Chapter-V

Electrical Conductivity
Widespread interest in the electrical conduction properties of metal complexes is a fairly recent phenomenon. In the 1960s a number of papers appeared which dealt with the conduction properties of complexes and pointed the way for future studies. It was realized that for conduction to occur in complexes it is necessary for there to be some form of electronic as opposed to magnetic interaction between either the metal atoms alone or the complexes as whole in the lattice. For high conductivity to be extended throughout the solid and not be restricted to the dimmer or cluster formation, since the spaces in the lattice between the delocalized clusters will be insulting. In coordination compound what supposed to simple compound it is very difficult to envisage interactions leading to conduction pathways in three dimensions are anisotropic. By far the most common type are system known as "One dimensional conductors". For significant electrical conductivity in metal complexes there has to be the correct combination of both structure and electronic features.

Inorganic semiconducting complexes constitute one of the most fascinating recent research topics, deeply involving both chemists and state physicists. Considerable interest has been shown in the synthesis and study of molecular complexes, which may behave like semiconducting materials or at least show high conductivities. Semiconducting organic solid materials, are frequently grouped into the categories of molecular crystal, charge transfer complexes and polymers [1]. Inorganic semiconductors stand on the threshold of a bright and exciting future. An organic semiconductor can be synthesis with properties comparable to those exhibited by inorganic semiconductor materials such as the development for transistors and the wide array of non-existing derivative devices and components of the electronic industry. Molecules materials with remarkable physical properties have been extensively studied [2].

The molecular semiconductors based on organic charge transfer solids have been an area of extensive research in the recent years. The materials based on electron-donor-acceptor complexes range from organic semiconductors, organic metals to organic semiconductors [3].
recent years, the investigation on the electrical conduction mechanism in metal organic compounds have been much intensified. This is mainly due to attracting properties of inorganic semiconductors for the technology of solid state devices.

Transition metal complexes of Schiff bases have among the most widely studied coordination compounds in the past few years because of their wide applicability. Metal complexes with ligand, capable of coordinating with two or more sites with metal ions evolved much interest in the field of coordination chemistry.

Metallic conductors are substance with an electrical conductivity that decreases with increase temperature (i.e. temperature coefficient is negative) and their resistivity range vary from $10^{-6}$ to $10^{-2} \ \Omega^{-1} \ \text{cm}^{-1}$. Semiconductors are materials which increase electrical conductivity with rise in temperature (i.e. temperature coefficient is positive). For such substances specific resistance varies within a wide range i.e. from $10^{-5}$ to $10^{5} \ \Omega^{-1} \ \text{cm}^{-1}$. Solid insulators are substances with a very low electrical conductivity and whose specific resistances exceed $10^8 \ \Omega^{-1} \ \text{cm}^{-1}$. However when that conductivity can be measured which is found to increase with temperature, such as semiconductors.

The electrical conductivity of some complexes and polychelates derived from organic compounds play an effective role in the conduction process and they act as semiconductors. Increasing in the conductivity values of organic compounds was observed owing to the inclusion of metal ions in to $\pi$ electron delocalization of the organic compounds [4-5]. Reduction in the conductivity value of organic compounds was also observed which is attributed to the localized bond between metal and organic compound [6-7].

Linear organic polymers which contain donor substitution may form coordination complexes with metal ions. The donor group can be so arranged that uni, bi and tetradentatione residues are present in the polymer. When metal ion is coordinated to more than one ligand unit to forms a bridge between the units which may be intra or intramaolecule
type. The complexes of organic ligands makes possible the formation of several different more or less separated electronic systems.

In recent years an extensive research efforts has been concentrated on organics metal polymers. The implies even looking for the polymers that are intrinsically good electrical conductors without the need of doping. To achieve this one need to have a complete understanding of the relationship between the chemical structure of polymer and its electronic and conduction properties. The conduction properties of an undoped polymer in term of band theory of solid such as band gap, ionisation potential and electron affinity.

Band gap of polymers is measure of its ability to show intrinsic conductivity while ionization potential and electron affinity value of a polymer determine its ability to form conductivity polymers through oxidizing and reducing doping respectively [8].

The applications in electronic industry and power sources depend on the band gap and conductivity of semiconductor. The organic semiconductor have the disadvantages of having low carrier mobilities, since the disordered structure of the electron get scattered which traveling through such materials.

The organic semiconductor structures, which still over willingly dominate semiconductor applications are being pushed a side in research more and more by chelate polymers mainly because of their carrier mobilities. The organic semiconductors have the disadvantages of having low carrier mobilities due to the following reasons:

1) The forces between the adjacent molecules are relativity weak as organic compounds form molecular crystal. Also due to little electronic coupling that exists between the adjacent molecules, it becomes difficult for the electrons to jump form one molecule to the other, and so the carrier mobilities in this kind of compounds increase with increasing molecules size.

2) Most of them are amorphous in the nature and due to the disordered structures the electrons get scattered while traveling
through such materials, when they try to flow through it and hence lower the conductivity.

In order to overcome these difficulties many chelate polymers have been synthesized in which transition metal have been used to bridge the ligand molecules, particularly with aromatic group through conjugation. This makes the dπ-pπ interaction with the adjacent ligand possible through the orbital of the metal. This π electron network facilitates the electrical conductivity.

**LITERATURE SURVEY**

The literature available on the electrical studies of the coordination polymers is scarce as compared to the organic polymers. However during the last two decades there have been significant international research efforts by several workers. In the fitness of the present investigation, relevant literature is presented in the following paragraph.

First systematic investigation on semiconductor electrolytes interphase was reported by Yahan et al [9]. The numbers dioximes and their transition metal complexes have been investigated for their electrical properties [10]. The exceptional stability and unique electronic properties of the complexes can be attributed to their planar structure, which is stabilized by hydrogen bonding [11]. The conducting properties of some azocomplexes of have been investigated [12]. Electrical conductivity properties of some o-substituted azoyleazo-barbiturate complex at different temperature were studied. It was observed that all the carboxylate, cobalt, and nitro complex and nickel-methyl complex were semiconducting behaioir [13].

Patel et al [14-15] have synthesized a large number of complexes and polychelates including those of VO(IV) and UO$_2$ (VI). They have extensively studied electrical conductivity of ligand and their polychelates over a wide of temperature. The low value of electrical conductivity may be due to the low molecular weight and undesirable morphology occurring during the preparation of pellets further more the low magnitude of activation energy may be due to the presence of large number of π
electrons. It was found that general behavior of electrical conductivity obeys the equation \( \sigma = \sigma_0 \exp \left( \frac{E_a}{kT} \right) \), where \( \sigma_0 \) is a constant, \( E_a \) is activation energy of conduction process, \( T \) is the absolute temperature and \( k \) is Boltzmann constants. The plots \( \log \sigma \) vs. \( 1/T \) show greater slope in higher temperature region and lower slope with lower activation energy in the lower temperature region. The results agrees with the observation of Shetty et al [23] that the activation energy approaches higher value at high temperature suggesting value due to extrinsic conduction. Electrical properties of of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) polychelates with Schiff bases ligands of terephthaldehyde and S-benzythiocarbazate have been studied by Paliwal et al [26-27]. The electrical conductivity lies in the range \( 6.33 \times 10^{-10} \) to \( 3.15 \times 10^{-11} \) \( \Omega^{-1} \) cm\(^{-1}\). They also studied the effect of iodine doping on electrical property.

A correlation between Schiff bases complexes and conductivity versus temperature behaviour have been investigated by Ahmed et al [22]. A fairly extensive study of electrical conductivities of poly (2,2 bipyridine-5-5 dinyl) by using Ni(II) complexes was reported by Maryyama [28] and studied electrical conductivity of poly(2,2′bipyridine-5-5dicyl) by using Ni(II) complexes.

Hassan et al [29] have studied the electrical conductivity of N-phenyl-3-carboxethoxy-4-methyl-5-cyanopyridazine-5-one and its Cr(III),Mn(III), Fe(III),Co(II) and Cu(II) complex. All the sample behaour as organic semiconductors. The delocalised d-orbital electrons contribution as charge carries. The conductivity showed a tendency to increase with the raising of temperature. The lower temperature region was the region of the extrinsic semiconductors, whereas the higher temperature region was the region of the intrinsic semiconductor. The activation energy was linearly dependant on the ionic radius. Complex of anthroquinons –O-Carboxylic phenylhydrozone with Cr(III), Mn(III), Fe(III), Ni(II) and Cu(II) metal ion were synthesized and their electrical conductivity was measured [26]. The electrical conductivity of these complex at 298 K follow the order Fe(III) > Cr(III) > Mn(III) > Ni(II) > Cu(II).
Chapter 5

Electrical Conductivity

Despite extensive work done on the preparation, properties, magnetic properties and structural aspects of transition metal complexes with quadridentate Schiff bases comparatively lattice work is available on the studies of electrical properties with solid state type of ligand. The interest in such studies is the increasing being shown by different schools of responders as an interdisciplinary field of study [31].

Aswar et al [32-35] have extensively studied the semiconductivity properties of large number of Schiff base ligand and their chelates with transition metal ions.

Experimental:

The electrical resistivity of the compounds can be measured either with ac or dc methods. However in the present work the dc method have been used for resistivity measurements over wide range of temperature i.e. from room temperature to 423 K. The measurement involved the following steps.

Preparation of Pellets:

In order prepare the pellets the Schiff bases and their metal complexes were ground separately to 300 mesh size in an agate pestle and mortar. The well powdered compounds were pelletized isostatically in steel die of 1.2 cm diameter under a pressure of 5-6 tons cm$^{-1}$ with the help of hydraulic press. The pellet thus obtained was crack-free and hard. The end faces of the pellets were gently ground over a zero number. Emery paper to ensure smooth surfaces and desired polishing a silver paste was used for good electrical contact. The surface continuity of the pellet was then tested by mean of a millimeter.

The average diameter of the pellet and its thickness were measured using a screw gauze. The actual diameter were measured by average the three measurements taken at three at three different places. The pellets were then stored in a desiccator till needed for conductivity measurements.
Sample Holder:
A typical sample holder is specially designed and fabricated for the purposes of resistively measurements. It consists of two brass electrode one of which is fixed to the asbestos plate by means of brass nuts. The other electrode is also of the asbestos plates which is specially loaded which pressure hard against the surfaces of the pellets.

Furnace for heating the sample:
For resistively measurements at different temperature a suitable electrical furnace was constructed by winding the standard resister kanthal wire over an alumina tube of 1.5 inch diameter and packing its with ceramic blankest in a tin box. Heating of the furnace was controlled with the help of a dimmerstat. The current to the furnace was achieved and recorded by means of standard chromel-alumel thermocouple connected with digital millimeter model No.435 in which the emf development in millvolt were measured. The measurement junction of the thermocouple and the pellet in the sample holder were at same level almost in the center of the furnace where were insulated with porcelain heads were taken out for connections.

Experimental Procedure:
The resistance of the pellets was measured by the voltage drop method using of the Systronics microvolt meter as a function of range 1V to 100V. The connecting wires of the samples holders from the furnace were connected to two terminals of the resistant. In this way corresponding resistance (R) of the pellet was measured directly by keeping the pellet in the sample holder.

\[ R = \frac{[V_t - V_r]}{V_r} \times 10^{-5} \Omega \]

Where \( V_t \) = Total voltage range applied.
\( V_r \) = Actual voltage across resistant.
Chapter 5  

Electrical Conductivity

Resistively \((\rho)\) was then calculated using relation.

\[
\text{Resistively } (\rho) = R \times A/t
\]

Where \(A\) = Area of the pellet.
\(t\) = Thickness of the pellet.
\(R\) = Resistance of the pellet.

The electrical conductivity \((\sigma)\) vary exponentially with absolute temperature according to well known relation.

\[
\sigma = \sigma_0 \exp (-\text{Ea}/kT)
\]

Where \(\sigma\) = Electrical conductivity at temperature \(T\).
\(\sigma_0\) = Electrical conductivity at temperature \(T = \infty\).
\(\text{Ea}\) = Activation energies of electrical conduction
\(K\) = Boltzman constant of electrical conduction
\(T\) = Absolute temperature.

This relation has been modified as

\[
\log \sigma = \log \sigma_0 + \left[ -\text{Ea} / 2.0303 kT \right]
\]

According to the relation a plot of \(\log \sigma\) vs. \(1/T\ 10^3\) would be linear with negative slope. Such plots were made on the basis of each set of data. The plots of temperature dependence of electrical conductivity for all these chelate have been drawn.

**Results and discussion:**

**Electrical conductivity of BNPSAP and its Polychelates -**

The results of electrical conductivities of BNPSAP and its chelate polymers are presented in table 5.1 and fig 5.1 and 5.2. The effect of temperature on electrical conductivity of the chelate and from the results of electrical conductivity of the following discussion can be made.

1) Linear dependence of \(\log \sigma\) vs. \(1/T\) was observed, which suggest the semiconducting behaviour of the ligand and its chelates.
Chapter 5

Electrical Conductivity

2) Electrical conductivity of these chelates lies in the range $8.789 \times 10^{-12}$ to $4.786 \times 10^{-9} \ \Omega^{-1} \ cm^{-1}$ at 373 K.

3) Electrical conductivity of these complexes at 373 K follow the order Ni > Cd > Cu > Zn > BNBSAP > Co > Mn > Fe.

4) The activation energies of electrical conduction of the complexes have been directly measured energy gap of semiconductor.

Electrical conductivity of BNBSAP and its Polychelates -

The temperature dependence of the conductivity of BNBSAP and its chelates reveals a linear trend figs 5.3 and 5.4 and data in table 5.1.

From the results following discussion can be made.

1) The electrical conductivity of the BNBSAP and its chelates show a tendency to increase by increasing the temperature.

2) The electrical conductivity this complex lies in the range $4.361 \times 10^{-11}$ to $7.241 \times 10^{-10} \ \Omega^{-1} \ cm^{-1}$ at 372 K.

3) The order of electrical conductivity of BNBSAP and its complexes at 373 K is found to be Zn > Ni > Cu > BNBSAP > Co > Mn > Cd > Fe.

4) The activation energies of electrical conduction of these complexes follow the order: Cd > Zn > Mn > Fe > Ni > Cu > Co > BNBSAP.
Fig. 5.1: Solid State Conductivity of BNPSAP, Mn(II), Fe(II), and Ni(II) Polychelates

1000/T vs Log ε
Fig. 5.2: Solid State Conductivity of Co(II), Cu(II), Zn(II), and Cd(II) Polythelates
Table No 5.1: Activation and Electrical Conductivity of Ligands and Its Polychelates at 373 K

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Comp.</th>
<th>Activ. Energy Ea eV</th>
<th>Electr. Cond. $\sigma \Omega^{-1} \text{cm}^{-1}$ at 373 K</th>
<th>Comp.</th>
<th>Activ. Energy Ea eV</th>
<th>Electr. Cond. $\sigma \Omega^{-1} \text{cm}^{-1}$ at 373 K</th>
<th>Comp.</th>
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<th>Electr. Cond. $\sigma \Omega^{-1} \text{cm}^{-1}$ at 373 K</th>
<th>Comp.</th>
<th>Activ. Energy Ea eV</th>
<th>Electr. Cond. $\sigma \Omega^{-1} \text{cm}^{-1}$ at 373 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BNPSAP</td>
<td>0.26</td>
<td>9.258 x 10^{-10}</td>
<td>BNBSAP</td>
<td>0.75</td>
<td>7.943 x 10^{-10}</td>
<td>BIPSAP</td>
<td>0.16</td>
<td>1.096 x 10^{-8}</td>
<td>BNESAP</td>
<td>0.31</td>
<td>9.70 x 10^{-11}</td>
</tr>
<tr>
<td>2</td>
<td>Mn</td>
<td>0.65</td>
<td>9.77 x 10^{-11}</td>
<td>Mn</td>
<td>0.37</td>
<td>1.905 x 10^{-10}</td>
<td>Mn</td>
<td>0.42</td>
<td>4.478 x 10^{-8}</td>
<td>Mn</td>
<td>0.60</td>
<td>7.244 x 10^{-10}</td>
</tr>
<tr>
<td>3</td>
<td>Fe</td>
<td>0.08</td>
<td>8.709 x 10^{-12}</td>
<td>Fe</td>
<td>0.38</td>
<td>4.073 x 10^{-11}</td>
<td>Fe</td>
<td>0.43</td>
<td>6.309 x 10^{-11}</td>
<td>Fe</td>
<td>0.35</td>
<td>5.75 x 10^{-11}</td>
</tr>
<tr>
<td>4</td>
<td>Co</td>
<td>0.34</td>
<td>7.413 x 10^{-10}</td>
<td>Co</td>
<td>0.54</td>
<td>7.413 x 10^{-10}</td>
<td>Co</td>
<td>0.35</td>
<td>1.20 x 10^{-9}</td>
<td>Co</td>
<td>0.62</td>
<td>6.606 x 10^{-9}</td>
</tr>
<tr>
<td>5</td>
<td>Ni</td>
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<td>7.79 x 10^{-9}</td>
<td>Ni</td>
<td>0.45</td>
<td>9.32 x 10^{-9}</td>
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<td>0.93</td>
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<td>Ni</td>
<td>1.61</td>
<td>1.047 x 10^{-9}</td>
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<tr>
<td>6</td>
<td>Cu</td>
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<td>1.657 x 10^{-9}</td>
<td>Cu</td>
<td>0.58</td>
<td>1.34 x 10^{-9}</td>
<td>Cu</td>
<td>0.62</td>
<td>6.06 x 10^{-12}</td>
<td>Cu</td>
<td>0.64</td>
<td>9.772 x 10^{-11}</td>
</tr>
<tr>
<td>7</td>
<td>Zn</td>
<td>0.51</td>
<td>1.584 x 10^{-9}</td>
<td>Zn</td>
<td>0.34</td>
<td>7.24 x 10^{-10}</td>
<td>Zn</td>
<td>1.10</td>
<td>1.621 x 10^{-9}</td>
<td>Zn</td>
<td>0.46</td>
<td>2.63 x 10^{-9}</td>
</tr>
<tr>
<td>8</td>
<td>Cd</td>
<td>0.62</td>
<td>3.311 x 10^{-9}</td>
<td>Cd</td>
<td>0.30</td>
<td>1.995 x 10^{-8}</td>
<td>Cd</td>
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<td>2.29 x 10^{-9}</td>
<td>Cd</td>
<td>0.18</td>
<td>9.772 x 10^{-15}</td>
</tr>
</tbody>
</table>
Chapter 5

Electrical Conductivity

Electrical conductivity of BIPSAP and its Polychelates:

Results of temperature dependance of electrical conductivity of BIPSAP and its complexes given in figs 5.4 to 5.6 and table 5.1 and are summarized as follows.

1) The plots of log $\sigma$ vs. $1/T$ are found to be linear over studied temperature range therefore it may be considered that these complexes behave as semiconductor.

2) The electrical conductivity of these complexes at 373 K lies in the range $6.666 \times 10^{-12}$ to $1.090 \times 10^{-6}$ $\Omega^{-1}$ cm$^{-1}$.

3) The order of electrical conductivity of these complexes at 373 K follow the order BIPSAP$>$Mn$>$Co$>$Cd$>$Zn$>$Fe$>$Ni$>$Cu.

4) The activation energies of the electrical conductance of these complexes is found to increase in the order Zn$>$ Ni$>$ Cd$>$ Fe$>$ Mn$>$ Co$>$ BIPSAP.

Electrical conductivity of BNESAP and its Polychelates:

The results of electrical conductivity are incorporated in table 5.1 and figs.5.7 and 5.8. The results observed that

1) The plots of log $\sigma$ vs. $1/T$ are found to be linear over measured temperature range (313-423 K).

2) The complexes have electrical conductivity in the range $9.77 \times 10^{-12}$ to $2.630 \times 10^{-8}$ $\Omega^{-1}$ cm$^{-1}$.

3) The order of electrical conductivity of these complexes 373 K increases Zn$>$ Co$>$ Ni$>$ Mn$>$ BNESAP$>$ Cu$>$ Fe$>$ Cd.

4) The activation energies of electrical conductivity of the complexes is found to increase in the order Ni$>$ Cu$>$ Co$>$ Mn$>$ Zn$>$ Fe$>$ BNESAP$>$ Cd.
Fig. 5.3 Solid State Conductivity of BNBSAP, Mn(II), Fe(II), and Ni(II) Polychelates
Fig. 5.4: Solid State Conductivity of Ni(II), Cu(II), Zn(II) and Cd(II) Polychelates
Fig. 5.5: Solid State Conductivity of BIPSAP, Mn(II), Fe(II), and Co(II) Polychelates
Fig. 5.6: Solid State Conductivity of Ni(II), Cu(II), Zn(II) and Cd(II) Polychelates
Fig. 5.8: Solid State Conductivity of Ni(II), Cu(II), Zn(II), and Cd(II) Polychelates
REFERENCES