Electrical Conductivity Study of Some Chelate Polymers

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Abstract

Metal polychelates of Cr(III), Fe(III), Mn(III), Ti(III), Zr(IV), VO(IV), MoO_2(VI) and UO_2(VI) with bis-bidentate Schiff base 4,4'-bis-[(N-propane salicylaldimine-5)-azo] biphenyl (BNPSAP) have been synthesised. All these polychelates were coloured solids and insoluble in water and common organic solvents. These have been characterized by elemental analysis, magnetic susceptibilities, spectroscopic (reflectance and IR) data, and TGA. The electrical conductivity of the ligand and polychelates has been measured in their pellet form at temperature 373 K. The room temperature electrical conductivity (σ)values of the polychclales lie in the range (3.12 x 10^{-10} to 9.55 x 10^{-13} Ω^{-1} cm^{-1}) typical of semiconductors. The plots of log *σ* vs 1/T are found to be linear, also indicating the semiconducting nature of the ligand and the polychelates in the studied range of temperature. The general behaviour of electrical conductivity *(σ)* obeys the relation $\sigma = \sigma_0 \exp(-E_a/kT)$, where σ_0 is a constant, E_a, the activation energy of conduction process, T the absolute temperature and k the Boltzman constant. The energy of activation (E_a) of BNPSAP and polychelates is obtained from the slopes of plots which is in the 0.084 – 1.17 eV range and increases in the order Mn(III) > UO_2(VI)>VO (IV) > MoO_2(VI) > Fe(III) > BNPSAP > Cr(III)>Ti(III)>Zr(IV).

Keywords: Electrical conductivity 1, Semiconducting 2, Polyschiff base 3.

Introduction:

The polymer metal complexes have gained much attention due to their semiconducting and catalytic properties [1]. Literature survey reveals that the most of the work has been done on the bivalent transition metal complexes of Schiff bases but few report are available on azo dye metal polychelates of tri- tetra- and hexavalent transition and inner transition metal ions with Schiff base ligand having an azo group [2]. Hence we have synthesised a new Schiff base ligand 4,4'-bis-[(N-propane Salicylaldimine -5)-azo] biphenyl (BNPSAP) and its polychelates with Cr(III), Fe(III), Mn(III), Ti(III), Zr(IV), VO(IV), MoO_2(VI) and UO_2(VI). These have been characterized by elemental analysis, magnetic susceptibilities, spectroscopic (reflectance and IR) data and TG analysis.

Experimental

The Schiff base ligand BNPSAP and its polychelates were prepared by the known methods reported earlier [3].The d.c. electrical conductivity was measured in the pellet form using d.c. micro volt meter. The well powdered compounds were pelletalisedisotactically in a steel die under a pressure of 5 x IO^7 kg m^{-2} with the help of hydraulic press. A thin aluminium foil was used for good electrical contact and the pellet was placed between two spring-loaded brass electrodes of a specially designed sample holder. For electrical conductivity measurement at different temperatures, a suitable electric furnace was used and the sample holder was kept in the centre of the furnace.

Results and Discussion:

The elemental analysis suggests 1:1 (metal; ligand) stoichiometry, I.R. spectral studies indicate that the ligand BNPSAP acts as a bis-bidentate molecule coordinating through phenolic oxygen and azomethine nitrogen atoms. The two chelating sites cannot interact with the same metal ion for steric reasons, therefore polymeric chain is formed. The formation of chelate polymer is also supported by the fact that all the polychelates obtained are coloured solids and insoluble in water or common organic solvents.

The electrical conductivity was studied at temperature 373 K, as shown in Table 1.

The electrical conductivity (σ) of the ligand and the polychelates, at room temperature, was found to be between 3.12×10^{-10} and 3.55×10^{-13} Ω^{-1} cm^{-1} indicating their semiconducting nature [4]. The electrical conductivity of these polychelates at 373 K decreases in the following order BNPSAP < Ti (III)<Zr(IV) <UO_2(VI) <VO(IV) <MoO_2(VI) <Cr(III) <Mn(III) <Fe(III).

The general behaviour of electrical conductivity *(σ)*obeys the relation (1).

$$\sigma = \sigma_0 \exp(-E_a / kT) \qquad (1)$$

Where σ_0 is a constant, E_a the activation energy of conduction process, T the absolute temperature and k the Boltzman constant. The temperature dependences of the electrical conductivity of the ligand and the polychelates are shown in Fig. 1. The plots of log σ vs 1/T are found to be linear indicating their semiconducting nature in the studied range of temperature. The plots of conductivity explain a positive temperature coefficient of conductivity. With conventional semiconducting behavior when the conductivity increase with increase in temperature and so, the plots indicating semiconducting behavior [5].

Activation energy is direct measure of band gap of semiconductors. Thus lower the activation energy lower will be band gap [6]. Among the studied polychelates, the electrical conductivity at 373 K varied in magnitude. This may be attributed to the difference in their conjugation or resonance and ionic radii of different metal ions.

The activation energy of electrical conduction of BNPSAP and polychelates is obtained from the slopes of these plots, in the higher temperature region, which lies in the range 0.084 - 1.17 eV, and increases in the order Mn(III) > UO_2(VI) > VO (IV)> MoO_2(VI)> Fe (III) > BNPSAP > Cr (III)> Ti(III)>Zr(IV).

The results indicate that the electrical conductivity and activation energy of polychclates vary with the metal ion, which may be clue to the incorporation of different metal ions in chelates, which increases the ionization tendency [7].

Table 1. Electrical data of ligand and polychelates

Ligand / Polychelates	Electrical Conductivity (σ) (Ω^{-1} cm^{-1})	Activation energy (E_a)(eV)	Band gap
BNPSAP	1.180×10^{-8}	0.592	1.18
$\{[Cr\ BNPSAP.2H_2O]Cl\}_n$	1.78×10^{-11}	0.565	1.13
$\{[Fe\ BNPSAP.2H_2O]Cl\}_n$	9.558×10^{-13}	0.609	1.21
$[MnBNPSAP.OAc]_n$	2.65×10^{-12}	1.17	2.28
$\{[Ti\ BNPSAP.2H_2O]Cl\}_n$	3.12×10^{-10}	0.496	0.992
$[Zr(OH)_2\ BNPSAP]_n$	3.98×10^{-10}	0.180	0.360
$[VO\ BNPSAP]_n$	6.17×10^{-10}	0.849	1.698
$[MoO_2\ BNPSAP]_n$	1.50×10^{-11}	0.084	0.169
$[UO_2\ BNPSAP]_n$	4.01×10^{-11}	1.02	2.04

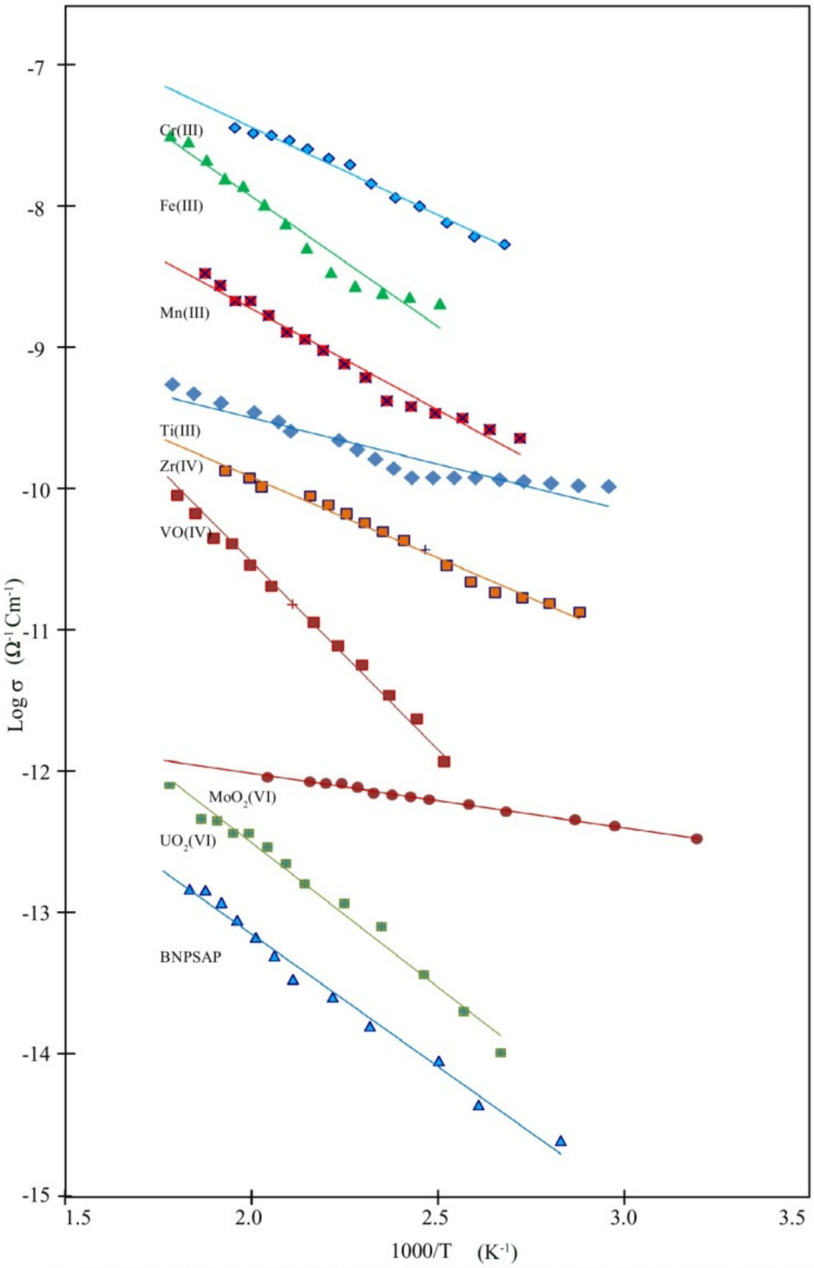

Fig. 1 SOLID STATE CONDUCTIVITY OF BNPSAP AND IT'S POLYCHELATES

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