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# Thermal, dielectrical properties and conduction mechanism of Cu(II) complexes of azo rhodanine derivatives



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#### ABSTRACT

A novel series of Cu(II) complexes of azo rhodanine derivatives  $[CuL_n(OAc)(OH_2)]2H_2O$  (n = 1,  $R = OCH_3$ ; n = 2, CH<sub>3</sub>; n = 3, H; and n = 4, NO<sub>2</sub>) have been synthesized. The alternating current conductivity ( $\sigma_{ac}$ ) and dielectric properties of Cu(II) complexes of azo rhodanine derivatives were investigated in the frequency range 0.1–100 kHz and temperature range 303–600 K. The values of the thermal activation energies of electrical conductivity  $\Delta E_1$  and  $\Delta E_2$  for all Cu(II) complexes [CuL<sub>n</sub>(OAc)(OH<sub>2</sub>)]2H<sub>2</sub>O were calculated at different frequencies. The conductivity depends on the substituents of the complexes. The correlated barrier hopping (CBH) is the dominant conduction mechanism for complexes [CuL<sub>n</sub>(OAc)(OH<sub>2</sub>)]2H<sub>2</sub>O (n = 1, 2 and 4) while for complex [CuL<sub>3</sub>(OAc)(OH<sub>2</sub>)]2H<sub>2</sub>O the small polarons tunneling (SPT) is the dominant conduction mechanism.

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## 1. Introduction

Azo rhodanine and its derivatives have wide industrial applications as intermediates in the synthesis of dyes, antioxidants and brightening additives in silver electroplating, as well as pharmacological [1], and biological activities [2–6]. Another interesting aspect of the chemistry of these compounds is their donating power to metal ions, which makes them strong ligands in coordination compounds [7–10]. These compounds are also used in analytical chemistry as highly sensitive reagents for heavy metals [11,12].

Azo rhodanine and its derivatives contain heteroatoms which are considered to be adsorption centers (nitrogen, sulphur, oxygen) and could be used as anti-corrosion agents for protection of metals. Azo rhodanine and its some derivatives were found to be good corrosion inhibitors for stainless steel [13], mild steel, [14] and carbon steel [15]. Rhodanine derivatives have been proven to be attractive compounds due to their outstanding biological activities and have undergone rapid development as anticonvulsant, antibacterial, antiviral and antidiabetic agents [16,17]. Heterocyclic compounds such as rhodanine and 2-thiohydantoin, which in spite of having only five-membered rings possess several different endoand exocyclic electron-donating atoms, are interesting as ligands because they can exist either as neutral molecules or as monocharged anions and, in solution, are also involved in tautomeric equilibria [18]. Azo rhodanine appear to be very important as far as biocidal potency is concerned, probably via incorporation of the N–C=S moiety, the importance of which has been stressed in many fungicides and bactericides [19,20].

The alternating current conductivity ( $\sigma_{ac}$ ) and dielectric properties of ligands (5-(4'-derivatives phenylazo)-2-thioxothiazolidin-4-one) were investigated [21]. The thermal activation energies of electrical conductivity,  $\Delta E_1$  and  $\Delta E_2$ , increase according to the following order p-(NO<sub>2</sub>>H>CH<sub>3</sub>>OCH<sub>3</sub>). This is in accordance with that expected from Hammett's substituent coefficients ( $\sigma^R$ ). The conductivities are found to be dependent on the structure of the ligands. The correlated barrier hopping (CBH) is the dominant conduction mechanism for the ligands.

Moreover, only a few reports are available on Pd(II) and VO(IV) complexes with 5-(4'-alkyl phenylazo)-2-thioxo-4-thiazolidinone [7,8]. These papers describe the synthesis, characterization and their electronic absorption spectra of mixed ligand (azo rhodanine and methylacetoacetate) and metal complexes. In addition to the novel complexes of Ru(III) with 5-(4'-alkyl phenylazo)-2-thioxo-4-thiazolidinone have been prepared and characterized [10] by different techniques.

The objectives of the present work are the synthesis of Cu(II) complexes of 5-(4'-derivatives phenylazo)-2-thioxo-4-thiazolidi-none (HL<sub>n</sub>). The thermogravimetric analysis (TGA) studies, the ac

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n=1, R = OCH<sub>3</sub>; n=2, R = CH<sub>3</sub>; n=3, R = H; and n=4, R = NO<sub>2</sub>

Scheme 1. The formation mechanism of azo rhodanine derivatives.

conductivity, dielectric properties and conduction mechanism of Cu(II) complexes of azo rhodanine derivatives, as well as the effect of substituents of complexes on these properties were discussed.

### 2. Experimental

All the chemicals used were of British Drug House (BDH) quality.

# 2.1. Preparation of 5-(4'-derivatives phenylazo)-2-thioxothiazolidin-4-one ( $HL_{\rm p}$ )

In a typical preparation, 25 ml of distilled water containing 0.01 mol hydrochloric acid were added to aniline (0.01 mol) or *p*-derivatives. To the resulting mixture stirred and cooled to 0 °C, a solution of 0.01 mol sodium nitrite in 20 ml of water was added dropwise. The formed diazonium chloride was consecutively coupled with an alkaline solution of 0.01 mol 2-thioxo-4-thiazo-lidinone, in 10 ml of pyridine as shown in Scheme 1. The colored precipitate, which formed immediately, was filtered through sintered glass crucible, washed several times with water and ether. The crude products was purified by recrystallization from hot ethanol, yield ~65% then dried in a vacuum desiccator over  $P_2O_5$  [21].

#### 2.2. Preparation of complexes

A hot ethanolic solution containing the 5-(4'-derivatives phenylazo)-2-thioxothiazolidin-4-one (HL<sub>n</sub>) was mixed with a hot ethanolic solution of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (1 mmol) as shown in Scheme 2. The mixture was then refluxed on a water bath for ~10 h and allowed to cool whereby the solid complexes were separated, which were filtered off, washed several times with ethanol, dried and kept in a desiccator over dried CaCl<sub>2</sub>.

# 2.3. Measurements

Elemental microanalyses of the compounds for C, H and N were determined on automatic analyzer CHNS Vario ELIII, Germany. The infrared spectra were recorded as KBr discs using a PerkinElmer 1340 spectrophotometer. The analyses were repeated twice to check the accuracy of the analyzed data. The metal content in the complexes was estimated by standard methods [8]. The magnetic moment of the prepared solid complexes was determined at room temperature using the Gouy's method. Mercury(II) (tetrathiocyanato) cobalt(II), [Hg{Co(SCN)<sub>4</sub>}], was used for the calibration of the Gouy's tubes. Thermogravimetric analysis (TGA) measurements were investigated using Simultaneous Thermal Analyzer (STA) 6000 with scan rate 15 °C/min under dynamic nitrogen atmosphere in the temperature range 40–800 °C. Ac conductivity measurements are performed on the samples in the form of discs



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Scheme 2. The structure of Cu(II) complexes.

Table 1
Analytical and magnetic moments of Cu(II) complexes

Complex	$\mu_{eff.}$ B.M.	Calc. (exp)%				
		С	Н	Ν	S	М
$[Cu(L_1)(OAc)(OH_2)]2H_2O$ (1)	1.83	32.54 (32.47)	3.84 (3.72)	9.49 (9.13)	14.46 (14.07)	14.36 (14.06)
[Cu(L <sub>2</sub> )(OAc)(OH <sub>2</sub> )]2H <sub>2</sub> O (2)	1.84	28.51 (28.40)	3.02 (2.89)	9.07 (8.78)	13.82 (13.65)	13.72 (13.47)
[Cu(L <sub>3</sub> )(OAc)(OH <sub>2</sub> )]2H <sub>2</sub> O (3)	1.85	33.76 (33.60)	3.99 (3.82)	9.85 (9.46)	15.01 (14.86)	14.90 (14.72)
[Cu(L <sub>4</sub> )(OAc)(OH <sub>2</sub> )]2H <sub>2</sub> O (4)	1.87	32.00 (31.86)	3.64 (3.44)	10.18 (9.87)	15.51 (15.27)	15.40 (15.17)

of thickness 0.4–0.8 mm and compressed at a pressure of 12 t cm<sup>-2</sup>. The surface of each sample was covered by a layer of silver, then was held between two copper electrodes and inserted vertically into a cylindrical electric furnace. The ac conductivity ( $\sigma_{ac}$ ) measurements of samples are measured as a function of temperature range from 303 to 600 K and frequency range 0.1–100 kHz using Stanford research systems Model SR 720 LCR METER. Ac conductivity was calculated from the measured values of capacitance ( $C_p$ ) and loss tangent (tan $\delta$ ) in parallel mode. The temperature is measured by NiCr–NiAl thermocouple. The range of temperature for electrical measurements is chosen according to TGA measurements.

# 3. Results and discussion

# 3.1. Structure of the metal complexes

The complexes were found to be insoluble in common organic solvents but soluble in coordinated solvents. The analytical data are given in Table 1. Magnetic measurements were conducted in order to obtain information about the geometry of the complexes. The magnetic susceptibility values (1.83–1.87 B.M.) suggesting the square planar geometry for the Cu(II) complexes of azo rhodanine derivatives (Table 1) [22].

### 3.2. Infrared spectra of complexes and nature of coordination

The broad/strong absorption bands in the ligands (HL<sub>n</sub>) located at ~3450–3434 and at ~1710–1695 cm<sup>-1</sup> region assigned to the v(NH) stretching vibrations mode and carbonyl stretching vibrations. The three bands in the 1600–1500 cm<sup>-1</sup> region are characteristic for most six-membered aromatic ring system. The frequencies for the N=N stretching lie in the region 1440–1435 cm<sup>-1</sup>. The region between 1500 and 1900 cm<sup>-1</sup> is due C–N stretching, N–H in plane or out of plane bending and outof-plane C–H bending vibrations [7,8,10]. In the IR spectra of all Cu(II) complexes (1–4) a number of changes are observed:

- 1) The appearance of a new bands around  $\sim 3380 \, {\rm cm}^{-1}$  and two sharp bands at  $\sim 715$  and  $420 \, {\rm cm}^{-1}$ , the latter two can be assigned to the wagging and rocking modes of vibration of the water molecule, respectively [23] in the prepared Cu(II) complexes (1–4) may be taken as a strong evidence for the presence of coordinated water. Such region, however, is not initially present in the free ligands. This is confirmed by the elemental analysis of these complexes (Table 1).
- 2) The N=N stretching frequency of the azo groups is shifted to lower frequency by ~15-25 cm<sup>-1</sup> due to the involvement of one of the azo nitrogen atoms in coordination with metal ion [7,24]. This lowering of frequency can be explained by the transfer of electrons from nitrogen atom to the Cu(II) ion due to coordination.
- 3) To confirm the presence of coordinating H<sub>2</sub>O molecules in the complex, we carried out thermogravimetric analysis of all the complexes. This study shows loss of weight corresponding to one water molecule in the temperature range above 190 °C, indicating that the water molecule in these complexes is coordinated to the metal ion.
- 4) The participation of the OH group in Cu(II) complexes is confirmed by the appearance of new bands in Cu(II) complexes at 555–525 cm<sup>-1</sup> for complexes related to the Cu–O vibration [24]. The acetate complexes show two new bands at 1600 and 1390 cm<sup>-1</sup> attributed to  $v_{as}$  and  $v_s$  of the acetate group. The difference between the two bands indicates the monodentate nature of the acetate group [22,25].

On the basis of all these data, the molecular structure of the Cu (II) complexes could be suggested based on: (i) the presence of anion, (ii) the disappearance of C=O, (iii) the coordination of azo-group and (iv) the presence of water.

 Table 2

 The thermal analysis data of the Cu(II) complexes.

Complex <sup>a</sup>	Temp. range (°C)	Found mass loss (calc.) %	Assignment
(1)	45-331	23.91 (25.52)	Loss of water molecules and one coordinated acetate group
	331-506	24.43 (26.88)	Further decomposition of a part of the ligand $(C_3H_7N_2SO)$
	506-709	14.38 (16.27)	Decomposition of a part of the ligand $(C_2H_2NS)$ leaving CuO residue with contaminated carbon atoms
(2)	45-316	23.22 (26.49)	Loss of water molecules and one coordinated acetate group
	316-533	20.47 (21.33)	Decomposition of a part of the ligand $(C_2H_7N_2S)$
	533-670	15.45 (16.87)	Decomposition of a part of the ligand (C <sub>2</sub> H <sub>2</sub> NS) leaving CuO residue with contaminated carbon atoms
(3)	45-273	26.52 (27.39)	Loss of water molecules and one coordinated acetate group
	273-514	18.06 (17.94)	Decomposition of a part of the ligand $(CH_2N_2S)$
	514-640	22.04 (21.57)	Decomposition of a part of the ligand $(C_3H_7NS)$ leaving CuO residue with contaminated carbon atoms
(4)	45-288	20.87 (24.7)	Loss of water molecules and one coordinated acetate group
	288-400	10.46 (10.05)	Loss of NO <sub>2</sub> group
	400-592	13.72 (15.74)	Decomposition of a part of the ligand ( $C_2H_2NS$ )
	592-670	22.44 (22.51)	Decomposition of a part of the ligand (C <sub>3</sub> H <sub>7</sub> N <sub>2</sub> S) leaving CuO residue with contaminated carbon atoms

<sup>a</sup> Numbers as given in Table 1.



Fig. 1. TGA curves for Cu(II) complexes (1-4).



**Fig. 2.** The relation between  $\ln K^*$  versus 1/T for Cu(II) complexes (**1–4**) (inset: the relation between  $E_a$  and Hammett's substituent coefficients ( $\sigma^R$ )).



Fig. 3. Variation of real dielectric constant,  $\varepsilon_n$  with frequency for Cu(II) complexes (1–4) at different temperatures.



**Fig. 4.** Variation of imaginary dielectric constant,  $\varepsilon_i$ , with frequency for Cu(II) complexes (1–4) at different temperatures.

According to the structure shown in Scheme 1 the ligands (HL<sub>n</sub>) takes its usual anionic form ( $L_n$ ) to chelate Cu(II) through N- of azo group and oxygen of hydroxy group (Scheme 2).

# 3.3. Thermogravimetric analysis of the complexes

The TGA of the isolated complexes was taken as a proof for the existence of water molecules as well as the anions in the coordination sphere. The thermal analyses data for the Cu(II) complexes (1–4) are summarized in Table 2. In the temperature range ~45–273 °C, the loss of water molecules as well as the loss of one coordinated acetate group occurs as shown in Fig. 1. According to the literature, the azo bonds in the azo metal complexes breakdown when the temperature is higher than 260 °C [22, 26–28]. The weight loss stages (~273–500 °C) are due to the decomposition of a part of the ligand. The final weight losses (~500–640 °C) are largely attributed to complete decomposition of other part of the ligand molecule. The remaining final product is CuO with contaminated carbon atoms.

The rate constant of the thermal degradation is plotted in Fig. 2 according to the Arrhenius relationship [21]:

$$\ln K^* = \ln A^\circ - \frac{E_a}{RT} \tag{1}$$

where  $K^*$  is the rate constant of the thermal degradation,  $A^{\circ}$  is a constant,  $E_a$  the thermal activation energy of decomposition, R is

the gas constant (=8.314  $JK^{-1}$  mol<sup>-1</sup>) and T is the absolute temperature. The thermal activation energies of decomposition  $(E_2)$  of Cu(II) complexes (1-4) are calculated from the slope of the straight line obtained from the plot  $\ln K^*$  versus 1/T as shown in Fig. 2, and the values found to be 40.98, 39.28, 38.88 and 45.13 kJ/ mol for complexes (1-4), respectively. The effect of the substituents of complexes on the thermal activation energies of decomposition  $(E_a)$  can be confirmed in terms of Hammett's substituent coefficients ( $\sigma^{R}$ ) are shown in the inset of Fig. 2. The effect of methoxy and methyl groups is to decrease the  $E_{a}$ , while the effect of nitro group is to increase  $E_a$ . The complex (4) is the highest value of  $E_a$ . This can be attributed to the fact that the effective charge experienced by the d-electrons increases due to the electron withdrawing p-substituent NO2 while it decreases by the electron donating character of OCH<sub>3</sub> and CH<sub>3</sub>. This indicates that the complex (4) is more thermally stable than the other complexes. This can be attributed to the strong withdrawing nature of the NO<sub>2</sub> as a function group [21,29]. It is important to note that the existence of a methyl and/or methoxy group enhances the electron density on the coordination sites.

#### 3.4. Analysis of ac measurements

The ac conductivity of a material can be determined in terms of its dielectric constant. The dielectric constant is an important



**Fig. 5.** The relation of conductivity ( $\sigma_{ac}$ ) as a function of temperature for Cu(II) complexes (1–4) at different frequencies.

parameter which gives valuable information about the electric properties of the material which is given by [21,30,31]:

$$\varepsilon^* = \varepsilon_r - i\varepsilon_i,\tag{2}$$

where  $\varepsilon_r$  is the real dielectric constant and  $\varepsilon_i$  is the imaginary dielectric constant. The real dielectric constant,  $\varepsilon_r$ , can be calculated from the measured capacitance in parallel mode by Eq. (3) [21,30,31]:

$$\varepsilon_r = \frac{C_p d}{\varepsilon_o A},\tag{3}$$

where  $C_p$  is the capacitance of the samples measured in parallel mode,  $\varepsilon_o$  is the permittivity of free space, A is the cross sectional area and d is the thickness of the samples. The imaginary part of the dielectric constant,  $\varepsilon_i$ , can be calculated using the equation below [21,30,31]:

$$\varepsilon_i = \varepsilon_r \tan \delta \tag{4}$$

where tan $\delta$  is the measured values of loss tangent. The value of  $\varepsilon_r$ and  $\varepsilon_i$  are calculated in the frequency range 0.1–100 kHz and temperature range 303–600 K. Both of  $\varepsilon_r$  and  $\varepsilon_i$  in general, are found to decrease with increasing frequency and increase with increasing temperature for all Cu(II) complexes (1–4) (The calculated data of  $\varepsilon_r$  and  $\varepsilon_i$ , not presented her). Figs. 3 and 4 show the frequency dependence of real and imaginary dielectric constants at different temperatures. It is evident that  $\varepsilon_r$  and  $\varepsilon_i$  decrease with increasing frequency and increase with increasing temperature.

The ac conductivity,  $\sigma_{ac}$ , for complexes can be calculated from Eq. (5) [21]:

$$\sigma = \omega \varepsilon_0 \varepsilon_i, \tag{5}$$

where  $\omega$  is the angular frequency. The calculated values of  $\sigma_{\rm ac}$  of Cu (II) complexes (1–4) under consideration as a function of temperature are investigated in the temperature range 303–600 K and in frequency range 0.1–100 kHz and are shown in Fig. 5. The calculated values of  $\sigma_{\rm ac}$  are found to increase with increasing temperature and frequency. The values of conductivity at temperatures higher than ~470 K show a remarkable increase. This behavior can be attributed to the decomposition process.

The ac electrical conductivity,  $\sigma_{ac}$ , for Cu(II) complexes (1–4) as a function of temperature which is given by [21,32]:

$$\sigma = \sigma_0 \exp\left(\frac{-\Delta E}{k_B T}\right),\tag{6}$$

where  $\sigma_o$  is the pre-exponential constant,  $\Delta E$  is the thermal activation energy of electrical conductivity and  $k_B$  is Boltzmann's constant. The relation between  $\ln \sigma_{ac}$  as a function of (1/T) for complexes is shown in Fig. 6 in the temperature range 303–470 K and frequency ranges under consideration. The temperature interval is chosen according to the TGA analysis. The data show a thermally activated behavior and are characterized by two thermal



**Fig. 6.** Dependence of  $\ln \sigma_{ac}$  versus 1/T for Cu(II) complexes (1–4) at different frequencies.

activation energies of electrical conductivity  $\Delta E_1$  and  $\Delta E_2$  in the regions I and II, respectively, depending on the temperature range.

The values of the thermal activation energies of electrical conductivity,  $\Delta E_1$  and  $\Delta E_2$ , for all complexes at different frequencies are determined and listed in Table 3. The relative low values of  $\Delta E_1$  ( $\Delta E_1 = 0.032 - 0.344 \text{ eV}$ ) in the lower temperature region proposes hopping and/or tunneling conduction mechanism. The variations in both  $\Delta E_1$  and  $\Delta E_2$  are attributed to the effect of the substituents [21]. This behavior has been observed from the ac and dc electrical conductivity of some rhodanine azodye compounds and their complexes [21,33]. The effect of the substituents on the thermal activation energies of electrical conductivity can be confirmed in terms of Hammett's substituent

coefficients ( $\sigma^R$ ) are shown in Fig. 7. It is clear that the values of  $\Delta E_1$  increase with increasing  $\sigma^R$ . This can be attributed to the fact that the effective charge experienced by the d-electrons increases due to the electron withdrawing *p*-substituent NO<sub>2</sub> while it decreases by the electron donating character of OCH<sub>3</sub>. This is in accordance with that expected from Hammett's substituent coefficients ( $\sigma^R$ ) as shown in Fig. 7. On the other hand the frequency dependence of the  $\Delta E_1$  and  $\Delta E_2$  for Cu(II) complexes (**1–4**) show that both of  $\Delta E_1$  and  $\Delta E_2$  tends to decrease with the increase of frequency. Thus, the increase of the applied frequency enhances the electronic jumps between the localized states [34,35].

To operating conduction mechanism for Cu(II) complexes (1–4) can be investigated by studying the behavior of  $\sigma_{\rm ac}$  with frequency

Table 3

The values of the thermal activation energies of electrical conductivity for Cu(II) complexes<sup>a</sup> at different frequencies.

F (kHz)	(1)		(2)	(2)		(3)		(4)	
	$\Delta E_1$ (eV)	$\Delta E_2 (eV)$	$\Delta E_1$ (eV)	$\Delta E_2 (\text{eV})$	$\Delta E_1$ (eV)	$\Delta E_2 (\text{eV})$	$\Delta E_1$ (eV)	$\Delta E_2 (eV)$	
0.1	0.107	0.488	0.117	0.344	0.092	0.211	0.164	0.240	
1	0.037	0.362	0.109	0.314	0.082	0.174	0.097	0.234	
10	0.043	0.262	0.074	0.282	0.055	0.176	0.086	0.225	
100	0.032	0.194	0.067	0.188	0.042	0.169	0.057	0.186	

<sup>a</sup> Numbers as given in Table 1.



**Fig. 7.** The relation between  $\Delta E_1$  (eV) and Hammett's substituent coefficients ( $\sigma^R$ ) for Cu(II) complexes (**1,3** and **4**).



$$\sigma = A^* \omega^s, \tag{7}$$

where  $A^*$  is a constant depending on temperature and S is the frequency exponent in which its behavior with temperature determines the operating conduction mechanism. In order to determine the conduction mechanism for a material, theoretical model has been reported to correlate the conduction mechanism with the behavior of the frequency exponent S [21,37]. The value of S is the slope of the straight line obtained from the relation between  $\log \sigma_{\rm ac}$  and  $\log \omega$ . The values of S as a function of temperature for Cu(II) complexes (1-4) are shown in Fig. 8. The behavior of *S* with temperature for complexes (1), (2) and (4) appear to be consistent with the hopping process of charge carriers between localized sites and suggests that the correlated barrier hopping (CBH) model is the best suitable model for conduction mechanism [21,30,32]. The value of S for complex (3) was found to increase with increasing temperature. This behavior can be explained in terms of small polaron tunneling (SPT) model for ac conduction [38]. The frequency exponent S based on this model is evaluated as,



**Fig. 8.** Plot of the frequency exponent, *S*, versus temperature, *T*, for Cu(II) complexes (**1-4**).



**Fig. 9.** The maximum barrier height,  $W_m$ , as a function of temperature for Cu(II) complexes (**1**, **2** and **4**) according to CBH conduction model.

$$S = 1 - \frac{4}{\ln[1/\omega\tau_{\rm o}] - W_{\rm H}/K_{\rm B}T},$$
(8)

where  $W_{\rm H}$  is the barrier height for infinite site separation,  $\tau_{\rm o}$  the relaxation time and  $\omega$  the angular frequency. According to this model, the ac conductivity is given by equation [38]:

$$\sigma_{ac(SPT)} = \frac{\pi^4 e^2 K_B T [N(E_F)]^2 \omega R_w^{\prime 4}}{24 \alpha},\tag{9}$$

where *e* is the electronic charge,  $\alpha$  is the spatial extent of polaron, *N* (*E<sub>F</sub>*) the density of states at the Fermi level and *R'*<sub>w</sub> is the tunneling distance.

In CBH model, S is given by Eq. (10) [21,32]:

$$S = 1 - \frac{6k_BT}{\left[w_m - k_BT\ln(1/\omega\tau_o)\right]},\tag{10}$$

where  $W_m$  is the maximum barrier height (the energy required to move the electron from a site to infinity).

The dependence of  $\sigma_{ac(CBH)}$  on temperature and frequency is given by Eq. (11) [37,39]:

$$\sigma_{ac(CBH)} = \frac{\pi^3}{24} [N(E_F)]^2 \varepsilon \varepsilon_0 \omega R_w^6, \tag{11}$$

where  $R_w$  is the distance between hopping states.

First approximation to Eq. (10) gives the expression:

$$w_m = \frac{6k_BT}{1-S} \tag{12}$$

The maximum barrier height,  $W_m$ , as a function of temperature for complexes (1), (2) and (4) is presented in Fig. 9. The value of maximum barrier height,  $W_m$ , for complex (1) decreases with increasing the temperature and have values in the range 0.35–0.80 eV. The values of  $W_m$  for complexes (2) and (4) are slightly increased with increasing temperature. This behavior may be attributed to probable increase of the hopping distance,  $R_w$ , of charge carrier from one site to another with heating.

# 4. Conclusions

In this paper, synthesis and characterization of a series of Cu(II) complexes of azo rhodanine derivatives. The complexes characterized by elemental analysis, IR spectra, magnetic measurements and thermogravimetric analysis (TGA). The complexes behave as monobasic bidentate ligands when react with Cu(II) salt and undergo coordination through azodye nitrogen, enolic oxygen atom. It is found that the change of substituent affects the thermal properties of the complexes. The values of the thermal activation energies of decomposition ( $E_a$ ) of complexes (1–4) are found to be 40.98, 39.28, 38.88 and 45.13 kJ/mol, respectively. The values of the thermal activation energies of electrical conductivity for Cu(II) complexes (1–4) under investigation were calculated at different frequencies and found to be in the range 0.032–0.164 eV for  $\Delta E_1$  and 0.170–0.488 eV for  $\Delta E_2$  depending on the test frequency. The conductivities are found to be dependent on the structure of the complexes. The correlated barrier hopping (CBH) is the dominant conduction mechanism for complexes (1), (2) and (4) while small polaron tunneling (SPT) is the dominant conductivities of the complexes affects the thermal properties and conductivities of the complexes.

#### References

- B.C.C. Contello, M.A. Cawhorne, D. Haigh, R.M. Hindley, S.A. Smith, P.L. Thurlby, Bioorg. Med. Chem. Lett. 4 (1994) 1181–1184.
- [2] M.I. Abou-Dobara, A.Z. El-Sonbati, Sh.M. Morgan, World J. Microbiol. Biotechnol. 29 (2013) 119–126.
- [3] S.L. Johnson, L.H. Chen, R. Harbach, M. Sabet, A. Savinov, N.J.H. Cotton, A. Strongin, D. Guiney, M. Pellecchia, Chem. Biol. Drug Design 71 (2) (2008) 131–139.
- [4] S.G. Alegaon, K.R. Alagawadi, P.V. Sonkusare, S.M. Chaudhary, D.H. Dadwe, A.S. Shah, Bioorg. Med. Chem. Lett. 22 (2012) 1917–1921.
- [5] P. Villain-Guillot, M. Gualtieri, L. Bastide, F. Roquet, J. Martinez, M. Amblard, M. Pugniere, J.P. Leonetti, J. Med. Chem. 50 (17) (2007) 4195–4204.
- [6] S. Yan, G. Larson, J.Z. Wu, T. Appleby, Y. Ding, R. Hamatake, Z. Hong, N. Yao, Bioorg. Med. Chem. Lett. 17 (2007) 63–67.
- [7] A.Z. El-Sonbati, A.A.M. Belal, M.S. El-Gharib, Sh.M. Morgan, Spectrochim. Acta A 95 (2012) 627–636.
- [8] A.Z. El-Sonbati, M.A. Diab, A.A.M. Belal, M. Sh. Morgan, Spectrochim. Acta A 99 (2012) 353–360.
- [9] A.Z. Él-Sonbati, A.A. El-Bindary, A. El-Dissouky, T.M. El-Gogary, A.S. Hilali, Spectrochim. Acta A 58 (2002) 1623–1629.
- [10] A.Z. El-Sonbati, A.A.M. Belal, S.A. Abd El-Meksoud, R.A. El-Boz, J. Mol. Struc. 1027 (2012) 200–206.
- [11] W.I. Stephen, A. Townshend, Anal. Chim. Acta 33 (1965) 257-265.

- [12] G.G. Alfonso, J.L.G. Ariza, Microchem. J. 26 (1981) 574-585.
- [13] M. Abdallah, Corros. Sci. 44 (2002) 717-728.
- [14] A. Döner, R. Solmaz, M. Özcan, G. Kardaş, Corros. Sci. 53 (2011) 2902–2913.
   [15] S.A. Abd El-Meksoud, A.M. El-Desoky, A.Z. El-Sonbati, A.A.M. Belal, R.A. El-Boz,
- Intern. J. Sci. Eng. Res. 4 (2013) 1986–1994. [16] A.K. Jain, A. Vaidya, V. Ravichandran, S.K. Kashaw, R.K. Agrawal, Bioorg. Med.
- Chem. 20 (2012) 3378–3395.
- [17] S. Ravi, K.K. Chiruvella, K. Rajesh, V. Prabhu, S.C. Raghavan, Eur. J. Med. Chem. 45 (2010) 2748–2752.
- [18] G.G. Alfonso, J.L.G. Ariza, Microchem. J. 26 (1981) 574-585.
- [19] N.S. Habib, S.M. Rida, E.A.M. Badawey, H.T.Y. Fahmy, H.A. Ghozlan, Eur. J. Med. Chem. 32 (1997) 759–762.
- [20] N.H. Metwally, M.A. Abdalla, M.A. Mosselhi, E.A. El-Desoky, Carbohydr. Res. 345 (2010) 1135–1141.
- [21] N.A. El-Ghamaz, A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, M.K. Awad, Sh.M. Morgan, Mater. Sci. Semicond. Process. 19 (2014) 150–162.
- [22] A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, Sh.M. Morgan, Spectrochim. Acta A 127 (2014) 310–328.
- [23] J.A. Dean, Lange's Handbook of Chemistry, fourteenth ed., McGraw-Hill, New York, 1992, pp. 35.
- [24] A.Z. El-Sonbati, A.A. El-Bindary, M.A. Diab, S.G. Nozha, Spectrochim. Acta A 83 (2011) 490–498.
- [25] A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, Stoichiometry and Research-The Importance of Quantity in Biomedicine, In Tech, Rijeka, Croatia, 2012, pp. 147–194 ISBN 978-953-51-0198-7.
- [26] M.A. Diab, A.Z. El-Sonbati, A.A. El-Bindary, A.M. Barakat, Spectrochim. Acta A 116 (2013) 428–439.
- [27] S. Amer, N. El-Wakiel, H. El-Ghamry, J. Mol. Struct. 1049 (2013) 326-335.
- [28] A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, A.M. Eldesoky, Sh.M. Morgan, Spectrochim. Acta A 135 (2015) 774–791.
- [29] N.A. El-Ghamaz, A.Z. El-Sonbati, Sh.M. Morgan, J. Mol. Struct. 1027 (2012) 92–98.
- [30] H.M. Zeyada, M.M. El-Nahass, Appl. Surf. Sci. 254 (2008) 1852-1858.
- [31] A.M. Afifi, E. Abd El-Wahabb, A.E. Bekheet, H.E. Atyia, Acta Phys. Pol. A 98 (2000) 401-409.
- [32] N.A. El-Ghamaz, M.A. Diab, M.Sh. Zoromba, A.Z. El-Sonbati, O. El-Shahat, Solid State Sci. 24 (2013) 140–146.
- [33] M.S. Aziz, A.Z. El-Sonbati, A.S. Hilali, Chem. Pap. 56 (2002) 305–308.
- [34] M.M. El-Nahass, H.A.M. Ali, Solid State Commun. 152 (2012) 1084-1088.
- [35] M.A.M. Seyam, Appl. Surf. Sci. 181 (2001) 128-138.
- [36] M.M. El-Nahass, A.A. Atta, M.A. Kamel, S.Y. Huthaily, Vacuum 91 (2013) 14-19.
- [37] S.R. Elliott, Adv. Phys. 36 (1987) 135–217.
- [38] T.M. Meaz, S.M. Attia, A.M. Abo El-Ata, J. Magn. Magn. Mater. 257 (2003) 296-305.
- [39] A.R. Long, Adv. Phys. 31 (1982) 553–637.