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ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
Vol. 5, No.4, pp. 797-801, October 2008

Electrical Conductivity Studies on Co(II), Cu(II), Ni(II) and Cd(II) Complexes of Azines

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Received 21 November 2007; Accepted 20 January 2008

Abstract: 1-Phenyl-4-(2'-hydroxyphenyl-1-yl)di-imino azine, {1P-4-(2' HPDA)} 1, 4(2'-hydroxyphenyl-1-yl)di-imino azine, {1, 4-(2' HPDA)} are derived from benzophenone hydrozone with different aldehydes in presence of few drops of concentrated hydrochloric acid in alcoholic medium. Metal(II) complexes have been prepared by salts of $CoCl_2$, $CuCl_2$, $NiCl_2$ and $CdCl_2$ reacting with azine ligands dissolved in alcohol in the molar ratio of (1:2). The prepared complexes were characterized by using various physical methods *viz*. elemental, molar conductance, magnetic susceptibility, IR, NMR, XRD and UV-Visible. Conductivity of the powder samples were measured by two probe method. Measured electrical conductivities of Co(II), Cu(II), Ni(II) and Cd(II) complexes of azines are reported in this paper. It is found that at room temperature these complexes show insulator behavior. At higher temperature conductivity increases linearly, showing semi conducting behavior.

Keywords: Electrical conductivity, Complexes of Azines, Benzophenone hydrozone

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. Semis conducting properties of poly chelates 2, 5–dihydroxy phthaldehyde and series of di and tetra amino compounds and monomaric Schiff bases and their chelates have been reported[4]. Coordination polymers of Cu(II) and Ni(II) with ethylene diaminetetrahalato and tetra thioazalatotetrathio flavane were prepared and their electrical conductivity has been studied[5-7]. In view of the above discussion, the present work deals with electrical conductivity studies on Co(II), Cu(II), Ni(II) and Cd(II) complexes of azines derived from benzophenone hydrozone with different aldehydes in presence of few drops of concentrated hydrochloric acid in alcoholic medium.

Experimental

Preparation of {1P-4-(2' HPDA)} and {1, 4-(2' HPDA)}

1-Phenyl-4-(2'-hydroxyphenyl-1-yl)di-imino azine, {1P-4-(2'-HPDA)} [Mol Formula $C_{14}H_{12}N_2O_2$, Yield=70%, M.P=216ºC], 1,4(2'-hydroxyphenyl-1-yl) di-imino azine,{1, 4-(2' HPDA)} [Moleuclar formula $C_{14}H_{12}N_2O$, yield=75%, m.p=187ºC] were derived from benzophenone hydrozone with different aldehydes in presence of few drops of concentrated hydrochloric acid in alcoholic medium has been reported in the literature[8].

Preparation of complexes

Metal complexes of azines were synthesized by adding 0.002 mole of ligand solute ion in ethanol and little quantity of dimethyl formamide to 0.001 mole of alcoholic solution metal(II) chloride. The contents were refluxed for about 3-4 hours on a water bath. Then the sodium acetate was added and continued refluxation for half an hour, allowed to cool and the reaction mixture was transferred into a beaker and the precipitation of the complex was initiated by adding distilled water. The precipitate was filtered, washed with alcohol and dried over fused calcium chloride.

Electrical measurement

The powdered complex was palletized isostatistically in a steel disk of 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 resistance of the pellets were measured on BPL – INDIA million mega meter R M 160 m K IIIA and D C micro voltmeter by voltage drop method[9].

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 404 - 540 K.

The DC transport measurements were made on three samples as a function of temperature, at 330 – 380 K and the results were indicated in Figure 1- 4. 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} behavior to $T^{-1/n}$ at low temperatures[10]. Accordingly, the mechanism of electrical conduction can be distinguishing as follows: (a) conduction due to carriers excited beyond the mobility shoulders into non-localized or extended states; (b) into the localized states at the band edges; (c) hopping (tunneling) between localized states near the Fermi energy. Therefore, the overall conductivity of the material in the finite temperature range can be written as:

$$\sigma_{Overall} = \sigma_{ext} + \sigma_{hop} \tag{1}$$

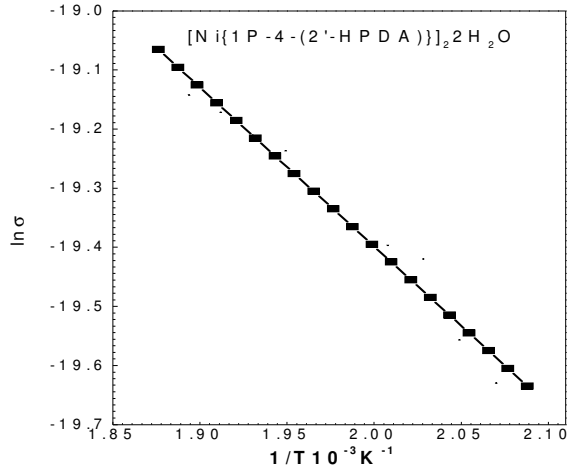

Figure 1. Temperature dependence of electrical conductivity

(The electrical conductivity of Ni[{1P-4-(2' HPDA)}]$_2$ $2H_2O$ varies from 4.857×10^{-5} mhos/cm to 2.749×10^{-5} mhos /cm over the temperature range 474-528 K)

At relatively high temperatures, the phonon energy will be very high compared to the energy gap between the nearest neighbor states at E_F. Hence the contribution to conduction by hopping will be considered is thermal excitation of carriers. The conductivity σ_{ext} variation with T is expressed by Arrhenius relation of the type

$$\sigma_{ext} = \sigma_M \exp\left(\frac{-\Delta E}{kT}\right) \tag{2}$$

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:

$$\sigma_M = \sigma_o \exp(-\gamma) \tag{3}$$

Where σ_o is the minimum conductivity at T = 0 of a metal below which undergoes a transition in to an insulator. The value of σ_o 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 behavior is called as variable range hopping or phonon assisted quantum mechanical tunneling[10]. Since the hops are phonon assisted, the hopping conductivity has a finite value at a finite temperature. The conductivity variation in this region can be expressed as:

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

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 $B=\left[\frac{\alpha^3}{kN(E_F)}\right]^{1/4}$ a constant depending on the random potential well decay length (α^{-1}) and N (E_F).

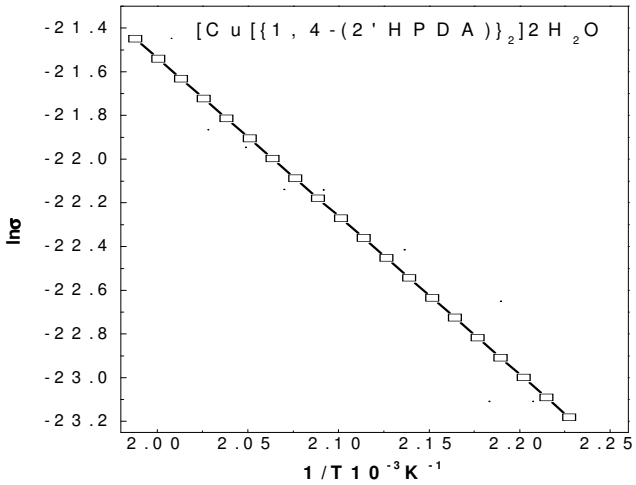

Figure 2. Temperature dependence of electrical conductivity

(The electrical conductivity of $Cu[\{1,4\text{-}(2'HPDA)\}]_2 2H_2O$ varies from 4.842×10^{-6} mhos/cm to 0.9×10^{-6} mhos/cm over the temperature range 454-498 K).

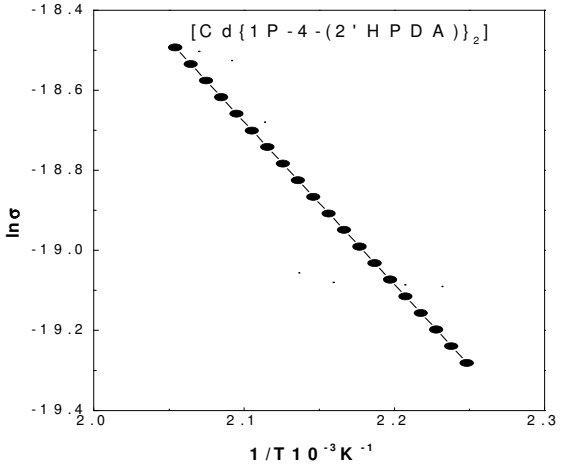

Figure 3. Temperature dependence of electrical conductivity

(The electrical conductivity of Cd[{1P-4-(2' HPDA)}] varies from 8.74×10^{-5} mhos/cm to 5.12×10^{-5} mhos/cm over the temperature range 444 – 524 K).

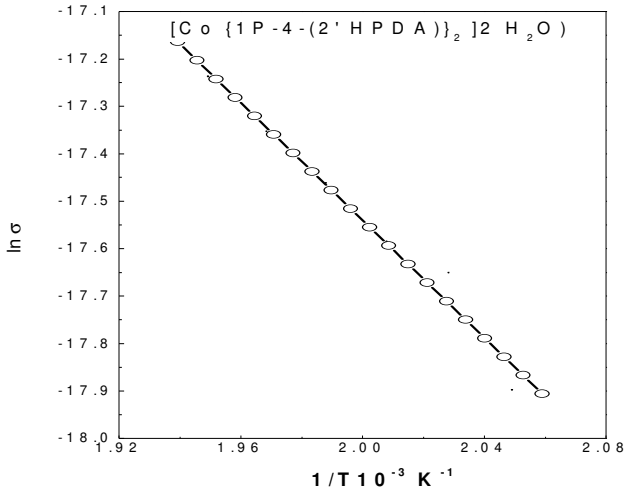

Figure 4. Temperature dependence of electrical conductivity
(The electrical conductivity of Co[{1P-4-(2' HPDA)}]$_2$ $2H_2O$ varies from $4.55x10^{-4}$ mhos/cm to $1.4x10^{-4}$ mhos/cm over the temperature range 478 – 540 K).

From the Arrhenius plots clearly indicates the effect of complexation with different transition metals on the electrical conductivity of *N*- azines. The conductivity of metal free ligand is insulator. After complexation, the conductivity increases as increase in the temperature when compared to that of ligand. At room temperature they behave as an insulator but higher temperature shows semi conducting nature. This may be due to the overlap between the electrons in the anti bonding π-orbitals of the σ donor ligand (*N*–azines), the empty *d*-orbitals of the different transition metal cation. It leads to delocalization of the π-electronic charges on the azine molecules. Based on spectral data and electrical measurement reveals that these complexes are monomeric in nature.

Conclusion

Activation energy of different azine metal complexes investigated in the range of 0.21-0.63eV. Figure 1-4 demonstrate the variation of logarithmic conductivity values as a function of reciprocal temperature. At lower temperature 25–100°C they behave as insulator, where as they show semi conducting behaviour in the temperature range 100–250°C. The orders of the activation energy for the metal complexes are as follows: Cu > Co > Cd > Ni.

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