Thermochimica Acta, 125 (1988) 9–16
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECT OF TEMPERATURE ON THE ELECTRICAL CONDUCTIVITY OF SOME 4-(SUBSTITUTED)-3-HYDROXY-2-QUINOLINE LIGANDS AND THEIR COMPLEXES

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(Received 22 April 1987)

ABSTRACT

Electrical conductivity measurements of 4-methyl-3-hydroxy-2-quinoline (**I**), 4-phenyl-3-hydroxy-2-quinoline (**II**) and *N*-methyl-4-phenyl-3-hydroxy-2-quinoline (**III**) ligands and their transition metal complexes were measured in the temperature range 20–150 ° C. The results indicated slight semiconducting behaviour for these systems. A discontinuity in the conductivity curve was obtained for ligands (**I**) and (**III**) with two different activation energies one below and one above the transition region. This phenomenon was retained with their metal complexes accompanied by change in the magnitude of the energy gap, and a reduction in the temperature range of the transition region. The conductivities were found to depend on the structure of the compounds. The metal ion forms a bridge between the ligands to facilitate the transfer of current carriers with some degree of delocalisation in the excited state. As the cobalt content in the complexes increased, a gradual increase in electrical conductivity occurred that might be due to lattice imperfections.

INTRODUCTION

The quinoline nucleus has long been known to play an important role in many areas of interest including coordination chemistry, analytical chemistry and chemotherapy. An important group of quinoline compounds having the general structure 4-(substituted)-3-hydroxy-2-quinoline exhibited a marked antibacterial activity and are considered to act as antibiotics [1,2]. As a continuation of our work on the physicochemical properties of this class of quinoline compounds and their transition metal complexes [3], it is desirable to throw light on the mechanism of the electrical conductivity of

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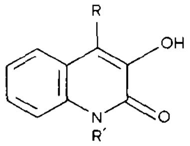
0040-6031/88/$03.50

these ligands and their Fe(III), Co(II), Ni(II) and Cu(II) complexes, and relate the mechanism to their physicochemical properties. This does not appear to have been reported before.

EXPERIMENTAL

The ligands under investigation, 4-methyl-3-hydroxy-2-quinoline (**I**), 4-phenyl-3-hydroxy-2-quinoline (**II**) and *N*-methyl-4-phenyl-3-hydroxy-2-quinoline (**III**) were synthesised following a published procedure [4]. The general structural formula for these ligands is given below.



R	R′	
$-CH_3$	H	(I)
$-C_6H_5$	H	(II)
$-C_6H_5$	$-CH_3$	(III)

A series of complexes were synthesised and characterised as described elsewhere [3]. For the 4-methyl (**I**) ligand the complexes were $Co(L) \cdot 2H_2O$, $Co(HL)_2 \cdot 2H_2O$ and $Ni(HL)_2 \cdot 4H_2O$; the 4-phenyl (**II**) complexes were $Fe(\bar{L})(H\bar{L})_2 \cdot 2H_2O$, $Co(\bar{L}) \cdot 2H_2O$, $Co(H\bar{L})_2 \cdot 2H_2O$, $Ni(H\bar{L})_2$ and $Cu(H\bar{L})_2$; and the *N*-methyl-4-phenyl (**III**) complexes were $Co(\bar{L})_2 \cdot 2H_2O$ and $Cu(\bar{L})_2$. H_2L, $H_2\bar{L}$ and $H\bar{L}$ denote the ligands (**I**), (**II**) and (**III**), respectively.

For electrical conductivity measurements samples were prepared in the form of tablets of thickness 0.1–0.2 cm at a pressure of 5 tons cm^{-2}. The samples were held between two copper electrodes with silver paste and were then inserted with the holder vertically into a cylindrical electric furnace. The potential across the heater was varied gradually through a variac transformer to produce a slow rate of increase in temperature in order to obtain accurate measurements. The electrical measuring circuit consisted of a Heathkit d.c. regulated power supply (0–400 V) and a Keithley electrometer type 610 C for measuring current with a sensitivity of up to 10^{-13} A. The temperatures of the samples were measured to within ± 0.1 K by means of Keithley 871 digital thermometer type KTC NiCr–NiAl. The conductivity of the sample was obtained during cooling using the general equation

$$\sigma = \frac{I}{V_c} \times \frac{d}{a}$$

where I is the current in ampere and V_c is the potential drop across the sample of cross-sectional area a and thickness d.

RESULTS AND DISCUSSION

The classification of organic compounds on the basis of semiconducting properties was originally proposed by Garrett [5]. His classification consisted of polymers, CT complexes and molecular crystals. Another mode of classification was given to four groups [6]: (1) molecular crystals bonded by relatively weak Van der Waals forces, (2) complexes which also exhibit, in addition to the Van der Waals interaction, a varying degree of covalent and coordinate bonding, (3) polymers which are really macromolecules held together by ionic and covalent bonding, and (4) the free radicals or their salts.

Figure 1 and Figs. 2, 3 and 4 show the variation in the logarithmic electrical conductivity values as a function of reciprocal absolute temperature for the ligands and their metal complexes, respectively. The dependence of the conductivity of semiconducting materials on temperature is expressed by the equation

$$\sigma = \sigma^{\star}\ e^{-\Delta E/2kT}$$

where ΔE is the activation energy for conduction, $\sigma^{\star}$ is a constant for the conductivity independent of temperature and k is the Boltzmann constant. The electrical conductivity data are collected in Table 1.

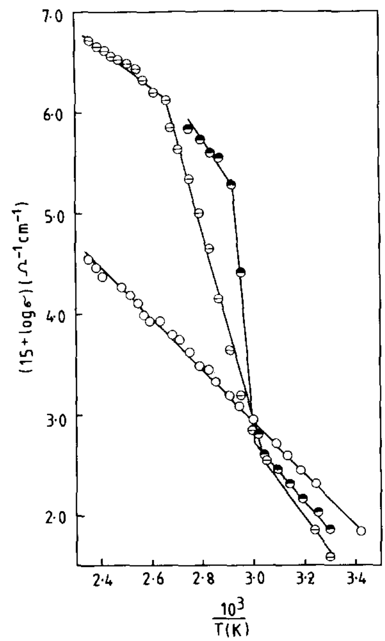


Fig. 1. Log σ vs. $1/T$ relationship for the ligands: ⊖, 4-methyl (**I**), ○, 4-phenyl (**II**) and ●, *N*-methyl (**III**).

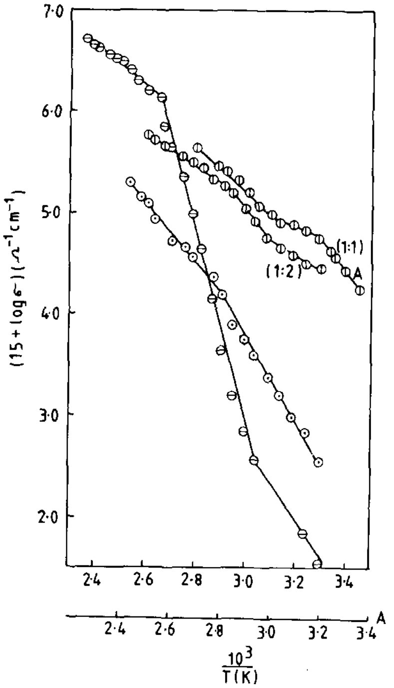


Fig. 2. Log σ vs. $1/T$ relationship for the ligand ⊖, 4-methyl (**I**) and its complexes: ⦶, Co(II) and ⊙ Ni(II).

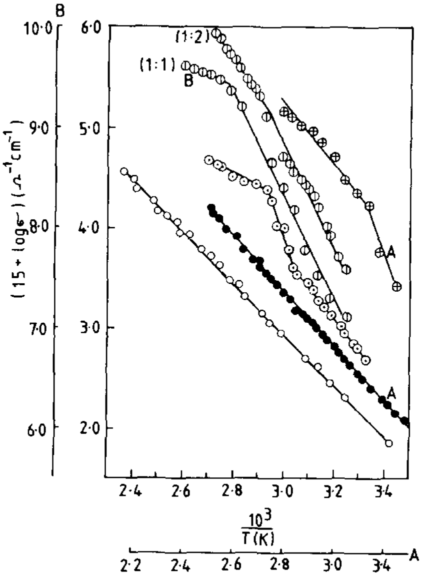


Fig. 3. Log σ vs. $1/T$ relationship for the ligand ○, 4-phenyl (**II**) and its complexes: ⊕, Fe(III), ⦶, Co(II), ⊙, Ni(II) and ●, Cu(II).

If we confine our discussion to the metal-free ligands (Table 1 and Fig. 1), where the conductivity was measured over the temperature range 20–150 ° C, the following observations can be made. A straight line is obtained in the case of the 4-phenyl (**II**) ligand with a ΔE value of 0.45 eV. A discontinuity in the conductivity curve of 4-methyl (**I**) is observed at a transition temperature of 78 ° C where two different values for the activation energy (0.69 and 0.28 eV), below and above the transition region respectively are obtained. The transition region is extended over a temperature interval of about 75 ° C with a ΔE value of 1.60 eV. A similar behaviour is exhibited by the *N*-methyl (**III**) ligand where the log σ vs. $1/T$ relationship showed two breaks. Two activation energies are obtained of nearly the same magnitude (0.49 and 0.51 eV) before and after the transition temperature (65 ° C), respectively. The transition region is located over a narrow temperature range of 60–70 ° C. It has been indicated [7] that there is no guarantee that the energy term will be the same for conduction along different crystal directions. ΔE can also be affected by ambient atmosphere, the presence of impurities, temperature [8] or pressure [9]. Here, it is apparent that ΔE is temperature dependent. The phenomenon of discontinuation in the conductivity curves can be ascribed to a molecular rearrangement or crystallographic transition [10]. A similar trend has been reported for chloropromazine [10] and metal-free phthalocyanine [11]. Furthermore, it is apparent

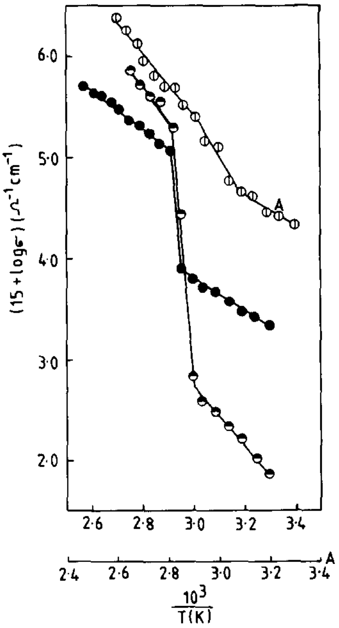


Fig. 4. Log σ vs. $1/T$ relationship for the ligand ◓, *N*-methyl (**III**) and its complexes: ⦶, Co(II) and ●, Cu(II).

that the conductivity is modified by the incorporation of a methyl group with its electron-donating character to the periphery of the quinoline nucleus in both 4-methyl (**I**) and *N*-methyl (**III**) ligands [12].

On dealing with the electrical conductivity properties of the metal complexes compared with their metal-free ligands (Figs. 2, 3 and 4, Table 1), the following could be deduced. The magnitudes of the conductivities of the ligands and their metal complexes, along with the values of the energy gaps indicate slight semiconducting properties. Hence the electrons in the available orbitals are not of high mobility. For the present purpose, the most realistic description of the complexes involves an interaction of the metal orbitals with ligands to give new molecular orbitals (MO), which are delocalised over the whole molecular complex. It is sufficient to consider qualitatively the behaviour of the lowest unoccupied π MO of the ligands that interact with the appropriate metal orbitals. The relevant ligand orbitals transform as B_{1u} and B_{2g}, which may interact with $4p_z$ and $3d_z2$ orbitals, respectively. The B_{1u}-type MOs are sufficiently stabilised on interaction with the $4p_z$ orbital to become occupied. This explains the possible resonating structures [13]. It has been proposed [14,15] that the first step in the conduction process is the excitation of a π electron from the uppermost filled π orbital to the lowest empty π MO. The electron is then assumed to tunnel to the equivalent empty level of the neighbouring molecule in the direction of the anode, whereas the positive hole moves in the opposite

TABLE 1

Conductivity data

Compound [b]	ΔE_1	ΔE_2	ΔE_3	Transition temperature (°C)	Transition region (°C)	log σ_{308} [a]
4-Methyl (**I**)	0.69	1.60	0.28	55–130	78	−13.44
$\mathrm{Co(L)\cdot 2H_2O}$ [b]	0.54	0.28	0.39	40– 60	50	−10.53
$\mathrm{Co(HL)_2\cdot 2H_2O}$	0.25	0.50	0.28	50– 66	59	−10.53
$\mathrm{Ni(HL)_2\cdot 4H_2O}$	0.70	0.48	–	–	–	−12.44
4-Phenyl (**II**)	0.45	–	–	–	–	−12.65 [a]
$\mathrm{Fe(\bar{L})(H\bar{L})\cdot 2H_2O}$	1.32	0.50	–	–	–	−11.57 [a]
$\mathrm{Co(\bar{L})\cdot 2H_2O}$	0.88	0.17	–	–	–	−7.84 [a]
$\mathrm{Co(H\bar{L})_2\cdot 2H_2O}$	0.92	0.59	–	–	–	−11.40 [a]
$\mathrm{Ni(H\bar{L})_2}$	0.55	0.89	0.22	56– 68	63	−12.02 [a]
$\mathrm{Cu(H\bar{L})_2}$	0.47	–	–	–	–	−12.84 [a]
N-Methyl (**III**)	0.49	–	0.51	60– 70	65	−13.14
$\mathrm{Co(\bar{\bar{L}})_2\cdot 2H_2O}$	0.26	0.79	0.55	50– 72	61	−10.66
$\mathrm{Cu(\bar{\bar{L}})_2}$	0.77	–	0.33	65– 70	68	−11.66

[a] log σ at 308 K.

[b] $\mathrm{H_2L}$, $\mathrm{H_2\bar{L}}$ and $\mathrm{H\bar{\bar{L}}}$ denote the ligands (**I**), (**II**) and (**III**), respectively.

direction towards the cathode. If initial excitation is involved in the complexes, it is no longer necessary that the electron in the uppermost π level comes from the highest occupied MO as it could also arise from an orbital, essentially positive centre. If the electron is assumed to arise from the highest MO, it must be placed in a state of different multiplicity in order to become sufficiently long-lived. The first excited singlet and the first triplet state will almost certainly be too far above the ground state to allow thermal population. Hence, it is conceivable that the population of the electrons in the lowest unoccupied π MO may be proportional to the absolute energy of the lowest empty orbital in the complexes [16].

On the basis of the insolubility of the complexes under investigation in most common organic solvents, interaction might occur between adjacent atoms in a metal-atom chain [17]. Furthermore, it is obvious that the activation energies for the ligands are affected to a great extent by the presence of a chelated metal atom. The discontinuity in the conductivity curves of the metal-free ligands is retained in their metal chelate complexes where the electrical conductivity against temperature relationship showed two or three segments with variable activation energies. This can be suggested to be due to different crystallographic or phase transitions [18]. Generally, it is seen that the incorporation of a metal atom to form the complex leads to the reduction of the transition region compared with the metal-free ligands. For example, the 4-methyl (**I**) transition region covers the range 55–130 °C whereas its Co(1 : 1) and Co(1 : 2) complexes exhibit a reduced transition region to 40–60 °C and 50–66 °C, respectively. This is accompanied by a drop in the resistivity of the ligands which might be due to the replacement of hydrogen atoms with the metal atoms. As the cobalt content in the prepared complex increased, a gradual increase of electrical conductivity with a decrease in activation energy occurred (Figs. 2 and 3). (ΔE values are 0.28 and 0.50 for (1 : 1) and (1 : 2) Co-4-methyl (**I**) complexes respectively, and 0.17 and 0.59 for (1 : 1) and (1 : 2) stoichiometries of Co-4-phenyl complexes, respectively). This might be due to distortions in the conduction pathways through the metal caused by lattice imperfections which affect the movement of electrons. Therefore, the delocalisation of electrons within the metal-atom chains play some role.

REFERENCES

1 D. Gottieb and P.D. Shaw,. Antibiotic II, Biosynthesis, Springer-Verlag, New York, 1967, p. 105.

2 H.C. van der Plas, L. Otvos and M. Simonyi, Bio-Organic Heterocycles, Elsevier Science Publishers, 1984, p. 180.

3 M.S. Masoud, F. Taha, E.M. Soliman and Y.S. Mohamed, Synth. React. Inorg. Met.-Org. Chem., submitted for publication.

4 Y.S. Mohamed, A.N. Gohar, F.F. Abdel-Latif and M.Z.A. Badr, Die Pharmazie, 40 (1985) 312.

5 C.G.B. Garrett, Mater. Des. Eng., 51 (1960) 12.
6 F. Gutmann and L.E. Lyons, Organic Semiconductors, Wiley, New York, 1967 p. 5.
7 C.G.B. Garrett, Organic semiconductors, in N.H. Hannay (Ed.), Semiconductors, Reinhold, New York, 1959, p. 25.
8 S. Aftergut and G.P. Brown, Organic Semiconductors, Macmillan, New York, 1962 p. 87.
9 H.A. Pohl and D.A. Opp, J. Phys. Chem., 66 (1962) 2121.
10 F. Gutmann and A. Netschey, J. Chem. Phys., 36 (1962) 2355; F. Gutmann and H. Keyzer, Nature, 205 (1965) 1102.
11 K. Wihksne and A.E. Newkirk, J. Chem. Phys., 34 (1961) 2184.
12 W. Noddack, H. Meier and A. Haus, Z. Phys. Chem., 212 (1959) 55
13 D. Alder and E.J. Yoffa, Can. J. Chem., 55 (1977) 1920.
14 Y. Nakamma, M. Naoi and M. Shimoji, Can. J. Chem., 55 (1977) 1975.
15 A. Schramzer, J. Am. Chem. Soc., 88 (1966) 4876.
16 M.S. Masoud, B.S. Farag, Y. Sawan, T.M. Salem and M.M. El-Essawy, J. Non-Cryst. Solids, 55 (1983) 209.
17 J.M. Thomas, Chem. Br., 13 (1977) 175.
18 A. Epstein and J. Wildi, J. Chem. Phys., 32 (1960) 324.