

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 $\log \sigma_0$ 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.

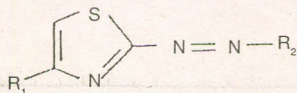
Introduction

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 2-aminothiazole and its 4-phenyl derivative (0.1 mole) in HCl (0.2 mole/25 ml distilled H₂O). The hydrochloric compounds were diazotized below 5°C with a solution of NaNO₂ (0.1 mole/30 ml distilled H₂O). 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 P₄O₁₀.

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	Barbituric acid (BA)
H	2-Thiobarbituric acid (SBA)
Ph	2-Thiobarbituric acid (SBA)
H	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 pre-exponential 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-2-thiazolylazo) 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 THIAZOLYL-AZO-PYRIMIDINE DERIVATIVES.

Complexes	Stoichiometry	Calculated (found) %				
		C	H	N	S	M
Co.Th.BA.	ML . 2H ₂ O	25.3	2.1	20.1	9.6	17.7
		(25.1)	(2.0)	(19.9)	(9.6)	(17.7)
Co.Th.SBA.	ML . 2H ₂ O	24.1	2.0	20.1	18.4	16.9
		(24.1)	(1.9)	(20.1)	(18.3)	(16.9)
Co.Th.TUr.	ML ₂ . 4H ₂ O	27.5	2.2	23.0	21.2	9.7
		(27.7)	(2.3)	(23.1)	(21.2)	(9.7)
Co.Th.φ.BA.	ML . 2H ₂ O	38.2	2.7	17.1	7.8	14.4
		(38.0)	(2.6)	(17.0)	(7.7)	(14.3)
Co.Th.φ.SBA.	ML . 2H ₂ O	36.7	2.6	16.5	15.1	13.8
		(36.5)	(2.4)	(16.4)	(15.0)	(13.8)
Ni.Th.BA.	M ₂ L . 6H ₂ O	18.2	3.3	15.1	6.9	25.3
		(18.2)	(3.1)	(15.0)	(6.7)	(25.1)
Ni.Th.φ.BA.	ML ₂ . 4H ₂ O	41.1	3.2	18.4	8.4	7.7
		(40.9)	(3.1)	(18.2)	(8.3)	(7.7)
Ni.Th.φ.SBA.	ML ₂ . 4H ₂ O	39.4	3.0	17.6	16.2	7.4
		(39.4)	(3.0)	(17.4)	(16.0)	(7.4)
Cu.Th.BA.	ML ₂ . 2H ₂ 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 ₂ . 2H ₂ O	27.5	1.9	23.0	21.1	10.4
		(27.4)	(1.7)	(23.0)	(21.0)	(10.4)
Cu.Th.TUr.	ML ₂ . 2H ₂ O	29.0	1.5	24.3	22.1	11.0
		(29.2)	(1.7)	(24.4)	(22.3)	(11.0)
Cu.Th.φ.BA.	ML ₂ . 4H ₂ O	40.8	3.1	18.3	8.4	8.4
		(40.7)	(3.1)	(18.1)	(8.4)	(8.3)
Cu.Th.φ.SBA.	ML ₂ . 2H ₂ O	39.2	3.0	17.6	16.1	7.9
		(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-φBA

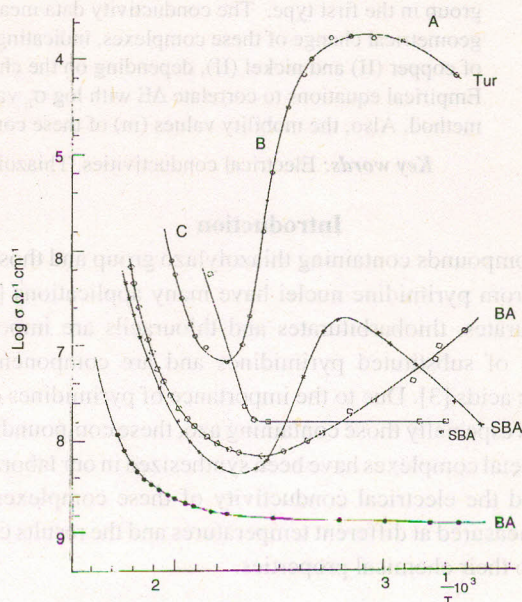


Fig. 1. Temperature dependence of electrical conductivity of complexes containing cobalt.

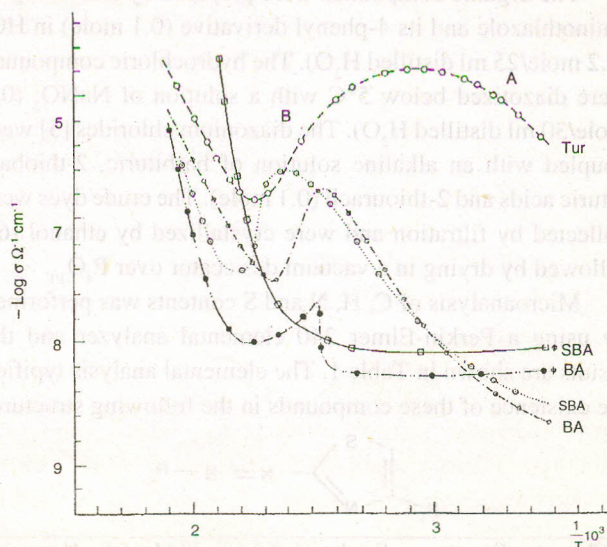


Fig. 2. Temperature dependence of electrical conductivity of complexes containing copper.

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- ϕ SBA, 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- ϕ 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 $\log \sigma - (1/T)$ relation for the Co-TUr ($ML_2 \cdot 4H_2O$) gives three segments. The first lies within the temperature

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

Complexes	Stoichiometry	Transitions temperature	ΔE (eV)	$\log \sigma_0$ (Ω^{-1}/cm)
Co.Th.BA.	$ML \cdot 2H_2O$	142	2.314	14.730
			0.293	-4.761
Co.Th.SBA.	$ML \cdot 2H_2O$	87	1.361	5.762
		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. ϕ .BA.	$ML \cdot 2H_2O$	169	0.777	-1.206
Co.Th. ϕ .SBA.	$ML \cdot 2H_2O$	149	1.962	15.475
Ni.Th.BA.	$M_2L \cdot 6H_2O$	77.8	0.366	-4.917
		171	-0.613	-15.927
			0.265	-3.390
Ni.Th. ϕ .BA.	$ML_2 \cdot 4H_2O$	25	0.444	-3.199
		32.2	0.074	-7.627
			-0.190	-11.942
Ni.Th. ϕ .SBA.	$ML_2 \cdot 4H_2O$	194	0.454	-4.199
			-0.301	-11.536
			0.268	-5.780
Cu.Th.BA.	$ML_2 \cdot 2H_2O$	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.	$ML_2 \cdot 2H_2O$	98	0.607	1.527
		142	-1.709	-26.065
		172	0.232	-3.020
Cu.Th. ϕ .BA.	$ML_2 \cdot 4H_2O$	167	0.286	-11.365
Cu.Th. ϕ .SBA.	$ML_2 \cdot 2H_2O$	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 sulphur atoms to give rise to higher conductivity. The reverse was observed for the copper complexes in $ML_2 \cdot 2H_2O$ 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-(2-thiazolylazo)-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_{1u} and B_{2g} , which may interact with $4p_z$ and $3d_z^2$ orbitals, respectively. The B_{1u} type MO's are sufficiently stabilized on the interac-

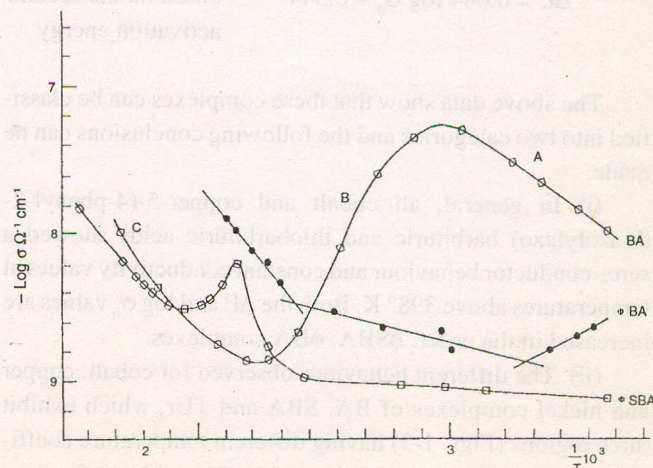


Fig. 3. Temperature dependence of electrical conductivity of complexes containing nickel.

tion with the $4p_z$ 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 long-lived. 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 $\log \sigma_0$ 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:

$$\Delta E = 0.081 \log \sigma_0 + 0.088 \quad \text{based on the first activation energy}$$

$$\Delta E = 0.87 \log \sigma_0 + 0.074 \quad \text{based on the second activation energy}$$

For the copper (II) complexes:

$$\Delta E = 0.087 \log \sigma_0 + 0.677 \quad \text{based on the first activation energy}$$

$$\Delta E = 0.084 \log \sigma_0 + 0.544 \quad \text{based on the second activation energy}$$

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 $\log \sigma_0$ values are increased in the order: ϕSBA , ϕBA complexes.

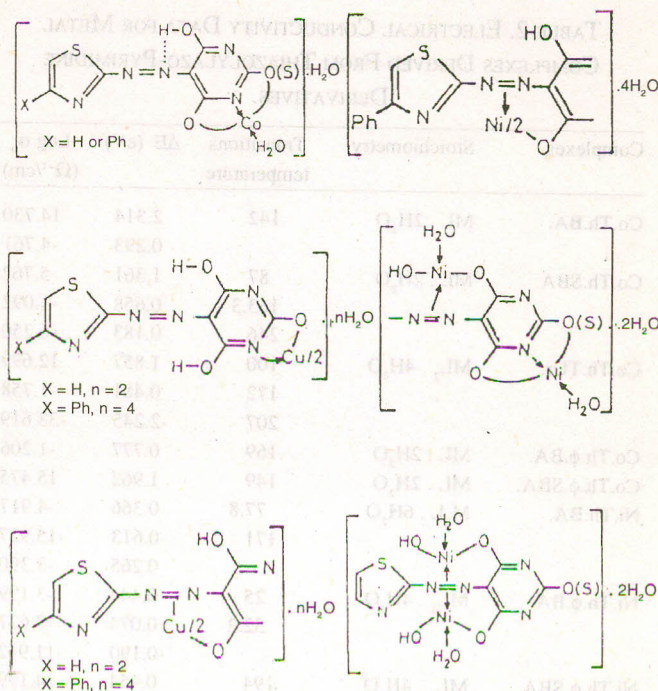
(ii) The different behaviour observed for cobalt, copper and nickel complexes of BA, SBA and TUr, which exhibit three regions (Figs. 1-3) having different temperature coefficients of electrical conductivity and positive values of activation energy is attributed to the steric effect of the phenyl group.

The mobility value (m) can be calculated from the following equation:

$$m = \frac{\sigma}{eN_0}$$

where $e = 1.6022 \times 10^{-19}$ coulombs is the electronic charge, $N_0 = 10^{21}$ is the number of charge carriers and σ is the conductivity ($\text{ohm}^{-1}/\text{cm}$). 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 $m = 10^{-8} - 10^{-9} \text{ cm}^2/\text{V sec} \ll 1$, which coincides with the hopping model that increases with temperature, e.g., $m = 1.08 \times 10^{-7}$ and $m = 7.10 \times 10^{-15} \text{ cm}^2/\text{V sec}$ for Co-BA and Cu-TUr, respectively.

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



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