Asian Journal of Chemistry Vol. 2, No. 4 (1990), 363-367

Electrical Properties of Some Polymeric Complexes

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The D.C. conductivities of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) polychelates of 4,4'-dihydroxy-3,3'-diacetyl biphenyl-dithiooxamide (DDBDO), 4,4'-dihydroxy 3,3'-diacetyl biphenyl diaminopyridine (DDBDP) and 4,4'-dihydroxy-3,3'-diacetyl biphenyl diaminonapthalene (DDBDN) have been studied in their pellet form. All the polychelates show semiconducting behaviour in the range 293 to 520°K. The value of activation energy lies in the range 0.163 to 0.642 eV.

INTRODUCTION

Semiconducting behaviour was systematically developed by Brattain *et al.*[1] The semiconducting properties of polymer metal complexes have gained sufficient ground in recent years. Although a variety of conjugated organic molecules are known to act as semiconductor, carrier mobility in them usually is very low. This is due to the difficulty which electrons experience in jumping from one molecule to another and so the carrier mobility in compounds of this kind increases with increasing molecular size[2, 3]. Till now a unified theory of the transport phenomena and of the generation mechanism of the charge carrier is not elaborated[4]. Some work on the semiconducting properties of polychelates of Schiff base was reported from this laboratory[5]. Pekaln and Kotosonov[6] have studied the electrical conductivity of Phenol-formaldehyde resin. An industrially useful semiconducting materials has been reported by Dewar *et al.*[7] Since delocalised electrons and conjugation impart semiconducting properties to compounds, the present study deals with electrical properties of some polychelates of polymeric ligands which may serve as potential semiconductors.

EXPERIMENTAL

The polychelates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) obtained from 4,4'-dihydroxy 3,3'-diacetyl biphenyl-dithiooxamide, (DDBDO) and 4,4'-dihydroxy-3,3'-diacetyl biphenyl diaminopyridine (DDBOP) and 4,4'-dihydroxy 3,3'-diacetyl biphenyl diaminonaphthalene (DDBDN) were prepared by interfacial polycondensation. All the polychelates in the form of coloured powders were found to be insoluble in common organic solvents.

The D.C. conductivity of the polychelates over a range 293–520 K of temperature were measured in their pellet form using BPL-India Million Megohmmeter RM-160 MK IIIA and Universal bridge TF–2700. The instrument could read and measure upto 10 MΩ to 10^6MΩ and 0.1 Ω to 10 MΩ

respectively and test voltage varied from 50 to 500 volts, the accuracy being at the lower range ± 5%. Pellets of 1.2 cm in diameter and 0.25–0.30 cm, were prepared by pressing finely powdered samples at $10t/cm^2$. On both sides of the pellets a thin layer of colloidal graphite was applied, which acts as electrode. The pellet of the test sample was put in a typical cell fabricated in this laboratory and resistance in Megohms was calculated using the expression

Resistance in Megohms
= Meter reading × Applied Voltage × Multiplying factor

multiplying factor being 10 10^2, 10^3 etc.

The sample was heated in a tubular furnace in which D.C. conductivity cell snugly fitted, the temperature of the furnace being increased by steps from room temperature to about 220°C and regulated by using Dimmerstat and sunvic dial.

The slope values obtained from log σ vs $10^3/T$ were converted to E_a values in eV by using expression[8].

$$\text{Slope } (-\text{ve}) = E_a/2.303 \times 0.864 \times 10^{-4}.$$

It is to be noted that resistivities σ of these sample were obtained only after subjecting them to several temperature increases. During the D.C. conductivity measurements several errors crop in. Grain boundaries are developed during compression, metallic particles of the die may get adhered during pelletisation or there may be an imperfect contact of the electrodes to the pellets due to slight deformation during pellet formation. In the present work author applied several compression cycles before taking the final results of the conductivity measurements and only limiting values were chosen as standard.

RESULTS AND DISCUSSION

The values of the thermal activation energy are given in Table 1. Also, in the same Table there are given the values of electrical conductivity at different temperatures. The resistance values of the pellets of the sample ranging from room temperature to 220°C were converted into conductivity values (σ) by taking into account the thickness of the pellet and its diameter and evaluating thickness/area parameter of the pellet of a particular sample. Generally the diameter of the pellet remained constant (1.20 cm) since the same die was used and the thickness varied from 0.25 to 0.30 cm according to the amount of sample pressed. The results of the D.C. conductivities are presented here in the form of plots of log σ vs 1000/T as the range of conductivities was found to be 1.101×10^{-5} to 1.78×10^{-12} ohm^{-1} cm^{-1}.

In the plots there are two distinct regions. In the low temperature region the slopes of plots have small values and the polychelates present extrinsic

TABLE 1

ELECTRICAL CONDUCTIVITY DATA OF DDBDO, DDBDP AND DDBDN POLYCHELATES

Metal	Ligand					
	DDBDO (324, 374, 514 K)	E_a(eV)	DDBDP (309, 374, 519 K)	E_a(eV)	DDBDN (318, 378, 518 K)	E_a(eV)
Manganese	5.011×10^{-12}		2.718×10^{-11}		2.301×10^{-3}	
	1.047×10^{-11}	0.163	6.116×10^{-11}	0.334	1.291×10^{-12}	0.397
	4.665×10^{-11}		2.038×10^{-9}		3.013×10^{-11}	
Iron	4.168×10^{-9}		2.324×10^{-11}		1.395×10^{-9}	
	5.623×10^{-8}	0.314	1.065×10^{-10}	0.238	2.166×10^{-9}	0.367
	1.064×10^{-7}		1.253×10^{-9}		2.415×10^{-8}	
Cobalt	6.108×10^{-10}		1.789×10^{-12}		1.905×10^{-12}	
	1.780×10^{-9}	0.642	4.473×10^{-12}	0.425	9.529×10^{-12}	0.241
	8.900×10^{-8}		1.789×10^{-10}		9.740×10^{-11}	
Nickel	6.160×10^{-11}		2.185×10^{-10}		8.616×10^{-11}	
	2.730×10^{-11}	0.543	4.304×10^{-10}	0.409	1.846×10^{-10}	0.397
	5.460×10^{-9}		4.735×10^{-9}		1.520×10^{-9}	
Copper	7.923×10^{-7}		2.472×10^{-11}		2.976×10^{-11}	
	3.671×10^{-6}	0.193	1.047×10^{-10}	0.463	9.923×10^{-11}	0.542
	1.101×10^{-5}		1.275×10^{-9}		7.412×10^{-10}	

conduction. In the high temperature region a linear dependence of log $\sigma = F(10^3/T)$ was observed. In this temperature domain the polychelates present intrinsic conduction[9]. There is an anomalous electrical conductance change with temperature in Ni(II), Co(II) and Fe(II)-DDBDO polychelates; that is, above room temperature to nearly 85°C, the conductance decreases as temperature increases and after 85°C the conductance increases with temperature *i.e.* initial trend is a typical of metallic conduction[10] where conductivity (σ) decreases as temperature rises while the latter part of behaviour is a characteristic of semiconduction[11]. The metal-metal interaction is may be responsible for anomalous behaviour of these polychelates[12,13].

In the intrinsic conduction domain, the temperature dependence of the electrical conductivity obeys the well known equation[14]

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

where,

k = Boltzmann constant

σ_0 = electrical conductivity at temperature $T \rightarrow \infty$

σ = electrical conductivity at temperature T = T

E_a = thermal activation energy of electrical conduction.

The value of the activation energy was determined from the high temperature part of the curves $\log \sigma = f\left(\frac{10^3}{T}\right)$. From the analysis of our results, it can be assumed that the difference in electrical properties of polychelates studied are determined mainly by their chemical structure[9]. Over the whole temperature range the values of the electrical conductivity vary between 7.67×10^{-7} to 5.73×10^{-12}, 1.27×10^{-9} to 1.78×10^{-12} and 2.16×10^{-9} to 9.50×10^{-12} ohm^{-1} cm^{-1} for DDBDO, DDBDP and DDBDN polychelates. The activation energy increased in the order Co > Ni > Fe> Cu > Mn, Cu > Co > Ni > Mn > Fe and Cu > Ni > Mn > Fe > Co respectively for DDBDO, DDBDP and DDBDN polychelates. After the comparison of the electrical properties of the polychelates of DDBDO, DDBDP and DDBDN, we conclude that the influence of nature of the metal atoms is small enough. The conductivities are in the order of 10^{-12} to 10^{-5} ohm^{-1} cm^{-1} due to comparatively small intra and intermolecular charge transfer of polymeric ligands and polychelates[15]. The nature of conduction (n or p type) in the polychelates investigated could not be established because of lack of instrumentation for measuring Hall-coefficients and the difficulty in getting the polychelates as well defined crystals.

ACKNOWLEDGEMENTS

Authors are thankful to Head of the Department of Chemistry, Nagpur University, for facilities. One of us (ASA) thanks the UGC, New Delhi for awarding JRF.

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[*Received*: 7 August 1989; *Accepted*: 15 December 1989] AJC-123