In the words of Linus Pauling: "The Chemistry of Molybdenum is complicated. It forms compounds with oxidation numbers of +2, +3, +4, +5 and +6." Smith summed up these three words, the behavior of Molybdenum: "Ambidextrous, bisexual, and polygamous." Molybdenum has also been found to possess coordination numbers of 4, 6 and 8 and also 5 as in $\text{MoCl}_5$. Due to these variations in properties exhibited by molybdenum, it presents a series of baffling chemical puzzles. Molybdenum compounds readily disproportionate to yield complex mixtures of compounds in which molybdenum shows any or all of its valence states, and shifts between the three coordination states take place only with slight variations in the controlling conditions. Clearly, any system containing molybdenum can only be extremely complex since two or more variables must each reach equilibrium independently to define a specific condition. These equilibria are independent of each other and are easily disturbed individually. The same can be said to be true in the case of the element, Tungsten, as it belongs to the same group in the periodic table as molybdenum, i.e., group VIA. Tungsten also shows variations in properties over a wide range of valence and coordination states.

The amphoteric nature of molybdenum and tungsten can be best explained on the basis of the characteristic properties of group VI elements.
The atomic numbers of molybdenum and tungsten are 42 and 74 respectively, and the electronic configurations, the most important aspect responsible for chemical behaviour of elements, especially complex formation, are as follows:

**Molybdenum**

<table>
<thead>
<tr>
<th>K</th>
<th>L</th>
<th>M</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2s</td>
<td>2p</td>
<td>3s 3p</td>
<td>3d</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2 6 10</td>
<td>2 6 5</td>
</tr>
</tbody>
</table>

**Tungsten**

<table>
<thead>
<tr>
<th>K</th>
<th>L</th>
<th>M</th>
<th>N</th>
<th>O</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2s</td>
<td>2p</td>
<td>3s 3p</td>
<td>3d</td>
<td>4s 4p 4d 4f</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2 6 10</td>
<td>2 6 10 14</td>
<td>2 6 4</td>
</tr>
</tbody>
</table>

Molybdenum and tungsten form three types of complex anions, the isopolymolybdates, and tungstates, the heteropoly acids exemplified by phospho- and silico-molybdic or tungstic acids, and thirdly, those formed by molybdenum and tungsten in lower valence states. The third type include, the halogen, cyanide and thiocyanate complexes of molybdenum and tungsten.

Many of the earlier workers studied the formation of
complexes of molybdenum and tungsten with organic ligands, only from the point of view of their preparations. Also, the findings of these workers often create contradictions rather than collaborations. As an example of this fact, the many views regarding the stoichiometry of the molybdo-oxalate complex, have been listed.

Oxalate ion was found to be stable to permanganate in a sulphuric acid medium in the presence of molybdic acid. The precipitation of phosphomolybdate was prevented by the addition of oxalate ion. These phenomena were explained on the basis of complex formation between oxalic and molybdic acids. The molybdo-oxalate complex was also studied by Pechard, Rosenheim and Spittle and Wardlaw. Later workers, including Ray and Sharma, and Rao and Banerjee, found the combining ratio of molybdate and oxalate ions to be 1:1. However, Ramana Rao and Pani have found this ratio to be 1:2 from a conductometric study, so that agreement on this point is yet to be reached.

Gernez, from a polarimetric study, reported a complex between alkali molybdate and tartaric acid in a combining ratio 1:1. The evidence of complex formation between molybdic and tartaric acids was also had from a pH and conductometric study carried out by Mazzucchelli, and Rosenheim and associates.
Biswas\textsuperscript{16} and Jackson and Britton\textsuperscript{17} corroborated Geine's view but Henderson and Barr\textsuperscript{18} and Raman and Vaishya\textsuperscript{19} supported the view that the combining ratio of molybdate and tartarate ions was 1:2. Henderson and Barr (loc. cit.) formulated the compound as \( \text{MoO}_2(\text{NaC}_4\text{H}_4\text{O}_6)_2 \).

On the strength of his polarimetric data Darmois\textsuperscript{20} suggested the existence of a complex, \( [\text{MoO}_3(\text{C}_4\text{H}_4\text{O}_5)_2]^{-2} \), formed by the reaction of molybdate and malic acid. But Theodoresco\textsuperscript{21} formulated the compound as \( (\text{MoO}_3\text{C}_4\text{H}_4\text{O}_5)^{-2}\cdot n\text{H}_2\text{O} \) on the evidence of his Raman Spectra.

Although much attention has been paid to the determination of stoichiometry of these complex forming reactions between \( \text{MoO}_3 \) and organic anions, no conclusive results are available regarding the structure and stability of these compounds. The study of a number of complexes was carried out by Fernandez\textsuperscript{22} from the point of view of their composition and not as regards their stabilities and structural formulae. He reported the combining ratio of \( \text{MoO}_3 \) and organic acids as 1:2 in all the cases.

Earlier workers in the field of molybdenum and tungsten have hardly taken recourse to the application of physico-chemical methods, but used only classical methods for their study. This, together with the fact that no attention was paid to the
structural problems, made the earlier investigations rather incomplete and inconclusive.

Molybdenum and tungsten have been found to form complex halides or oxyhalides in their di-, tri-, penta-, and hexavalent states. Mo(III) forms fluoro- and chloro-complexes of the types, \([\text{MoX}_5(\text{H}_2\text{O})]^2\) and \([\text{MoX}_6]^3\), whereas only the dimeric anion \([\text{W}_2\text{Cl}_9]^3\) is known for W(III)\(^{24}\). The most stable oxyhalo-complexes of molybdenum and tungsten in their penta- and hexavalent states are fluoro complexes such as, \([\text{MoVI}_2\text{O}_2\text{F}_4]^2\), \([\text{WVI}_2\text{O}_2\text{F}_4]^2\) and \([\text{MoVOF}_5]^2\). The affinity of fluoride ion for Mo(VI) and W(VI) can best be illustrated from the masking effect of fluoride ion on the colour reactions and precipitations of molybdates and tungstates\(^{25}\).

Probably the most widely studied compounds are the octacyanides of molybdenum and tungsten, which have the formulae, \(M_4(\text{CN})_8\) and \(M_3(\text{CN})_8\). Hoard and Nordsieck\(^{26}\) have shown the existence of individual octacyanomolybdate ions, with the eight cyanide groups arranged at the apices of a dodecahedron. Some of the substituted octacyanides which have been reported are \([\text{W(OH)}_3(\text{CN})_5]^4\), \([\text{Mo(OH)}_4(\text{CN})_4]^4\) and \([\text{Mo(OH)}_3(\text{CN})_4\text{H}_2\text{O}]^4\).

Molybdenum and tungsten have also been found to form dye complexes along with other metals.\(^{31}\) Phosphomolybdic and
phosphotungstic acids have been used as mordants. The structures of the resulting complex mordanted products have been suggested to be:

$$\text{R} \rightarrow \text{Complex inorganic acid} \rightarrow \text{R} \quad \text{with R as the dye molecule.}$$

Molybdenum (II) forms bridged complexes of the type $[\text{Mo}_6\text{Cl}_8](\text{OH})_4\cdot 14\text{H}_2\text{O}$, $\text{Mo}_6\text{Cl}_{12}\cdot 8\text{H}_2\text{O}$, and $\text{HMo}_3\text{Cl}_7\cdot 3\text{H}_2\text{O}$ having interesting structures.

Bhaduri and Ray$^{36}$ estimated molybdenum colorimetrically using as reagents aromatic hydroxamic acids. A yellow coloured solution was obtained with molybdate at pH 6.3 - 7.02. The authors explained the formation of colour due to the formation of a Mo(V) complex.

A number of complexes have been reported by Kuan Pan, Sui-Fong Lin and Hwa-Sheng Cheng$^{37}$ between tungstic and organic acids. These authors formulated the complex ions as $[\text{R} - (\text{COO})_2\text{W(OH)}_2\text{O}_2]^{-2}$ and $[\text{R} - (\text{COO})_2\text{W(COO)}_2\text{R}]^{-2}$.

Reaction between ammonium molybdate and ammonium salicylate was studied by Zvyagintsov, Sudarikov and Goncharova$^{38}$ who reported an orange coloured complex with Mo: $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$ 1:6.

The same authors$^{39}$ found two complexes with mole ratios
of salicylic acid and tungsten as 1:5 at pH 7.5 and a
coloured compound with the stoichiometric proportion of WO₃
and C₆H₄OHCOOH as 1:6 at pH 8.5.

It was shown after a spectrophotometric study, by
Plško⁴⁰ that Na₂MoO₄ and Na₂WO₄(II) form two complexes with
pyrogallol (I). The coloured ions in aqueous medium existed
at pH 6.0 - 8.0 with a ratio 2(I) : (II) and at pH 3.5 for
(I) : (II). The dissociation constants for the Mo- and W-
dipyrrogallolates were calculated to be 2.1 x 10⁻⁶ and
4.6 x 10⁻⁸ respectively.

A spectrophotometric study of the molybdenum - gallic
acid system showed the formation of a yellow complex of the
empirical formula MoR which shows an absorption maximum at
305 μm.⁴¹ The complex had a dissociation constant equal to
0.6 ± 0.1 x 10⁻⁴.

Murgier and Cordier⁴² studied the mutarotation of
the solution formed by mixing equimolar solutions of tartaric
acid and H₂W₄O₁₃. They observed the formation of two compounds,
an l-compound, whose formation was favoured at 0⁰C, and a
d-compound, which was best studied at 20⁰C. Some of the data
indicated the formation of a complex with a 1:1 ratio of
components, but the values for mutarotation did not support this.
According to the same authors\textsuperscript{43}, a study of the optical rotation of solutions of sodium tungstate, tartaric acid and hydrochloric acid indicates the formation of complex, $\text{WO}_3\text{C}_4\text{H}_6\text{O}_6$ with rotation 15 to 30 times that of tartaric acid and showing mutarotation.

Rao\textsuperscript{44} has investigated the citrate and tartarate complexes of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ and found that the complexes are formed at equimolecular proportions of the acids and tungstate. Banerjee and Rao\textsuperscript{45} have studied the systems of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ with acetic and oxalic acids using pH and conductivity data. They found that a 1 : 1 complex with oxalic acid is formed with the structure $[\text{WO}_3(\text{C}_2\text{O}_4)\cdot \text{H}_2\text{O}]^{-2}$. This complex decomposes to its components on ageing.

This author has also reported some complexes of molybdenum and tungsten with organic ligands like tartaric\textsuperscript{46}, lactic\textsuperscript{47}, mandelic\textsuperscript{48} and glycollic acids\textsuperscript{49}, as a result of the physico-chemical studies carried out by him involving pH and conductance measurements.

After reviewing the work so far done in the field of complex compounds of molybdenum and tungsten, the author thought it worthwhile to undertake a systematic study of some reactions involving $\text{Na}_2\text{WO}_4$ and $\text{Na}_2\text{MoO}_4$ and organic acids by physico-chemical methods. The investigation has been based on the
study of three different molecular properties of the systems e.g., pH, conductance and optical density. Use has been made of the monovariation and continuous variation methods. The organic ligands used belong to the hydroxy, dicarboxylic and unsaturated series of acids. A complete study, regarding the composition, stability and structure of the complex systems has been attempted.
# References

2. Killeffer & Linz, ibid.
17. Biswas, J. Ind. Chem. Soc., 21, 149 (1944); 22, 351 (1945); 24, 103, 335 (1947).
19. Henderson & Barr, ibid, 542 (1899); 1456 (1896).
24 Olsson, Ber., 46, 566 (1913).
33 Brosset, Arkiv Kemi, 1, 353 (1949).
34 Brosset, Arkiv Kemi, Mineral Geol., A20, No.7(1945).
35 Brosset, ibid, A22, No.11 (1946).
36 Bhaduri & Ray, (Univ. College of Science, Cal.), Science and Culture (India), 18, 97-8(1952).
37 Kuan Pan, Sui-Fong Lin & (National Taiwan Univ., Taiwan) Hwa-Sheng Cheng, Chemistry, (Taiwan) No.2,17-25(1954).

39 Zvyagintsov, Sudarikov ibid, 92-94 (1955).

& Goncharova,


42 Murgier & Cordier, Compt. rend., 213, 729-30 (1941).

43 Murgier & Cordier, ibid, 213, 836-7 (1941).


45 Banerjee & Rao, ibid, p. 76 - 83 (1954).


