CHAPTER IV

SYNTHESIS AND CHARACTERIZATION OF MOLYBDENUM-BENZOinoximate
AND ITS USE AS ELECTRON ION EXCHANGER
The analytical applications of ion exchangers are increasing at an exponential rate, and newer areas of their use are being actively sought. Many synthetic inorganic ion exchangers have been used as electron ion exchangers and as redox ion exchangers. The chemical reductions are important processes in modern industries. Electron ion exchangers are important due to their insolubility in the redox medium. This facilitates their removal from the reaction medium without causing any chemical perturbation to the redox medium.

In the present work, a new electron ion exchanger is synthesized by the reaction of α-benzoinoxime and molybdate. Many oximes possess valuable analytical properties. They form salts either by the replacement of a hydrogen from the oxime or by coordination to the oxime nitrogen. Several transition metal complexes of different oximes have been reported and characterized. A survey of literature shows that not much work has been done on α-benzoinoxime derived from α-acyloinoximes. Besides other important reactions and properties of these oximes, their reducing properties are worth mentioning. It was in this light that oxime was complexed with molybdenum, whereby it, with its reducing properties reduced molybdenum from an oxidation state of six to an oxidation state of five. Molybdenum by itself, is also a reducing agent, when the complex is brought in contact with an aqueous solution of a reducible species.
(copper as an example) the Mo(V) is reconverted to Mo(VI) by a redox reaction whereby copper (II) is reduced to the cuprous ion and molybdenum is oxidized and attains its maximum oxidation state (six). It was therefore considered worthwhile to carry out electron exchange studies on this material. In the present work, the material prepared by α-benzoinoimine and molybdate has been utilized as electron ion exchanger and the reductions of Cu$^{2+}$, Cr$^{6+}$, Ce$^{4+}$, V$^{5+}$, Fe$^{3+}$, As$^{5+}$ and Sn$^{4+}$ have been successfully achieved on the columns of this material.

EXPERIMENTAL

Reagents: Sodium molybdate, VEB Labor chemic Apolda (Germany), α-benzoinoimine, Riedel (Germany) were used. All other chemicals used were of A.R. grade.

Synthesis:

Molybdenum-benzoinoimine was synthesized by mixing 0.10 M solution of sodium molybdate to 0.10 M alcoholic solution of α-benzoinoimine in the volume ratio of 1:2. The pH of sodium molybdate and ligand solution was set at 1.5 by adding HCl. The initial white precipitate obtained on mixing the two slowly and completely changed to yellowish green after 2 h of continuous stirring. It was then filtered and washed with 3:1 water-alcohol mixture and dried in air oven at $40^\circ$C. The results of the synthesis of molybdenum-benzoinoimine are given in table 24.
## RESULTS

### Table 24

**Conditions for the synthesis of Molybdenum-benzoinoximinate**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Conditions of Synthesis</th>
<th>Molarity of Reagents</th>
<th>Mixing ratio</th>
<th>pH</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sodium molybdate</td>
<td>α-benzoinoxime</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(M)</td>
<td>(M)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>0.10</td>
<td>0.10</td>
<td>1:1</td>
<td>1.5</td>
<td>Dissolution of precipitate on standing.</td>
</tr>
<tr>
<td>2.</td>
<td>0.10</td>
<td>0.10</td>
<td>1:2</td>
<td>1.5</td>
<td>Yellowish green colored precipitate</td>
</tr>
<tr>
<td>3.</td>
<td>0.10</td>
<td>0.10</td>
<td>1:2</td>
<td>4.0</td>
<td>Incomplete precipitation</td>
</tr>
<tr>
<td>4.</td>
<td>0.10</td>
<td>0.10</td>
<td>1:3</td>
<td>1.5</td>
<td>Blue colored precipitate</td>
</tr>
<tr>
<td>5.</td>
<td>0.10</td>
<td>0.10</td>
<td>2:1</td>
<td>1.5</td>
<td>Dissolution of precipitate on standing</td>
</tr>
<tr>
<td>6.</td>
<td>0.10</td>
<td>0.10</td>
<td>3:1</td>
<td>1.5</td>
<td>Dissolution of precipitate on standing</td>
</tr>
</tbody>
</table>

**Chemical stability:**

In order to check the chemical stability 0.500 g of this material was shaken for 6 h. in the desired solution and then the supernatant liquid was checked for molybdenum and α-benzoinoximine.

**Conductometric titrations:**

Freshly prepared α-benzoinoximine solution was always used for conductometric titrations. The stock solution of sodium molybdate was prepared in 3:1 water-alcohol mixture.
Rate of reduction:

In order to determine the rate of reduction, weighed amount of the exchanger was shaken with the concerned solution, after appropriate intervals of time, the contents of the flask were filtered and the reduced species were determined. The results are plotted in figure 26.

Redox Studies:

Reductions of $\text{Cu}^{2+}$, $\text{Cr}^{6+}$, $\text{Ce}^{4+}$, $\text{V}^{5+}$, $\text{Fe}^{3+}$, $\text{As}^{5+}$ and $\text{Sn}^{4+}$ in their respective lower oxidation states were performed by passing their solutions through the column containing 0.500 gm of the exchanger. The reductions were performed in CO$_2$ atmosphere and the effluent was collected in H$_2$SO$_4$. The results are given in tables 25-31.

Table 25
Reduction of Cu(II) to Cu(I)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amount of exchanger taken (g)</th>
<th>Amount of Cu(II) taken (mg)</th>
<th>Amount of Cu(I) found (mg)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.500</td>
<td>98.00</td>
<td>98.00</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>0.500</td>
<td>110.00</td>
<td>109.50</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>0.500</td>
<td>140.00</td>
<td>138.70</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>0.500</td>
<td>280.00</td>
<td>277.00</td>
<td>1.770</td>
</tr>
<tr>
<td>5.</td>
<td>0.500</td>
<td>330.00</td>
<td>326.00</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>0.500</td>
<td>370.00</td>
<td>368.10</td>
<td></td>
</tr>
</tbody>
</table>
Amount of exchanger taken = 500 mg
Amount of Ce⁴⁺ taken = 50 mg

Fig: 26 - Plot of rate of reduction of Ce⁴⁺ to Ce³⁺ by batch process
### Table 26
Reduction of Cr(VI) to Cr(III)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amount of exchanger taken (g)</th>
<th>Amount of Cr(VI) taken (mg)</th>
<th>Amount of Cr(III) found (mg)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.500</td>
<td>102.00</td>
<td>99.50</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>0.500</td>
<td>142.00</td>
<td>139.00</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>0.500</td>
<td>166.00</td>
<td>164.00</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>0.500</td>
<td>208.00</td>
<td>204.60</td>
<td>0.804</td>
</tr>
<tr>
<td>5.</td>
<td>0.500</td>
<td>230.00</td>
<td>228.10</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>0.500</td>
<td>246.00</td>
<td>245.00</td>
<td></td>
</tr>
</tbody>
</table>

### Table 27
Reduction of Ce(IV) to Ce(III)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amount of exchanger taken (g)</th>
<th>Amount of Ce(IV) taken (mg)</th>
<th>Amount of Ce(III) found (mg)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.500</td>
<td>43.00</td>
<td>41.80</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>0.500</td>
<td>68.00</td>
<td>67.80</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>0.500</td>
<td>73.00</td>
<td>72.00</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>0.500</td>
<td>89.00</td>
<td>87.00</td>
<td>1.160</td>
</tr>
<tr>
<td>5.</td>
<td>0.500</td>
<td>134.00</td>
<td>131.00</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>0.500</td>
<td>164.00</td>
<td>162.40</td>
<td></td>
</tr>
</tbody>
</table>
Table 28
Reduction of V(V) to V(IV)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amount of exchanger taken (g)</th>
<th>Amount of V(V) taken (mg)</th>
<th>Amount of V(IV) found (mg)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.500</td>
<td>81.00</td>
<td>80.70</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>0.500</td>
<td>102.00</td>
<td>102.00</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>0.500</td>
<td>143.00</td>
<td>139.60</td>
<td>1.570</td>
</tr>
<tr>
<td>4.</td>
<td>0.500</td>
<td>182.00</td>
<td>179.00</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>0.500</td>
<td>225.00</td>
<td>224.00</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>0.500</td>
<td>250.00</td>
<td>246.00</td>
<td></td>
</tr>
</tbody>
</table>

Table 29
Reduction of Fe(III) to Fe(II)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amount of exchanger taken (g)</th>
<th>Amount of Fe(III) taken (mg)</th>
<th>Amount of Fe(II) found (mg)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.500</td>
<td>34.00</td>
<td>34.00</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>0.500</td>
<td>68.00</td>
<td>66.90</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>0.500</td>
<td>100.00</td>
<td>99.00</td>
<td>1.050</td>
</tr>
<tr>
<td>4.</td>
<td>0.500</td>
<td>134.00</td>
<td>132.00</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>0.500</td>
<td>201.00</td>
<td>198.00</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>0.500</td>
<td>230.00</td>
<td>227.00</td>
<td></td>
</tr>
</tbody>
</table>
### Table 30

Reduction of As(V) to As(III)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amount of exchanger taken (g)</th>
<th>Amount of As(V) taken (mg)</th>
<th>Amount of As(III) found (mg)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.500</td>
<td>10.00</td>
<td>9.50</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>0.500</td>
<td>30.00</td>
<td>27.00</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>0.500</td>
<td>40.00</td>
<td>38.00</td>
<td>1.090</td>
</tr>
<tr>
<td>4.</td>
<td>0.500</td>
<td>80.00</td>
<td>78.20</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>0.500</td>
<td>100.00</td>
<td>97.30</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>0.500</td>
<td>120.00</td>
<td>118.00</td>
<td></td>
</tr>
</tbody>
</table>

### Table 31

Reduction of Sn(IV) to Sn(II)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amount of exchanger taken (g)</th>
<th>Amount of Sn(IV) taken (mg)</th>
<th>Amount of Sn(II) found (mg)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.500</td>
<td>80.00</td>
<td>79.00</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>0.500</td>
<td>120.00</td>
<td>119.00</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>0.500</td>
<td>179.00</td>
<td>179.00</td>
<td>1.240</td>
</tr>
<tr>
<td>4.</td>
<td>0.500</td>
<td>198.00</td>
<td>196.30</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>0.500</td>
<td>230.00</td>
<td>227.00</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>0.500</td>
<td>245.00</td>
<td>241.40</td>
<td></td>
</tr>
</tbody>
</table>
Electronic and IR spectra:

The electronic spectra was monitored in the range 200-800 nm by Bausch and Lomb Spec. 1001. The solvent used was DMSO (Baker Analyzed Reagent). The IR spectra was recorded by the standard KBr disc method. The IR spectra of the complex is plotted in figure 27.
DISCUSSION

The conditions under which molybdenum-benzoinoximate was synthesized are given in table 24. For complete precipitation of molybdenum-benzoinoximate, equimolar solutions of sodium molybdate (PH=1.5) and α-benzoinoxime (PH=1.5) were mixed in 1:2 volume ratio. It was found that any alteration in PH of these solutions resulted either in dissolution or incomplete precipitation, while alteration in the volume ratio resulted in the formation of blue colored precipitate which was found ineffective for reduction purposes. The yellowish-green precipitate gave good reduction properties. The gradual change from an initial white to yellowish green color is probably due to the slow reduction by α-benzoinoxime of Mo(VI) to Mo(V).

The material, molybdenum-benzoinoximate was found to be quite stable in de-ionized water, ethyl alcohol, methyl alcohol, acetone and dilute solution of acids and bases but is sparingly soluble in chloroform and carbon tetrachloride, and soluble in Dimethyl Sulphoxide (DMSO).

The conductometric titrations show sharp peaks leading to the metal ligand ratio of 1:2. The results of ratio were further confirmed by elemental analysis.

Spectroscopic studies:

It is quite evident from the infrared spectra (figure 27) that the exchanger exhibits all fundamental bands characteristics of C = N, C = O, Mo = O and Mo = N vibrations. The structure of molybdenum-benzoinoximate is highly complicated like other oxime complexes with other metal ions. An indication of the
possible structure may be discussed in the light of its IR spectrum. It is quite evident from the spectrum of the complex that the phenolic hydrogen of oximate is replaced by the metal because the band at 3200 cm\(^{-1}\) does not appear in the complex while it can very well be seen in the spectrum of the ligand. A peak at 1610 cm\(^{-1}\) assigned to C = N stretching is shifted to 1640 cm\(^{-1}\) and the peak at 985 cm\(^{-1}\) of medium intensity in the ligand assigned to N – O stretching vibration shifts to 1005 cm\(^{-1}\) in the complex. These changes in the absorption frequencies of C = N and N – O give a good indication for the donation of lone pairs from the nitrogen to the metal to form chelate. The IR spectrum also shows well resolved doublet at 920 and 960 cm\(^{-1}\) indicating an Mo – O – Mo bridging\(^{14-16}\). The Mo-N bending is indicated by a weak band at 500 cm\(^{-1}\).

The electronic spectrum recorded in DMSO shows two bands at 630 and 670 nm of very low intensity, which may be due to ligand field transition characteristic of Mo(V) in an octahedral array of ligands. However, the \(\mu\) eff. value is only 0.4 BM (Bohr Magneton) which is very low from that expected for d\(^{1}\) system\(^{17}\). Lowering in magnetic moment values from theoretically expected values may also be due to the existence of Mo – O – Mo bridging similar to that reported in MoO\(_3\)Cl\(_4\) (bi py)\(_2\) complex\(^{18}\).

Thus on the basis of the above discussion and elemental
analysis, the following structure for the complex seems plausible.

\[
\begin{array}{c}
\text{R} \\
\text{C} \\
\text{0} \\
\text{R}_0 - \text{Mo} - \text{0} - \text{C} \\
\text{C= N} \\
\text{V I} \\
\text{OH} \\
\text{H'} \\
\text{R} \\
\end{array}
\]

where \( R = C_6H_5 \)

**Redox Studies:**

It is clear from figure 26 that only 50 minutes are required for the complete conversion of \( Ce^{4+} \) to \( Ce^{3+} \). The results of table 25-31 show that the material molybdenum-benzoinoximate has a remarkable reducing property. We have utilized this material for the reduction of \( Cu^{2+} \), \( Cr^{6+} \), \( Ce^{4+} \), \( V^{5+} \), \( Fe^{3+} \), \( As^{5+} \) and \( Sn^{4+} \) to their respective lower oxidation states. It was found that this material could not be used for the reduction of \( Ti(IV) \) to \( Ti(III) \) which has a redox potential equal to 0.06 but it can reduce \( Sn^{4+} \) to \( Sn^{2+} \)
which has redox potential equal to 0.10, on this basis it was concluded that molybdenum/benzoinoxime couple has a redox potential somewhere between 0.06 - 0.10 and it can reduce only those substances which have redox potential higher than its own. After reducing a substance, molybdenum-benzoinoximate gets oxidized, it can be re-reduced by passing 0.10 M solution of thiosulfate. For regeneration of 0.500 g of this exchanger about 50 ml of 0.10 M solution of thiosulfate should be passed through the column at the rate of 0.50 ml per minute.
REFERENCES


17. Lewis, J. and Wilkins, R.G., 'Modern Coordination Chemistry'