Electrical Conduction in Some Ternary Metallo-Organic Solid Complexes of Biological Importance and Compensation Effect

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Synopsis. The electrical conduction in some ternary solid complexes of Cu(II) with 2,2′-bipyridyl/1,10-phenanthroline and several amino acids (e.g., α-alanine, leucine, tryptophan, glycine, and norvaline) is studied as a function of temperature. These materials show semiconductivity. Results suggest that true compensation effect is valid for most of the materials studied. Importance of characteristic temperature (T_o) in biological process is pointed out.

Investigations on the electrical conduction properties in biologically important solid materials may bring significant contribution[1,2] to the field of 'bioenergetics'. In general, ternary complexes (mixed ligand complexes) of different metal ions play an important role in biolgical system.[3,4] Copper is one of the essential trace elements[3] present in living organism and in general copper exists in complexed form either with small molecules like amino acids or with macromolecules such as proteins. Several ternary complexes of Cu(II) containing amino acids have been detected recently in human serum.[5–7] The ternary complexes of Cu(II) formed by the interaction of one amino acid and a nonionized ligand like 2,2′-bipyridyl, 1,10-phenanthroline are typical examples[8–11] of such complexes present in biological systems.[3] Such complexes are expected to take part actively in the biological process[12] involving (i) electron transport and (ii) dioxygen transport and metabolism. In spite of the importance of metallo-organic complexes in biological process scant attention has been paid to the measurment of their electrical properties. Therefore, it was though worthwhile to study the electrical properties of some ternary solid metallo-organic complexes. This present paper concerns the validity of compensation rule[13–15] in the electrical conduction process in some ternary solid complexes of Cu(II) with 2,2′-bipyridyl/1,10-phenanthroline and amino acids.

In case of some organic semiconductors as reported[13–15] earlier the different values of activation energy (E) obtained by adsorption of vapors on semiconductor powders and the specific conductivity $\sigma(T)$ at a temperature T are related by the three constant expression

$$\sigma(T)=\sigma_o' \exp(E/2kT_o)\exp(-E/2kT) \qquad (1)$$

where k is the Boltzmann constant and the parameters σ_o' and T_o are constants for a particular semiconductor. Thus, the pre-exponential factor σ_o in the usual semiconduction expression

$$\sigma(T)=\sigma_o \exp(-E/2kT) \qquad (2)$$

is related to the activation energy (E) by the expression

$$\sigma_o=\sigma_o' \exp(E/2kT_o) \qquad (3)$$

As evidenced from expression (3), $\log \sigma_o$ is linearly related to E which is known as compensation effect (or rule). The origin of this effect and the physical significance of T_o is not yet clear. In this paper it is shown that the true compensation effect is valid for some ternary complexes of Cu(II) containing amino acids. The origin of this effect in this case and the possible role of T_o in biological system are discussed.

Experimental

The ternary metallo-organic solid complexes used in this investigation are of the type $[Cu(II)\cdot A.L]Cl\cdot H_2O$ where A represents 2,2′-bipyridyl/1,10-phenanthroline and LH=α-alanine, leucine, tryptophan, glycine, and norvaline. These complexes were synthesized and characterized by usual procedure.[10,11] The reagent chemicals used were of AR or GR quality (E.Merck, BDH, LOBA). This synthesis work was carried out by Prof. M. C. Saxena and his co-workers in the Deptt. of Chemistry, Dr. H. S. Gour University, Sagar: 470003, India. These samples were dried under vacuum before use. The finely powdered sample pressed in a sandwich cell[13,16] between a conducting glass and a stainless steel electrode at moderate pressure by spring clips. The separation between the electrodes was maintained by a two mil (1 mil=0.00254 cm) thick Teflon spacer. The sample cell was then placed in a suitably designed conductivity chamber[13,16] made of brass and fashioned with Teflon. A dc voltage of 27 volts from a dry battery pack was applied across the sample cell. The dark conductivity was measured in vacuum [10^{-3} Torr (1 Torr=133.322 Pa)] using an electrometer, model no. 617, of Keithley Inst. Inc., U.S.A. The thermo emf was measured by a digital panel meter, model no. HIL: 2301, India. Details of the experimental arrangement is similar to that described earlier.[13,16]

Results and Discussion

The electrical conductivity of the materials under investigation was studied in the temperature range 298 K to 345 K. In all the cases an increase in conductivity with increasing temperature was observed which indicates that these materials behave like semiconductors. Each measurement was repeated several times in vacuum. All the measurements gave consistent results. The $\log \sigma$ vs. $1/T$ plots for some complexes under study are shown in Fig. 1. It is seen that all the linear plots intersect the ordinate at wide variety of positions but all they meet at a point of intersection corresponding to a fixed tempereture (307 K) showing that the conductivity at this temperature is same for all these meterials. The linear plots for the complexes containing (bipy·α-ala) and (1,10-phen·leu) are not included in Fig. 1 as the corresponding linear plots do not pass through the common point of intersection.

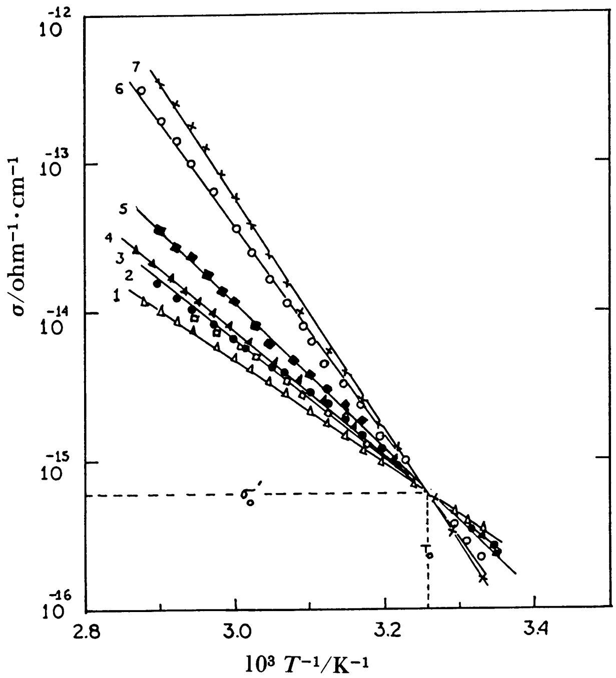

Fig. 1. Plot of $\log \sigma$ value vs. $1/T$ for some ternary solid complexes[††] of Cu(II) with 2,2′-bipyridyl/1,10-phenanthroline and several amino acids.
The line (1) for [Cu(II)·1,10-phen·ala]Cl·H_2O [—△—]; (2) for [Cu(II)·bipy·trp]Cl·H_2O [—□—]-this almost overlaps with (3); (3) for [Cu(II)·bipy·leu]Cl·H_2O [—●—]; (4) for [Cu(II)·bipy·norval]Cl·H_2O [—▲—]; (5) for [Cu(II)·1,10-phen·trp]Cl·H_2O [—■—]; (6) for [Cu(II)·1,10-phen·gly]Cl·H_2O [—○—]; and (7) for [Cu(II)·bipy·gly]Cl·H_2O [—×—].
These lines were fitted by the method of least squares. For each linear plot at least 20 data points were considered. To avoid overcrowding of data points (particularly near T_o) only few representative data points are shown for each complex.
The value of T_o=307 K; σ_o'=6.2×10^{-16} (Ω·cm)$^{-1}$.
††Standard abbreviations used.

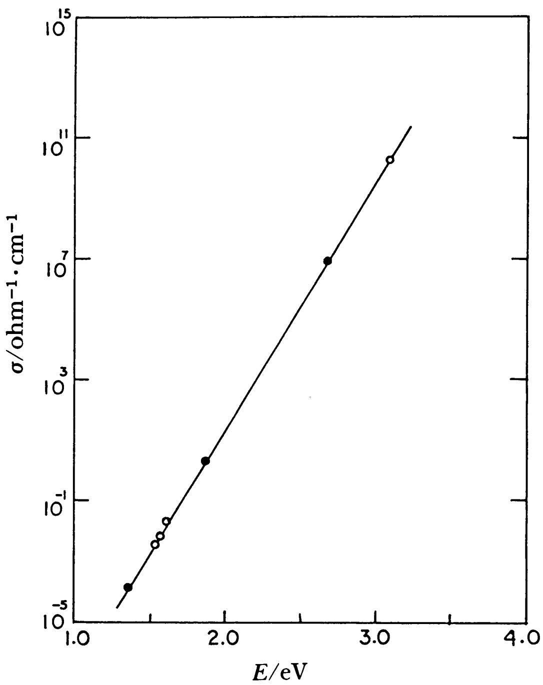

Fig. 2. Plot of $\log \sigma_o$ value vs. E for some ternary solid complexes of Cu(II) with 2,2′-bipyridyl/1,10-phenanthroline and several amino acids.
—○— for complexes with 2,2′-bipyridyl and amino acids; —●— for complexes with 1,10-phenanthroline and amino acids. Value of T_o=307 K; σ_o'=7.55×10^{-16} (Ω·cm)$^{-1}$.

The reason for this anomally is discussed latter on. The values of E and measured values of σ_o for the complexes are shown in Table 1. The temperature where all the materials show equal conductivity, $\sigma(T_o)$, is known as characteristic or compensation temperature (T_o). The value of σ at T_o gives σ_o' value. The values of T_o and σ_o' obtained from the $\log \sigma$ vs. $1/T$ plots are 307 K and 6.2×10^{-16} (Ω·cm)$^{-1}$ respectively. To test the validity of compensation effect $\log \sigma_o$ was plotted against E and a linear plot as expected from expression (3) is shown in Fig. 2.

The compensation effect is thought[17] to arise from the existence of a linear relationship between the activation energy and activation entropy of the system. It has been pointed out by Johnston and Lyons[17] that if a true linear free energy relationship (LFER) does hold for a dark conduction process a definite point of intersection for the Arrhenius plots of the experimental data must exist as we have observed in Fig. 1. In the experiment of Johnston and Lyons[17] the $\log \sigma_o$ vs. E plot was linear, but a very poor correlation between $\log \sigma$ and E was observed in one component crystal of anthracene by changing its purity and doping with tetracene. On the basis of that experimental results it was concluded that a simple linear relation between $\log \sigma_o$ and E is not sufficient for judging the validity of compensation effect. However, in the present case it is clearly seen that the true compensation effect is valid.

There are number of theses (models) as mentioned in earlier communications[13,14] about the mechanism

Table 1. The Values of E and σ_o for Some Ternary Solid Complexes[a)] of Cu(II) with 2,2′-Bipyridyl/1,10-Phenanthroline and Several Amino Acids

Complexes studied	$\frac{E}{\text{eV}}$	Measured value of $\sigma_o/\Omega^{-1}\cdot\text{cm}^{-1}$
[Cu(II)·bipy·leu]Cl·H_2O	1.53	3.54×10^{-3}
[Cu(II)·bipy·trp]Cl·H_2O	1.57	6.41×10^{-3}
[Cu(II)·bipy·norval]Cl·H_2O	1.61	1.64×10^{-2}
[Cu(II)·bipy·ala]Cl·H_2O[b)]	1.63	4.25×10^{-2}
[Cu(II)·bipy·gly]Cl·H_2O	3.07	1.71×10^{10}
[Cu(II)·1,10-phen·ala]Cl·H_2O	1.35	1.07×10^{-4}
[Cu(II)·1,10-phen·trp]Cl·H_2O	1.86	1.72
[Cu(II)·1,10-phen·leu]Cl·H_2O[b)]	1.88	5.84
[Cu(II)·1,10-phen·gly]Cl·H_2O	2.66	7.72×10^{6}

a) Standard abbreviations used. b) Compensation effecct is not valid for this complex.
(The samples are arranged separately for each primary ligand in order of increasing E-value).

of conduction in organic semiconductors leading to compensation effect. The applicability of different models has already been discussed.[13,14] A models depending on the interaction between the electrons and the vibrational motion[18] of the molecules appears suitable[13] to give a possible mechanism behind such compensation effect in case of some polyene[13,14] and nitroaromatic[15] semiconductors.

It has been reported by Sigel et al.[19] that the ternary metal complexes under investigation exist predominantly in a 'folded form'. Similar to common biopolymers (peptides, proteins, DNA), these complexes posses defined conformation[20] in their normal state. In the normal condition each atom performs thermally excited movements around its mean position. Also several energetically similar positions may be occupied by the same groups with comparable probability. Any change of external parameters such as temperature, pressure, electric field etc. will influence this dynamics and flexibility of the structure which may lead to changes[20] of conformations. The particular electronic properties of a complex in its normal state will obviously change with the change in its precise conformation. A change in electronic state (as involved in transport) gives rise to an activation entropy[18] because of a change in vibrational frequencies associated with the conformatinal changs. Each compound possesses a definite value of activation entropy arising from the temperature-dependent conformational changes in the temperature range under consideration. The variation in both the electronic energy gap (E_g) and activation entropy (S) can account for compensation effect if the changes in these parameters are given by[18]

$$E_g = E_{g_0} + nE_{g_1} \text{ and } S = S_0 + nS_1$$

where n is a definite number for each compound and E_{g_0}, E_{g_1}, S_0, and S_1 are same for all the compounds. In this case the characteristic temperature is given by

$$T_0 = E_{g_1}/(2S_1).$$

Unfortunately due to the fact that the nature of these complexes is not precisely known at present, the activation entropy S (hence S_1) is a relatively obscure quantity and any quantitative estimate of T_0 could not be done.

The compensation behavior depends on the molecular property[13-15] of the complexes/materials involved and T_0 plays an important role in dark conduction process. Though attempts have been made to understand the compensation behavior as mentioned in the earlier communications,[13,14] the factors on which the value of T_0 depends is not yet clear. It should be mentioned here that compensation effect is not valid for the ternary complexes of Cu(II) with 2,2′-bipyridyl and alanine; and 1,10-phenanthroline and leucine ligands possibly due to different types of conformational changes in these complexes on thermal agitation. Such anomaly has also been observed[15] previously in some nitroaromatics on adsorption of several vapors related to an experiment on compensation effect.

The observed value of T_0 in most of the reported data is either much higher[13] or lower[14,15] than physiological tempereture. It is interesting to note that the characteristic tempereture for the materials under investigation is near the physiological temperature. Since at this temperature (T_0) the collective electronic properties of these materials are significantly changed, the presence of these materials in a biological system may have some important role in the biological processes involving transfer of electrons (charges) near physiological temperature. Investigation with complexes containing other amino acids as well as other metal ions could be of much interest but unfortunately such experiment could not be performed as the materials were not available at this moment.

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