

Synthesis, Spectroscopic, and Thermal Characterization of Thiazole Metal Complexes: Biological Activity Studies

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Metal complexes of the organic ligand with N azomethine and N thiazole donation sites, derived from 3-(2-(2-(2,6dichlorobenzylidene)hydrazinyl)-4-oxo-4,5-dihydrothiazol-5-yl) acetic acid (H₂L), with some transition metal ions, namely Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II), are reported. They are characterized based on elemental analyses, IR, ¹H NMR, solid reflectance, magnetic moment, and molar conductance. The ionization constants are found to be 5.57 and 11.50, which can be attributed to loss of the hydrazo and the carboxylic acid protons, respectively. The stability constants of metal chelates, is calculated spectrophotometrically at 25°C, and the order of stability follows the Irving and Williams order. The chelates are found to have octahedral geometrical structures. The ligand (H_2L) and its binary chelates are subjected to thermal analyses, and the different activation thermodynamic parameters are calculated using Coats-Redfern equation. The ligand and its metal complexes show a remarkable biological activity against the desert locust Schistocerca gregaria (Forsk) (Orthoptera - Acrididae) and its adult longevities.

Keywords biological activity, thermal analyses, thiazole ligand, transition metal complexes, spectroscopy

INTRODUCTION

It has long been known that metal ions are involved in the biological processes of life and have been a subject of interest. The modes of action of these metal ions are often complex, but are believed to involve bonding to the hetero-atoms of the heterocyclic residues of biological molecules, i.e., proteins, enzymes, nucleic acids, etc.^[11] Organic ligands and their metal complexes played an important role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to physicochemical ^[2] and biochemically relevant studies of metal complexes, ^[3-5] and

found a wide range of applications. Thiazoles represent a very interesting class of compounds because of their wide applications in pharmaceutical, phytosanitary, analytical and industrial aspects,^[6,7] and have biological activities.^[8,9] In recent years, thiazole-based chemisensors have also been investigated and shown to be successfully applicable in biological systems.^[10] It is known that 2-aminothiazole is a biologically active compound with a broad range of activity, and it is also an intermediate in the synthesis of antibiotics and dyes. Numerous thiazole derivative organic ligands and their transition metal complexes have been investigated by various techniques.^[11–18] From these points of view, it is interesting to study different types of transition metal complexes of this biologically active ligand.

In this article, the synthesis and characterization of the first row transition metal complexes with the formulae $[M(H_2L)_2Cl].xH_2O$ (where M is Mn(II), Co(II), Ni(II), Cu(II), and Zn(II); x = 0-4) and $[Fe(H_2L)Cl_2]Cl$, and H_2L is a protonated ligand, (2-(2-(2,6-dichlorobenzylidene)hydrazinyl)-4-oxo-4,5-dihydrothiazol-5-yl) acetic acid, have been studied. The N of azomethine and N thiazole coordination sites are helpful as they will do a cavity around the metal ions and hence they can be used as analytical reagents for determination of metal ions. The structure of the studied complexes is elucidated using elemental analyses, IR, ¹H NMR, solid reflectance, magnetic moment, molar conductance, and thermal analysis measurements. The biological activity of the parent organic ligand and its metal complexes are reported. The structure of ligand is given in Figure 1.

EXPERIMENTAL

Materials and Reagents

The chemicals used included CuCl₂.2H₂O (Sigma), CoCl₂.6H₂O and NiCl₂.6H₂O (BDH); MnCl₂ (sigma), ZnCl₂.2H₂O (Ubichem), and FeCl₃.6H₂O (Prolabo), thiosemicarbazide and maleic anhydride (Merck). Organic solvents (spectroscopic pure from BDH) used included absolute ethyl alcohol, diethylether and dimethylformamide (DMF). Hydrogen peroxide and chloride, carbonate and hydroxide salts of sodium (A.R.) were used. Hydrochloric and nitric acids (Merck) were used.

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FIG. 1. Structure of H₂L ligand.

Solutions

Fresh stock solution of 5×10^{-4} M ligand; H₂L, was prepared by dissolving the accurately weighed amount (0.173 g/L) in the appropriate volume of absolute ethanol. 5×10^{-4} M Stock solution of the metal salts was prepared by dissolving the accurately weighed amounts of the metal salts in the appropriate volume of de-ionized water. The metal salt solutions were standardized by the recommended procedures.^[32] Dilute solutions of the metal ions and organic ligand under study were prepared by accurate dilution. 1.0 N Stock sodium hydroxide solution was prepared by accurate dilution and used for pH adjustment. Mixture of 0.04 M phosphoric, acetic and boric acids was prepared to obtain universal buffer solutions of the required pH values from 2–13. The pH was adjusted by adding 0.2 N NaOH solution to 100 mL of the acid mixture.^[33]

Instruments

The molar conductance of solid chelates in DMF was measured using Sybron-Barnstead conductometer (Meter-PM.6, E = 3406). Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer in wavenumber region 4000– 400 cm⁻¹. The spectra were recorded as KBr pellets. The solid reflectance spectra were measured on a Shimadzu 3101pc spectrophotometer. The molar magnetic susceptibility was measured on powdered samples using the Faraday method. The diamagnetic corrections were made by Pascal's constant and Hg[Co(SCN)₄] was used as a calibrant.

The mass spectrum was recorded by the EI (Electron Ionization) technique at 70 eV using MS-5988 GS-MS Hewlett-Packard instrument. The ¹H NMR spectra were recorded using 300 MHz Varian-Oxford Mercury. The deuterated solvent used was dimethylsulphoxide (DMSO) and the spectra extended from 0 to 15 ppm. The thermal analyses (TG, DTG and DTA) were carried out in dynamic nitrogen atmosphere (20 mL.min⁻¹) with a heating rate of 10° C min⁻¹ using Shimadzu TG-60H and DTA-60H thermal analyzers.

Biological Activity

The susceptible strain of locust, Schistocerca gregaria was obtained from Locust Research laboratory, Entomology Department, Faculty of Science, Cairo University. A stock colony was reared in cages 40x50x65 cm. Except for the front side, which was made of glass; all the other three sides of the cages were made of wood, with a small window closed by wire gauze for ventilation. Each cage was supplied every morning with a suitable amount of fresh food, consisting of clover or maize leaves. The cages were provided with pots of moistened, sieved sand to serve as ovipositional sites. The locust culture and the experimental tests, unless otherwise mentioned, were kept in a dark room covered with thick black curtains. Light was provided by a set of 60-watt electric bulbs. A bulb was hung in front of the glass side of each cage. All bulbs were connected to a time switch (a 24 hour automatic program timer) that would turn the lights on at 4.00 a.m. and off at 6.00 p.m., approximately corresponding to the times of sunrise and sunset in Egypt. Temperature in the cages was recorded to range between 30 and 35°C, while the relative humidity fluctuated between 60 and 80%.

Susceptible strain of *Schistocerca gregaria* was reared away from any insecticidal contamination. 5th Nymphal instars of Sch. gregaria nymphs, were treated with the novel chemicals of thiazole derivatives using topical treatment techniques according to method of Nassar.^[34] After preliminary test, three groups of 5th nymphal instars (5 insects of each group) were received $2\mu g/insect$ of all tested compounds. Treatment was replicated three times, and not less than 15 insects were treated with each tested compound. Starting with the day after treatment, all mortalities, malformation and adult longevities were recorded. Mortality % was calculated for the next instars considering the initial number of treated hoppers, irrespective of the instars under test. All experiments were performed as triplicate and data plotted were the mean value.

RESULTS AND DISCUSSION

Synthesis of Organic Ligand (H₂L)

A mixture of 2,6-dichlorobenzaldehyde and thiosemicarbazide (0.005 mol) and maleic anhydride (0.0055 mol) in anisole (3 mL) was refluxed for 15 min. After cooling, ethanol (10 mL) was added and the solid precipitate was collected and recrystallized from DMF/H₂O mixture.



Synthesis of Metal Complexes

The metal complexes were prepared by the addition of hot ethanolic solution (60° C, 10 mL) of the appropriate metal chloride (1 mmol) to the hot ethanolic solution (60° C, 10 mL) of the organic ligand (0.173 g H₂L, 1 mmol). The resulting mixture was stirred whereupon the complexes precipitated. They were collected by filtration, washed several times with ethanol and diethyl ether for further purification and dried under vaccum.

Characterization of Organic Ligand

The organic ligand is prepared and subjected to elemental analyses, mass, ¹H NMR, and IR spectral analyses. The results of elemental analyses are presented in Table 1. The results obtained are in good agreement with those calculated for the suggested formula and the melting point is sharp indicating the purity of the prepared organic ligand.

Mass spectrum of the organic ligand

The important peaks and its relative intensities for the molecular ions are shown in Scheme 1. Mass spectrum of the studied organic ligand is characterized by moderate to high relative intensity molecular and fragment ion peaks. Scheme 1 shows a well-defined parent peak of H₂L at m/z = 346 (R.I. = 2%). Fragment at m/z = 58 (R.I. = 100%, base peak) is attributed to C₂H₂S ion as shown in the mass spectrum of H₂L.

Absorption Spectra of the Organic Ligand

The absorption spectrum of 1×10^{-4} M solution of H₂L ligand under investigation in buffer solutions of varying pH values from 2–13 are scanned in the wavelength range from 200 to 700 nm, against the same solvent as a blank. The absorption spectrum of H₂L ligand shows sharp bands at 290 ($\epsilon = 1970$ L.mol⁻¹cm⁻¹) and 310 ($\epsilon = 2098$ L.mol⁻¹cm²). These bands can be attributed to $\pi - \pi^*$ transitions within the azomethine group of the organic ligand molecule.

Ligands dissociation and metal-ligand stability constants

The ligand dissociation constant was calculated using the half height method.^[19] H₂L ligand is found to have two pK_a values of 5.57 and 11.50, which can be attributed to loss of the hydrazo group and the carboxylic acid protons, respectively. The free energy change, ΔG^{o} , was also calculated and found to be 356.4 and 506.9 kJ mol⁻¹ for the first and second ionizations, respectively. The positive values indicate the spontaneous character of dissociation reaction.

The stability constants of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) complexes are determined spectrophotometrically using Taneja method.^[20] The mean $\log \beta_1$ and $\log \beta_2$ values are listed in Table 1. The complex-forming abilities of the transition metal ions are frequently characterized by stability orders. The order of stability constants is found to be Mn²⁺ < Co²⁺ < Ni²⁺ < Cu²⁺ > Zn²⁺ in accordance with the Irving and Williams order^[21] for divalent metal ions of the 3d series. It is clear from Table 1 that the stability of Cu(II) complex is considerably larger as compared to other metals of the 3d series. Under the influence of the ligand field, Cu(II) (3d⁹) will receive some extra stabilization^[22] due to tetragonal distortion of octahedral symmetry in its complexes. The Cu(II) complexes will be further stabilized due to the Jahn-Tellar effect.^[23] The free energy of formation, ΔG° , accompanying the complexation reaction has been determined at 25°C (Table 1). From this table, it is apparent that the negative values of ΔG° show that the complexation reaction proceeds spontaneously.

Elemental Analyses of the Complexes

The results of elemental analyses are in good agreement with those required by the proposed formulae given in Table 1.

Molar Conductance Measurements

Table 1 shows the molar conductance values of the 10^{-3} M concentration complexes in DMF solvent at $25 \pm 2^{\circ}$ C. It is concluded from the results that the Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes have a molar conductivity values in the range 17.60–31.40 Ω^{-1} mol⁻¹ cm², which indicates the nonionic nature of these complexes, and they are considered as non-electrolytes. Fe(III) complex is found to has molar conductance value of 79.50 Ω^{-1} mol⁻¹ cm², indicating that it is 1:1 electrolyte.

IR Spectral Studies

The IR spectral data of the organic ligand and its complexes are listed in Table 2. The IR spectra of the complexes are compared with the free ligand in order to determine the coordination sites that may involved in chelation. Upon comparison, it is found that the $v(C=N)_{azomethine}$ and the $v(C=N)_{thiazole}$ stretching vibrations are found in the free H₂L ligand at 1623 and 1583 cm⁻¹, respectively. However, the participation of the (C=N)_{azomethine} and $v(C=N)_{thiazole}$ groups in chelation are ascertained from the shift of the bands to higher wavenumbers in the spectra of the complexes to 1625–1654 and 1590–1586 cm⁻¹, respectively, indicating the participation of the azomethine and thiazole nitrogen in coordination (M—N)).^[24]

The v(C=O), $v_{asym}(COO)$ and $v_{sym}(COO)$ stretching vibrations are observed at 1731, 1409, and 1094 cm⁻¹ for H₂L ligand, respectively. These stretching vibrations are shifted to higher or lower frequencies in the region 1721–1733, 1402–1430, and 1059–1097 cm⁻¹ in the complexes, respectively. Although, the carboxylate O atom not involvement in the complexes formation,^[25] the shift in position of the v(C=O), $v_{asym}(COO)$ and $v_{sym}(COO)$ stretching vibrations may be due to hydrogen bond formation and formation of stable six membered ring. The IR spectrum of the H₂L ligand shows a broad band at 3445 cm⁻¹, which can be attributed to the carboxylic OH group. This band is still broad in all complexes (Table 2), and the shift in position of this band can support the hydrogen bond formation.

	Analytical, ph	ıysical, a	nd the calc	ulated st	TABL ability con	E 1 Istants dat	a of H ₂ L li	igand and	its metal co	omplexes		
					% Found	l (calcd.)				$\Lambda_m \Omega^{-1}$	$\log eta_1^*$	$\log eta_2^*$
Compound	Color (%yield)	M.p. (°C)	U U	н	z	s	G	M	$\mu_{\rm eff.}$ (B.M.)	mol ⁻¹ cm ²	$(-\Delta G_1^0; kJ mol^{-1})$	$(-\Delta G_2^0; kJ mol^{-1})$
H ₂ L C ₁₂ H ₉ Cl ₂ N ₃ O ₃ S	yellowish	256	41.62	5.20	12.14	9.25	20.52					
	white (83)		(41.46)	(5.33)	(12.13)	(69.6)	(20.61)					
$[Mn(H_2L)_2Cl_2]$	pale yellow	234	35.25	2.20	10.28	7.83	26.07	6.34	5.24	17.60	8.44	3.43
$C_{24}H_{18}Cl_6MnN_6O_6S_2$	(62)		(35.08)	(2.75)	(11.07)	(7.18)	(26.72)	(6.73)			(229)	(133)
$[[Fe(H_2L)_2Cl_2]Cl$	black	76	33.70	2.11	9.83	7.49	29.08	6.94	5.87	79.50	8.09	3.96
$C_{24}H_{18}Cl_7FeN_6O_6S_2$	(63)		(33.95)	(2.26)	(10.15)	(7.81)	(29.23)	(6.55)			(225)	(148)
$[Co(H_2L)_2Cl_2]$	blue	110	35.04	2.19	10.22	7.79	25.91	7.30	4.94	28.90	8.86	3.65
$C_{24}H_{18}Cl_6CoN_6O_6S_2$	(63)		(35.93)	(2.39)	(10.4)	(7.59)	(25.99)	(7.18)			(248)	(139)
$[Ni(H_2L)_2Cl_2].4H_2O$	pale green	247	35.04	2.19	10.22	7.79	25.91	7.70	3.28	18.90	9.22	3.83
$C_{24}H_{26}Cl_6NiN_6O_{10}S_2$	(63)		(35.99)	(2.59)	(10.17)	(7.82)	(25.33)	(7.18)			(239)	(144)
$[Cu(H_2L)_2Cl_2]$	pale green	215	34.85	2.18	10.16	7.74	25.77	7.80	1.97	22.20	10.38	4.56
$C_{24}H_{18}Cl_6CuN_6O_6S_2$	(63)		(34.89)	(2.63)	(10.78)	(7.94)	(25.80)	(7.68)			(252)	(163)
$[Zn(H_2L)_2Cl_2]$	white (61)	308	34.78	2.17	10.15	7.73	25.72	7.55	Diam.	31.40	9.81	4.18
$C_{24}H_{18}Cl_6N_6O_6S_2Zn$			(34.16)	(2.12)	(10.43)	(7.80)	(25.50)	(7.85)			(246)	(154)
* [H ₂ L] = 5×10^{-4} M, []	$\Lambda] = 5 \times 10^{-4} \mathrm{M}, \lambda_{\mathrm{m}}$	$_{\text{lax}} = 310$	nm.									

	TABLE 1	al, physical, and the calculated stability constants data of H ₂ L ligand and its metal comp
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	ik spec		1 (4000–400	cm ⁻) 01	$\Pi_2 L$ ligand a	nd its meta	a complex	es		
Compound	v(OH) carboxylic	υ(NH)	v(C=O) carboxylic	v(C=O) carbonyl	v(C=N) azomethine	v(C=N) thiazole	v(COO) v(asym.)	v(COO) (sym.)	v(M-N)	v(M-O)
H ₂ L	3445br	3086br	1731sh	1699sh	1623sh	1583sh	1409sh	1094m		
$[Mn(H_2L)_2Cl_2]$	3471br	3058s	1725sh	1701s	1640sh	1588m	1428m	1060m	544s	442s
[Fe(H ₂ L) ₂ Cl ₂]Cl	3396br	3069br	1732m	1700s	1648sh	1586s	1430m	1060s	578s	409m
$[Co(H_2L)_2Cl_2]$	3411br	Dis.	1721m	1704s	1625m	1589m	1402s	1097s	540w	451w
$[Ni(H_2L)_2Cl_2].4H_2O$	3355br	Dis.	1724m	1700s	1651sh	1588s	1430m	1059m	544w	447s
$[Cu(H_2L)_2Cl_2]$	3393br	3016br	1726sh	1700s	1637sh	1588sh	1402m	1095m	542s	448s
$[Zn(H_2L)_2Cl_2]$	3448br	3077s	1733sh	1695s	1654m	1590m	1424m	1090s	538s	445s

TABLE 2R spectral data (4000–400 cm $^{-1}$) of H2L ligand and its metal complexes

sh = sharp, m = medium, br = broad, s = small, w = weak.

Therefore, from the IR spectra, it is concluded that H_2L behaves as neutral bidentate ligand in all the complexes coordinating to the metal ions via azomethine N and thiazole N atoms.

¹H NMR Spectral

The ¹H NMR data for H₂L ligand and its Zn(II) complex, recorded in DMSO-d₆, show a sharp signal at 8.547 and 8.537 ppm, which may be assigned to the azomethine protons (-CH=N, 1H), respectively. However, a multiple at 7.589–7.426 and 7.576-7.444 ppm may be attributed to the phenyl protons (4H, 3Ar-H, 1 thiazolyl-H) and (8H, 6Ar-H, 2 thiazolyl-H) for H₂L ligand and its Zn(II) complex, respectively. Another multiple observed at 3.048–2.851 and 3.017–2.858 ppm for H_2L and Zn(II) complex, corresponds to the methylene protons (-CH₂; 2H) and (CH₂; 4H), respectively. A multiple bands at 4.398-4.356 (NH, 1H) and 4.470-4.444 ppm (NH, 2H) for HL and Zn(II) complex, respectively, may reasonably be assigned to secondary amine protons. A broad band observed at 12.00 ppm may be attributed to the COOH proton (-COOH; 1H). This signal is found at 11.797 ppm in Zn(II) complex. This indicates the non-involvement of the COOH group in chelation and this shift can be assigned to hydrogen bond and formation of stable six membered ring.

Magnetic Susceptibility and Electronic Spectral Studies

The diffused reflectance spectrum of the Mn(II) complex shows three bands at 16.350, 22.080, and 27.390 cm⁻¹ assignable to ${}^{4}T_{1g} \rightarrow {}^{6}A_{1g}, {}^{4}T_{2g}(G) \rightarrow {}^{6}A_{1g}$ and ${}^{4}T_{1g}(D) \rightarrow {}^{6}A_{1g}$ transitions, respectively.^[36,37] The magnetic moment value 5.24 B.M. indicates the presence of Mn(II) complex in octahedral structure. From the diffused reflectance spectrum, it is observed that the Fe(III) chelate exhibits a band at 21,340 cm⁻¹, which may be assigned to the ${}^{6}A_{1g} \rightarrow T_{2g}(G)$ transition in octahedral geometry of the complex.^[37] The ${}^{6}A_{1g} \rightarrow {}^{5}T_{1g}$ transition appears to be split into two bands at 17,460 cm⁻¹ and 13,220 cm⁻¹. The observed magnetic moment value of Fe(III) complex is found to be 5.87 B.M., indicating octahedral geometry involving d^2sp^3 hybridization in Fe(III) ion.^[37] The spectrum shows also a band at 25,420 cm⁻¹ which may be attributed to ligand to metal charge transfer.

The studied Ni(II) complex is high spin with a room temperature magnetic moment value of 3.28 B.M., which indicates octahedral geometry.^[37] Three bands, in the solid reflectance spectrum at ν_1 : 13,257 cm⁻¹: ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$, ν_2 : 14,780 cm⁻¹: ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$ and ν_3 : 22,444 cm⁻¹: ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (P) are displayed. The spectrum shows also a band at 25,333 cm⁻¹ which may be attributed to ligand to metal charge transfer. The electronic spectrum of the Co(II) complex gives three bands at 12,870, 15,974, and 21,208 cm⁻¹. The region at 25,445 cm⁻¹ refers to the charge transfer band. The bands observed are assigned to the transitions ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F) (\nu_{1}), {}^{4}T_{1g}(F)$ \rightarrow ⁴A_{2g}(F) (ν_2) and ⁴T_{1g}(F) \rightarrow ⁴T_{2g}(P) (ν_3), respectively, suggesting an octahedral geometry around Co(II) ion.^[38] The magnetic moment value is found to be 4.94 B.M. indicating of octahedral geometry.^[37] The reflectance spectrum of the Cu(II) chelate consists of a broad band centered at 15,575 and 17,640 cm⁻¹. The ${}^{2}E_{g}$ and ${}^{2}T_{2g}$ states of the octahedral Cu(II) ion (d^9) split under the influence of the tetragonal distortion and the distortion can be such as to cause the three transitions ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$; ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ to remain unresolved in the spectrum.^[39] The magnetic moment of 1.97 B.M. falls within the range normally observed for octahedral geometry.^[39] A moderately intense peak observed at 21,750 cm⁻¹ is due to ligand to metal charge transfer transition.^[40] The Zn(II) complex is diamagnetic and according to the empirical formula, an octahedral geometry is proposed.

Thermal Analyses (TG, DTG and DTA) Studies

The TG curve of H₂L ligand (Figure 2a) exhibits a first estimated mass loss of 51.68% (calcd.51.73%) at 200–390°C, which may be attributed to the liberation of 3NO, 2HCl and CH₄ molecules as gases. In the 2^{nd} stage within the temperature range from 390–750°C, the remaining organic part (C₁₁H₃S) is lost with an estimated mass loss of 48.32% (calcd. 48.27%). The loss of C₁₁H₃S molecule can also be estimated in the



SCH. 1. Mass fragmentation pattern of H₂L ligand.

mass spectrum of the ligand at m/z =165 (f. =167, R.I. = 2%) is observed. This fragment ion, $C_{11}H_3S$, is fragmented to give different fragment ions (see scheme 1), which is observed as single decomposition step in the TG curve. The TG curve of the [Fe(H₂L)₂Cl₂]Cl chelate represents four decomposition steps as illustrated in Figure 2b and Table 3. The first step of decomposition within the temperature range 30–85°C corresponds to the loss of 3HCl molecules with a mass loss of 12.28% (calcd. 12.81%). The remaining steps of decomposition within the temperature range 85–720°C correspond to the removal of

the remaining ligand as gases. The overall weight loss amounts to 90.43% (calcd. 90.64%). Figure (2b) shows the DTA curve which shows six exothermic peaks at (81, 238, 333, 477, 632, and 733°C) and one endothermic peak at (200°C). The appearance of many exothermic and endothermic peaks are due to the removal of the anions and ligand molecules as gases. The TG curve of the Co(II) chelate is shown in Figure 2c. It decomposes in five steps in the temperature range 30–950°C. The first step is accounted to the loss of 3HCl molcules with a mass loss of 13.54% (calcd. 13.32%). The mass losses of the remaining steps



FIG. 2. Thermal analyses (TG, DTG and DTA) of H₂L and its complexes. Where (a) H₂L ligand, (b) Fe(III), (c) Co(II), and (d) Ni(II) complexes.

(T = 100–950°C) correspond to the removal of $C_{24}H_{12}N_6O_6S_2$ and 3HCl molecules as gases (estimated mass loss = 78.10%; calcd. = 77.55%). These steps are accompanied by exothermic peaks (298 and 568°C) and endothermic peaks (54, 137, and 875°C). On the other hand, [Ni(H₂L)₂Cl₂].4H₂O chelate exhibits three decomposition steps (Figure 1d) within the temperature range from 30–650°C. The estimated mass loss = 20.71% (calcd. 20.36%) of the first step within the temperature range from 30–175°C can be attributed to the loss of 4HCl and 2H₂O molecules. According to the data listed in Table 5, the total mass loss of the decomposition steps are found to be 91.64% (calcd. 91.60%) and NiO is suggested as a residue. The DTA data are listed in Table 3 and represented graphically in Figure 2d. It is clear from these data that these mass losses have two exothermic (262 and 572°C) and two endothermic (76 and 465°C) peaks.

Calculation of Activation Thermodynamic Parameters

The thermodynamic activation parameters of decomposition processes of dehydrated complexes namely activation energy (E^{*}), enthalpy (Δ H^{*}), entropy (Δ S^{*}) and Gibbs free energy change of the decomposition (Δ G^{*}) are evaluated graphically by employing the Coats-Redfern relation.^[30] The activation energies of decomposition are found to be in the range 61.42–264.9 kJmol⁻¹ and the data is summarized in Table 4 and Figures 3 and 4. The high values of the activation energies calculated from the thermal decomposition reflect the thermal stability of the complexes. The entropy of activation is found to have negative values in all the complexes that indicate that the decomposition reactions proceed spontaneously.

2.10. Structural Interpretation

On the basis of the above observations and from the magnetic and solid reflectance measurements, octahedral and tetrahedral geometry is suggested for the investigated complexes. The structures of the complexes are shown in Figure 5.



FIG. 3. Coats-Redfern plot of the decomposition steps of Fe(III)-H₂L complex.

Biological Activity

The main aim of the production and synthesis of any antimicrobial compound is to inhibit the causal microbe without any side effects on the patients. In addition, it is worthy to stress here on the basic idea of applying any chemotherapeutic agent that depends essentially on the specific control of only one biological function and not multiple ones. The biological activities of H_2L and its metal complexes are studied against the different



FIG. 4. Coats-Redfern plot of the decomposition steps of Co(II)-H₂L complex.

			Thern	noanalytical resu	lts (TG, DTG,	and DTA) of H_2L and its metal comp	plexes	
Compound	TG range (°C)	DTG _{max} (°C)	ц*	Mass loss calcd (estim) %	Total mass loss	Assignment	Metallic residue	DTA (°C)
H ₂ L	200-390 390-750	270 547		51.73 (51.68) 48.27 (48.32)	100 (100)	-Loss of CH ₄ , 3NO and 2HCl. -Loss of C ₁₁ H ₃ S.		255(+), 274(-) 530(-)
(1)	30-85 85-720	48 204 317 632	- "	12.81 (12.28) 77 82 (78 15)	90 64 (90 43)	-Loss of 3HCl. Loss H-1 ² and 3/20.	$^{1}/_{2}$ Fe ₂ O ₃	81(-), 200(+), 238(-) 333(-), 477(-), 632(-), and 733(-)
(2)	30-100	48) -	13.32 (13.54)		-Loss of 3HCl.	C_0O	54(+) 54(-)
(3)	100-950 30-175	133,283,2/2,884 67	4 –	(1.87) cc.77 20.36 (20.71)	90.87 (91.64)	-Loss of C ₂₄ H ₁₂ N ₆ O ₆ S ₂ , and 3HCl. - Loss of 2H ₂ O and 4HCl	NiO	13/(+), 298(-), 508(-), 8/2(+) 76(+)
	175-470 470-650	262 567		45.80 (46.70) 25.84 (24.23)	91.61 (91.64)	-Loss of 2H ₂ O, H ₂ L ² and N ₂ -Loss of C ₁₂ H ₉ NO ₂ S		262(-) 465(+), 572(-)
	her of decom	mosition stens						

TABLE 3 ermoanalytical results (TG, DTG, and DTA) of H ₂ L and its metal comple

n^{*} = number of decomposition steps. (1) [Fe(H₂L)₂Cl₂)]Cl (2) [Co(H₂L)₂Cl₂)] (3) [Ni(H₂L)₂Cl₂].4H₂O. (⁻) = exothermic, (+) = endothermic.

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FIG. 5. Structure of metal complexes.

developmental stages of the desert locust *Schistocerca gregaria* Forsk. The data are listed in Table 5. On comparing the biological activity of the organic ligand and its metal complexes with specific control of only one biological function and not multiple ones, the following results are obtained:

I-Effect of H₂L Ligand and its Metal Complexes on the 5th Nymphal Instars of *Schistocerca gregaria*

The results of the effect of novel benzylidene complexes on 5th instars nymph of *Schistocerca gregaria* is recorded in Table 5. It is observed from this table that treatment of newly ecdysed

5th instar nymphs with the complexes is found to cause different mortality after 24 hr post treatment. A dose (2 μ g/insect) mortality of complexes can be easily observed in Table 5. Thus the highest mortality is found to be 100%, which is obtained after nymphal treatment with [Cu(H₂L)₂Cl₂] complex. Meanwhile, 80% mortality is recorded after nymph treatment with the [Fe(H₂L)₂Cl₂]Cl, [Co(H₂L)₂Cl₂] and [Zn(H₂L)₂Cl₂] complexes. On the other hand, different nymphal deformation is obtained due to the effect of thiazole complexes against *Schistocerca gregaria* nymphs. The lowest deformation is 20% when nymph is treated with [Ni(H₂L)₂Cl₂].4H₂O complex. The

	Thermodynamic data of	the thermal deco	omposition of H	l_2L and its metal c	omplexes	
Complex	Decomp. Temp. ^î C	E* kJmol ⁻¹	$A s^{-1}$	$\Delta S^* k Jmol^{-1}$	$\Delta H^* k Jmol^{-1}$	$\Delta G^* \text{ kJmol}^{-1}$
H ₂ L	25-390	78.37	1.1×10^{6}	-130.7	75.29	123.6
	390-650	121.8	4.8×10^{6}	-121.9	117.3	183.9
[Fe(H ₂ L) ₂ Cl ₂]Cl	25-85	134.6	1.1×10^{8}	-56.10	130.6	157.6
	85-248	174.5	4.8×10^{7}	-75.40	157.6	311.4
	248-386	140.5	1.0×10^{8}	-72.40	114.1	343.7
	520-716	61.42	1.8×10^{7}	-112.0	56.16	127.0
$[Co(H_2L)_2Cl_2]$	22-100	104.0	4.7×10^{14}	-70.40	103.6	100.2
	100-200	82.10	1.3×10^{8}	-63.20	71.03	155.1
	200-425	63.19	2.3×10^{8}	-65.00	39.64	223.5
	425-625	117.5	2.3×10^{8}	-70.80	70.00	47.48
	625-1000	74.71	1.9×10^{10}	-57.10	123.6	50.58
$[Ni(H_2L)_2Cl_2].4H_2O$	22-176	264.9	8.4×10^{5}	-100.0	259.4	32.64
	176-320	217.6	2.4×10^{6}	-83.30	195.8	41.42
	472-620	220.4	2.4×10^{13}	-76.20	215.7	212.2

 TABLE 4

 Thermodynamic data of the thermal decomposition of H₂L and its metal complexes

TABLE 5
Biological effect of H ₂ L and its metal complexes on the desert locust Schistocerca gregaria and adult longevities of Schistocerca
gregaria (Forsk) (Orthoptera – Acrididae)

		Desert lo	cust Schistoce	erca gregaria		adult longevities of Schistocerca gregaria		
	% Nymp	ohal instar	Ģ	% Adult stage		Adult lon	gevities (Days \pm S.E)	
Dose of the complexes 2μ g/insect	Nymph mortality	Deformed nymphs	% Emerged	% Deformed	% normal	Male	Female	
(H ₂ L)	40	34	26	15	11	86±4.3*	79±2.7*	
$[Mn(H_2L)_2Cl_2]$	40	19	41	22	19	92±4.4*	$88{\pm}4.2^{*}$	
$[Fe(H_2L)_2Cl_2]Cl$	80	15	5	00	00	00	00	
$[Co(H_2L)_2Cl_2]$	80	6	14	00	00	00	00	
$[Ni(H_2L)_2Cl_2].4H_2O$	20	22	58	32	26	89±4.3*	$87{\pm}5.1^{*}$	
$[Cu(H_2L)_2Cl_2]$	100	00	00	00	00	00	00	
$[Zn(H_2L)_2Cl_2]$	80	00	20	6	14	$76 \pm 5.2^{*}$	$72 \pm 4.2^{*}$	
control	00	00	00	00	98.8	129.2 <u>+</u> 5.2	120.7 <u>+</u> 4.5	

*: Significance at P < 0.05

(NS): Nonsignificance at P < 0.05

mortalities obtained reveal that many of adult deformations are inversely proportional with normal adults. $[Zn(H_2L)_2Cl_2]$ complex is found to produce 14% deformation of normal adult, while the adult malformation is 6%. In conclusion, the data obtained reveal that $[Cu(H_2L)_2Cl_2]$ complex is the highest effective compounds. A remarkable mortal potency of the studied organic compound and its complexes against the 5th nymphal instar of the desert locust *Schistocerca gregaria* is estimated as compound dependent mortalities. This may be explained by the inhibition of nymphal development induced by unbalance caused by the presence of chemicals in insect blood. These results suggest that thiazole complexes act directly on feeding inhibition. These compounds are found to play an important role in regulating activity and oviposition rhythm of locust *Schistocerca gregaria*.

Effect of Different H₂L Ligand and its Metal Complexes on the Adult Longevity of *Schistocerca gregaria*

Data listed in Table 5 reveal different varieties of adult longevity that emerged from treated 5th nymphal instars of *Schistocerca gregaria* with the different complexes, whereas adult longevity depends on healthy immature stages. The male longevity is found to be more or less increased than the female longevity, i.e., the produced adult males is less effective than females. The higher male longevity is found to be non-significant (P<0.05) at 112 days and significance (P>0.05) at 66 days after nymphal treatment with the [Mn(H₂L)₂Cl₂] complex in comparison to 92 days of control male longevity. The same previous complex is found to cause no significance (110 days) and significance (88 days) on female longevity in comparison to 120 days of control female longevity (Table 5). These results agree with the application of different chemicals against locusts *Schistocerca Gregaria*.^[31]

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