CHAPTER II
SUMMARY OF THE PRESENT WORK
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The present work was undertaken (i) to isolate new compounds of quinquevalent molybdenum, (ii) to show that the properties of "molybdenyl cation" MoO$_3^{\text{3+}}$ in RH$_2$[MoOX$_5$] are dependent on both the nature of halogen $^r_X$ and the organic base $^r_R$ (iii) Mechanistic study of the hydrolytic equilibria involving the oxomolybdenum species MoO$_3^{\text{3+}}$ and last of all to characterise the new compounds isolated by the present author by analytical and various other physico-chemical investigations.

The earlier investigations on the chemistry of quinquevalent molybdenum are based mainly upon the electrochemical reduction$^3$ of hexavalent molybdenum. Recently, Saha and his coworkers$^{19}$ have developed an excellent method for the preparation of quinquevalent molybdenum compounds by chemical method of reduction of MoO$_3$. New oxopentachloro and oxopentabromomolybdates(V) of the organic bases $\alpha$-picoline and piperidine were isolated by this new method$^{19}$ of preparation by the present author for the first time.

Pyridine(Py)  $\alpha$-Picoline($\alpha$-Pic)  Piperidine (Pip)

Except these, the corresponding pyridine salt$^3$ was also prepared in pure state by this method. The principle of reduction of MoO$_3$ by HI
in presence of concentrated HCl and also by HBr are based on the following reactions.

\[
2\text{MoO}_3 + 2\text{HI} + 10\text{HCl} = 2\text{MoOCl}_5^- + I_2 + 4\text{H}^+ + 4\text{H}_2\text{O}
\]

and

\[
2\text{MoO}_3 + 12\text{HBr} = 2\text{MoOBr}_5^- + 4\text{Br}_2 + 4\text{H}_2\text{O} + 4\text{H}^+
\]

Now it is known that the chemistry of quinquevalent molybdenum is mainly dominated by the oxometal entity MoO\textsuperscript{3+} which is commonly known as "molybdenyl cation". The present author has studied the reactions of (PyH)\textsubscript{2}MoO\textsubscript{X}
\textsubscript{5} (where X = Cl and Br) with (i) dehydrated ethanol and (ii) acetyl acetone (acae).

(i) Ethanolysis of RH\textsubscript{2}MoO\textsubscript{X}
\textsubscript{5}

It has already been shown by Saha and his coworkers\textsuperscript{20,21} that the chloro-compound BipyH\textsubscript{2}MoOCl\textsubscript{5} on ethanolysis yields paramagnetic nonelectrolytic oxotrichloro(2,2'-bipyridyl) molybdenum(V) \(\text{MoOCl}_3\text{bipy}\), whereas, the bromocompound BipyH\textsubscript{2}MoOBr\textsubscript{5} under identical condition yields the feebly paramagnetic nonelectrolytic compound oxo- \(\mu\)-oxodibromo (2,2'-bipyridyl) molybdenum(V) \(\text{Mo}_2\text{Br}_3\text{bipy}\). The present author has found that both bipyridinium oxopentachloromolybdate(V) (PyH)\textsubscript{2}MoOCl\textsubscript{5} and bipyridinium oxopentabromo molybdate(V) (PyH)\textsubscript{2}MoOBr\textsubscript{5} on ethanolysis yield well crystalline copper-red solid of the composition \(\text{Mo}_2\text{O}_2\text{OH}\)\textsubscript{2}Cl\textsubscript{4}Py\textsubscript{2} and \(\text{Mo}_2\text{O}_2\text{OH}\)\textsubscript{2}Br\textsubscript{4}Py\textsubscript{2}. Both these compounds are diamagnetic and
contain the oxobridge i.e.

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{Cl} & \quad \text{O} & \quad \text{Cl} \\
\text{Mo} & \quad \text{O} & \quad \text{Mo} \\
\text{Cl} & \quad \text{O} & \quad \text{Cl} \\
\text{Py} & \quad \text{Py}
\end{align*}
\]

and

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{Br} & \quad \text{O} & \quad \text{Br} \\
\text{Mo} & \quad \text{O} & \quad \text{Mo} \\
\text{Br} & \quad \text{O} & \quad \text{Br} \\
\text{Py} & \quad \text{Py}
\end{align*}
\]

It is really interesting to note here that the corresponding \(\alpha\)-picoline and piperidine salts do not yield any such products. The oxopentahalomolybdates of alkalimetals, of ammonium and other strong bases like ethylenediamine etc. also behave identically. On ethanolysis a brown solution containing the solvated \(\text{MoOCl}_3\) species is obtained with the simultaneous separation of the solid halides of bases i.e. \(\text{KX}, \text{NH}_4\text{X}\) and \(\text{C}_2\text{H}_4\text{N}_2\text{HX}\) (where \(X = \text{Cl and Br}\)). From these observations it appears that \(\text{BipyH}_2\text{MoOCl}_3\) by simple dehydrohalogenation in dehydrated ethanol yields paramagnetic \(\text{MoOCl}_3\cdot\text{bipy}\) whereas, \(\text{BipyH}_2\text{MoOBr}_5\) undergoes both dehydrohalogenation and partial hydrolysis to yield feebly paramagnetic one oxobridged species \(\text{Mo}_2\text{O}_3\text{Br}_4\text{bipy}_2\). But the pyridine salts \((\text{PyH})_2\text{MoOCl}_5\) undergoes dehydrohalogenation and complete hydrolysis to yield double oxobridged compounds \(\text{Mo}_2\text{O}_2(\text{OH})_2\text{Cl}_4\text{py}_2\) and \(\text{Mo}_2\text{O}_2(\text{OH})_2\text{Br}_4\text{py}_2\) as shown below:

\[
\begin{align*}
\text{BipyH}_2\text{MoOCl}_3 & \underset{\text{Ethanolysis}}{\longrightarrow} \text{MoOCl}_3\cdot\text{bipy} & \text{red-paramagnetic (A)} \\
2 \text{BipyH}_2\text{MoOBr}_5 & \underset{\text{Ethanolysis}}{\longrightarrow} \text{Mo}_2\text{O}_3\text{Br}_4(\text{bipy})_2 & \text{pink-feebly paramagnetic (B)} \\
2(\text{PyH})_2\text{MoOCl}_5 & \underset{\text{Ethanolysis}}{\longrightarrow} \text{Mo}_2\text{O}_2(\text{OH})_2\text{Cl}_4\text{py}_2 & \text{copper red diamagnetic (C)}
\end{align*}
\]

(where \(X = \text{Cl and Br}\))
The main oxometal entity in (A), (B) and (C) may be pictured as follows:

\[
\begin{align*}
\text{red-paramagnetic (MoO}^3+) & \quad \text{Pink-feeably paramagnetic (Mo}_{2}\text{O}^4+) \\
\text{solid (A)} & \quad \text{solid (B)}
\end{align*}
\]

The feebly acidic nature of the aqueous solution of \(\text{Mo}_{2}\text{O}_2(\text{OH})_2\text{X}_4\text{Py}_2\) is quite consistent with the structure of these compounds proposed by the present author. It is also evident that the oxometal ions \(\text{MoO}^3+, \text{Mo}_{2}\text{O}^4+\text{ and } \text{Mo}_{2}\text{O}^2+\) play a dominant role in the chemistry of quinquevalent molybdenum.

(ii) Reactions with Acetylacetone (acac)

When dipyridinium oxohalomolybdates(V)\((\text{PyH})_2\text{MoO}_5\sqrt{\text{X}}\) (where \(X = \text{Cl}\) and \(\text{Br}\) were boiled with acetyl acetone and the solution was concen •
treated and cooled, brown shining crystalline solids of the composition $\text{PyH}_2\text{MoOX}_3\cdot\text{acac}$ were obtained. On the other hand, $\text{BipyH}_2\text{MoOX}_5$ and $\text{Phen H}_2\text{MoOX}_5$ (where phen = 1,10-phenanthroline) under identical conditions yielded green shining crystalline solid of the composition $\text{MoOX}_3\cdot\text{bipy}$ and $\text{MoOX}_3\cdot\text{phen}$, which were found to have identical properties like trans-$\text{MoOX}_3\cdot\text{L}$ (where L = 2,2'-bipyridyl and 1,10-phenanthroline) previously isolated by Saha and his coworkers $^{20-21}$.

The reactions may be pictured as:

$$(\text{PyH})_2\text{MoOX}_3 \rightarrow \text{CH}_3\text{COCH}_2\text{COCH}_3 \rightarrow \text{PyH}_2\text{MoOX}_3(\text{CH}_3\text{COCH}_2\text{COCH}_3) + \text{PyHX} + \text{HX} \quad .. (1)$$

and

$\text{IH}_2\text{MoOX}_5 \rightarrow \text{CH}_3\text{COCH}_2\text{COCH}_3 \rightarrow \text{MoOX}_3\cdot\text{L} \quad \text{trans-} \rightarrow \quad \text{MoOX}_3\cdot\text{L} \quad .. (2)$

It is interesting to note here that in reaction (1) acetyl acetone acts as a coordinating ligand to the oxometal entity $\text{MoO}^{3+}$ whereas, in (2) it simply acts as solvent helping dehydrohalogenation of $\text{IH}_2\text{MoOX}_5$ yielding trans-$\text{MoOX}_3\cdot\text{L}$ just as acetonitrile.$^{20-21}$ When pyridinium oxotrichloro-acetylacetonato molybdate(V) $\text{PyH}_2\text{MoOX}_3\cdot\text{acac}$ was slowly heated in a metal block furnace, dehydrohalogenation took place and an interesting nonelectrolytic paramagnetic greyish green solids of the composition $\text{MoOX}_3(\text{acac})(\text{py})$ were obtained:

$$\text{PyH}_2\text{MoOX}_3(\text{acac}) \overset{\text{Heated}}{\rightarrow} \text{MoOX}_3(\text{acac})(\text{py}) \text{greyish green paramagnetic solid} \quad .. (3)$$

No such products could be obtained in the case of oxohalomolybdates of $\alpha$-picoline, piperidine, alkalimetal ions, ammonium, ethylenediamine etc. It is thus evident that the reactions of the molybdenyl cation $\text{MoO}^{3+}$ in
with acetylacetone are functions of the base $R$ of the oxohalomolybdates.

(iii) **Mechanistic study of the hydrolytic equilibria of Mo$^3+$**

The compounds $^{20,21}$ cis-oxotrihalo(2,2'-bipyridyl)molybdenum(V) i.e. Cis-$\text{MoOX}_3\text{bipy}$ and Cis-oxotrihalo(1,10-phenanthroline) molybdenum(V) Cis-$\text{MoOX}_3\text{phen}$ were found to react with water at room temperature very slowly yielding acidic yellow coloured solutions. These reactions were found to be greatly accelerated by raising the temperature. But under identical condition no appreciable reactions were noticed with the trans-variety.

$$\text{Paramagnetic, Cis-}_{\text{MoOX}_3\text{L}}$$

It seems probable then that the weakening of the Mo-$X$ bond trans-to oxygen in the Cis-compound leads to hydrolysis yielding acidic solution. The present author was thus able to isolate the nonelectrolyte diamagnetic dioxobridged compounds $\text{Mo}_{4}O_4X_2L_2$ by the trans-elimination reaction of Cis-$\text{MoOX}_3\text{L}$ in aqueous solution. The Cis-compounds (red and reddish pink) were simply boiled with limited quantity of water and the solution on simple cooling yield crystalline
yellowish brown diamagnetic solids of the compositions $[\text{Mo}_2\text{O}_4\text{X}_2\text{L}_2]^-$. The hydrolytic equilibria may be pictured as

\[
\begin{align*}
\text{Stable solid phase} & \quad \text{(unstable intermediate containing one} \\
\text{Mo}_2\text{O}_4\text{X}_2\text{L}_2 \text{containing} & \quad \text{oxobridged unit Mo}_2\text{O}_4^4 \text{+ could not be} \\
\text{the unit Mo}_2\text{O}_4^4 \text{having} & \quad \text{isolated in hydrolytic equilibria)} \\
\text{the oxobridges} & \quad 
\end{align*}
\]

In the proposed scheme of hydrolysis the first step (i) involves the trans-elimination of the halide ion $X^-$ followed by aquation. In the second step (ii) deprotonation gives rise to the unstable hydroxo-derivative as the possible intermediate but this quickly dimerises in step(iii) giving rise to the mono-oxobridged unstable intermediate containing the entity $\text{Mo}_2\text{O}_4^4_+$. And finally, in step (iv) the dioxo-bridged diamagnetic solid phase $[\text{Mo}_2\text{O}_4\text{X}_2\text{L}_2]$ is obtained which is exceptionally stable and does not react with water any further, although, the theoretical possibility of complete dehalogenation cannot be ruled out. But in practice, the end product $[\text{Mo}_2\text{O}_4(\text{OH})_2\text{L}_2]$ could not be
isolated in hydrolytic equilibria of Cis-\( \text{MoO}_3 \). This might be due to the stabilisation by 2,2'-bipyridyl and 1,10-phenanthroline. The interesting compounds given in table III have been isolated in pure state by the present author. These compounds have been studied and characterised by (a) Chemical analysis (b) Conductance measurements (c) Determination of oxidation state of the metal, (d) Magnetic susceptibility measurements, (e) Infra-red spectra and (f) Electronic spectra.
<table>
<thead>
<tr>
<th>Types of reactions used</th>
<th>Compounds isolated and studied</th>
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</thead>
<tbody>
<tr>
<td>(i) Salts : Reduction of MoO$_3$</td>
<td>(PyH)$_2$MoOCl$_5$</td>
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<tr>
<td></td>
<td>(PyH)$_2$MoOBr$_5$</td>
</tr>
<tr>
<td></td>
<td>($\alpha$-PicH)$_2$MoOCl$_5$</td>
</tr>
<tr>
<td></td>
<td>($\alpha$-PicH)$_2$MoOBr$_5$</td>
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<tr>
<td></td>
<td>(PipH)$_2$MoOCl$_5$</td>
</tr>
<tr>
<td></td>
<td>(PipH)$_2$MoOBr$_5$</td>
</tr>
<tr>
<td>(ii) Derivatives of salts : Reaction with dehydrated ethanol</td>
<td>Mo$_2$O$_2$(OH)$_2$Cl$_2$(py)$_2$</td>
</tr>
<tr>
<td></td>
<td>Mo$_2$O$_2$(OH)$_2$Br$_2$(py)$_2$</td>
</tr>
<tr>
<td>(iii) Derivatives of salts : Reactions with acetylacetone</td>
<td>PyHMoOCl$_3$(acac)</td>
</tr>
<tr>
<td></td>
<td>PyHMoOBr$_3$(acac)</td>
</tr>
<tr>
<td></td>
<td>MoOCl$_2$(acac)(py)</td>
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<td></td>
<td>MoOBr$_2$(acac)(py)</td>
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<td>trans-MoOCl$_3$·bipy</td>
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<td>trans-MoOBr$_3$·bipy</td>
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<td>trans-MoOBr$_3$·phen</td>
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<tr>
<td>(iv) Derivatives of Cis-MoO$_x$L</td>
<td>Mo$_2$O$_4$Cl$_2$(bipy)$_2$</td>
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<td></td>
<td>Mo$_2$O$_4$Cl$_2$(phen)$_2$</td>
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<tr>
<td></td>
<td>Mo$_2$O$_4$Br$_2$(bipy)$_2$</td>
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<tr>
<td></td>
<td>Mo$_2$O$_4$Br$_2$(phen)$_2$</td>
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