V\) oxo compounds. A large number of these compounds are of the form \([\text{MoOCl}_3\text{L}_n]\) (n=1,2) and commonly involve 0 or S donor ligands\(^{27-32}\).

The reduction of nitrate and nitrite by a number of monomeric oxomolybdenum (V) complexes, including \([\text{MoOCl}_3(\text{OPPh}_3)_2]\), \([\text{MoOCl}_3\text{L}]\) (L=bipy, phen), and \([\text{MoOClL}_2]\) (L=ox, tox), has been studied\(^{23,33-35}\). These reactions have relevance to the reduction of nitrate and the competitive inhibition by nitrite which occurs at the molybdenum centre of the nitrate reductases. Complexes of the type \([\text{MoO(SR)}_4]^-\) are important, both in their own right as interesting chemical species and as systems which provide information of relevance to the molybdenum centres of the oxomolybdoenzymes\(^{36-42}\).
Monomeric oxomolybdenum (V) complexes are paramagnetic, with magnetic moments in the range 1.65-1.73 BM due to the single unpaired electron. Monomeric Mo(V) oxo complexes in solution have characteristic EPR spectrum with a strong central line and EPR provides the most direct and definitive means of distinguishing this form\(^{43-45}\). The vibrational spectra of oxomolybdenum (V) complexes display an intense band in the range 940 to 1020 cm\(^{-1}\) due to \(\nu(Mo=O)^2\). The electronic spectra of the six-coordinate monomeric oxomolybdenum (V) complexes having \(C_4v\) symmetry show three d-d transitions\(^{37,38,46}\) corresponding to \(2E \rightarrow 2B_2\) (600 - 850 nm), \(2B_1 \rightarrow 2B_2\) (400-450 nm) and \(2A_1 \rightarrow 2B_2\) (shoulder \(\sim 280 \text{ nm}\)) transitions.

Dimeric species play a major role in the chemistry of molybdenum (V), and of particular importance are compounds containing one or more oxygen bridges. Examples\(^{16}\) of complexes bridged by sulphur, selenium, nitrogen or halogen are also known. Many dimeric compounds are diamagnetic due to interaction between the two molybdenum (V) atoms, either directly and/or via the bridging a-toms, which lead to spin-pairing of the two unpaired electrons. However, in some (Mo\(^V\))\(_2\) systems spin-pairing does not occur or is incomplete and EPR signals are observed characteristic of monomeric species, with one electron associated with each molybdenum. Compounds containing Mo\(_2O_3\)^{4+} and Mo\(_2O_4\)^{2+} core are common. The
former contains one bridging 'O' and the latter contains two bridging 'O'. IR spectra of these complexes exhibit molybdenum-terminal oxygen stretching in the region 900 - 1000 cm⁻¹. Unlike the Mo₂O₃⁴⁺ dimers, those containing an Mo₂O₄²⁺ core do not exhibit any characteristic absorption in their electronic spectra.

In the coordination chemistry of molybdenum (VI) mononuclear examples are dominant. A substantial number of dinuclear complexes of Mo (VI) are also known. Mo (VI) coordination chemistry has been considered in recent reviews.

The tetrahedral molybdate ion serves as the starting point for many of the preparative schemes in the chemistry of Mo (VI) and directly or indirectly, often for low oxidation state chemistry as well. Complexes containing the MoO₂²⁺ core are by far the most common in Mo (VI) chemistry. An MoO₂²⁺ unit is likely to be present in the oxidized form of sulphite oxidase and in the desulfo form of xanthine dehydrogenase. The reactivity of the MoO₂²⁺ unit has been thoroughly studied, especially with regard to oxygen atom transfer reactions. The MoO₂²⁺ group manifests itself in the infrared and/or Raman spectrum in the form of an intense two-band pattern corresponding to the symmetric and asymmetric Mo-O stretching vibrations at ~920 and ~885 cm⁻¹. The
method of choice for the preparation of many dioxo Mo (VI) complexes involves the use of MoO₄²⁻ and acac⁻ by adjusting the pH. Complexes with MoO₂²⁺ core containing schiff base chelating ligands have been extensively studied.

Large number of peroxo complexes of Mo (VI) have been prepared. Early work on peroxo compounds of molybdenum has been reviewed. Most mononuclear peroxo complexes have one Mo-O⁻ in addition to one or two peroxo ligands. Dinuclear peroxo complexes have been structurally characterized with a single bridging oxo or fluoride ligand or with a set of two bridging hydroperoxo ligands. Spectroscopically, in the IR region the O-O stretch can be identified between 845 and 895 cm⁻¹.

Peroxomolybdenum complexes have been used stoichiometrically to effect a variety of organic conversions and catalytically, usually with t-butylhydroperoxide or H₂C₂O₂, to effect similar reactions.

The dinuclear complexes of Mo (VI) are diverse in structure. They can have a single, double or triple bridge. The single bridge is almost always a lone oxo group. The double bridge contains either a single oxo plus a non-oxo ligand or, more commonly, two non-oxo ligands. There are a number of dinuclear complexes of Mo (VI) containing MoO₂O₇²⁻,
Mo$_{2}O_{3}^{6+}$ and Mo$_{2}O_{5}^{2+}$ core. The most common among these is the Mo$_{2}O_{5}^{2+}$ core having Mo-O-Mo type bridging, which can be detected by characteristic IR absorption band in the region 650-770 cm$^{-1}$, in addition to the IR bands corresponding to the cis-MoO$_{2}$ core.

The biological importance of molybdenum, the great variety of oxidation states and coordination numbers exhibited by molybdenum, and the attempts to develop reaction systems as functional models of the molybdoenzymes, have been considerable stimuli for the present work.

This thesis contains investigations on coordination compounds of molybdenum (V) and molybdenum (VI) with a variety of biologically relevant ligands.

The thesis is set out into four chapters, as detailed: Chapter I presents a brief account of the coordination chemistry of molybdenum.

Chapter II deals with the synthesis and characterization of molybdenum (V) oxo complexes with bis(2-benzimidazoly1) alkanes.

Chapter III deals with the study of Schiff base complexes of molybdenum (V). This chapter is divided into three parts.

Part I - Molybdenum (V) complexes with Schiff bases derived from thiosemicarbazide/ 2-hydrazinobenzothiazole and biace-
Part II: Molybdenum (V) complexes with Schiff bases derived from 2,6-diaminopyridine and salicylaldehyde / substituted salicylaldehydes.

Part III: Molybdenum (V) complexes with Schiff bases derived from 3-methyl-4-amino-5-mercapto-1,2,4-triazoles and salicylaldehyde / substituted salicylaldehydes.

Chapter IV includes the study of molybdenum (VI) complexes. This chapter is divided into two parts.

Part I: Peroxo complexes of molybdenum (VI) with thio-carbohydrazones.

Part II: Molybdenum (VI) complexes with aldoximes.

Each chapter includes an exhaustive and up-to-date survey of relevant literature.
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