ELECTRICAL CONDUCTIVITY PROPERTIES OF SOME THIAZOLYLAZO-PYRIMIDINE DERIVATIVE COMPLEXES AT DIFFERENT TEMPERATURES

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The electrical conductivities of complexes of some thiazolylazo-pyrimidine derivative complexes have been investigated at different temperatures. The complexes were found to be of two types; the first one has a semi-conductor behaviour and a constant conductivity value above 398° K, whereas the second type shows three segments with variable activation energy. The dissimilarity between the two types of complexes is attributed to the steric effect of the phenyl group in the first type. The conductivity data measured in the temperature range 298° - 570° K were correlated to the geometrical change of these complexes, indicating that the cobalt (II) complexes have higher conductivity than those of copper (II) and nickel (II), depending on the chemistry of the metal ion and the molecular structure of complexes. Empirical equations to correlate ΔE with log σ_0 values for the complexes were deduced by the use of the least square method. Also, the mobility values (m) of these complexes were calculated.

Key words: Electrical conductivities, Thiazolylazo-pyrimidine derivative complexes, Temperature.

Introduction

Compounds containing thiazolylazo group and those derived from pyrimidine nuclei have many applications [1,2]. Barbiturates, thiobarbiturates and thiouracils are important classes of substituted pyrimidines and are components in nucleic acids [3]. Due to the importance of pyrimidines compounds especially those containing azo, these compounds and their metal complexes have been synthesized in our laboratory [4], and the electrical conductivity of these complexes has been measured at different temperatures and the results correlated to their chemical properties.

Experimental

The organic compounds were prepared by dissolving 2aminothiazole and its 4-phenyl derivative (0.1 mole) in HCl (0.2 mole/25 ml distilled H_2O). The hydrochloric compounds were diazotized below 5°C with a solution of NaNO₂ (0.1 mole/30 ml distilled H_2O). The diazonium chlorides [5] were coupled with an alkaline solution of barbituric, 2-thiobarbituric acids and 2-thiouracil (0.1 mole). The crude dyes were collected by filtration and were crystallized by ethanol [6], followed by drying in a vacuum desiccator over P_4O_{10} .

Microanalysis of C, H, N and S contents was performed by using a Perkin-Elmer 240 elemental analyzer and the results are shown in Table 1. The elemental analysis typified the existence of these compounds in the following structure:



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$R_1 = H$		R ₂ =Barbituric acid (BA)
	Ph Ph	Barbituric acid (BA)
	a.i.(TbHib) o	2-Thiobarbituric acid (SBA)
	Ph	2-Thiobarbituric acid (SBA)
	the solution	2-Thiouracil (TUr)

The complexes of these compounds were prepared by refluxing an alcoholic solution of the metal (II) chloride; M = Co, Ni and Cu; (0.01 mole/20 ml) with an ammoniacal alcoholic solution of the organic compounds (0.1 mole/40 ml alc. + few drops NH₃) for 2 hr. The precipitated complexes were separated by filtration and washed with ethanol and dried in a desiccator over anhydrous CaCl₂. All the complexes have melting points greater than 300°C. The metal ions were determined volumetrically by standard EDTA titration methods [6].

The electrical conductivity of the complexes were measured in the temperature range 298-570° K with a stability and accuracy of ± 0.1 K. The measuring circuit consisted of an oscillator (10 Hz -10 MHz) BM 492 and a millivoltmeter (10 Hz - 1 MHz) BM 494. The samples were prepared in the form of tablets of thickness 0.1-0.3 cm at a pressure of about 5 tons/ cm². The tablets were covered on both sides with silver paste to improve the contact with measuring electrodes, The temperature was measured by using a precalibrated Cu-constantan thermocouple attached to the sample.

The electrical conductivity was measured by applying a stabilized D.C. voltage across the potential difference. The conductivity of the sample was obtained during heating using the general equation:

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

where I is the current in amperes and V_c is the potential drop across the sample of cross section area a and thickness d.

Results and Discussion

The variation in the logarithmic electrical conductivity values with the reciprocal absolute temperature for metal complexes derived from thiazolylazo-pyrimidine derivatives is presented in Figs. 1-3. The dependence of the conductivity of the semiconducting materials on temperature is expressed by the equation.

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

where ΔE is the activation energy for conduction, σ^* is a preexponential conductivity factor independent of temperature and k is the Boltzman constant. The values of electrical conductivity (σ_0), activation energy (ΔE) and the energy gap (E_g) of these complexes are collected in Table 2. These results allowed the following observations:

(a) The curves of the cobalt and copper 5-(4-phenyl-2thiazolylazo) barbituric and thiobarbituric acids show a negative temperature coefficient of resistance (dR/dT), i.e. of semi-

TABLE 1. THE ELEMENTAL ANALYTICAL DATA OF METAL COMPLEXES DERIVED FROM THIAZOLYLAZO-PYRIMIDINE DERIVATIVES.

Complexes	Stoichio-	Calculated (found) %				
nd als. + lan	metry	C	H	N	S	M
Co.Th.BA.	ML.2H,O	25.3	2.1	20.1	9.6	17.7
	rale brie Joins	(25.1)	(2.0)	(19.9)	(9.6)	(17.7)
Co.Th.SBA.	ML.2H,O	24.1	2.0	20.1	18.4	16.9
	mail read he	(24.1)	(1.9)	(20.1)	(18.3)	(16.9)
Co.Th.TUr.	ML, . 4H,0	27.5	2.2	23.0	21.2	9.7
	1.200 . * 1.000 * 1.1	(27.7)	(2.3)	(23.1)	(21.2)	(9.7)
Co.ThBA.	ML.2H,O	38.2	2.7	17.1	7.8	14.4
	enno.X~0	(38.0)	(2.6)	(17.0)	(7.7)	(14.3)
Co.Th SBA.	ML.2H,O	36.7	2.6	16.5	15.1	13.8
	illim a bus	(36.5)	(2.4)	(16.4)	(15.0)	(13.8)
Ni.Th.BA.	M,L.6H,O	18.2	3.3	15.1	6.9	25.3
		(18.2)	(3.1)	(15.0)	(6.7)	(25.1)
Ni.Th.ø.BA.	ML, . 4H,0	41.1	3.2	18.4	8.4	7.7
	na istratio	(40.9)	(3.1)	(18.2)	(8.3)	(7.7)
Ni.Th SBA.	ML, . 4H,O	39.4	3.0	17.6	16.2	7.4
	() bolindiles	(39.4)	(3.0)	(17.4)	(16.0)	(7.4)
Cu.Th.BA.	ML, . 2H,O	29.1	2.1	24.3	11.1	11.0
		(29.0)	(2.1)	(24.1)	(11.0)	(11.0)
Cu.Th.SBA.	ML, . 2H,0	27.5	1.9	23.0	21.1	10.4
		(27.4)	(1.7)	(23.0)	(21.0)	(10.4)
Cu.Th.TUr.	ML, . 2H,0	29.0	1.5	24.3	22.1	11.0
	2 2	(29.2)	(1.7)	(24.4)	(22.3)	(11.0)
Cu.Th.ø.BA.	ML, . 4H,0	40.8	3.1	18.3	8.4	8.4
	2 2	(40.7)	(3.1)	(18.1)	(8.4)	(8.3)
Cu.Th.ø.SBA.	ML, . 2H,O	39.2	3.0	17.6	16.1	7.9
States and states	2 . 2	(39.0)	(2.8)	(17.5)	(16.0)	(7.8)

conductor properties. These complexes show a constant conductivity value at temperatures above 398° K (Figs. 1-3), indicating that they possess insulator properties under these conditions.

(b) The temperature dependence of the conductivity curves for the cobalt and copper complexes of the SBA, TUr and those of BA, SBA and Ni-BA complex exhibit three regions: A, B, C. In some cases the regions A and C are with a positive temperature coefficient of electrical conductivity. The region B has a negative value. On the other hand, the electrical activation energies of these complexes reveal positive values in the regions A and C (except for Co-TUr and Ni- ϕ BA







Fig. 2. Temperature dependence of electrical conductivity of complexes containing copper.

complexes). The region A exhibits an increase of conductivity as the temperature is increased, with a relatively low activation energy [7]. The region B has a negative value in Ni-BA, Ni-\$BA, Cu-SBA and Cu-TUr. This region is characterized by the decrease of conductivity as the temperature is increased. The region C has a positive temperature coefficient except for Co-TUr and Ni- BA complexes, with an activation energy lower than that of region A. However, the lower activation energies are related to the electron hopping which is a thermally activated process [8]. This may be the result of a relatively weak electronic coupling between the donor and the acceptor molecules [9]. The phenomenon of discontinuation observed in the electrical conductivity-temperature relationship showed two of the three segments with variable activation energies, probably due to different crystallographic transition or molecular arrangement [10].

(c) The log σ - (1/T) relation for the Co-TUr (ML₂.4H₂O) gives three segments. The first lies within the temperature

TABLE 2. ELECTRICAL CONDUCTIVITY DATA FOR METAL
COMPLEXES DERIVED FROM THIAZOLYLAZO-PYRIMIDINE
DEDRUATIVES

Complexes	Stoichiometry	Transitions temperature	ΔE (eV)	Log $σ_0$ (Ω ⁻¹ /cm)
Co.Th.BA.	ML . 2H,O	142	2.314	14.730
			0.293	-4.761
Co.Th.SBA.	ML.2H2O	87	1.361	5.762
	San Diego - Cino	163.3	0.658	-1.092
		246	0.183	-6.250
Co.Th.TUr.	$ML_2 \cdot 4H_2O$	100	1.857	12.699
		172	0.481	-1.758
		207	-2.245	-33.619
Co.Th.ø.BA.	ML.2H ₂ O	169	0.777	-1.206
Co.ThSBA.	ML.2H ₂ O	149	1.962	15.475
Ni.Th.BA.	M ₂ L.6H ₂ O	77.8	0.366	-4.917
		171	-0.613	-15.927
			0.265	-3.390
Ni.ThBA.	$ML_2 \cdot 4H_2O$	25	0.444	-3.199
		32.2	0.074	-7.627
			-0.190	-11.942
Ni.Th SBA.	$ML_2 \cdot 4H_2O$	194	0.454	-4.199
			-0.301	-11.536
			0.268	-5.780
Cu.Th.BA.	ML ₂ . 2H ₂ O	122	0.853	2.206
			0.415	-2.646
		152	0.529	0.729
Cu.Th.SBA.	$ML_2 \cdot 2H_2O$	167	1.013	3.480
			-0.792	-16.299
		181.5	0.284	-3.630
Cu.Th.TUr.	ML ₂ .2H ₂ O	98	0.607	1.527
		142	-1.709	-26.065
		172	0.232	-3.020
Cu.ThBA.	ML ₂ .4H ₂ O	167	0.286	-11.365
Cu.Th SBA.	ML, . 2H,O	152.5	0.280	-4.390

range 25°-100°C followed by the second one up to 172°C and the third region above the transition temperature 172°C. The first is due to the dehydration of the complex, i.e. loss of water in the outer sphere and the second is due to the lattice defect of dehydrating the complex which is characterized by a decrease in the conductivity and the activation energy values. This is related to the electron hopping which is a thermally activated process [8]. The third region has a positive temperature coefficient. The same behaviour was also observed for the Cu-TUr complex, with three transition temperatures at 98°, 142° and 172°C.

(d) Based on the ΔE_1 , values, the electrical conductivity of cobalt-5-(2-thiazolylazo)-barbituric acid complex is higher than that of the thiobarbituric complex, due to electronegativity difference between the oxygen and the sulpher atoms to give rise to higher conductivity. The reverse was observed for the copper complexes in ML₂. 2H₂O for both barbiturate and thiobarbiturate complexes which have the tetrahedral geometric structure. The electrical conductivity of 1:1 tetrahedral cobalt complexes derived from 5-(2-thiazolylazo)-barbituric acid, 5-(2-thiazolylazo)-2-thiobarbituric acid and 5-(2thiazolylazo)-2-thiouracil is found to be higher than the corresponding copper complexes. This is probably due to the bidentate nature of the ligands on complexation to Cu(II) and tridentate behaviour through reaction with Co (II) [11]. The unpaired 3d electron in copper will occupy the uppermost filled orbital and will be likely to take part in intermetallic interactions. In these cases, as the molecular weight increases, the electrical conductivity decreases. The metal orbitals interact with those of the organic compounds to give new molecular orbitals (MO) which are delocalized over the whole molecular complex. The relevant ligand orbital transforms as B_{10} and B_{20} , which may interact with 4p, and 3d, 2 orbitals, respectively. The B_u type MO's are sufficiently stabilized on the interac-



Fig. 3. Temperature dependence of electrical conductivity of complexes containing nickel.

tion with the 4p, orbital to become occupied [12]. However, the first step for conduction is the excitation of electron from the uppermost filled π -orbital to the lowest MO [13,14]. 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 is moving in the opposite direction, i.e. towards the cathode. 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 longlived. The excited singlet and the first triplet state will almost certainly be above the ground state to allow thermal population. This assumes that the population of electrons in the lowest occupied π -MO depends on the absolute energy of the lowest empty orbital in the complex [15]. In most of the complexes, an additional increase in the electrical conductivity occurs, probably indicating a discontinuity of the chemical bond existing in the compounds. However, the following extra comments are recorded:

On plotting ΔE against log σ_0 for thiazolylazo-complexes having the same metal ion, cobalt (II), nickel (II) and copper (II), straight lines are obtained in case of both the cobalt and copper complexes. However, in case of nickel complexes, such relation gave scattered points. Therefore, the following empirical equations are deduced:

In case of cobalt (II) complexes:

 $\Delta E = 0.081 \log \sigma_0 + 0.088$

based on the first activation energy based on the second activation energy

For the copper (II) complexes:

 $\Delta E = 0.87 \log \sigma_0 + 0.074$

 $\Delta E = 0.087 \log \sigma_0 + 0.677$ $\Delta E = 0.084 \log \sigma_0 + 0.544$ based on the first activation energy based on the second activation energy

The above data show that these complexes can be classified into two categories and the following conclusions can be made:

(i) In general, all cobalt and copper-5-(4-phenyl-2-thiazolylazo) barbituric and thiobarbituric acids showed a semi-conductor behaviour and constant conductivity values at temperatures above 398° K. Both the ΔE and log σ_0 values are increased in the order: ϕ SBA, ϕ BA complexes.

(ii) The different behaviour observed for cobalt, copper and nickel complexes of BA, SBA and TUr, which exhibit three regions (Figs. 1-3) having different temperature coefficients of electrical conductivity and positive values of activation energy is attributed to the steric effect of the phenyl group. The mobility value (m) can be calculated from the following equation:

m

σ

eN

where $e = 1.6022 \times 10^{-19}$ coulombs is the electronic change, N₀ = 10²¹ is the number of charge carriers and σ is the conductivity (ohm⁻¹/cm). From this equation, it seems that there is a direct proportionality between the conductivity and mobility. However, the low activation energy in some complexes is related to the electronic hopping which is a thermally activated process. This is also confirmed by the mobility value m=10⁻⁸-10⁻⁹ cm²/V sec << 1, which coincides with the hopping model that increases with temperature, e.g., m = 1.08 x 10⁻⁷ and m = 7.10 x 10⁻¹⁵ cm²/V sec for Co-BA and Cu-TUr, respectively.

In general, these complexes are reported [11] to possess the following structures:



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lieft in many countries of the world. There is increasing interest in the output of this species in mugliadesh. The dependence on mutual sources for the supply of the use of the fitning accessfully indeced to reproduce using bormones [1-3]. However, as cossitulinge scale remarg of the remains a major biowever, as cossitulinge scale remarg of the remains a major constraint for the development and expansion of farming the species. Remarg of *Claran sourcehar* larvee with his effect the species from got *Claran sourcehar* larvee with his effect the species from got *Claran sourcehar* larvee with his effect the species from got *Claran sourcehar* larvee with his effect the species from got *Claran sourcehar* larvee with his effect the species from got *Claran sourcehar* larvee with his effect the species from got *Claran sourcehar* larvee with his effect the species from got of the negative of the provident of the major statistical for the species of the effect of source the species contrained for the species at the collections of the provident has from another the development has a species of the species of the species from dulation have as food for rearrow disc larves and the species of source discussion of the species of the species of the statistical four dulation haves as food for rearrow disc larves at *Claran and apprecies* of the species of the

Materials and Methods

The present work, was undertaken for a period of twelve drive in laboratory from Oct. 2 to Oct.13, 1990 with five day old confish (Clorens ball achue) fry $(9.3 \pm 0.2 \text{ mm}, 0.009 \pm 0.0012 \text{ mm}, 0.0012 \text{ m$

litteen equal size (47.5 cm dia, 20.5 cm h) howie were filled with conditioned no water and one hundred by were stocked in each bowl. Four teads were tested each with three replicates. Treatment 1 was fed with five plankton, treatment 2 with frozen plankton, treatment 3 with dired plankton, treatment 4 with Tahriev and matmant 5 acted as a control where no feed was given.

Crive phytoplankton and zoophakton were collected from meaning point with a plankton net (much size follower viceter). Some of the collected phasi ton were frozzo to a refrigaritor for it lease? daws in the cool chamber, other sization were three.

from drams in and around Fisherics Research Institute. Food was given once daily in the moning at the time of outer change. The how's were actated throughout the period of experiment kept at room temperature (25-29°C) in the fahoretory. The dead fishes were removed as soon as they were seen at 3 days interval. The length and number of dead fishes were recorried. The pH, temperature and the dissolved oxygenoffice water were measured by pH meter and oxygen preter daily berecorried. The pH, temperature and the dissolved oxygenoffice water were measured by pH meter and oxygen preter daily betering of mean fish weight and in precentage of survival. The opperimental that were then an investing of survival. The isot design and ANOVA were computed in completely randomized design and ANOVA were computed. Dancen's Yew isod to further analysis of the results.

Reader and Discussion

The surveys and mean length of earlich try fed wate different dieu are presented in 1 able 1, fauticity, faitmontakey was high in all the treatmonts but with the coartanation of experiment the montainy decreteed appreciably. Statistical analysis indicated that feed had very significant effect on sec result (Table 2). It was evident that it's planten resulted in a bottor surved rate up to 11 theys of eac but Tublifix, were gave better survest from 1 th days of eac but Tublifix, were mon. Highest mentality was ebsorved to amonts throughout the experiment. It is already similar with the factings of age of 15 days the stomach of (faring tagens that upto the anticity cooplication. Fats is in conformity with the factings of entitely cooplication. Fats is in conformity with the Hogendoorn is [who found that its dry leads were not single to be experiment to a stomach of (faring tagens comprised of entitely recomplication. Fats is in conformity with the Hogendoorn is [who found that its dry leads were not single to fats and the days of the stomach of the days of the store fats and the hogen-

Allydre iny died in the control bowls at 15th day, which supressed that the water used for the experiment contained.