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Electrical Conductivity Studies on Aldazine Metal Complexes

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***Abstract*— Electrically conducting organometallic complexes are considered to be the most interesting area among the transition metal containing complexes. Because of their great flexibility, paramagnetic properties and diverse structural aspects, a wide range of N-azine based transition metal complexes has been prepared and their complexation behavior was explored. Transition metal-aldazine complexes have been of crucial concern for many years because such transition metal complexes play a vital role in the conduction of molecular materials, which exhibits distinctive conducting properties and finds applicability in diverse areas such as material chemistry and biochemistry. In this present work, author has put an effort to prepare different transition metal-aldazine complexes by microwave method using N-azines as ligands. The investigation of D.C electrical properties of synthesized metal-aldazine complexes was done at a varied temperature from 424K to 540 K.**

***Index Terms*— Transition metal complexes, activation energies, conductivity, aldazines, ligands**

I. INTRODUCTION

Since 1980, the scientific community have been publishing the review articles in the field of organometallic complexes and utmost attention has been focused on the preparation and compatibility of conducting transition metal complexes [1-5]. Possible applications for such materials include high temperature coatings, electrode materials, LED's, lasers and homogeneous catalysts**.** The electrically conducting organometallic complexes are considered to be the most interesting area among the transition metal containing complexes. Because of their great flexibility, paramagnetic properties and diverse structural aspects, a wide range of N-azine based transition metal complexes has been prepared and their complexation behaviour was explored.

II. METHODS AND MATERIAL

Metal (II) chlorides (0.002M) were refluxed for about 4-5 hours, with azine ligands taken in a round bottom flask in an ethanolic medium. Then to the reaction mixture, sodium acetate was added and the resulting reaction mixture was irradiated by microwave with the intensity 50% for about 2-3 min. The metal (II) complexes separated was filtered and washed with excessive distilled water followed by ethanol and dried in vacuum. The obtained complexes were purified by soxhlet extraction using alcohol. The same procedure was followed for preparing Fe (III), VO (II) complexes of the aldazine ligands. But ZrO (II) complexes were prepared in methanol medium and same procedure was adopted. The obtained complex was powdered and extracted with chloroform in a soxhlet thimble for about 3-4hrs. The so obtained product was then subjected to successive filtration using ethanol and dried to achieve constant weight [6-7].

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III. RESULTS AND DISCUSSION

The variation of electrical conductivity with the inverse of temperature for the synthesized complexes was depicted in the Fig.1 (a-c). It was seen that conductivity decreases with increase in temperature ($T^{-1/4}$).The variation in electrical conductivity with raising temperature in a sample material with partial localization of charge carrier changes from T^{-1} behaviour to $T^{-1/n}$ at low temperatures. As a consequence, the charge transport mechanism can be summarized here: (i) conduction because of excitation of charge carriers surpassing the mobility shoulders into delocalized states; (ii) transition of charge carriers between the confined states near the fermi energy. It is seen in the Fig.1 (a-c), the d.c conductivity of the prepared aldazine solid complexes depends on the $T^{-1/4}$ predicting three-dimensional hopping approach for the electrical charge carriers transported. M.S. Masoud et.al. reported that, at temperature between 330 and 380 K, these complexes lies in the semi-conducting regime when the conductivity enhances profoundly with increase in temperature. At varied temperature from 324K to 380 K, the electrical activation energies of the prepared complexes show positive values and presented positive temperature coefficient of electrical conductivities. The σ_{dc} of the synthesized aldazine complexes exhibit increase in trend with rise in absolute temperature according to the equation:

$$\sigma = \sigma_o Exp^{(-Ea/KT)}$$

The activation energies of the prepared aldazine solid complexes were computed from the slopes of the obtained graphs as shown in the Fig. 1(a-c) and are depicted in Table 1. Among these complexes, $Fe(C_{14}H_{12}N_2O_2)_2.H_2O$ exhibit relatively high activation energy compared to $ZrO(C_{14}H_{12}N_2O_2)_2$ and $VO(C_{14}H_{12}N_2O_2)_2$ complexes, this can be attributed to the activation from the valance band to the conduction band, which is obvious an intrinsic behavior.

Table 1: Calculated activation energies of the synthesized complexes

Samples	Activation Energy, Ea (ev)
$ZrO(C_{14}H_{12}N_2O_2)_2$.	0.4873
$VO(C_{14}H_{12}N_2O_2)_2$.	0.3142
$Fe(C_{14}H_{12}N_2O_2)_2 .2 H_2O$	1.5049

The electrical conductivity trend of these prepared complexes can be interpreted on the basis, that they have semi-conducting properties [10-11]. The electron or hole movement in these complexes may be due to hopping process of charge carriers. Accordingly, the hopping mechanism can be distinguished as follows:

I. the charge carriers drifts from one localized centre to the neighboring centre. When it rests on a new site it makes the neighboring ions to take position into their localizations and the charge carriers isolated transiently in the potential well yielding atomic polarization,

II. the electron relaxed at its new site get relocated to its nearest centre when thermally activated [12-17].

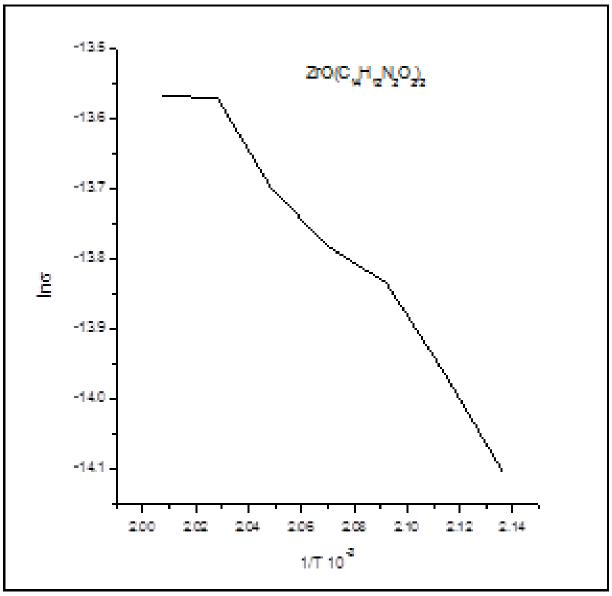

Fig: 1(a)

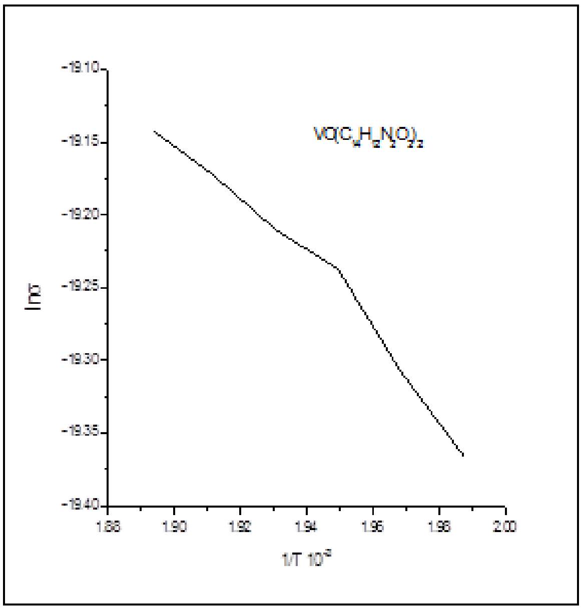

Fig: 1(b)

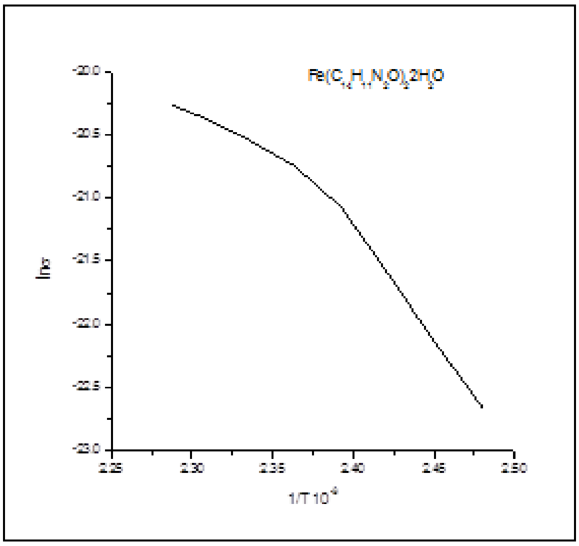

Fig: 1(c)

Fig: 1 shows the behavior of D.C electrical conductivity with 1/T for (a) ZrO $(C_{14}H_{12}N_2O_2)_2$, Fig: (b) VO $[C_{14}H_{12}N_2O_2]_2$ and Fig: (c) Fe $[C_{14}H_{12}N_2O_2]_{2}.2H_2O$

IV. CONCLUSION

In the present work, different transition metal-azine complexes were successfully synthesized by microwave method using N-azines as ligands. Different metal-aldazine complexes investigated were followed over the temperature range 423-526K. The $\sigma_{d.c}$ of the synthesized aldazine complexes increases with increasing temperature. At temperature range 300-370K they unveiled non-metallic behavior; however they show semi-conducting behaviour at elevated temperature range 372-526K. The hierarchy of the activation energies for the prepared aldazine complexes follows the order: Fe >Zr> VO.

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