CHAPTER I
INTRODUCTION
Introduction

Chemistry of molybdenum has been the subject of immense interest to chemists in recent times due to its versatility in displaying many interesting characteristics in different oxidation states. The formation of the stable oxo-species MoO$_3^+$ i.e., "molybdenyl ion" is the main nucleus which plays a dominant role in the chemistry of quinquevalent molybdenum and enters in many biochemical reaction especially in the chemistry of enzymes. The present author has studied certain interesting reactions of this entity MoO$_3^+$ as would be evident from the contents of the next Chapters heitherto unravelled by the previous workers in this line.

Molybdenum, a member of group VIA of "Mendeleeff's periodic classification of elements" finds its place in between chromium and tungsten in the vertical column in Gr. VIA and between niobium (Group VA) and technitium (Group VIIA) in the horizontal period which is pictured in the miniature periodic table given below:

<table>
<thead>
<tr>
<th>Gr VA</th>
<th>Gr VIA</th>
<th>Gr VIIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
</tr>
<tr>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
</tr>
<tr>
<td>Ta</td>
<td>W</td>
<td>Re</td>
</tr>
</tbody>
</table>

The neutral molybdenum atom contains in addition to the completed shell of 36-electrons in Krypton, five more electrons in N shell and one in O shell. The complete electronic configuration is,
Mo\(\text{42} \quad 2\cdot8\cdot6\cdot2\cdot6\cdot10\cdot2\cdot6\cdot5\cdot1\)

and the ground state spectroscopic term is 7s\(_3\)

it is a member of 4-d transition series.

Some characteristic properties of molybdenum like paramagnetism, tendency to form coloured ions, to exhibit variable oxidation states, to form complex compounds and its usefulness as good catalyst and alloy forming abilities may be attributed to the incomplete filling up of 4d-shell. Molybdenum in these respects show good analogy with its fellow members Cr(3d member) and W(5d member) but does not resemble its horizontal predecessor and successor Nb and Tc. There is also little similarity to the sulphur group( i.e. Gr. VII B) except in stoichiometric similarities in simple sulphates and molybdates i.e. \(\text{SO}_4^{2-}\) and \(\text{MoO}_4^{2-}\). Like molybdenum, chromium and tungsten also exhibit \(+2, +3, +5\) and \(+6\) oxidation states, but it should be noted that as we pass from Cr\(\rightarrow\)Mo\(\rightarrow\)W, the lower oxidation states become more and more unstable, whereas, the higher oxidation states specially \(+6\) becomes exceptionally stable, which is also apparent from the potentiality of the dichromates, molybdates and tungstates as oxidants. The coordination characteristics of different oxidation states of molybdenum are given in table - 1.
<table>
<thead>
<tr>
<th>Oxidation states</th>
<th>Co-ordination number</th>
<th>Geometry</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(-II)</td>
<td>5</td>
<td>?</td>
<td>$\left[\text{Mo(CO)}_5\right]^{2-}$</td>
</tr>
<tr>
<td>Mo(0)</td>
<td>6</td>
<td>Octahedral</td>
<td>$(\text{CO})_3$ where $\left[\text{Mo (Py)}_3\right]^-$ Py = pyridine</td>
</tr>
<tr>
<td>Mo(I)</td>
<td>-</td>
<td>Sandwich bonding</td>
<td>$(\text{C}_3\text{H}_5\text{Mo})^+$</td>
</tr>
<tr>
<td>Mo(II)</td>
<td>4</td>
<td>Tetrahedral</td>
<td>$\left[\text{Mo(OOCH)}_3\right]_2^2$</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>$\left[\text{Mo(diars)}_2(\text{CO})_2\right]^+$ (where diars = ditertiary arsine and $X$ = halide ion)</td>
<td></td>
</tr>
<tr>
<td>Mo(III)</td>
<td>8</td>
<td>Dodecahedral</td>
<td>$\left[\text{Mo(CN)}_7(\text{OH})_2(\text{NO})\right]^{4-}$</td>
</tr>
<tr>
<td>Mo(IV)</td>
<td>4</td>
<td>Distorted tetrahedral</td>
<td>$(\text{N}-\text{C}_5\text{H}_5)_2\text{MoH}_2$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Octahedral</td>
<td>$\left[\text{Mo(SCN)}_6\right]^{2-}$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Trigonal prism</td>
<td>$\text{MoS}_2$</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>Dodecahedral</td>
<td>$\left[\text{Mo(CN)}_8\right]^{4-}$</td>
</tr>
<tr>
<td>Mo(V)</td>
<td>5</td>
<td>Trigonal bipyramid</td>
<td>$\text{MoCl}_8(s)$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Octahedral</td>
<td>$\left[\text{MoOCl}_5\right]^{2-}$</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>Dodecahedral</td>
<td>$\left[\text{Mo(CN)}_8\right]^{3-}$</td>
</tr>
<tr>
<td>Mo(VI)</td>
<td>4</td>
<td>Tetrahedral</td>
<td>$\left[\text{MoO}_4\right]^{2-}$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Octahedral</td>
<td>$\left[\text{MoO}_6\right]^{3-}$ in polyacids</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td></td>
<td>$\left[\text{MoF}_8\right]^{2-}$</td>
</tr>
</tbody>
</table>
Molybdenum is widely used in production of alloy steels and its compounds are used for wool and silk dying, in colouring leather and rubber and as a blue pigment for porcelain. The role of quinquevalent molybdenum in biochemical processes is interesting and comparable to that of iron, which has made it very important in biochemical studies.

Chemistry of Quinquevalent molybdenum:

Hexavalent molybdenum may be reduced in hydrochloric acid medium by mild reducing agents like \( Sn^{2+}, SO_3^{2-}, H_2S \), etc. in acid medium. The main product "Molybdenum blue" has been characterised as containing a mixture of oxides and hydroxides of both stoichiometric and non-stoichiometric composition. The compounds may be listed as follows:

<table>
<thead>
<tr>
<th>Mean oxidation state</th>
<th>Crystalline</th>
<th>Compounds</th>
<th>amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.76</td>
<td>Mo(_{2.88})H(_2)O</td>
<td>Mo(_{2.88})X H(_2)O</td>
<td></td>
</tr>
<tr>
<td>5.66</td>
<td>...</td>
<td>H (\sim)Mo(_{3.09})</td>
<td></td>
</tr>
<tr>
<td>5.50</td>
<td>Mo(<em>{2.50})(OH)(</em>{0.5})</td>
<td>Mo(_{2.75})X H(_2)O</td>
<td></td>
</tr>
<tr>
<td>5.20</td>
<td>Mo(_{2.60})X H(_2)O</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>5.00</td>
<td>Mo(_{2.00})(OH)</td>
<td>...</td>
<td></td>
</tr>
</tbody>
</table>

The reason for the blue colour is not clearly known. The reduction of hexavalent state to pentavalent state may be represented as

\[
\text{MoO}_2^{2+} + 2H^+ + e^- \rightarrow \text{MoO}_3^{3+} + H_2O
\]

and \( E^0 = 0.53 \) volt in 2N HCl
But in or above 8N HCl, a green solution containing $\left[\text{MoOCl}_5\right]^{2-}$ is formed by reducing agents like Sn$^{2+}$ and I$^-$. Mercury and silver in 2N HCl and Ti$^{3+}$ salts in 3 - 5N hydrochloric acid medium cause this reduction$^2$.

The reduction proceeds further to the trivalent state with Cd$^0$, Cr$^{2+}$ and Ti$^{3+}$ in strong HCl medium.

$$\text{MoO}_3^+ + \text{H}_2\text{O}, E^0 = 0.11 \text{ volt in 2N HCl}$$

$$\text{MoO}_3^+ + 2\text{H}^+ + 2e^- \xrightarrow{\text{(green)}} \left[\text{MoCl}_6\right]^{3-}, E^0 = 0.26 \text{ volt in 8N HCl}$$

The reduction of hexavalent molybdenum to penta- and trivalent molybdenum may also be effected by electrolytic method$^3$.

Simple compounds formed by molybdenum in quinquevalent state are not numerous but quite a large number of complex compounds have already appeared in the literature. Simple compounds in quinquevalent state are unstable in most cases and are susceptible to moist air. The pentoxide is known as violet black powder and is obtained by heating Mo$^{\text{III}}_2\text{O}(\text{SO}_4)_2$ in nitrogen at 750°C. The light brown MoO(OH)$_3$ and black Mo$_2\text{S}_5$ are also known. The pentachloride MoCl$_5$ sublimes as black crystals on heating the metal or MoCl$_2$ in dry chlorine. This is decomposed by water to MoOCl$_3$ which gives interesting series of salts of the oxopentachloromolybdate(V) - anion $\left[\text{MoOCl}_5\right]^{2-}$. It is the oxo-eation Mo$^{3+}$ which plays important role in the chemistry of quinquevalent molybdenum.
Stabilisation of this state by complex formation has been achieved using various types of ligands like (a) σ-donor type (halo complexes) (b) π and π'-donor type (oxohalo-complexes) (c) σ-donor and π'-acceptor type (cyano complexes) etc. It may be noted here that excepting cyano complexes, the oxospecies MoO$_3^{3+}$ retains its identity either as such or in dimeric or polymeric halo- or oxo-bridged complexes. Possible structures of some of these species are given in fig. 1, (where X = Cl or Br and N$_2$) is a bidentate nitrogenous ligand like 2,2'-bipyridyl or 1,10-phenanthroline).
(Feebly paramagnetic)
Containing $\text{Mo}_2\text{O}_2^{2+}$-unit
Fig. 1A. Mono-oxobridge.

(Almost diamagnetic)
Containing $\text{Mo}_2\text{O}_4^{2+}$-unit
Fig. 1B. Di-oxobridge.
Chemistry of Molybdenyl Cation (MoO$_3^+$)

The general chemistry of molybdenum(v) is reminiscent of that of iron(III) in some aspects like (1) the cations form complexes with a very similar series of ligands (2) ferric ions like Mo(V) ions have a tendency to polymerise and (3) the complexes of ferric ion also have spectrophotometric properties in common with Molybdenum(v) complexes. It is known that some flavoproteins contain both iron and molybdenum. The facts that both iron and molybdenum complexes show charge transfer spectra and that these complexes are semi-conductors in solid state make it possible that the oxidation reduction reactions utilise the electron transport path.

$\text{Fe-substrate} \rightarrow \text{coenzyme,Mo}$, where a direct exchange of an electron takes place between a coenzyme and a substrate. From the literature, it appears that the complexes $R_2\text{MoOX}_5$, $R\text{MoOX}_4(H_2O)$, where $X = \text{Cl, Br}$ and $R\text{MoO}_2\text{Cl}_2$, $2H_2O$ are prepared by electrolytic or chemical reduction of a solution of molybdenum trioxide in concentrated halogen hydracids or by dissolving MoCl$_5$ or Mo(OH)$_3$ in concentrated halogen hydracid followed by addition of the appropriate halide RX. Anhydrous complexes $R\text{MoOCl}_4$ have been prepared from molybdenum pentachloride and RCl in liquid $SO_2$ and $PyH\text{MoOBr}_4$ by treating the pentabromocomplex with $SO_2$. It has been suggested that the $\text{MoOX}_4$ species are binuclear with halogen rather than oxygen bridges.

Complexes of quinquevalent molybdenum with organic ligands have been prepared mainly from (NH$_4$)$_2\text{MoOCl}_5$ and in a few cases from MoCl$_5$ and MoOCl$_3$. Compounds isolated are in most cases diamagnetic or feebly paramagnetic containing oxygen bridge, except in a few
cases like MoOCl₃L (where L is a bidentate ligand like 1,10-phenanthroline or 2,2'-bipyridyl) and MoOCl₃L₂' (where L' is a unidentate ligand like triphenyl phosphine etc.). In the case of diamagnetic and feebly paramagnetic species it has been proposed that the compounds contain the units Mo₂O₄²⁺ and Mo₂O₃⁴⁺ i.e.,

\[
\begin{array}{c}
\text{Mo} \quad \text{Mo} \\
\text{O} \\
\end{array}
\]

\[\text{MoO} \rightarrow \text{MoO} \]

The oxalato-complexes have been studied by Wardlaw and his co-workers⁴,⁹.

By using electrolytic³ method of reduction, various alkali metal salts, pyridinium, quinolinium and trimethylammonium salts of the series R₂[MoOCl₅] and R₂[MoOBr₅] have been isolated by Wardlaw and his coworkers³,¹³. Later, Allen et al reported the dimethyl ammonium and methyl ammonium salts. Isolated examples of a few nonelectrolytic bromo complexes⁶ have also appeared in the literature which are mostly the products of metathesis. But all the workers in this line uptill now have mainly concentrated on the isolation of salts by metathetical reactions and none have studied their chemistry systematically.

Interest in oxomolybdenum compounds is centered on determination of structures, interpretation of their vibrational and electronic spectra and their magnetic and chemical properties. This needs an introduction of the recent theories on chemical bonding namely the "ligand field theory" and "Molecular orbital theory" in
preference to valence bond theory for this purpose. Since in these complexes the metal penultimate d- and outermost s- and p- orbitals take part, the angular factors of these orbitals are shown in fig. 2.

Molecular orbital theory as applied to coordination compounds

According to this theory, the electrons in a molecule are placed in polycentric molecular orbitals being delocalised over the whole molecule. The electrons are placed in molecular orbitals in order of increasing energy following Pauli exclusion principle and Hund's maximum multiplicity rule. The necessary condition that atomic orbitals may combine to form molecular orbitals are (a) The orbitals should possess similar energy (b) They should overlap appreciably and (c) They should have the same symmetry with respect to the bonding molecular axis.

Considering the particular case of an octahedral complex, the central metal atom being a transition metal with \((n-1)d\), ns and np orbitals available for bonding where \(n\) is the outermost quantum shell and the ligands possessing six \(\sigma\)-symmetry orbitals and capable of forming \(\sigma\)-bond only. We may construct the molecular orbital picture qualitatively as follows. For convenience the six ligands around the central metal atom are specified by numbers 1, 2, 3, 4, 5 and 6 given in fig. 3(a).

Since the molecule considered is purely octahedral, the character table for \(O_h\) symmetry group reveals that the metal valence shell orbitals belong to the following irreducible representations.
Fig. 2. Diagrammatic representations of the angular factors of the s, p, and d orbitals.
Fig. 3(a). Six ligand orbitals along the axis.

Fig. 3(b). Schematic diagram of ligand A\(^1\)g orbital after linear combination.

Fig. 3(c). Schematic diagram of ligand Eg orbital after linear combination.
Now the actual M.O.S are constructed by making linear combination of ligand orbitals to form M.O.'s of proper symmetry which then combine with the metal orbitals of appropriate symmetry. For construction of \( \text{A}_{1g} \) orbital the normalised expression is

\[
\psi_{A_{1g}} = \frac{1}{\sqrt{6}} \left( \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6 \right)
\]

because all the \( \sigma \)-orbitals are permutable with one another by symmetry operations.

Similarly,

\[
\psi_{E_g}^\alpha = \frac{1}{\sqrt{2}} \left( \sigma_1 + \sigma_4 - \sigma_2 - \sigma_5 \right)
\]

These two may be pictorially represented in fig. 3(b) and 3(c).
In the same way we get
\[ \psi_{E_g}^{b} = \frac{1}{\sqrt{2}} \left( 2 \sigma_3 + 2 \sigma_6 - \sigma_1 - \sigma_2 - \sigma_4 - \sigma_5 \right) \]
\[ \psi_{T_{1u}}^{a} = \frac{1}{\sqrt{2}} \left( \sigma_1 - \sigma_4 \right) \]
\[ \psi_{T_{1u}}^{b} = \frac{1}{\sqrt{2}} \left( \sigma_2 - \sigma_5 \right) \]
\[ \psi_{T_{2u}} = \frac{1}{\sqrt{2}} \left( \sigma_3 - \sigma_4 \right) \]

Now, this six M.O.'s of ligand will combine with the metal orbitals to form the molecular orbitals of the complex. A schematic diagram of the energy levels of molecular orbitals is given in Fig. 4. In the above case \( \pi \)-interaction is not taken into account and the difference in energy between nonbonding \( t_{2g} \) level and \( e_g^* \) orbital gives the value of 10 Dq. or \( \Delta \).

**\( \pi \)-Interaction:**

But if there is \( \pi \)-interaction i.e., if one or more ligands possess \( \pi \)-orbitals of appropriate symmetry, there will be interaction between the metal \( T_{2g} \) orbitals and the corresponding ligand \( \pi \)-orbitals and the M.O. picture will be a bit more complicated. This will not only change the M.O. picture but along with it the spectral, magnetic and other related properties. \( \pi \)-interaction may be of two types mainly:
(i) Interaction between filled $\pi$-orbital or ligand and vacant $T_{2g}$ metal orbital. (The orbitals $T_{2g}$ and $E_{g}^{*}$ in fig. 4 are essentially metal orbitals and are termed as such in the fig.) This may be represented in fig. 5(a). In this case the bonding $T_{2g}$ M.O. is occupied by ligand electrons and $T_{2g}^{*}$ is essentially metal orbital, which is high in energy than $t_{2g}$ A.O. of metal and hence $\Delta$ is lowered.

(ii) In the second case $\pi$-interaction may occur between filled metal $T_{2g}$ level and vacant ligand $\pi$-orbital. This may be represented pictorially in Fig. 5(b).

($E_{g}$ orbitals in both fig. 5(a) and 5(b) are the antibonding $E_{g}$ orbitals of fig. 4, because the bonding $E_{g}$ orbitals are occupied by ligand electrons). In this case the metal electrons will occupy the $T_{2g}$ bonding M.O. and hence the $\Delta$ value is increased.

The two cases described above are two extreme cases and there may be a number of other intermediate cases e.g., ligand may possess such orbitals which will interact with only one or two orbitals of $T_{2g}$ degenerate level (i.e., any one or two among $d_{x^2-y^2}, d_{xy},$ and $d_{z^2}$). In that case the degeneracy of the $T_{2g}$ level as a whole will be lifted, because only two or one will interact and others will remain as nonbonding. This will change the symmetry of the molecule as a whole and hence the properties related therein. A very good example of this is $\Gamma^{2-}$ molecule ion which belongs to $C_{4v}$ point group and the detailed M.O. will be discussed later.

Thus, $\pi$-bonding changes the M.O. picture and consequently the energies of electronic transitions expected in a purely octahedral environment. This is observable in the visible and u.v. spectra of the complex. Also, this will cause a change in magnetic behaviour of the compound.
Fig. 4. Molecular orbital energy level diagram of an octahedral complex without \( \pi \)-interaction.
Fig. 5(a). $\Pi$-interaction of metal T$_{2g}$ orbitals with ligand T$_{2g}$ orbitals having lower energy than metal T$_{2g}$ orbitals.

Fig. 5(b). $\Pi$-interaction of metal T$_{2g}$ orbitals with ligand T$_{2g}$ orbitals having higher energy than metal T$_{2g}$ orbitals.
Ligand Field theory

The theory accounts for the nature of bonding in coordination compounds thereby explaining the characteristic properties. Let us take the particular case of an octahedral complex, where the central atom is a transition metal, and the ligands form σ-bond only, with the metal ion. In a symmetrical octahedral coordination sphere, the ligands are placed on the axes and these interact preferentially with \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals which have lobes directed along the axes. This interaction lifts the degeneracy of the d-orbitals and these are split up into

(a) a doubly degenerate level consisting of \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals called \( e_g \) level (\( e \) indicating doubly degenerate state and \( g \) indicating the possession of inversion symmetry) and

(b) one triply degenerate level consisting of \( d_{xy}, d_{yz}, \) and \( d_{xz} \) orbitals called \( t_{2g} \) level.

(\( t \) indicates triply degenerate state, 2 indicates antisymmetry with respect to rotation axis and \( g \) as before)

This can be pictorially represented in fig. 6. The energy of separation between the two levels is represented by \( \Delta \) or \( 10Dq \). The difference in energy of the two levels from the mean energy is given for \( e_g = +3/5 \Delta \) or \( 6Dq \) and for \( t_{2g} = -2/5 \Delta \) or \( -4Dq \). Thus for each electron being placed in \( t_{2g} \) level the ligand field stabilisation energy is \( -4Dq \) (minus sign indicating lowering of energy) and for one electron being placed in \( e_g \) level + \( 6Dq \).
Fig. 6. Splitting of $d$ levels in an octahedral field.
(positive sign indicating increase in energy or destabilisation).

The value of \( \Delta \) or \( 10\Omega q \) depends upon the charge on the ion, since a large ionic charge causes a large polarisation of the ligand electrons and thereby increases the electrostatic field; with the hexahydrates of bivalent ions of the first transition series \( \sum_{i=0}^{2+} \), for instance, the \( \Delta \) values are around 10,000 cm\(^{-1}\), as compared with the values of about 20,000 cm\(^{-1}\) for the analogous tervalent ions. \( \Delta \) also increases by about 30 percent on passing from ions of the first transition series to those of the second transition series. The value of \( \Delta \) further depends as might be expected on the nature of ligands, since the field produced by the ligands will be related to the ease with which the ligand electrons are distorted by the ion.

The ligands may be placed in order of decreasing crystal field effect, an order which is independent of the particular metal ion to which they are attached.

\[
\begin{align*}
\text{CN}^- & \succ \text{NO}_2^- \succ \text{Phen} \succ \text{Bipy} \succ \text{en} \succ \text{NH}_3 \sim \text{Py} \succ \text{CNS}^- \\
\text{H}_2\text{O} & \sim \text{C}_2\text{O}_4^{2-} \succ \text{OH}^- \succ \text{F}^- \succ \text{Cl}^- \succ \text{Br}^- \succ \text{I}^-
\end{align*}
\]

The spectra of complexes are explained from the expected d-d transitions and also the magnetic behaviour considering the d-level splitting. The theory satisfactorily explains the properties of complexes when overlap between metal-orbitals and ligand-orbitals are not considerable. This happens with metals in their usual
oxidation states. But in cases of metals in their unusual oxidation states where overlap is expected to be considerable, the theory is modified by adjusting the values of the ligand field parameters B and C (the Racah parameters) and ∆, the spin orbit coupling constant. A better explanation in these cases is offered by "molecular orbital theory" which has also been discussed in brief.

The Molecular Orbital Description of Oxohalomolybdate(V) ion \( \text{MoOBr}_5^{2-} \)

The \( \text{MoOBr}_5^{2-} \) ion may be assumed to have a tetragonal structure with a short Mo-O bond where the molecular field is dominated by the axial MoO\(^{3+}\) interaction. In \( C_{4v} \) symmetry the bonding in the molecule ion may be described (Fig. 7) as, a strong σ-bond of symmetry \( a_1 \) between the sp σ-oxygen hybrid orbital and the \( \sum \text{5s} + 4 \text{dz}^2 \) metal hybrid orbital; two π-bonds of symmetry e between the oxygen 2 \( p_x \) and 2 \( p_y \) orbitals and the metal 4d\(_{xz}\) and 4d\(_{yz}\) orbitals, making a total of three metal-oxygen bonds in MoO\(^{3+}\); four σ-bonds involving 4 \( p_z \) orbitals of the equivalent bromines (\( d_{\alpha} \)) and the metal \( \sum \text{5s} + 4d_x 2 \) (\( a_1 \)), 5 \( p_x \) and 5 \( p_y \) (e) and 4d\(_{x^2-y^2}\) (\( b_1 \)) orbitals, the axial bromine is considered to be bonded to the remaining metal 5p\(_z\)(\( a_1 \)) orbital. Finally, neglecting the \( \pi \)-bonding between the metal and bromine, the 4d\(_{xy}\)(\( b_2 \)) metal orbital is nonbonding. By placing the seventeen(17) valence-electrons (10 from five bromines, 6 from oxygen, one from molybdenum) in the molecular orbitals of lowest energy and increasing therefrom, a ground state \( ^2B_2 \):

\[
\left[ (1a'_1)^2 (1a'_1)^1 (b_1^1)^1 (b_1^0)^1 (3a'_1)^0 (c_2^0)^0 (b_2^1)^1 \right]
\]
a. Structure of \((\text{MoOX}_5)^{2-}\) ion and reference axes \((X=\text{Cl and Br})\).

(b) Molecular orbitals of the complex ion \([\text{MoOX}_5]^{2-}\) in the center is built up from the \(\pi\) orbitals of oxygen and \(\sigma\) orbitals of oxygen and halogen and metal orbitals. Crystal field transitions originate in the nonbonding \(dxy\) orbital and the charge transfer transitions in the \(\pi^b\) orbitals. Number of electrons in orbitals as shown in parenthesis.

Fig. 7.
is obtained. For explanation of electronic spectra we may conveniently divide the excited states into two classes (1) those involving promotion of the $b_2$ electron into the $e^*,b_1^*$, and $1a^*$ levels and (2) those involving the promotion of an $e_\pi$ electron into the $b_2$, $e_\pi^*,b_1^*$ and $1a^*$ levels. Transitions of the first category are crystal field transitions and those of the second category are charge transfer transitions. The expected transitions with identical scheme agree very closely with experimental result in the case of $\text{MoOCl}_5^{2-}$ ion.

**Results of $\text{MoOCl}_5^{2-}$ ion**

<table>
<thead>
<tr>
<th>Band in maxima in cm$^{-1}$</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 13,600</td>
<td>$2_{B_2} \rightarrow 2_E$ (I)</td>
</tr>
<tr>
<td>(2) 23,000</td>
<td>$2_{B_2} \rightarrow 2_B$ (I)</td>
</tr>
<tr>
<td>(3) 26,700</td>
<td>$2_{B_2} \rightarrow 2_E$ (II)</td>
</tr>
<tr>
<td>(4) 32,100</td>
<td>$2_{B_2} \rightarrow 2_{B_2}$ (I)</td>
</tr>
<tr>
<td>(5) 35,700</td>
<td>$2_{B_2} \rightarrow 2_{B_2}$ (II)</td>
</tr>
<tr>
<td>(6) 41,700</td>
<td>$2_{B_2} \rightarrow 2_E$ (III)</td>
</tr>
</tbody>
</table>

Here the first two are expected d-d transitions. Another d-d transition has been covered by more intense charge transfer transition, i.e., the third one above and the rest are charge transfer transitions. The results and discussions for $\text{MoOBr}_5^{2-}$ ion are given in the experimental section.
Molecular Orbital Configuration of the β-diketo complexes of Quinquevalent Molybdenum

The β-diketocomplexes of oxovanadium and some oxomolybdenum complexes have recently been studied by Selhin and his co-workers. The co-ordinate system chosen is given in Fig. 8. It has been assumed that the β-diketone ligand lies completely in a plane perpendicular to the metal oxygen multiple bond, rather than having one point of attachment in the axial position. Thus we expect that stronger ligand oxygen (from β-diketone) will not prefer a site trans-to the multiple bonded oxygen and furthermore all β-diketone complexes of VO^{2+} whose structures are known have the ligand atoms in equatorial plane. Under these circumstances the ion will belong to a point group Cs if the β-diketone is symmetrical (R₁ is identical with R₂) and C₁ for the symmetrical ligands.

In each compound a relatively low intensity broad band is found at a frequency of approximately in the region 14 KK (1 KK = kilo kaiser units = 1000 cm⁻¹). The frequency, intensity and broadness of this transition indicate that it is almost surely analogous to that assigned as d → (dₓ, dᵧ, d₂) by Gray and Hare. In the coordinate system used here the transition would be designated as dₓ² → (dₓ, dᵧ, d₂). The moderate intensity band in the region 20 KK is presumably due to dₓ² → dₓ transition which is in agreement with Gray and Hare's proposal of (NH₄)₂MoOCl₅.
Fig. 8. Coordinate system used in $C_s$ symmetry for the complexes $[MoOA_3(\beta$-diketonate)]$^-$ (where $A=Cl^-$ and $Br^-$).
Although the intensity is higher than usual d-d transition, this is completely unreasonable for very low symmetry compounds. The third d-d band \( \frac{2}{x^2-y^2} \rightarrow d_\sigma^2 \) has not been assigned and is thought to lie at much higher frequency and covered by intense charge transfer and intra ligand bands. Gray and Hare suggested that the three intense band in the ultra violet spectrum of MoOCl\(_5^{2-}\) are charge transfer transitions due to excitation of an electron from a bonding \( e_\Pi^{\Pi} \) molecular orbital to the antibonding levels consisting primarily of metal d-orbitals. They neglect completely the possibility of metal-chlorine \( \Pi^-\) bonding and presume that \( \Pi^-\) orbitals from the oxo-group are the predominant component of the \( e_\Pi^{\Pi} \) level. However, Horner & Tyree and others\(^{17-18}\) are of the opinion that

1. Gray-Hare scheme be modified by including a substantial contribution from the halogen \( \Pi^-\) orbitals in the bonding \( \zeta_\Pi^{\Pi} \) level

2. highest energy filled bonding molecular orbital for the oxohalomolybdate(V) complexes is a \( \zeta_\Pi^{\Pi} \) level and that the transition of an electron from this level to molecular orbitals consisting primarily of the metal d-orbitals is the best explanation of the charge transfer bands observed in these complexes. The metal-oxygen bond is very important and that the strength of the metal halogen bonds in these complexes is so weak that excitation of an electron from a \( \zeta^-\) bonding halogen orbital will require less energy than the transition from the \( \Pi^-\) levels.

The anion \( [\text{MoO}_3(\text{acac})]^- \) has a moderate intensity band (occassionally a pair appears in the region 20 - 26 KK which are
probably charge-transfer in origin. The similarity in frequency as well as the magnitude of the splitting between the two bands leads us to suggest that they are all similar in origin and the splitting is caused by vibrational progression. If the bands represent excitation of an electron from the oxogroup to the metal, it is difficult to understand why the substitution of the \( \beta \)-diketone for the halogroup should cause a shift of several kilokalories, especially when the frequency of first d-d transition remains much the same as that observed in \( \text{MoOCl}_3^{2-} \). On this basis it is judged unlikely that this particular set of absorption bands involves any substantial contribution from the Oxo group or \( \sigma \) and \( \pi \) levels of the halogen ligands. If this seems most likely that this is charge transfer transition involving the \( \beta \)-diketone and the lowest energy metal d-orbital. It is considered most likely that this 20-26 KK band is a ligand metal charge transfer i.e., \( \pi \rightarrow d \) transition. Here \( d_{x^2-y^2} \) orbital is thought to lie between the \( \pi_3 \) and \( \pi_4 \) of \( \beta \)-diketone levels because if this half filled orbital were higher in energy than the empty \( \pi_4 \) level, the electron would tend to drop into the lower energy empty orbital there by oxidising the metal. Similarly the molybdenum would tend to be reduced if the half-filled metal orbital were lower in energy than \( \pi_3 \). Thus this charge-transfer transition originate in \( \pi_3 \) level of \( \beta \)-diketone.

Although the region beyond 26 KK is really complicated, yet one intense absorption which will surely appear in this region is the \( \pi_3 \rightarrow \pi_4 \) intra ligand transition.
Sometimes, this transition appears between 30 and 40 KK for the free ligands and various \( \beta \)-diketone complexes. In a less polar solvent CH\(_2\)Cl\(_2\), \( \pi_3 \rightarrow \pi_1 \) band is expected to be shifted towards higher frequency relative to its position in the strongly polar acetonitrile.

No firm assignments can be attempted for the bands beyond 35 KK. The absorption at about 40 KK in the compound containing C\(_6\)H\(_5\) group is probably \( \pi \rightarrow \pi^* \) transition in benzene ring but the spin-allowed \( \pi_3 \rightarrow \pi_5 \) and \( \pi_2 \rightarrow \pi_4 \) intraligand transitions may also be found in this region.

Thus the electronic spectra of \( \beta \)-diketo complexes of quinquevalent molybdenum can be expected mainly to involve the following transition:

### Results of \( \text{MoO}_3\text{(acac)}_7 \) ions

<table>
<thead>
<tr>
<th>Band maxima ( \nu ) in cm(^{-1} )</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>14,000 ( d ) ( x^2-y^2 ) ( \rightarrow ) ( (d_x, d_y) )</td>
<td></td>
</tr>
<tr>
<td>20,000 ( d ) ( x^2-y^2 ) ( \rightarrow ) ( d_{xy} )</td>
<td></td>
</tr>
<tr>
<td>26,000 ( \pi ) ( \rightarrow ) ( d_{x^2-y^2} )</td>
<td></td>
</tr>
<tr>
<td>32,000 ( \pi_3 ) ( \rightarrow ) ( \pi_4 )</td>
<td></td>
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