NOTES

Chemistry of oxometal ions—VII. Reactions of cis-oxotrihalo(2,2'-bipyridyl) molybdenum(V) and oxotrihalo (1,10-phenanthroline) molybdenum(V) and new synthesis of the trans-isomers

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In continuation of our investigations of the chemistry of oxospecies of quinquevalent molybdenum we have recorded certain interesting observations, which are described in the present communication. We have already reported[1-4] the isolation and study of the sterioisomers of the non-electrolytic complexes of the type \([\text{MoO}_X^3\text{L}]\) (where \(X = \text{Cl and Br}\) and \(L = 2,2'\)-bipyridyl and 1,10-phenanthroline) for the first time. It is apparent from the configuration (Fig 1) of the trans-isomer that it would be more stable than the corresponding cis-isomer because of the weakening of the Mo-X bond trans to the multiple molybdenum-oxygen bond in the latter. This interesting property of the molybdenum-oxygen bonding interactions has been utilized in the present work to study the hydrolytic reaction of cis-isomers. The reaction may be viewed to proceed in four distinct steps (Fig. 2), (i) trans-elutionation of \(X\) with the simultaneous formation of the squated cation \([\text{I}]\), (ii) hydrolysis and ionization yielding the intermediate \([\text{II}]\), (iii) dimerization leading to the mono-oxobridged species \([\text{III}]\) and finally, (iv) further hydrolysis including steps (i), (ii) and (iii) yielding the ultimate product \([\text{IV}]\).

The intermediates suggested in the proposed scheme of hydrolysis could not be isolated. The ultimate product \([\text{Mo}_2\text{O}_4\text{X}_2\text{L}_2]\) was formed in pure state and good yield by the prolonged boiling of cis-isomer in water. Kinetic study by spectrophotometric method could not be attempted due to low solubility of the cis-isomer in water at room temperature. But the reaction is greatly accelerated on boiling the aqueous suspension and the filtrate reacts acidic. Regeneration of the parent compounds from \([\text{Mo}_2\text{O}_4\text{X}_2\text{L}_2]\) has already been described[1-4].

It has already been shown[1-4] that the non-electrolytic complexes \([\text{MoO}_X^3\text{L}]\) can be directly obtained by dehydrohalogenation of the parent salts \(\text{LH}_2[\text{MoOX}_3]\), both in solid state and in solvents. In an attempt to synthesise the mixed ligand complexes of oxomolybdenum cation MoO\(^{++}\) these salts \(\text{LH}_2[\text{MoOX}_3]\) were refluxed in acetylacetone. The final product was in the form of solid of the composition \([\text{MoOX}_3\text{L}]\) having colours identical with the trans-isomers[1-4], i.e. green for \(X = \text{Cl}\) and chocolate for \(X = \text{Br}\). These are not affected by water and common organic solvents both at room temperature and on heating. Thus it is evident that acetylacetone like acetonitrile[1-4] serves as a good solvent for the efficient synthesis of trans \([\text{MoOX}_3\text{L}]\) by dehydrohalogenation.

EXPERIMENTAL

All reagents used were of A.R. Grade. The salts \(\text{LH}_2[\text{MoOX}_3]\) and the cis-isomers of \([\text{MoOX}_3\text{L}]\) were prepared by the methods described earlier and analysis of molybdenum, halogen and nitrogen was carried out by standard methods[1-4]. Oxidation states were found out by ceric sulphate titration and magnetic susceptibility measurements were carried out by Guoy balance. The results are given in Table 1.

Synthesis of dioxobridged compounds

About 2 g of the cis-\([\text{MoOX}_3\text{L}]\) were slowly boiled with 40 ml of water for about an hour. Water was added from time to time in order to keep the volume constant. The colour of the original non-electrolytic complexes gradually changed to red or reddish brown. This was filtered, washed with water and dried in vacuum desiccator. In each case the yield was about 60-70 per cent. Results of analysis and ceric sulphate titration are given in Table 1.

\[
\begin{align*}
\text{LH}_2[\text{MoOX}_3] & \quad \xrightarrow{\text{Refluxed in acetylacetone}} \text{trans-isomer.} \\
\text{LXMo-O-MoXL} & \quad \xrightarrow{-2\text{H}_2\text{O}} \\
\end{align*}
\]

Fig. 1.

\[
\begin{align*}
\text{cis-[MoOX}_3\text{L}] & \quad \text{trans-[MoOX}_3\text{L]} \\
\end{align*}
\]

Fig. 2.

Table 1

<table>
<thead>
<tr>
<th>Product</th>
<th>Reaction</th>
<th>Conditions</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{MoOX}_3\text{L}])</td>
<td></td>
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<td>(60-70%)</td>
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</table>

Fig. 1.

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Synthesis of trans-[MoOX$_3$. L]

About 2 g of the salt LH$_2$[MoOX$_5$] were refluxed with 20 ml of acetylacetone with a device under positive pressure of the solvent. Initially the suspension had a brownish red colour but gradually green and chocolate coloured crystalline precipitate began to separate. After about an hour this was filtered under strong suction, washed with very dilute alcohol and dried in a vacuum desiccator. The yield was about 50–60 per cent in each case. Results of analysis and ceric sulphate titration are given in Table 1.

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REFERENCES