Chapter - V
RUTHENIUM (III) MIXED LIGAND COMPLEXES
An important goal in the area of research in homogeneous catalysis has been to develop catalyst systems for mild and selective oxidation of hydrocarbons [1,2]. As discussed earlier, the system studied in the past include metal complexes of Porphyrin [3-5], Schiff bases [6-8] and nitrogen macrocycles [9].

Of particular interest are Ruthenium complexes of Polypyridyl ligand which impart stability to the complex and also increase the oxidation potential of Ru=O complex, thus weakening the Ru=O bond [10]. However, among the polypyridyl Ruthenium oxo systems studied [11-14], some are non catalytic [15,16]. Another class of Ru(III) complexes reported to be versatile catalysts for oxidation of organic compounds are amino carboxylate complexes [17]. Keeping in view, the above two types of ligands, we have synthesised mixed ligand complexes of Ru(III) with 2,6-dipicolinic acid (DPA) as one ligand and ethylenediamine (en), 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) as another ligand, to have the advantage of both pyridyl and carboxylate coordination with the metal ion.

This chapter presents an account of the synthesis of the above mixed ligand complexes and their use as catalysts in the oxygen atom transfer from terminal oxidants to organic substrates.
SYNTHESIS:

A solution of dipicolinic acid (1mmol) in water (10 ml) and ethanol (40 ml) was added, dropwise to a stirred solution of RuCl₃·3H₂O (1mmol) in ethanol (50 ml) and the mixture was stirred at room temperature for 1h. To the above solution, diamine (1mmol) in ethanol (50 ml) was added dropwise with a vigorous stirring and the mixture was stirred for 30 min. The mixture was refluxed under atmospheric condition for 6h. and then left overnight. The crystalline material separating out was filtered, washed with ethanol and dried under vaccum at 100°C.

RESULT AND DISCUSSION:

The elemental analyses of the complexes (1-3) were found in good agreement with the proposed formulae [Table 5.1]. The complexes (1-3) are non electrolyte in nitroethane but when dissolved in water-dioxane (1:1 v/v) the conductance values correspond to 1:1 electrolyte. The magnetic moments of the mixed ligand Ru(III) complexes are in the range 1.78 - 1.84 B.M., which is slightly lower than the predicted value for an unpaired electron.

The IR spectrum of 2,6-dipicolinic acid show bands at 1700 and 1300 cm⁻¹, due to asym (COO) and sym (COO) vibrations, respectively. In the mixed ligand complexes these bands appear at 1660 cm⁻¹ and 1470-1400 cm⁻¹, respectively, indicating the involvement of carboxylic group in the bond formation. Moreover, in the complex the OH band in the range of 3600-3200 Cm⁻¹ is found to be absent. This indicates that the -COOH group gets deprotonated on addition to the metal ion. This is supported by appearance of bands at 320-340 cm⁻¹ assignable to ~M-O.In complex (1) the ~N-H band appears at 3280 and
Table 5.1: Analytical, Conductance Data, gav Values and Magnetic Moment for the Complexes (1-3)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Analysis a %</th>
<th>Conductance</th>
<th>g Values in DMF at 298 K</th>
<th>Magnetic Moment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>Nitroethane</td>
</tr>
<tr>
<td>1</td>
<td>30.15</td>
<td>3.10</td>
<td>11.52</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(29.87)</td>
<td>(3.04)</td>
<td>(11.61)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>44.70</td>
<td>2.42</td>
<td>9.09</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(44.58)</td>
<td>(2.40)</td>
<td>(9.17)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>47.21</td>
<td>2.92</td>
<td>8.75</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(47.35)</td>
<td>(2.28)</td>
<td>(8.72)</td>
<td></td>
</tr>
</tbody>
</table>

a - Calculated value in Parentheses
3160 cm⁻¹, which is slightly lower than the N-H in free diamine, indicating that enthylene diamine is coordinated to the metal ion.

In the EPR spectrum of complex (1) in DMF, the \( g_{\|} \) and \( g_{\perp} \) are found to be 2.25 and 1.9, respectively. Similarly for complex (2) the \( g_{\|} \) and \( g_{\perp} \) values are 2.29 and 2.25, respectively. However, the complex (3) exhibits a broad signal with \( g_{\perp} \ 2.29 \) [Table 5.1]. EPR spectra of the complexes correspond to one unaired electron system in a tetragonally distorted octahedral field. The structure of the complex can be shown in Figure 5.1.

\[
\begin{align*}
\text{Ru} & \quad \text{Cl} \\
N & \quad \text{N} \\
1. & \quad \text{en} \\
2. & \quad 2,2'\text{-bpy} \\
3. & \quad 1,10\text{-phen}
\end{align*}
\]

CYCLIC VOLTAMMETRIC STUDIES:

The cyclic voltammetry of complex (1) shows first reduction potential at -0.06v which corresponds to Ru(IV)/Ru(III) and another at -0.26v which is due to Ru(III)/Ru(II) couple. Similarly, oxidation peaks for Ru(II)/Ru(III) and Ru(III)/Ru(IV) appear at -0.18v and -0.34v, respectively. In complex (2) the two reduction potentials are observed at +0.24v and +0.05v for Ru(IV)/Ru(III) and Ru(III)/Ru(II), respectively and the oxidation potentials,
observed at +0.13v and +0.30v, correspond to Ru(II)/Ru(III) and Ru(III)/Ru(IV) oxidations, respectively. The redox process in these systems are reversible. The reduction potential for complex (3) was observed at +0.28v and +0.08v, which corresponds to Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples, respectively. In the reverse cycle the first oxidation potential was observed at +0.16v due to Ru(II)/Ru(III), whereas second oxidation potential was observed at +0.36v due to Ru(III)/Ru(IV). Thus, it is observed that the oxidation potentials for Ru(II)/Ru(III) and Ru(III)/Ru(IV) are higher in case of the mixed ligand complexes containing bipyridyl and phenanthroline than for the mixed ligand complex with ethylenediamine. This shows that replacing the \( \sigma^* \) saturated amines by \( \pi \) aromatic amines increases the oxidation potential (Figure 5.2).

**CATALYTIC ACTIVITY OF THE COMPLEXES:**

The oxidation reactions were carried out using iodosylbenzene as oxidant. Norbornene, cis-cyclooctene, and cyclohexanol gave good yield of norbornene oxide, cyclooctene oxide and cyclohexanone, respectively. Cyclohexane showed poor reactivity. The oxidation of styrene gave benzaldehyde, besides styrene oxide. This may be due to oxidative cleavage of styrene. In oxidation of cyclohexene, allylic oxidation products were formed in addition to the epoxide [Table 5.2].

The oxidation reactions were repeated with t-BuOOH as an oxidant in case of norbornene. It was observed that the oxidation is much slower with t-BuOOH as compared to the case where PhIO is used as an oxidant. However, in the reaction with t-BuOOH there was complete utilisation of the oxidant for epoxide formation [Figure 5.3].
Table 5.2: Oxidation of Organic Substrates with PhIO Catalysed by Ruthenium Complexes (1-3)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Yield (%#) Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>Norbornene</td>
<td>Norbornene oxide</td>
<td>10</td>
</tr>
<tr>
<td>cis-Cyclooctene</td>
<td>cis-Cyclooctene oxide</td>
<td>25</td>
</tr>
<tr>
<td>Styrene</td>
<td>Styrene oxide</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Phenyl acetaldehyde</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Benzaldehyde</td>
<td>3</td>
</tr>
<tr>
<td>trans 4-Octene</td>
<td>trans 4-Octene oxide</td>
<td>7</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>Cyclohexene oxide</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>2-Cyclohexen-1-one</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2-Cyclohexen-1-ol</td>
<td>2</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>Cyclohexanone</td>
<td>41</td>
</tr>
</tbody>
</table>

a - Substrate Oxidant catalyst, mole ratio 250 50 1, solvent, water-dioxane (1:6, \(\sqrt{v}\)) Reaction time, 1 h.

b - Yield based on iodosylbenzene charged
Figure 5.2

Cyclic voltammogram of \([\text{Ru(DPA)(en)}\text{Cl}]\)\(\text{--}\) and \([\text{Ru(DPA)(2,2'}\text{-bipy)}\text{Cl}]\)\(\text{----}\) in water-dioxane with \(\text{NaClO}_4\text{(0.1M)}\) at platinum electrode and a scan rate of 50 mV s\(^{-1}\).

Figure 5.3

Rates of epoxidation of norbornene with t-BuOOH using complexes (1-3) as catalysts. Reaction conditions as in table 1.
Among the three complexes, (2) and (3) were found to be more active as catalysts, compared to complex (1) which showed poor catalytic activity. This is in accordance with the order of oxidation potentials observed in cyclic voltammetry.

**STUDY OF INTERMEDIATE AND TERMINATING SPECIES:**

On addition of iodosylbenzene to a solution of metal complex (2) and alkene, the colour of the solution immediately changed from yellow to brown. Oxidation sets in, and PhIO is completely consumed in 45 min, resulting in a green solution. On charging of additional PhIO (0.5 mmol), it was observed that there was marginal increase in the yield of epoxide after 2h. Most of the iodosylbenzene was found to be unreacted indicating that the green species formed has poor catalytic activity.

When PhIO is added to complex (2) solution, the colour of the solution changes from yellow to brown. The UV-visible spectrum of the brown solution showed a new band at 560 nm. This may be Ru(V) oxo species. This is proposed to be the intermediate in Ru(III) complex catalysed oxidation of alkenes. Similar band was observed either on addition of TBHP as an oxidant or by bubbling molecular oxygen through the complex(2) solution. This indicates that all the three different oxidants, form same active intermediate.

In case of molecular oxygen, the Ru (III) complex may be forming Ru(IV) peroxo species which gets further cleaved into two molecules of Ru(V) oxo species as suggested earlier.
The known oxo intermediate in the present system could not be isolated, as Ruthenium oxo complexes containing π-aromaticamines are unstable in aqueous medium. The characterisation of intermediate brown and greenspecies, formed at the end of the reaction, was carried out in solution by electronic spectral study.

On addition of norbornene to the brown solution, obtained by addition of oxidant to the complex, the band at 560 nm slowly disappeared with the change in colour of the solution to green. There was appearance of a new band at 680 nm. [Figure 5.4], may be due to the formation of oxo species.
The formation of oxo complex could further be confirmed by isolating the crystalline solid and characterising it. The oxo could be isolated by two methods (a) In the first method, the brown solution formed by the reaction of metal complex(2) in water- dioxane (1:1 v/v) with iodosylbenzene (3 equivalent) was extracted with ether to remove iodobenzene. The aqueous solution of oxo complex turned green on standing overnight and the crystals separated out. (b) In the second method a solution of metal complex (2) was stirred, keeping exposed to the atmosphere The solution turned green after 5 h, and on standing overnight, crystals deposited, which are washed with acetone and dried.

The green compound isolated by either of the above methods, gave satisfactory elemental analysis, corresponding to the expected composition \([\{\text{Ru}(IV)\text{-}(\text{DPA})(2,2'-\text{bpy})\}_2\text{O}\]. Both the compounds showed a new band at 866 cm\(^{-1}\) in IR due to \([\text{Ru}(IV)\text{-O-Ru}(IV)]\) stretching and a band at 680 nm was observed in the UV-visible spectrum. Similar oxo dimer of the type \([(L)\text{Ru}(IV)-o-\text{Ru}(IV)(L)]\) has been isolated and characterised by Collman and Coworkers, where \(L\) is sterically unhindered porphyrin.

ELECTROCHEMISTRY OF INTERMEDIATE AND TERMINAL SPECIES:

The redox potentials of the intermediate brown and green species were determined as follows. To a solution of complex (2) in water-dioxane (1:1 v/v), stoichiometric amount of iodosylbenzene was added and the mixture was stirred under nitrogen atmosphere for 10 min. The cyclic voltammogram of the brown solution shows a shift in redox potential as compared to the potential of original complex, supporting the formation of Ru(V) oxo intermediate. The cyclic voltammogram shows potentials \(\text{Ru(V)}/\text{Ru(IV)}\) at +0.28v and \(\text{Ru(IV)}/\text{Ru(III)}\) at +0.02v. The corresponding two oxidation potentials \(\text{Ru(III)}/\text{Ru(IV)}\) are observed at +0.08v and \(\text{Ru(IV)}/\text{Ru(V)}\) at +0.32v.
On standing, the solution turns green. Its cyclic voltammogram shows only one redox couple. The reduction potential is observed at +0.03v due to Ru(IV)/Ru(III) and the oxidation potential is observed at +1.0v due to Ru(III)/Ru(IV) couple [Figure 5.5] The cycles are repeated many times indicating that the \( \kappa \)-oxo system is very stable. This suggests that the formation of \( \kappa \)-oxo species causes termination of catalytic reaction.

**CONCLUSION:**

The study of the Ruthenium mixed ligand complexes as the catalysts for the epoxidation of organic substrates described in this chapter provides an insight into the nature of the intermediate active catalytic species, responsible for oxygen transfer, and dimeric \( \kappa \)-oxo complex, responsible for the termination of catalytic reaction. It is also observed that the replacement of \( \sigma \) saturated amines by a \( \pi \)-aromatic amine increases the oxidation potential of the Ru(III) centre, resulting in its greater catalytic activity.
References:


21. See Ref. 10 and reference therein.