S U M M A R Y

SUMMARY

Intrinsic semiconductivity of chelate polymers of various metal-ligand systems has been studied in recent years. A metal atom introduced into the organic ligand so that through-conjugation may result can increase the mobility of charge-carriers and hence the conductivity of the system. It may be influenced by the coplanarity of the system and by inter-molecular bonding or separation of the molecular chains.

With a view to study the semiconductivity of metal chelates and chelate polymers wherein metal may be 4,5 or 6 coordinate. We planned,

(1) to prepare various ligands and their chelate polymers.

(2) to prepare molecular complexes of transition metal chelates with halogens.

(3) to determine the magnetic susceptibility, IR absorption spectra etc. of some of them and

(4) to study their electrical resistivity over a range of temperature.

Ligands :

The ligands used for the preparation of metal complexes and metal chelate polymers were 2,5-dihydroxy-p-benzoquinone, naphthazarin, quinizarin, anthrarufin, dioxime of 1,5-diacetyl-2,6-dihydroxy naphthalene, 1,5-diamino-2,6-dihydroxy naphthalene, 5,8-dihydroxy quinoxaline,

4,6-diacetyl resorcinol, oxalyl bis(salicylidene hydrazide), α-diphenyl glyoxime, dimethyl glyoxime and 2,3-dioxobutyranilide dioxime.

These were prepared by the known methods.

Amines :

The amines used for the preparation of ammino chelate polymers were pyridine,benzidine,p-phenylene-diamine, thioaniline and azoaniline. Thioaniline and azoaniline were prepared by the known methods.

Metal ions :

The transition metal ions used were cobalt(II), nickel(II), copper (II) and iron (II).

Chelate polymers of 2,5-dihydroxy-p-benzoquinone :

(a) Cobalt (II) chelate polymers :

" Aquo" and ammino cobalt chelate polymers (amine = pyridine,benzidine,azoaniline and thioaniline) of 2,5-dihydroxy-p-benzoquinone were prepared. Some of these polymers contained molar fractional amounts of amine per cobalt atom. They are insoluble in all common solvents and do not melt upto 400 ^{o}C. On the basis of analysis and magnetic moment they are formulated as chelate polymers consisting of octahedral monomeric units. Thermal studies of BQCo B and BQCo Py and IR spectral studies of BQCo B were made. The results are used to elucidate their structures.

The plots of $\log_{10}$ (resistivity) vs. reciprocal temperature for these polymers are linear as expected by

the equation (a).

$$\rho = \rho_0 \times e^{\frac{E}{2kT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(a)$$

Hence ρ_0 and E are evaluated. It is found that when F=0 (or F=1)

$$\rho_0 = \gamma \times e^{-\beta E} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(b)$$

where F is the molar fraction of the amine per cobalt atom and γ and β are constants.

Hence,

$$\rho = \gamma \times e^{E\left[\frac{1}{2kT} - \beta\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(c)$$

When $F \neq 0$,

$$\rho_0 = \gamma^{\frac{(1+F)}{2}} \times e^{-E\beta\left(\frac{1+F}{2}\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(d)$$

and

$$\rho = \gamma^{\frac{(1+F)}{2}} \times e^{E\left[\frac{1}{2kT} - \beta\left(\frac{1+F}{2}\right)\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(e)$$

(b) Nickel chelate polymers :

" Aquo" and ammino nickel chelate polymers (amine = pyridine, p-phenylenediamine, thioaniline and azoaniline) of 2,5-dihydroxy-p-benzoquinone were prepared. They are insoluble in all common solvents and do not melt upto 400 ^{o}C. On the basis of analysis and magnetic moment they are formulated as chelate polymers consisting of

octahedral monomeric units. IR spectrum of BQNi was obtained.

The plots of $\log_{10}$ (resistivity) vs. reciprocal temperature are linear. Hence E and ρ_o are evaluated. The relation between ρ_o and E for ammino polymers is shown by the equation,

$$\rho_o = \gamma^{n\left(\frac{1+F'}{2}\right)} \times e^{-\beta E n\left(\frac{1+F'}{2}\right)}$$

where n is the number of rings associated with the amine molecule, F' represents half the number of ammino groups coordinated per nickel atom and β and γ are constants.

Hence,

$$\rho = \gamma^{n\left(\frac{1+F'}{2}\right)} \times e^{E\left[\frac{1}{2kT} - \beta n\left(\frac{1+F'}{2}\right)\right]}$$

when $F'=0$, $\rho_o = \gamma \times e^{-\beta E}$ and $\rho = \gamma \times e^{E\left[\frac{1}{2kT} - \beta\right]}$

(c) Copper chelate polymers :

" Aquo " and ammino copper chelate polymers (amine = pyridine, benzidine, thioaniline and azoaniline) of 2,5-dihydroxy-p-benzoquinone were prepared. They are insoluble in all common solvents and do not melt upto 400 ^{o}C. On the basis of analysis and magnetic moment, they are formulated as chelate polymers consisting of square

or square pyramidal monomeric units. IR spectrum of BQCu A was obtained.

The plots of $\log_{10}$ (resistivity) vs. reciprocal temperature are linear. From these E and ρ_o are evaluated and the relation between ρ_o and E for the ammino chelate polymers is shown by the equation,

$$\rho_o = \gamma \left(\frac{2}{1+F}\right)^2 \times e^{-\beta E \left(\frac{2}{1+F}\right)^2}$$

and

$$\rho = \gamma \left(\frac{2}{1+F}\right)^2 \times e^{E\left[\frac{1}{2kT} - \beta\left(\frac{2}{1+F}\right)^2\right]}$$

when $F = 0$, $\rho_o = \gamma \times e^{-\beta E}$ and $\rho = \gamma \times e^{E\left[\frac{1}{2kT} - \beta\right]}$.

(d) Iron chelate polymers :

" Aquo" and ammino iron chelate polymers (amine = pyridine, benzidine, thioaniline and azoaniline) of 2,5-dihydroxy-p-benzoquinone were prepared. They are insoluble in all common solvents. On the basis of analysis and magnetic moments they are formulated as chelate polymers consisting of octahedral monomeric units. IR spectrum of BQFe was obtained.

The plots of $\log_{10}$ (resistivity) vs. reciprocal temperature are linear. From these, the values of ρ_o and E are evaluated. The relation between ρ_o and E for the ammino chelate polymers is shown by the equation,

$$\rho_0 = \gamma \times e^{\frac{1}{1+F} - \beta E\left(\frac{1}{1+F}\right)}$$

hence,

$$\rho = \gamma \times e^{\frac{1}{1+F} E\left[\frac{1}{2kT} - \beta\left(\frac{1}{1+F}\right)\right]}$$

when $F = 0$, $\rho_0 = \gamma \times e^{-\beta E}$ and $\rho = \gamma \times e^{E\left[\frac{1}{2kT} - \beta\right]}$

(e) Complexes with organic bases :

Addition products of 2,5-dihydroxy-p-benzoquinone with a diamine (benzidine, p-phenylenediamine and azoaniline) were prepared. Their spectra in solution in the ultraviolet region were studied. The conductivity of BQ B in solution was also investigated and related to its structure.

The plots of $\log_{10}$ (resistivity) vs. reciprocal temperature are linear and from these the values of E and $\log \rho_0$ are evaluated. ρ_0 and E are related by the equation

$$\rho_0 = \gamma \times e^{-\beta E}$$

and $$\rho = \gamma \times e^{E\left[\frac{1}{2kT} - \beta\right]}$$

(f) General :

It has been observed that the curves of $\log_{10}\gamma$ or β vs. atomic number of the metal atom have the same

nature as the CF stabilisation curves.

For the aquo chelate polymers of 2,5-dihydroxy-p-benzoquinone, the equation found suitable is

$$\rho_o = \gamma \times e^{-\beta E}$$

It is considered that this equation may be modified as follows when chelate polymers of other ligands are considered.

$$\rho_o = \gamma \times e^{-U \beta E} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (g)$$

where U is termed as correlation factor.

Chelate polymers of naphthoquinones and anthraquinones :

(a) Chelate polymers of naphthazarin :

Copper and cobalt chelate polymers of naphthazarin were prepared and their magnetic moments were determined.

Plots of $\log_{10}$ (resistivity) vs. reciprocal temperature are linear. From these the values of E and ρ_o are evaluated. These values are used to calculate U.

(b) Chelate polymers of quinizarin :

Copper and cobalt chelate polymers of quinizarin were prepared and their magnetic moments were determined.

Plots of $\log_{10}$ (resistivity) vs. reciprocal temperature are linear. From these, the values of E and ρ_o are evaluated. These values are used to calculate U.

(c) Chelate polymers of anthrarufin :

Copper, cobalt and nickel chelate polymers of anthrarufin were prepared.

Plots of $\log_{10}$ (resistivity) vs. reciprocal temperature are linear. From these, the values of E and ρ_0 are evaluated and these values are used to calculate U.

(d) General :

For the cobalt chelate polymers (BQCo, NQCo, AQCo, AQRCo), a relation has been established that

$$U = \omega\pi + Z \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (h)$$

where π represents the effective number of π-bonds of the chelating ligands per cobalt atom and ω and Z are constants.

In the case of nickel chelate polymers the value of U does not change appreciably with the change in the number of π bonds.

In the case of copper chelate polymers the value of U does not show any uniform variation.

Chelate polymers of naphthalene and quinoxaline derivatives :

(a) Chelate polymers of the dioxime of 1,5-diacetyl-2,6-dihydroxynaphthalene :

Copper and cobalt chelate polymers of the dioxime of 1,5-diacetyl-2,6-dihydroxynaphthalene were prepared.

Plots of $\log_{10}$ (resistivity) vs. reciprocal temperature are linear. Hence values of E, ρ_0 and U are

determined.

(b) Cobalt chelate polymer of 1,5-diamino-2,6-dihydroxy-naphthalene :

Cobalt chelate polymer of 1,5-diamino-2,6-dihydroxy-naphthalene was prepared. Plot of $\log_{10}$ (resistivity) vs. reciprocal temperature is linear. Hence values of E, ρ_o and U are determined.

(c) Chelate polymers of 5,8-dihydroxy quinoxaline :

Copper, nickel and cobalt chelate polymers of the above ligand were prepared.

Plots of $\log_{10}$ (resistivity) vs. reciprocal temperature are linear. Hence the values of E, ρ_o and U are determined.

The values of U obtained by using the equations (g) and (h) for ONCo and QCo are in close agreement.

Cobalt and Nickel complexes :

Cobalt complex of 4,6-diacetyl resorcinol and dinuclear nickel complex of oxalyl bis(salicylidene hydrazide) were prepared.

Plots of $\log_{10}$(resistivity) vs. reciprocal temperature are linear. Hence values of E, ρ_o and U are determined. It is suggested that the value of U for nickel complexes and chelate polymers depends on the number of rings formed by the chelating ligands with nickel.

The halogen adducts of the transition metal complexes of glyoximes :

Bromine adducts of copper, nickel and cobalt complexes of 2,3-dioxobutyranilide dioxime, cobalt complex of diphenylglyoxime and nickel complex of dimethylglyoxime, and iodine adduct of the copper complex of 2,3-dioxobutyranilide dioxime were prepared and magnetic moments of some of them (OOCu Br, OOCo Br) were determined. They are considered to be inclusion type molecular complexes.

Plots of $\log_{10}$ (resistivity) vs. reciprocal temperature are linear. Hence the values of E, ρ_0 and U are determined. Applicability of equations (g) and (h) to the cobalt complexes is considered.

General :

(a) Conjugation :

We find that the conductivity for the cobalt chelate polymers increases in order

$$BQ < NQ < AQ$$

and be related to factor U. However, for copper chelate polymers, conductivity is increasing in order,

$$AQR < AQ \sim NQ < BQ$$

The results indicate that factors other than conjugation are of greater importance in deciding their conductivity.

(b) Metal :

We find that in the case of chelate polymers of copper and cobalt the conductivity shows a variation with the ligands as follows :

BQ : Cu > Co

NQ : Cu ~ Co

AQ : Cu < Co

(c) Anisotropy :

It is suggested that conduction anisotropy may be exerting considerable influence on the conductivity of copper chelate polymers of different ligands.

(d) Long range order :

The degree of polymerisation obtainable in the case of conducting chelate polymers may be 10 or less. This short range order is considered sufficient for conductivity considerations.

(e) Mobility :

From the results of Many, Harnik and Gerlich a relation is derived,

$$\log \sigma_0 \approx 10E^{1} - 13$$

We have suggested a relation

$$\rho_0 = \gamma \times e^{-U \beta E}$$

where γ and β are constants depending on the nature of the metal and the ligand and U is a constant depending on the π- bonds in the ligand or the number of rings formed by the ligand with the metal and a good correlation is established for the complexes and chelate polymers of cobalt and nickel.