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# Computational studies of the first order kinetic reactions for mononuclear copper(II) complexes having a hard-soft NS donor ligand

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#### ABSTRACT

The chelation behaviour of 4-((*E*)-2-(1-(thiophen-2-yl)ethylidene)hydrazinyl)-1-(4-methoxyphenyl)-1H-pyrrole-3-carbonitrile (HL) towards Cu(II) ions has been investigated. These Cu(II) complexes are characterized by elemental analyses, molarsolid conductance, ESR, FTIR and electronic spectral studies. Also, the kinetic and thermodynamic parameters (*Ea*, *A*,  $\Delta H$ ,  $\Delta S$ ,  $\Delta G$ ) for all thermal decomposition steps have been evaluated using Coats-Redfern and Horowitz-Metzger methods. Furthermore, antimicrobial activity of the ligand and its complexes were studied against Gram-negative bacteria: *Escherichia coli*, Gram-positive *Bacillus cereus*, *Bacillus subtilis* and pathogenic fungi *pseudomonas aeruginosa* by using minimum inhibitory concentrations (MICs) method.

**Keywords**: Copper(II) complexes; FTIR; ESR; Thermal analysis; Antimicrobial activity

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#### 1. Introduction

A literature survey reveals that the pyrrolidine ring is important for antimycobacterial activity [1]. In addition, many hetero-nitrogen and sulfur derivatives exhibit a wide variety of biological activities, such as antimicrobial [2], anti-inflammatory [3], antihistaminic [4], antihypertensive [5], hypnotic [6] and anticonvulsant [7] activity. From previous work, Schiff bases are known to possess at least antimicrobial and genotoxicity activities [8–13]. Also, transition metal ions with different oxidation state have a strong role in bio-inorganic chemistry and redox enzyme systems and may provide the basis of models for active sites of biological systems [14]. Copper is the third most abundant metallic element in the human body, following iron and zinc. It also plays a role in the action of a multitude of enzymes that catalyze a great variety of reactions [15-17]. Superoxide dismutase has normal Cu(II) enzyme active sites containing tetragonally coordinated Cu(II) ion. DTA and TG were used to study the modes of thermal decomposition of some divalent copper complexes of Schiff bases [18, 19]. In this work we aim to study the thermal analysis (DTA and TG) as well as the kinetic parameters of decomposition of some Cu(II) complexes prepared from 4-((E)-2-(1-(thiophen-2-yl) ethylidene) hydrazinyl)-1-(4methoxyphenyl)-1*H*-pyrrole-3-carbonitrile Schiff base.

#### 2. Experimental

#### 2.1. Materials and reagents

All manipulations were performed under aerobic conditions. All metal salts and other reagents used were pure (Fluka, Aldrich, or Merck). They included thiophene-2-carboxaldehyde; 4-hydrazinyl-1-(4-methoxyphenyl)-1*H*-pyrrole-3carbonitrile, Cu(CH<sub>3</sub>COO)<sub>2</sub>.H<sub>2</sub>O, CuCl<sub>2</sub>.2H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O and CuSO<sub>4</sub>.5H<sub>2</sub>O. Organic solvents used included absolute ethyl alcohol, diethyl ether and dimethyl sulphoxide. These solvents were spectroscopic pure from BDH.

#### 2.2. Apparatus

The molar conductance of the complexes were determined by preparing  $10^{-3}$  M solutions of the complexes in DMSO at room temperature and measured on an YSI Model 32 conductivity bridge. The electrical conductivity was measured using METRISO 5000A electrometer. The samples were in the form of discs of diameter 13

mm and thickness of 1-3 mm which were pressed under a pressure of ca 300 kg/cm<sup>-2</sup>. Good contact area was achieved by liquid silver painting on the two opposite surfaces of each disc. The temperature was measured in air using Cu-CuNi thermocouple placed close to the sample. Thermogravimetric analysis was performed using an automatic recording thermobalance type (DuPont 951 instrument). Magnetic moment values were evaluated at room temperature  $(25+1^{\circ}C)$  for triplet samples using a Johnson Matthey magnetic susceptibility balance using  $Hg[Co(SCN)_4]$  as calibrant. The electronic spectra of the complexes were recorded in DMSO solution on a Unicam UV<sub>2</sub>-UV-visible spectrometer, in the range 200–900 nm. Infrared spectra of the complexes and parent ligand were recorded on Mattson 5000 FTIR spectrophotometer, in the range 4000–400 cm<sup>-1</sup> in KBr disk. ESR spectra of Cu(II) complexes were obtained on a Bruker EMX Spectrometer working in the X-band (9.78 GHz) with 100 kHz modulation frequency. The microwave power was set at 1 mW and modulation amplitude was set at 4 Gauss. The low-field signal was obtained after four scans with a tenfold increase in the receiver gain. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature. Carbon and hydrogen content for the ligand and its complexes were performed with a Perkin-Elmer 2400 series II analyzer. Cu(II), Cl<sup>-</sup> and  $SO_4^{2-}$  contents in the complexes were determined by the well known standard methods [20].

#### 2.3. Synthesis of ligands

The 4-((E)-2-(1-(thiophen-2-yl)ethylidene)hydrazinyl)-1-(4-methoxyphenyl)-1H-pyrrole-3-carbonitrile (Scheme 1- Supplementary Materials) was prepared by condensing 1:1 molar ratios of thiophene-2-carboxaldehyde in absolute ethanol with 4-hydrazinyl-1-(4-methoxy-phenyl)-1H-pyrrole-3-carbonitrile in ethanolic solutions. The reaction mixtures were refluxed in a water bath for 3 h in the presence of few drops of glacial acetic acid. On heating, pale yellow crystals were formed, filtered off, washed with absolute ethanol and diethyl ether and recrystallized from EtOH. The purity of the compound was checked by TLC. The proposed formula of the ligand is in good agreement with the stoichiometric concluded from its analytical data (Table 1).

#### 2.4. Synthesis of copper(II) complexes

The complexes were prepared by mixing equimolar amounts of 4-((E)-2-(1-(thiophen-2-yl)ethylidene)hydrazinyl)-1-(4 methoxyphenyl)-1H-pyrrole-3-carbonitrile (HL) with ethanolic and/or aqueous solution of CuSO<sub>4</sub>.5H<sub>2</sub>O, CuCl<sub>2</sub>.2H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O and Cu(CH<sub>3</sub>COO)<sub>2</sub>.H<sub>2</sub>O. The reaction mixture was refluxed on a water bath for 1–3 h. The precipitate was filtered off, washed with hot water, hot absolute ethanol and diethyl ether and finally dried in a vacuum desiccator over anhydrous CaCl<sub>2</sub>.

#### 2.5. Antimicrobial activity

The minimum inhibitory concentration (MIC) was carried out using the micro dilution susceptibility method in Muller-Hinton Broth and sabouraud liquid medium. The compounds, ampicillin and gentamycin were dissolved in DMSO at concentration of 1mg/ml. The twofold dilutions of the solution were prepared. The microorganism suspensions at 10 CFU/ml (colony forming unit/ml) concentrations were inoculated to the corresponding wells. The plates were incubated at 36 °C for 24 and 48 h for the bacteria and fungi, respectively. The MIC values were determined as the lowest concentration that completely inhibited visible growth of the microorganism as detected by unaided eye.

#### 3. Results and Discussion

The isolated solid complexes are stable in air and easily soluble in DMF and DMSO. The complexes decompose on heating in the range 235-300 °C. The molar conductance values in DMSO are 3-9 Ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup> indicating that all complexes are non-electrolytes. The colors, melting points and elemental analyses of the isolated complexes are listed in Table 1.

#### 3.1. IR spectra

The bonding of the ligand to Cu(II) ion has been judged by a careful comparison of the infrared spectra of the complexes with that of the free ligand (Table 2). A few significant bands have been selected to observe the effect on ligand vibration in the complexes. Ligand show a medium-intensity broad band, due to v(NH) at 3240 cm<sup>-1</sup> [21]. In all Cu(II) complexes v(NH) appears at nearly the same or slightly higher frequencies, suggesting that this group does not take part in bonding. Whereas, the bands attributed to thiophen sulfur (C=S) and azomethine nitrogen (C=N) groups appears at 805 and 1644 cm<sup>-1</sup>, respectively [22]. In all the complexes

v(C=N) and v(C=S) is shifted to lower frequency indicating coordination of thiophen sulphur and azomethine nitrogen to the metal. So, the ligand acts as a neutral bidentate ligand via the thiophen sulphur and azomethine nitrogen. Also, the spectra of Cu(II) complexes show new bands in (503-512) and (405-423)  $\mbox{cm}^{-1}$  region assignable to v(Cu-O) and v(Cu-N), respectively [23,24]. The appearance of new bands in [Cu(HL)<sub>2</sub>(SO<sub>4</sub>)] complex at 1055 and 917 cm<sup>-1</sup> assignable to the SO stretching vibrations suggest bidentate sulphate [25]. In addition, [Cu(HL)(OAc)<sub>2</sub>].3H<sub>2</sub>O complex shows two bands at 1448 and 1541 cm<sup>-1</sup> attributable to the  $v_{as}(O-C-O)$  and  $v_s(O-C-O)$  of the acetate group. The difference (93 cm<sup>-1</sup>) between those two bands indicating the bidentate bonding for the acetate group [26].

#### 3.2. Magnetic moments and electronic spectra

The magnetic susceptibility ( $\mu_{eff}$ ) varies between 1.75 and 2.20 B.M., when spin–spin coupling between unpaired electrons belonging to different copper ions is absent, depending on the geometries of the complexes due to the difference in orbital contribution [27]. The observed  $\mu_{eff}$  values for the copper(II) complexes in this study are in the 1.92–2.05 B.M. range, corresponding to one unpaired electron. Electronic absorption spectra arise from the electronic transitions within a molecule or ion from a lower to a higher electronic energy level. The transition metal ions generally show a number of d–d transition bands depending on their electronic configuration from d<sup>1</sup> to d<sup>9</sup> in UV–vis regions. The copper(II) complexes generally show a broad band in the 13000–18000 cm<sup>-1</sup> region assigned to the envelop of  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g} + {}^{2}B_{2g} + {}^{2}A_{1g}$ transitions [28]. In the present study, all of the isolated complexes show a broad band in the 16000–16667 cm<sup>-1</sup> region in DMSO with a shoulder in the 14184–14285 cm<sup>-1</sup> regions (Table 3), suggesting a distorted octahedral geometry for all the complexes.

#### 3.3. ESR spectra

The room temperature solid state spectra of copper complexes (Fig. 1) exihibit axially symmetric g-tensor parameters with  $g_{\#} > g_{\perp} > 2.0023$ . The g values reflect that Cu(II) center has a tetragonally distorted octahedral geometry with the unpaired electron residing in the  $d_{x2-y2}$  orbital [29].

No band corresponding to the forbidden magnetic dipolar transition for the complexes were observed at half-field (*ca.* 1500 G, g = 4.0), ruling out any Cu–Cu

interaction and indicating that the complex is mononuclear Cu(II) complex. The g-values in axial symmetry given by,  $G = (g_{\parallel} - 2)/(g_{\perp} - 2) = 4$  which measure the exchange interaction between copper centers in solid.

According to Hathaway [30], if the value of G is greater than 4, the exchange interaction between Cu(II) centres in the solid state is negligible, whereas when G is less than 4, a considerable exchange interaction is indicated in the solid complex. The calculated G values were given in Table 3. The G values are greater than four Gsuggesting no copper–copper exchange interaction and these results are well consistence with the values of effective magnetic moments.

In hexacoordinated Cu(II) complexes, tetragonal distortion from the octahedral symmetry due to the Jahn-Teller distortion is very common. Such complexes with different ligands are attractive mainly due to the variation in the coordination geometry and the spectral features. [31, 32].

Superhyperfine structures for complexes were not seen at higher fields excluding any interaction of the nuclear spins of the nitrogen (I = 1) with the unpaired electron density on Cu(II). The absence of <sup>14</sup>N hyperfine coupling may be due to a relatively higher tetrahedral distortion for this complex [33]. Molecular orbital coefficients,  $\alpha^2$  (A measure of the covalency of the in-plane  $\sigma$ -bonding between a copper 3d orbital and the ligand orbitals) and  $\beta^2$  (covalent in-plane  $\pi$ -bonding), were calculated by using the following equations, [34–37].

where  $\alpha^2 = 1$  indicates complete ionic character, whereas  $\alpha^2 = 0.5$  denotes 100% covalent bonding, with the assumption of negligibly small values of the overlap integral.

$$\alpha^{2} = \left(\frac{A_{//}}{0.036}\right) + \left(g_{//} - 2.0023\right) + \frac{3(g_{\perp} - 2.0023)}{7} + 0.04$$
$$\beta^{2} = \frac{(g_{//} - 2.0023)E}{-8\lambda\alpha^{2}}$$

where  $\lambda = -828 \text{ cm}^{-1}$  for the free copper ion and *E* is the electronic transition energy. From table 4, the  $\alpha^2$  and  $\beta^2$  values indicate that there is a substantial interaction in the in-plane  $\sigma$ -bonding whereas the in-plane  $\pi$ -bonding is almost ionic. The higher value of  $\beta^2$  compared to  $\alpha^2$  indicates that the in-plane  $\pi$ -bonding is less

covalent than the in-plane  $\sigma$ -bonding. The  $\alpha^2$  value for Cu(II) complex indicates a considerable covalency in the bonding between the copper(II) ion and the ligand.

#### 3.4. Thermal analysis

The TG of the isolated complexes was taken as a proof for the existing of H<sub>2</sub>O molecules as well as the anions to be outside and/or inside the coordination sphere. The water of crystallization lost in 30–110 °C regions. The complexes show thermal stability rather than the ligand where the beginning of its decomposition shifts to higher temperature (252-320 °C). In general, all complexes are thermally stable;  $[Cu(HL)_2(NO_3)_2](H_2O)_2$  is the highest one. It is thermally stable up to 320 °C. In the temperature range 320–716 °C, the TG curve displays 47.4% weight loss which could be ascribed to the elimination of the two loosely bound ( $C_{12}H_{10}ON_3$ ) fragments. The final weight loss of 27.4% ending at 860 °C, is largely attributed to complete decomposition of the remaining more two tightly bound fragment ( $C_6H_6NS$ ). The remaining final fired product is Cu metal, representing 7.1%. The data of the different decomposition steps of all isolated complexes are shown in Table 4.

A realistic explanation for the anion effect can be provided by defect diffusion model [38]. When a reaction takes place in a solid, the formation of transition state results in a point defect in the lattice. These defects are analogous to the substituted ion Schotty and Frenkel defects [39]. When a volatile ligand like water is lost from a complex, a situation analogous to the Frenkel defect is formed. This introduces distortion in the structure of the crystal leading to transition state. The fraction of free space in crystal increases as the difference between the size of the cation and anion increases [40, 41]. The activation energies in Tables 5, 6 of the reported Cu(II) complexes for deaquation reaction decreases in the order sulphate > chloride > acetate > nitrate. The fraction of free space is much lower when cation and anions are of equal size.

#### 3.5. Kinetic data

Non-isothermal calculations were used extensively to evaluate the thermodynamic and kinetic parameters for the different thermal decomposition steps of the Cu(II) complexes were determined using the Coats-Redfern [42] and Horowitz-Metzger [43].

The rate of decomposition of a solid depends upon the temperature and the amount of material. The expression for the thermal decomposition of a homogeneous system has the following general form:

$$\frac{d\alpha}{dt} = K(T)g(\alpha) \tag{1}$$

Where t is the time, T is the absolute temperature and  $\alpha$  is the degree of transformation defined as:

$$\alpha = \frac{\frac{w - w}{o}}{\frac{w - w}{o}}$$

In which  $w_o$ ,  $w_t$  and  $w_\infty$  are the weights of the sample before the degradation, at temperature t and after total conversion, respectively. K(T) is the rate coefficient that usually follows the Arrhenius equation. The differential conversion function,  $g(\alpha)$ may present various functional forms but its most commonly form for solid-state reactions is  $g(\alpha)=(1-\alpha)n$ , where n is the reaction order, assumed to remain constant during the reaction [44, 45].

The rate constant is normally expressed by the Arrhenius equation:

$$K = A \exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

Where *Ea* is the activation energy, *A* is the Arrhenius pre-exponential factor which indicates how fast the reaction occurs and *R* is the gas constant in  $(\text{Jmol}^{-1}\text{K})$ . Substituting in equation 1, we get:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right)g(\alpha)$$
(3)  
$$\ln(1-\alpha) = -\frac{A}{\beta} \int_{T_0}^{T} \exp(-\frac{E}{RT}) dT$$
(4)

On the basis of equation (4), it is possible to analyze experimental data by the integral method, in order to determine the degradation kinetic parameters A and Ea.

The temperature integral in the right-hand side of equation (4) has no exact analytical solutions and several kinds of approximations are generally used. Two methods that differ on the way of resolving equation (4) are compared using the TGA data of the studied complexes. These methods are:

#### 3.5.1. Coats-Redfern method:

The Coats-redfern [42] method is as follows:

$$\ln[\frac{g(\alpha)}{T^2}] = \ln\left(\frac{AR}{\beta E}\right) - \frac{Ea}{RT}$$

Where  $g(\alpha) = 1 - (1 - \alpha)1 - n/1 - n$  for  $n \neq 1$  and  $g(\alpha) = -\ln(1 - \alpha)$  for n = 1, *R* is the universal gas constant. The correlation coefficient, r, was computed using the least square's method for different values of n (n=0.33, 0.5, 0.66, and n=1) by plotting  $\ln[\frac{g(\alpha)}{T^2}]$ 

(5)

method for different values of n (n=0.33, 0.5, 0.66 and n=1) by plotting  $T^2$  versus 1/T for the investigated metal complexes are shown in Figures from 2–4. The n-value which gave the best fit (r  $\approx$ 1) was chosen as the order parameter for the decomposition stage of interest. The slope of the straight line equal (*Ea/R*) and the intercept the pre-exponential factor, *A* can be determined (Fig. S1–Supplementary Materials). The data obtained are represented in Table 4.

#### 3.5.2. Horowitz-Metzger method:

The Horowitz-Metzger [43] relation was used to evaluate the degradation kinetics is

$$\ln[-\ln(1-\alpha)] = \frac{Ea\theta}{RT_s^2}$$
For n=1
(6)
$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] = \ln\left(\frac{A}{\beta}\frac{RT_s^2}{E}\right) - \frac{E_a}{RT_s} + \frac{E_a\theta}{RT_s^2}$$
For  $n \neq 1$ 
(7)

Where  $\theta = T \cdot T_s$ ,  $T_s$  is the DTG peak temperature, T the temperature corresponding to weight loss Wt. In this method a straight line should be observed between  $\ln[-\ln(1-\alpha)]$  and  $\theta$  with a slope of  $\frac{Ea}{RT_s^2}$ . The figures 5 & 6 show the Horowitz-

Metzger plots for the metal complexes under study (Figs. 2S, 3S - Supplementary Materials). The obtained data are recorded in Table 6.

#### 3.5.3 Thermodynamic parameters:

The other thermodynamic parameters of activation can be calculated by Eyring equation [46, 47]:

$$\Delta H = Ea-RT \tag{8}$$

A

(10)

$$\Delta S = R \left( \ln \frac{hA}{k_B T} - 1 \right) \tag{9}$$

$$\Delta G = \Delta H \text{-} T \Delta S$$

Where  $\Delta H$  is the enthalpy of activation (kJ/mol),  $\Delta S$  is the entropy of activation (kJ/mol.K) and  $\Delta G$  is the Gibbs free enthalpy of activation (kJ/mol), *h* is the Planck constant and  $k_B$  the Boltzmann constant. The kinetic parameters evaluated by Coats-Redfern (CR) and Horowitz-Metzger (HM) methods are listed in Tables 5 and 6, respectively. From the results the following remarks can be pointed out:

i) The kinetic parameters (*Ea*, *A*,  $\Delta H$ ,  $\Delta S$  and  $\Delta G$ ) of all isolated complexes have been calculated by using CR and HM methods (Table 5 and 6). The values obtained from the two methods are quite comparable.

ii) The thermodynamic data obtained with the two methods are in harmony with each other.

iii) The correlation coefficients of the Arrhenius plots of the thermal decomposition steps were found to lie in the range 0.9820–0.9996, showing a good fit with linear function.

iv) The activation energy *Ea* increases somewhat through the degradation steps revealing the high stability of the remaining part suggesting a high stability of complexes characterized by their covalence.

v) The negative value of the entropy of activation,  $\Delta S$  of some decomposition steps in case of the ion exchanger and its metal complexes with all investigated metal ions indicates that the activated fragments have more ordered structure than the undecomposed ones and the later are slower than the normal [48, 49].

vi) The positive sign of activation enthalpy change,  $\Delta H$  indicates that the decomposition stages are endothermic processes.

vii) The high values of the energy of activation, *Ea* of the complexes reveals the high stability of such chelates due to their covalent bond character [50].

viii) The positive sign of  $\Delta G$  for the investigated complexes reveals that the free energy of the final residue is higher than that of the initial compound, and hence all the decomposition steps are non-spontaneous processes. Moreover, the values of  $\Delta G$ increase significantly for the subsequent decomposition steps of a given compound. This results from increasing the  $T\Delta S$  clearly from one step to another which override the values of  $\Delta H$  reflecting that the rate of removal of the subsequent species will be lower than that of the precedent one [51]. This may be attributed to the structural rigidity of the remaining complex after the expulsion of one or more ligands, as compared with the precedent complex, which requires more energy,  $T\Delta S$ , for its rearrangement before undergoing any decomposition change.

3.6. Electrical conductivity measurements

The relation between solid state electric conductivity (log  $\sigma$ ) and temperature (1000/T) was found to be Arrhenius ( $\sigma = \sigma_o \exp(-\Delta E_a / KT)$ ) where  $\sigma_o$  is the preexponential factor given by ( $\sigma_o = nq^2 d^2 f/2KT$ ) where *n* is the concentration of mobile ions, *q* is the ionic charge, *d* is the average distance between the holes, *f* is the vibration frequency of the ion,  $\Delta E_a$  is the activation energy, *K* Boltzman constant and *T* is the absolute temperature. The activation energy was calculated from the linear portion of obtained data [52].

The electrical resistivity can be expressed by Kuivalainen et al. [53] model:

$$\rho = \frac{KT}{0.45e^2\alpha(T)^2} \frac{R_o^2}{\xi} \frac{(y_p + y_{bp})^2}{y_p y_{bp}} \frac{1}{\exp(\frac{-2.78R_o}{\xi})}$$
(11)

where,  $y_p$  and  $y_{bp}$  are the concentration of polarons and bipolarons, respectively;  $R_o$  is the hopping distance (separation) between impurities;  $\zeta$  is the average decay length of the polaron and bipolaron wave function. The electronic transition rate (T) between polaron and bipolaron states can be expressed as [54]:

$$\alpha(T) = A(\frac{T}{300K})^n \tag{12}$$

where A, is a constant equal to  $1.2 \times 10^{17}$ .

By using a computer-aided program, the order of magnitude of in the present system was adjusted. Taking  $y_p=y_{bp}$  for simplicity, which is an acceptable approximation, and using equations (11) and (12), we can obtain the values of the hopping distance  $R_0$  [55].

The calculated values of  $R_0$  was found to range from 8.04 nm to 12.10 nm depending on chemical composition. It was found also that the electrical conductivity and activation energies of metal complexes were lower than the ligand itself. This may be due to the increased electron delocalization or depends on the ionic radius of the cation and its ligand field's strength.

The inflection observed can be attributed to a change in conduction mechanism. It is assumed that at lower temperatures the conduction process is essentially due to the electronic conduction through  $\pi$ -electron delocalization while the conduction at higher temperatures is due to the excitation of an electron from the upper most filled  $\pi$ -molecular orbital to the lowest unfilled  $\pi$ -molecular orbital of these compounds (Table 1).

#### 3.7. Antimicrobial Activity

Minimum inhibitory concentration (MIC) [56, 57] was determined for each of the active compounds along with ampicillin and gentamycin as standard controls; results are shown in tables 7, 8. This screening was performed against the Gramnegative Escherechia coli and the Gram-positive Bacillus cereus, Bacillus subtilis in addition to pseudomonas aeruginosa. The tested compounds were dissolved in DMSO at a concentration of 8 mg/ml. Amongst all the compounds tested, [Cu(HL)(OAc)<sub>2</sub>].3H<sub>2</sub>O demonstrated the most potent antimicrobial activity against Bacillus subtilis. Escherechia coli and pseudomonas aeruginosa and [Cu(HL)<sub>2</sub>Cl<sub>2</sub>].3H<sub>2</sub>O against *Escherechia coli*. It is noteworthy that the observed antimicrobial activity was highly dependent on the metal complex, in which copper complexes played an important role in achieving an excellent level of biological activity. It is observed from these studies that most of the metal chelates have a higher

activity than the free ligand. Such increased activity of the metal chelates can be explained on the basis of Overtone's concept and chelation theory [58]. According to Overtone's concept of cell permeability the lipid membrane that surrounds the cell favours the passage of only lipid soluble materials due to which liposolubility is an important factor that controls antimicrobial activity. On chelation, the polarity of the metal ion is reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of *p*-electrons over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complexes into lipid membranes and blocking of metal binding sites on the enzymes of the microorganism.

#### 4. Conclusion

4-((*E*)-2-(1-(thiophen-2-yl)ethylidene)hydrazinyl)-1-(4-methoxyphenyl)-1Hpyrrole-3-carbonitrile (HL) and its Cu(II) complexes were prepared and characterized. It is obvious from this study that the ligand acts as a neutral bidentate *via* the thiophen sulphur and azomethine nitrogen. Also, the ESR, electronic spectra of the complexes and their magnetic moments suggesting octahedral geometry around Cu(II) center. The stability of complexes was explained and kinetic parameters (*Ea*, *A*,  $\Delta H$ ,  $\Delta S$ ,  $\Delta G$ ) of all thermal decomposition stages have been evaluated using Coats–Redfern method and Horowitz-Metzger methods. Moreover, the biological activities of the ligand and its complexes against bacterial and fungal organisms have been evaluated by using minimum inhibitory concentrations (MICs) method.

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**Fig. 1.** Solid state X-band ESR spectra for (A)  $[Cu(HL)(OAc)_2](H_2O)_3$ , (B)  $[Cu(HL)_2Cl_2](H_2O)_3$ , (C)  $[Cu(HL)_2(NO_3)_2](H_2O)_2$  and (D)  $[Cu(HL)_2(SO_4)]$  complexes at room temperature.



**Fig. 2.** Coats-Redfern plots of  $[Cu(HL)(OAc)_2](H_2O)_3$  (A) first step, (B) second step, (C) third step and (D) fourth step.

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**Fig. 3.** Coats-Redfern plots of  $[Cu(HL)_2Cl_2](H_2O)_3$  (A) first step, (B) second step, (C) third step and (D) fourth step.



**Fig. 4.** Coats-Redfern plots of  $[Cu(HL)_2(NO_3)_2](H_2O)_2$  (A) first step, (B) second step, (C) third step and (D) fourth step.



**Fig. 5.** Horowitz-Metzger plots of  $[Cu(HL)(OAc)_2](H_2O)_3$  (A) first step, (B) second step, (C) third step and (D) fourth step.



Fig. 6. Horowitz-Metzger plots of [Cu(HL)<sub>2</sub>(SO<sub>4</sub>)] (A) first step, (B) second step.

 Table 1

 Analytical and physical data of ligand and its Cu(II) complexes.

Compound		Colour	M.P.	Yield		%Foun	d (Calcd.)		Molar conductance	Ele	ectrical conduc	tance
Empirical Formula (F.W.)		Colour	(°C)	(%)	С	Н	М	X Cl <sup>°</sup> or SO <sub>4</sub> <sup>2-</sup>	$\Lambda_m$ in DMSO ( $\Omega^{-1}$ cm <sup>2</sup> mol <sup>-1</sup> )	Ea (eV)	$\sigma_0 \left( \text{S/cm} \right)$	R <sub>o</sub>
$\begin{array}{c} HL \\ C_{18}H_{16}ON_4S \end{array} (336.419) \end{array}$	(1)	Pale Yellow	215	80	64.50 (64.43)	4.54 (4.79)	-	-	-	2.35	11.52	8.04
$ \begin{array}{c} [Cu(HL)(OAc)_2](H_2O)_3 \\ CuC_{22}H_{28}O_8N_4S  (572.094) \end{array} \end{array} $	(2)	Green	> 300	75	46.27 (46.29)	4.88 (4.93)	11.14 (11.1)	-	3	1.18	11.12	9.11
$ \begin{bmatrix} Cu(HL)_2Cl_2 ](H_2O)_3 \\ CuC_{36}H_{38}O_5N_8SCl_2 & (861.424) \end{bmatrix} $	(3)	Green	> 300	75	50.31 (50.20)	4.39 (4.45)	7.45 (7.38)	8.19 (8.24)	7	1.38	11.07	10.82
$ \begin{bmatrix} Cu(HL)_2(NO_3)_2 \end{bmatrix} (H_2O)_2 \\ CuC_{36}H_{36}O_{10}N_{10}S_2  (896.409) \\ \end{bmatrix} $	(4)	Brown	235	79	48.34 (48.24)	4.12 (4.10)	7.04 (7.10)	-	9	1.06	10.98	12.10
	(5)	Brown	243	83	51.83 (51.94)	3.90 (3.87)	7.51 (7.63)	11.42 (11.5)	4	1.19	11.15	11.92
			2									

Table 2 Infrared data for the ligand and its Cu(II) complexes (cm<sup>-1</sup>).

Compound	μ <sub>eff.</sub> (B.M.)	Band position (cm <sup>-1</sup> )	g_	$g_{\perp}$	$A_{\parallel}$ (cm <sup>-1</sup> )	G	$g_{\parallel}/A_{\parallel}$	$\alpha^2$	$\beta^2$
2	1.98	14211; 16667	2.25	2.07	159	3.5	141	0.75	0.86
3	1.92	14285; 16393	2.21	2.06	162	6.3	136	0.72	0.63
4	2.05	14285; 16667	2.30	2.08	140	4.6	164	0.75	0.99
5	1.98	14184; 16000	2.27	2.06	162	4.5	140	0.78	0.84
									2

#### Table 3 Magnetic moment, electronic spectra and ESR data of Cu(II) Complexes.

#### Table 4

Complex	Temp. range (°C)	Decomp (Formu	p. prod. lla wt.)	Wt. lo Found	oss (%) Calcd.
2	35-150	3H <sub>2</sub> O	(54 045)	9.40	9.5
-	150-285	$2C_2H_2O_2$	(118.090)	20.8	20.6
	285-396	$C_{12}H_{10}ON_3$	(212.234)	37.0	37.1
	396-641	CeHeNS	(124.122)	21.8	21.7
	> 641	Residue, Cu	(63.540)	11.0	11.1
3	117-156	3H <sub>2</sub> O	(54.045)	6.4	6.3
	156-252	$Cl_2$	(71.000)	8.0	8.2
	252-670	$2C_{12}H_{10}ON_3$	(424.468)	49.4	49.3
	670-850	$2C_6H_6NS$	(248.243)	28.7	28.9
	> 850	Residue, Cu	(63.540)	7.5	7.4
4	35-161	$2H_2O$	(36.030)	4.0	4.0
	161-320	NO <sub>3</sub>	(124.013)	13.8	13.8
	320-716	$2C_{12}H_{10}ON_3$	(424.468)	47.4	47.4
	716-860	$2C_6H_6NS$	(248.243)	27.7	27.7
	> 860	Residue, Cu	(63.540)	7.1	7.1
5	200-598	$SO_4 + 2C_{12}H_{10}C_{10}$	DN <sub>3</sub> (520.468)	62.3	62.5
	598-875	$2C_6H_6NS$	(248.243)	29.9	29.8
	> 875	Residue. Cu	(63.540)	7.9	7.7

								-
Complay	naal	Mid.	Ea	A	$\Delta H^*$	$\Delta S^*$	$\Delta G^*$	
Complex	реак	Temp(K)	kJ∖mol	$(S^{-1})$	kJ\mol	kJ\mol.K	kJ∖mol	
2	$1^{st}$	365	218.08	4.90E-6	215.05	-0.34823	342.16	
	$2^{nd}$	491	175.86	9.95E-7	171.78	-0.36395	350.49	7
	$3^{rd}$	614	1011.29	4.11E-6	1006.18	-0.35401	1223.55	
	$4^{\text{th}}$	790	1643.33	1.09E-5	1636.76	-0.34800	1911.69	
								*
3	$1^{st}$	411	329.87	3.10E-5	326.45	-0.33388	463.68	
	$2^{nd}$	478	239.18	3.10E-6	235.21	-0.35427	404.55	
	$3^{rd}$	780	415.62	5.24E-7	409.13	-0.37312	700.17	
	$4^{\text{th}}$	1057	3037.01	1.94E-6	3028.22	-0.36477	3413.79	
4	$1^{st}$	371	147.42	5.83E-8	144.33	-0.38521	287.25	
	$2^{nd}$	515	523.93	1.51E-5	519.65	-0.34172	695.63	
	3 <sup>rd</sup>	791	1093.80	2.41E-6	1087.23	-0.36054	1372.42	
	$4^{\text{th}}$	1047	3552.21	5.59E-6	3543.51	-0.35590	3916.14	
5	$1^{st}$	672	429.38	3.93E-7	423.79	-0.37427	675.31	
	$2^{nd}$	997	1310.33	1.22E-6	1302.04	-0.36811	1669.05	

 Table 5

 Kinetic Parameters of Cu(II) complexes evaluated by Coats-Redfern equation.

-								
	Complex	Peak	Mid.	Ea	Α	$\Delta H^*$	$\Delta S^*$	$\Delta G^*$
	-		Temp(K)	kJ∖mol	$(S^{-1})$	kJ∖mol	kJ\mol.K	kJ∖mol
-	2	$1^{st}$	365	218.96	5.13E-6	215.92	-0.34786	342.89
		$2^{nd}$	491	175.08	1.06E-6	170.99	-0.36346	349.46
		$3^{rd}$	614	1011.83	3.99E-6	1006.72	-0.35426	1224.25
		$4^{\text{th}}$	790	1642.24	1.01E-5	1635.68	-0.34860	1911.07
	3	$1^{st}$	411	329.28	3.29E-5	325.79	-0.33338	462.81
		$2^{nd}$	478	239.90	4.06E-6	235.92	-0.35204	404.21
		$3^{rd}$	780	414.98	5.09E-7	408.49	-0.37338	699.73
		$4^{\text{th}}$	1057	3037.63	2.03E-6	3028.84	-0.36442	3414.04
	4	$1^{st}$	371	148.96	6.32E-8	145.88	-0.38455	288.55
		$2^{nd}$	515	515.08	1.93E-5	510.80	-0.33972	685.76
		$3^{rd}$	791	1093.49	2.69E-6	1086.92	-0.35965	1371.40
		$4^{\text{th}}$	1047	3553.68	5.86E-6	3544.98	-0.35551	3917.21
	5	$1^{st}$	672	428.16	3.94E-7	422.57	-0.37428	674.09
		$2^{nd}$	997	1309.38	1.21E-6	1301.09	-0.36818	1668.17
				2				
				4				
				9				
			,0	4				
				4				

# Table 6 Kinetic Parameters of Cu(II) complexes evaluated by Horowitz-Metzger equation.

#### Table 7

Antimicrobial activities of ligand and Cu(II) its complexes.

			Inhibi	tion zone (mm)	
	Compounds	Bacillus Cereus	Bacillus Subtillis	Pseudomonas Aeruginosa	Esherichia Coli
	1 2 3 4 5	3.5 6.5 5.5 6.5 3.5	0 17 1 5 3	3 12 11 7 4	2.5 12 12.5 5.5 4
	Ampicillin	7.5	13.5	11	16.5
		12	18	16.5	11.5
P					

	Minimu	m inhibitory	concentration (MI	C) ( $\mu g/ml$ )
Compounds	Bacillus	Bacillus	Pseudomonas	Esherichia
-	Cereus	Subtillis	Aeruginosa	Coli
1	3000	6000	3000	3000
2	375	93.75	187.5	93.75
3	1500	3000	93.75	93.75
4	750	1500	1500	750
5	1500	3000	1500	1500
Ampicillin	187.5	187.5	187.5	93.75
Gentamicin	93.75	93.75	187.5	375

#### Table 8 Antimicrobial activities of ligand and Cu(II) its complexes in terms of MIC (µg/mL).

Graphical abstract



 $\label{eq:modelling} Molecular modelling of 4-((E)-2-(1-(thiophen-2-yl)ethylidene)hydrazinyl)-1-(4-methoxyphenyl)-1H-pyrrole-3-carbonitrile (HL)$ 

#### Highlights

- Synthesis of mononuclear Cu(II) hydrazone complexes.
- The Cu(II) complexes structure was elucidated using different characterization techniques.
- Computational studies of the first order kinetic reactions.

• Antimicrobial activities of all isolated compound were studied.