Research Article

Electrical Conductivity Studies on Co(II), Cu(II), and Ni(II) Complexes of 6-(trifluoromethoxy) benzothiozole-2-amine Schiff base

Smita D Revankar, Jyothi C Ajbani and Revanasiddappa M*

Department of Engineering Chemistry, PESIT, Bangalore South campus, Bangalore, Karnataka, India

Abstract

Microwave assisted synthesis of Schiff base ligands1-[(E)-{[6-(trifluoromethoxy)-1,3-benzothiazol-2-yl]imino}methyl] naphthalen-2-ol, 4-chloro-2-[(E)-{[6-(trifluoromethoxy)-1,3-benzothiazol-2-l]imino} methyl]phenol and 2-{(1E)-N-[5-(trifluoromethoxy)-1,3-benzothiazol-2-yl]ethanimidoyl} phenol derived from condensation of Riluzole[6-(trifluoro methoxy) benzothiozole-2-amine] with different aldehydes. The Co(II), Ni(II) and Cu(II) complexes have been prepared by using above said ligands are dissolved in an appropriate amount of ethanol as solvent. The prepared complexes were characterized by using various physical methods *viz.* elemental, molar conductance, magnetic susceptibility, IR, NMR, XRD and UV-Visible spectroscopy. Metal complexes have been obtained in the form of powder and then the sample was pressed in hydraulic press to get the pallets. Conductivity of the pallets was measured by two probe method. DC electrical conductivity data shows at room temperature insulator in nature but at higher temperature theses complexes are reveals semiconducting behaviour.

Keywords: Electrical conductivity, Metal Complexes and Riluzole Schiff base
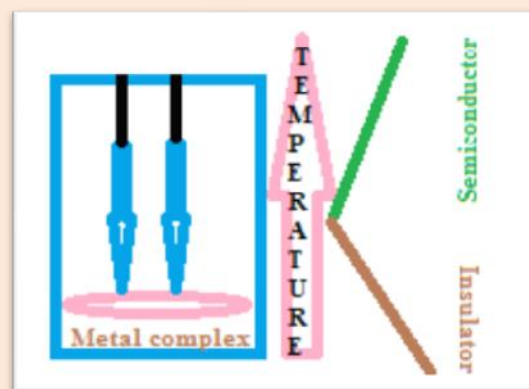
*Correspondence
Author: M Revanasiddappa
Email: revanasiddappam@pes.edu

Introduction

One of the most interesting areas of research is that of electrically conducting organometallic polymers [1-2]. The method of choice for producing conducting organometallic polymers involves complexing transition metals with conjugated bridging ligands. The ability to alter the oxidation state of the metal ion, and thus the charge density along the polymer backbone, provides an alternative route to charge carrier creation as opposed to redox doping. Polyamides and their poly chelates have σ values at 298K of about 10^{-6}-10^{-11} ohm-1 cm-1. The temperature dependant σ has a typical break point at 410- 450 K with lower ΔE values at higher temperature. Marcu and Dima [3] have prepared the polymers of dimethyl–4,4'–[*p*–phenylene–*bis* (methylidene nitrilo)] disalicylate with Co(II), Ni(II) and Cu(II) in DMF and reported that these polymers are heat stable, semi conducting in nature. Semiconducting properties of poly chelates 2, 5–dihydroxy phthaldehyde and series of di and tetra amino compounds and monomeric Schiff bases and their chelates have been reported [4]. Electrical conducting properties of metal chelates of azines have been reported [5]. Coordination polymers of Cu(II) and Ni(II) with ethylene diamine tetrahalato and tetra thioazalatotetrathio flavane were prepared and their electrical conductivity has been studied [6-12]. In view of the above discussion, the present work deals with electrical conductivity studies on Co(II), Cu(II) and Ni(II) complexes of Schiff base derived from Riluzole with different aldehydes.

Experimental
Synthesis of ligands and metal complexes

Microwave assisted synthesis of these ligands RN[1-[(E)-{[6-(trifluoromethoxy)-1,3-benzothiazol-2-yl]imino} methyl] naphthalen-2-ol], RCS [4-chloro-2-[(E)-{[6-(trifluoromethoxy)-1,3-benzothiazol-2-l]imino} methyl]phenol]

and RAP [2-{(1E)-N-[5-(trifluoromethoxy)-1,3-benzothiazol-2-yl]ethanimidoyl}phenol] ligands and its metal complexes has been reported in the literature [13].

Electrical measurement

The powdered complex was palletized in a circular dies and plunger with specific diameter under pressure of 5 – 6 tons per cm^2 with the help of hydraulic press; the pellet thus obtained was crack free and hard. These pellets were coated with silver paste to make good electrical contacts. The DC electric measurements for the obtained pallets were performed within the temperature range 300-500 K using the two-probe technique, with a Keithly 224 constant current source and a Keithly 617 digital electrometer [14].

Results and Discussion

The prepared complexes were characterized by using various physical methods viz. elemental, molar conductance, magnetic susceptibility, IR, NMR, XRD and UV-Visible. All these data reveals that the formation of metal complexes through the donor sites of O- and N-atoms [7]. The measurements of DC resistivity of the complexes were carried out in the temperature range of 313 - 438K.

The DC transport measurements were made on six samples as a function of temperature, and the results were indicated in **Figures 1-6**. The logarithmic conductivity increases linearly with temperature. It was found that conductivity increases with increasing T and decreasing as $T^{-1/4}$. Whenever an electron moves in an electric field which is disordered, as in an amorphous solid and semiconductor, some or all the electrons will be localized depending on the degree of disorder. The conductivity variation with increasing temperature in a material with partial localization of carriers changes from T^{-1} behaviour to $T^{-1/n}$ at low temperatures [15]. Accordingly, the mechanism of electrical conduction can be distinguishing as follows: (a) conduction due to carriers excited beyond the mobility shoulders into nonlocalized or extended states; (b) into the localized states at the band edges; (c) hopping (tunnelling) between localized states near the Fermi energy. Therefore, the overall conductivity of the material in the finite temperature range can be written as:

$$\sigma_{overall} = \sigma_{ext} + \sigma_{hop} \qquad (1)$$
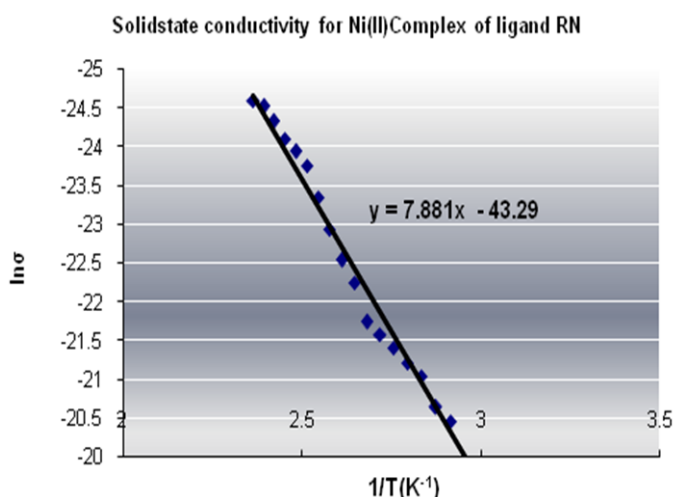
Figure 1 Plot of lnσ against 1/T. The electrical conductivity of Ni[RN]$_2$2H$_2$O varied from 4.8x10^{-10} S/cm to 0.92x10^{-8} S/cm over the temperature range 318 – 423 K
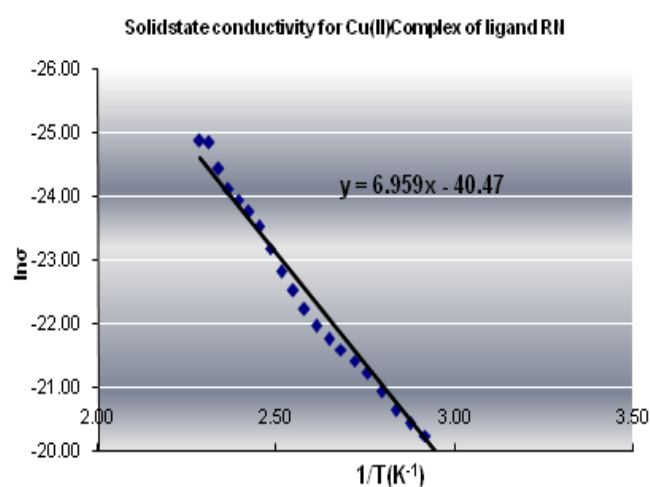
Figure 2 Plot of lnσ against 1/T. The electrical conductivity of Cu[RN.Cl.3H$_2$O] varied from 6.27x10^{-10} S/cm to 1.53x10^{-8} S/cm over the temperature range 313 – 438 K

At higher temperatures, the phonon energy will be very high compared to the energy gap between the nearest neighbour states at E_F. Hence the contribution to conduction by hopping will be considered is thermal excitation of carriers. The conductivity σext variation with T is expressed by Arrhenius relation of the type
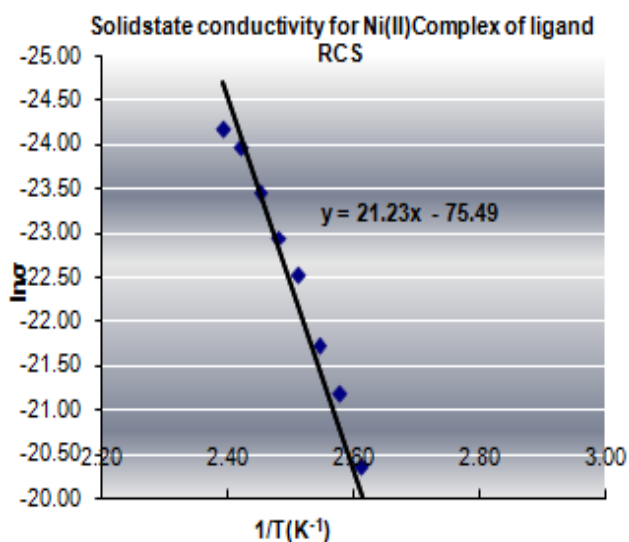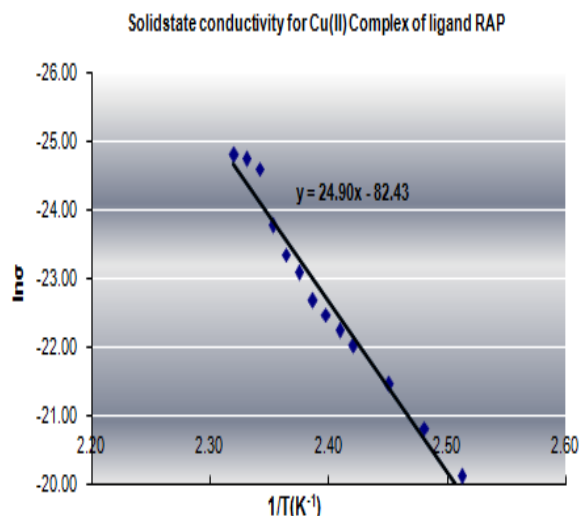
Figure 3 Plot of lnσ against 1/T. The electrical conductivity of Ni[L^2]$_2$2H$_2$Ovaried from 3.1x10^{-10} mhos/cm to 0.63x10^{-8} S/cm over the temperature range 373 – 418 K
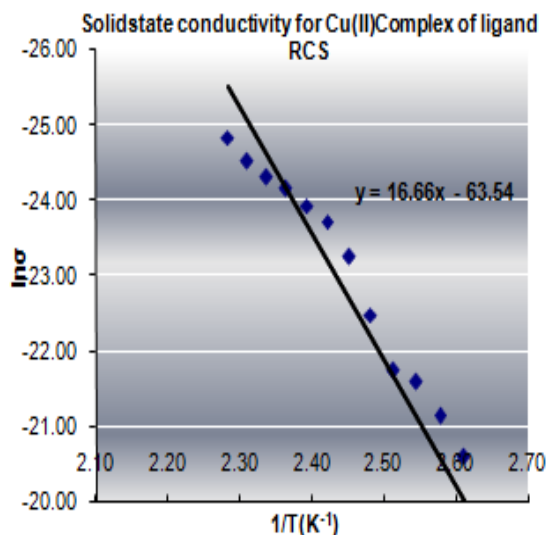
Figure 4 Plot of lnσ against 1/T. The electrical conductivity of Cu[RCS Cl.3H$_2$O]varied from 4.2x10^{-10} mhos/cm to0.31x10^{-8} S/cm over the temperature range 373 – 438 K
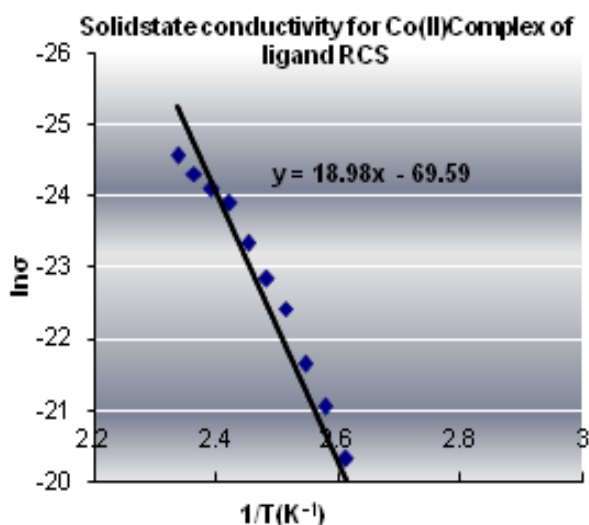
Figure 5 Plot of lnσ against 1/T. The electrical conductivity of Co[L^2]$_2$2H$_2$Ovaried from 4.6x10^{-10} S/cm to 0.61x10^{-8} S/cm over the temperature range 373 – 428 K

Figure 6 Plot of lnσ against 1/T. The electrical conductivity of Cu[L^3]$_2$2H$_2$Ovaried from 5.8x10^{-10} S/cm to 0.3x10^{-8} S /cm over the temperature range 383 – 431 K.

$$\sigma_{ext} = \sigma_M \exp -(\Delta E /kT) \qquad (2)$$

Where σ$_M$is the pre-exponential constant corresponding to 1/T = 0, ΔE the activation energy for electron transfer and k the Boltzmann's constant. The activation energy ΔE in eq (2) is found to be from Figure 3. The pre-exponential in the conductivity eq (2) is represented as:

$$\sigma_M = \sigma_o \exp (-\gamma) \qquad (3)$$

Where σ_0 is the minimum conductivity at T = 0 of a metal below which undergoes a transition in to an insulator. The value of so for 3D conduction has been predicated to be ~ 0.03 e^2/ha, where 'a' is the lattice constant, 'e' is the electron charge and 'h' the Plank's constant. As shown in Figure 4 the hopping conductivity σ_{hop} vary with temperature of $T^{-1/4}$. This type of transport behaviour is called as variable range hoppingor phonon assisted quantum mechanical tunnelling [10]. Since the hops are phonon assisted,the hopping conductivity has a finite value at a finite temperature. The conductivityvariation in this region can be expressed as:

$$\sigma_{hop} = A \exp (- B\ T^{\ -1/n}) \qquad\qquad (4)$$

Where 'A' is the pre-exponential factor which depends on the hopping distance, phonon frequency and the density of states(DOS) at E_F, $N(E_F)$; and B=$[\ \alpha^3\ /kN(E_F\ )]^{1/4}$a constant depending on the random potential well decay length (α^{-1}) and N (E_F).
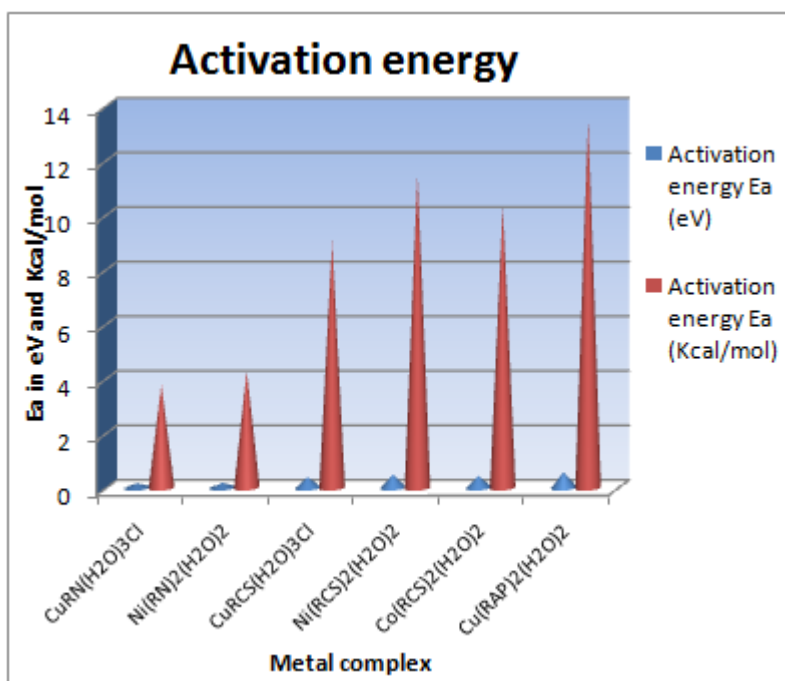
Figure 7 Activation energy chart for metal complexes

Temperature dependence of electrical conductivity

From the Arrhenius plots clearly indicates the effect of complexation with different transition metals on the electrical conductivity of Riluzole Schiff bases. The conductivity of metal complexes increases as increase in the temperature. From the above data the effect of complexation with different transition metals on the electrical conductivity of Riluzole drugs can be seen. Metal complex of ligand RN show semiconducting behaviour in the temperature range 40–150 °C. Metal complexes of ligands RCS and RAP behave as insulators at lower temperature 25–100°C, where as they show semiconducting behaviour in the temperature range 100–150 °C. This may be due to the overlap between the electrons in the antibonding π – orbitals of the σ donor ligand and the empty d-orbitals of the different transition metal cations. It leads to delocalization of the π – electronic charts on the Riluzole Schiff base molecules. Activation energy of different Riluzole Schiff base metal complexes investigated is in the range of 0.164-0.586eV (Figure 7). Based on spectral data and electrical measurement reveals that these complexes are monomeric in nature.

Conclusion

Metal complex of ligand RN shows semiconducting behaviour at room temperature. Metal complexes of ligands RCS and RAP behave as insulators at lower temperature 25–100°C, but they show semiconducting behaviour in the

temperature range 100–150 °C. The orders of the activation energy for the metal complexes are as follows: Cu <Ni< Co and for the ligands is as follows: RN<RCS<RAP.

Acknowledgement

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