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Metal complexes of a novel Schiff base derived from sulphametrole and varelaldehyde. Synthesis, spectral, thermal characterization and biological activity

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ABSTRACT

Metal complexes of a novel Schiff base (HL = 3-(4′-ethylazomethinobenzene sulphonamide)-4-methoxy-1,2,5-thiadiazole) derived from condensation of sulphametrole and varelaldehyde are reported and characterized based on elemental analyses, IR, solid reflectance, magnetic moment, molar conductance, and thermal analysis (TG). From the elemental analyses data, 1:1 metal complexes are formed having the general formulae $[MCl_3(HL)(H_2O)]\cdot 3H_2O$ (M = Cr(III), Fe(III)) and $[MCl_2(HL)(H_2O)_2]\cdot yH_2O$ (where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II), y = 0–3). The important infrared (IR) spectral bands corresponding to the active groups in the ligand and the solid complexes under investigation were studied. IR spectra show that HL is coordinated to the metal ions in a neutral bidentate manner with ON donor sites of the enolic sulphonamide-*OH* and thiodiaza-*N*. The solid complexes have been synthesized and studied by thermogravimetric analysis. The thermal dehydration and decomposition of these complexes were studied kinetically using the integral method applying the Coats–Redfern equation. All the metal chelates are found to be non-electrolytes. From the magnetic and solid reflectance spectra, the complexes have octahedral structures. The antibacterial and antifungal activities of the synthesized ligand and its metal complexes were screened against bacterial species (*Escherichia coli and Staphylococcus aureus*) and fungi (*Candida and Aspergillus flavus*). The activity data show that the metal complexes have a promising biological activity comparable with the parent Schiff base ligand against bacterial and fungal species.

1. Introduction

Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions. The development in the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species [1–5]. Schiff base ligands are considered "privileged ligands" because they are easily prepared by the condensation between aldehydes and imines. Schiff base ligands are able to coordinate many different metals [6–10], and to stabilize them in various oxidation states. The Schiff base complexes have been used in catalytic reactions [11] and as models for biological systems [12,13]. During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors [14–19]. This may be attributed to their stability, biological activity [20] and potential applications in many fields such as oxidation catalysis [21], and electrochemistry [22]. The complexes make these compounds effective and stereospecific catalysts for oxidation, reduction and hydrolysis and they show biological activity, and other transformations of organic and inorganic chemistry [23]. It is well known that some drugs have higher activity when administered as metal complexes than as free ligands [23].

Sulphametrole (SMR) was designated by chemical abstracts as N^1-(4-methoxy-1,2,5-thiadiazol-3-yl)sulphanilamide. It had the molecular formula $C_9H_{10}N_4O_3S_2$ (F.W = 286.33 g/mole). Sulfametrole is a sulphonamide antibacterial drug. Synthesis, spectroscopic, thermal and antimicrobial studies of some metal complexes of Schiff base derived from and 2-thiophene carboxaldehyde [24] and o-vanilin [25] were reported. The present study deals with the preparation of novel Schiff base ligand and its chelates with some transition metals, e.g. Cr(III), Mn(II), Fe(III), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II). The solid complexes have been synthesized and studied by elemental analyses, molar conductance, solid reflectance, IR and thermogravimetric analysis (TG). The thermal dehydration and decomposition of these complexes were studied kinetically using the integral method applying the Coats–Redfern. The biological activity of the parent Schiff base and its complexes was studied.

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2. Experimental

2.1. Materials and reagents

All chemicals used were of the analytical reagent grade (AR), and of highest purity available. Sulphametrole, varelaldehyde and ferrous chloride were purchased from Sigma. Copper (II) chloride dihydrate, ferric and chromium chlorides hexahydrates were obtained from Prolabo. Manganese (II), cobalt (II) and nickel (II) chlorides hexahydrate and the organic solvents (ethyl alcohol, diethylether, and dimethylformamide (DMF)), were purchased from BDH. Zinc chloride dihydrate was obtained from Ubichem. They included also Zinc oxide, disodium salt of EDTA (Analar), ammonia solution (33% v/v) and ammonium chloride (El-Nasr pharm. Chem. Co., Egypt). Hydrochloric and nitric acids from Merck were used. De-ionized water collected from all glass equipments was usually used in all preparations.

2.2. Instruments

The molar conductance of solid complexes in DMF was measured using Sybron-Barnstead conductometer (Meter-PM.6, $E = 3406$). Elemental microanalyses of the separated solid chelates for C, H, N and S were performed at the Microanalytical Center, Cairo University. The analyses were repeated twice to check the accuracy of the data. Infrared spectra were recorded, as KBr pellets, on a Perkin–Elmer FT-IR type 1650 spectrophotometer in wave number region 4000–400 cm^{-1}. 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 thermogravimetric analysis (TG) was carried out in dynamic nitrogen atmosphere (10 mL min^{-1}) with a heating rate of 10 $°\text{C min}^{-1}$ using Shimadzu TG-60H thermal analyzer. The ^{1}H NMR spectra were recorded using 300 MHz Varian-Oxford Mercury. The biological activity was carried out at the Microanalytical Center, Cairo University.

2.3. Synthesis of Schiff base (HL)

Ethanolic hot solution (60 °C) of varelaldehyde (0.58 g, 10 mmol) was mixed with ethanolic hot solution (60 °C) of sulphametrole (2.54 g, 10 mmol) in 50 mL quickfit flask. The resulting mixture was left under reflux for 3 h and the formed solid product was separated by filtration, purified by crystallization from ethanol, washed with diethyl ether and dried in a vacuum over anhydrous calcium chloride. The yellow product is produced in 90% yield.

2.4. Synthesis of metal complexes

The following detailed preparation is given as an example and the other complexes were obtained similarly. The Cu(II) complex was prepared by the addition of hot solution (60 °C) of the Cu(II) chloride (0.17 g, 1 mmol) in an ethanol–water mixture (1:1, 25 mL) to the hot solution (60 °C) of the Schiff base (0.294 g, 1 mmol) in the same solvent mixture (25 mL). The resulting mixture was stirred under reflux for one hour whereupon the complex precipitated. It was collected by filtration, washed with a 1:1 ethanol: water mixture and diethyl ether.

2.5. Biological activity

Antimicrobial activity of the tested samples was determined using a modified Kirby-Bauer disc diffusion method [26]. One hundred microliters of the tested bacteria or fungi were grown in 10 mL of fresh media until they reached account of approximately 108 cells/mL for bacteria and 105 cells/mL for fungi [27]. One hundred microliters of microbial suspension was spread onto agar plates corresponding to the broth in which they were maintained. Isolated colonies of each organism that might be playing a pathogenic role should be selected from primary agar plates and tested for susceptibility by disc diffusion method [28]. Of the many media available, NCCLS recommends Mueller–Hinton agar due to its results in good batch-to-batch reproducibility. Disc diffusion method for filamentous fungi tested by using approved standard method (M38-A) developed [28]. For evaluating the susceptibilities of filamentous fungi to antifungal agent, the disc diffusion method was applied for yeast developed by using approved standard method (M44-P) [28]. Plates inoculated with filamentous fungi as *Asprgillus* flavus at 25 °C for 48 h; Gram (+) bacteria as *Staphylococcus aureus;* Gram (−) bacteria as *Escherichia coli,* they were incubated at 35–37 °C for 24–28 h and yeast as *Candida albicans* incubated at 30 °C for 24–28 h and, then the diameters of the inhibition zones were measured in millimeters [28]. Standard discs of tetracycline (antibacterial agent), and amphotericin B (antifungal agent) served as positive controls for antimicrobial activity but filter discs impregnated with 10 μL of solvent (distilled water, chloroform, DMSO) were used as a negative control. The agar used is Mueller–Hinton agar that is rigorously tested for composition and pH. Further the depth of the agar in the plate is a factor to be considered in the disc diffusion method. This method is well documented and standard zones of inhibition have been determined for susceptible and resistant values. Blank paper discs (Schleicher and Schuell, Spain) with a diameter of 8.0 mm were impregnated with 10 μL of tested concentration of the stock solutions. When a filter paper disc impregnated with a tested chemical is placed on agar, the chemical will diffuse from the disc into the agar. This diffusion will place the chemical in the agar only around the disc. The solubility of the chemical and its molecular size will determine the size of the area of chemical infiltration around the disc. If an organism is placed on the agar, it will not grow in the area around the disc if it is susceptible to the chemical. This area of no growth around the disc is known as zone of inhibition or clear zone. For the disc diffusion, the zone diameters were measured with slipping calipers of the national committee for clinical laboratory standards [28]. Agar based methods such Etest and disc diffusion can be good alternatives because they are simpler and faster than broth-based methods [29].

3. Results and discussion

3.1. Schiff base characterization

The new prepared Schiff base (HL = 3-(4′-ethylazomethinobenzene sulphonamide)-4-methoxy-1,2,5-thiodiazole) is subjected to elemental analyses, IR and ^{1}H NMR spectral studies. The results of elemental analyses (C, H, N, S) with molecular formula and the melting point 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 Schiff base. The structure of the Schiff base under study is given below in Fig. 1. The IR spectral data of HL Schiff base is listed in Table 2. It was found that the $\nu(C{=}N)$ of the azomethine group and $\nu(C{=}N)$ of the thiadiazole moiety occur at 1597 and 1650 cm^{-1},

Table 1
Analytical and physical data of HL ligand and its metal complexes.

Compound	m.p. (°C)	Colour (% yield)	% Found (calcd.)					$\mu_{eff.}$ (B.M.)	Λ_m Ω^{-1} mol^{-1} cm^2
			C	H	N	S	M		
HL, $C_{12}H_{14}N_4O_3S$; 294 g/mol	205	Yellow (90)	48.70 (48.98)	4.41 (4.76)	18.93 (19.05)	10.62 (10.88)	–	–	–
$[CrCl_3(HL)(H_2O)]\cdot 3H_2O$, $C_{12}H_{22}Cl_3CrN_4O_7S$; 524.5 g/mol	>300	Green (66)	27.52 (27.45)	4.46 (4.19)	10.42 (10.68)	6.23 (6.10)	10.05 (9.91)	5.52	13.56
$[MnCl_2(HL)(H_2O)_2]\cdot H_2O$, $C_{12}H_{20}Cl_2MnN_4O_8S$; 473 g/mol	>300	Yellowish brown (69)	30.42 (30.38)	4.08 (4.22)	11.63 (11.81)	7.03 (6.75)	11.28 (11.60)	5.42	17.82
$[FeCl_3(HL)(H_2O)]\cdot 3H_2O$, $C_{12}H_{22}Cl_3FeN_4O_7S$; 528.5 g/mol	>300	Brownish Black (71)	27.54 (27.25)	4.05 (4.16)	10.10 (10.60)	5.73 (6.05)	10.3 (10.60)	5.69	19.28
$[FeCl_2(HL)(H_2O)_2]\cdot 2H_2O$, $C_{12}H_{22}Cl_2FeN_4O_7S$; 493 g/mol	>300	Yellow (63)	29.15 (29.21)	4.34 (4.46)	11.10 (11.36)	6.10 (6.49)	11.02 (11.36)	5.15	10.96
$[CoCl_2(HL)(H_2O)_2]\cdot 3H_2O$, $C_{12}H_{24}Cl_2CoN_4O_8S$; 514 g/mol	>300	Green (65)	28.25 (28.02)	4.31 (4.67)	10.95 (10.89)	6.18 (6.23)	11.52 (11.48)	5.06	17.30
$[NiCl_2(HL)(H_2O)_2]\cdot 3H_2O$, $C_{12}H_{24}Cl_3NiN_4O_8S$; 514 g/mol	>300	Yellowish Brown (70)	27.85 (28.02)	4.76 (4.67)	10.48 (10.89)	6.03 (6.23)	11.66 (11.48)	3.87	11.92
$[CuCl_2(HL)(H_2O)_2]\cdot 2H_2O$, $C_{12}H_{26}Cl_2CuN_4O_9S$; 500.5 g/mol	>300	Green (70)	26.74 (26.84)	5.06 (4.85)	10.12 (10.44)	5.78 (5.96)	12.03 (11.84)	2.07	9.18
$[ZnCl_2(HL)(H_2O)_2]$, $C_{12}H_{18}Cl_2N_4O_5SZn$; 466 g/mol	>300	White (62)	31.11 (30.90)	3.60 (3.86)	11.86 (12.02)	6.65 (6.87)	14.07 (13.95)	diam.	23.83

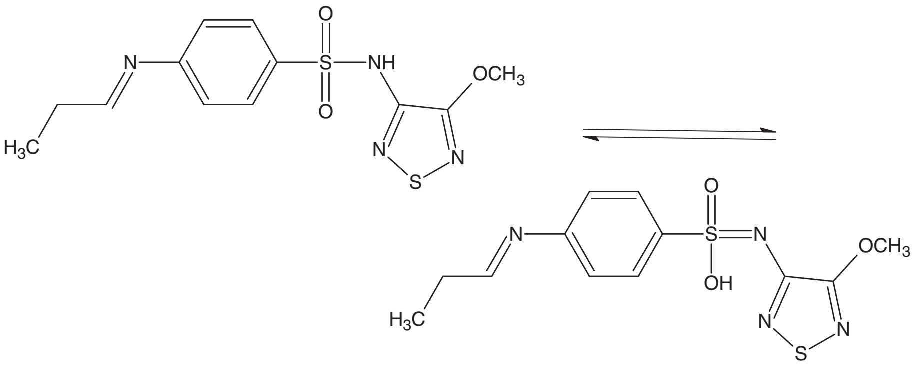


Fig. 1. Structure of Schiff base ligand (HL).

Table 2
IR spectra (4000–400 cm^{-1}) of the HL ligand and its metal complexes.

Compound	ν(NH)	ν(OH) enolic	$\nu(SO_2)$ (asym)	$\nu(SO_2)$ (sym.)	ν(CH=N) azomethine	ν(C=N) thiodiaza	$V(H_2O)$ (coord.)	ν(M—O)	ν(M—N)
HL	3381br	–	1321sh	1158sh	1597sh	1650sh	–	–	–
$[CrCl_3(HL)(H_2O)]\cdot 3H_2O$	–	3178s	1308sh	1174m	1594br	1645sh	830m 782m	550w	420w
$[MnCl_2(HL)(H_2O)_2]\cdot H_2O$	–	3100br	1321m	1145m	1598m	1628sh	820s 782s	554w	440w
$[FeCl_3(HL)(H_2O)]\cdot 3H_2O$	–	3150br	1321w	1160m	1595m	1622sh	836m 742m	520s	430w
$[FeCl_2(HL)(H_2O)_2]\cdot 2H_2O$	–	3230w	1323m	1155m	1598sh	1631m	887m 742m	520m	434w
$[CoCl_2(HL)(H_2O)_2]\cdot 3H_2O$	–	3150br	1322m	1155w	1597m	1625m	834m 774m	522w	430w
$[NiCl_2(HL)(H_2O)_2]\cdot 3H_2O$	–	3250br	1320sh	1154m	1597m	1628m	834m 774m	586m	466w
$[CuCl_2(HL)(H_2O)_2]\cdot 2H_2O$	–	3168br	1320m	1147m	1596sh	1625sh	822m 752m	532m	441w
$[ZnCl_2(HL)(H_2O)_2]$	–	3170br	1324m	1135m	1596m	1620sh	845m 725m	525m	432w

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

respectively. In addition, the ligand exhibits two bands at 1321 and 1158 cm^{-1} which is attributed to $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$ stretching vibrations, respectively [24,25]. Also, it has a band at 3412 cm^{-1} which attributed to ν(NH). The ^{1}H NMR data for HL ligand (Fig. 2A), recorded in DMSO-d$_6$, show a sharp signals at 9.80 and 3.986 ppm which may be assigned to the azomethine (s,

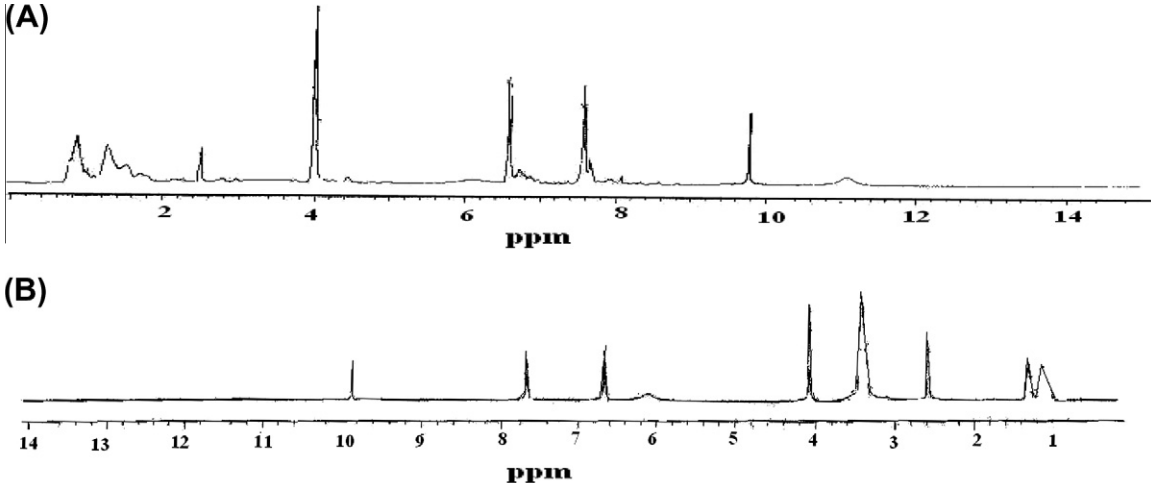


Fig. 2. ^{1}H NMR spectra of (A) HL and (B) Zn complex.

—CH=N, 1H) and methoxy (s, —OCH_3; 3H) protons, respectively. A multiple observed in the region 0.858 and 1.267 ppm for HL corresponds to the methyl protons (m, CH_3—CH_2—CH=N; 3H) and (m, CH_3—CH_2—CH=N; 2H), respectively. Another doublet–doublet bands at 6.60 and 7.577 and 6.70 and 7.70 ppm for HL may reasonably be assigned to phenyl protons (d,d, C_6H_4; 4H; $J = 8.65$ Hz). A broad band observed at 11.04 ppm may be attributed to the secondary amine proton (—SO_2—NH; 1H).

3.2. Composition and structures of Schiff base complexes

The isolated solid complexes of Cr(III), Mn(II), Fe(III), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) ions with the Schiff base ligand were subjected to elemental analyses (C, H, N, S and metal content), IR, ^{1}H NMR, magnetic studies, molar conductance, and thermal analysis (TG), to identify their tentative formulae in a trial to elucidate their molecular structures. The results of elemental analyses, Table 1, are in good agreement with those required by the proposed formulae. The complexes are insoluble in water and most organic solvents and soluble in DMF and DMSO solvents.

3.3. Molar conductivity measurements

The chelates were dissolved in DMF and the molar conductivities of their solutions (10^{-3} M) at 25 ± 2 °C were measured. It is concluded from the results reported in Table 1 that the chelates have molar conductance values of 9.18–23.83 Ω^{-1} mol^{-1} cm^2 indicating that these chelates are non-electrolytes. It also indicates the bonding of the chloride anions to the metal ions. The relative high values obtained may be attributed to the replacement of the coordinated chloride ions by solvent molecules, a phenomenon usually encountered in complexes containing chloride ions.

3.4. IR spectral studies

The IR spectral data of HL Schiff base and its complexes are listed in Table 2. It was found that the ν(C=N) of the azomethine group occurs at 1597 cm^{-1} in the free HL ligand; after complexation, this band is slightly shifted to lower wavenumbers (1594–1598 cm^{-1}) indicating the non-involvement of the azomethine nitrogen in chelate formation. However, the band due to the thiadiazole moiety; ν(C=N), in the free ligand is observed at 1650 cm^{-1} and shifted to lower frequency values at (1620–1645 cm^{-1}) upon complexation suggesting the coordination via thiadiazole nitrogen (N → M). In addition, the ligand exhibits two bands at 1321 and 1158 cm^{-1} due to $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$ stretching vibrations, respectively [24,25]. Also, it has a band at 3412 cm^{-1} which attributed to ν(NH). The bands due to asymmetric and symmetric SO_2 group are shifted to lower frequencies (Table 2) upon complexation. While the ν(NH) is disappeared or hidden under the broad bands at 3450–3100 cm^{-1} in the spectra of the complexes as the result of the presence of coordinated water molecules which in turns make it difficult to confirm the enolization of the sulphonamide group. The blue shift of the SO_2 stretching vibration to lower frequencies and the appearance of new absorption band for enol ν(OH) stretching mode at 3150–3250 cm^{-1}, confirm the tautomerization (—SO(OH)=N) as a result of complex formation to give more stable six-membered ring [24,25,30]. The IR bands of $\nu(H_2O)$ of coordinated water appeared at 820–887 and 725–782 cm^{-1}, indicating the binding of water molecules to the metal ions. In the far IR spectra of all the complexes, the non-ligand bands observed at 520–586 and 420–466 cm^{-1} regions can be assigned to ν(M—O) and ν(M—N), respectively [31,32]. Therefore, the IR spectra reveal that HL coordinated to the metal ions via enolic —OH of sulphonamide group and thiadiazole-N.

3.5. ^{1}H NMR spectra

The ^{1}H NMR data for HL ligand (Fig. 2A) and its Zn(II) complex (Fig. 2B), recorded in DMSO-d$_6$, show a sharp signal at 9.80 and 9.90 ppm which may be assigned to the azomethine protons (—CH=N, 1H), respectively. However, a singlet at 3.986 and 4.08 ppm may be attributed to the methoxy protons (—OCH_3; 3H). A multiple observed in the region 0.858 and 1.267 and 1.10 and 1.30 ppm for HL and Zn(II) complex corresponds to the methyl protons (CH_3—CH_2—CH=N; 3H) and (CH_3—CH_2—CH=N; 2H), respectively. Another doublet–doublet bands at 6.60 and 7.577 and 6.70 and 7.70 ppm for HL and Zn(II) complex, respectively, may reasonably be assigned to phenyl protons (C_6H_4; 4H; $J = 8.65$ Hz). A broad band observed at 11.04 ppm may be attributed to the secondary amine proton (—SO_2—NH; 1H). It is found that the enolic S(O)OH signal, appeared in the spectrum of Zn(II) complex at 6.10 ppm indicating that —SO_2—NH is enolized to the —S(O)OH=N— and participation in the chelation with Zn(II) ion [24,25]. The signal observed at 3.40 ppm with an integration corresponding to four protons in Zn(II) complex is assigned to two water molecules [24,25]. However, the resonance signals obtained for

Zn(II) complex shows downfield shift as compared to the corresponding ligand indicating the coordination of ligand to Zn(II) ion.

3.6. Magnetic susceptibility and electronic spectra measurements

From the diffused reflectance spectrum, the Fe(III) chelate (Fig. 3) exhibits a band at 22,010 cm^{-1}, which may be assigned to the $^6A_{1g} \rightarrow T_{2g}$ (G) transition in octahedral geometry of the complexes [33]. The observed magnetic moment of Fe(III) complex is 5.69 B.M. Thus, the complex formed has the octahedral geometry [25,33]. The spectrum shows also a band at 27,995 cm^{-1} which may attribute to ligand to metal charge transfer. The diffused reflectance spectrum of the Mn(II) complex (Fig. 3) shows three bands at 15,579, 22,145 and 26,977 cm^{-1} assignable to

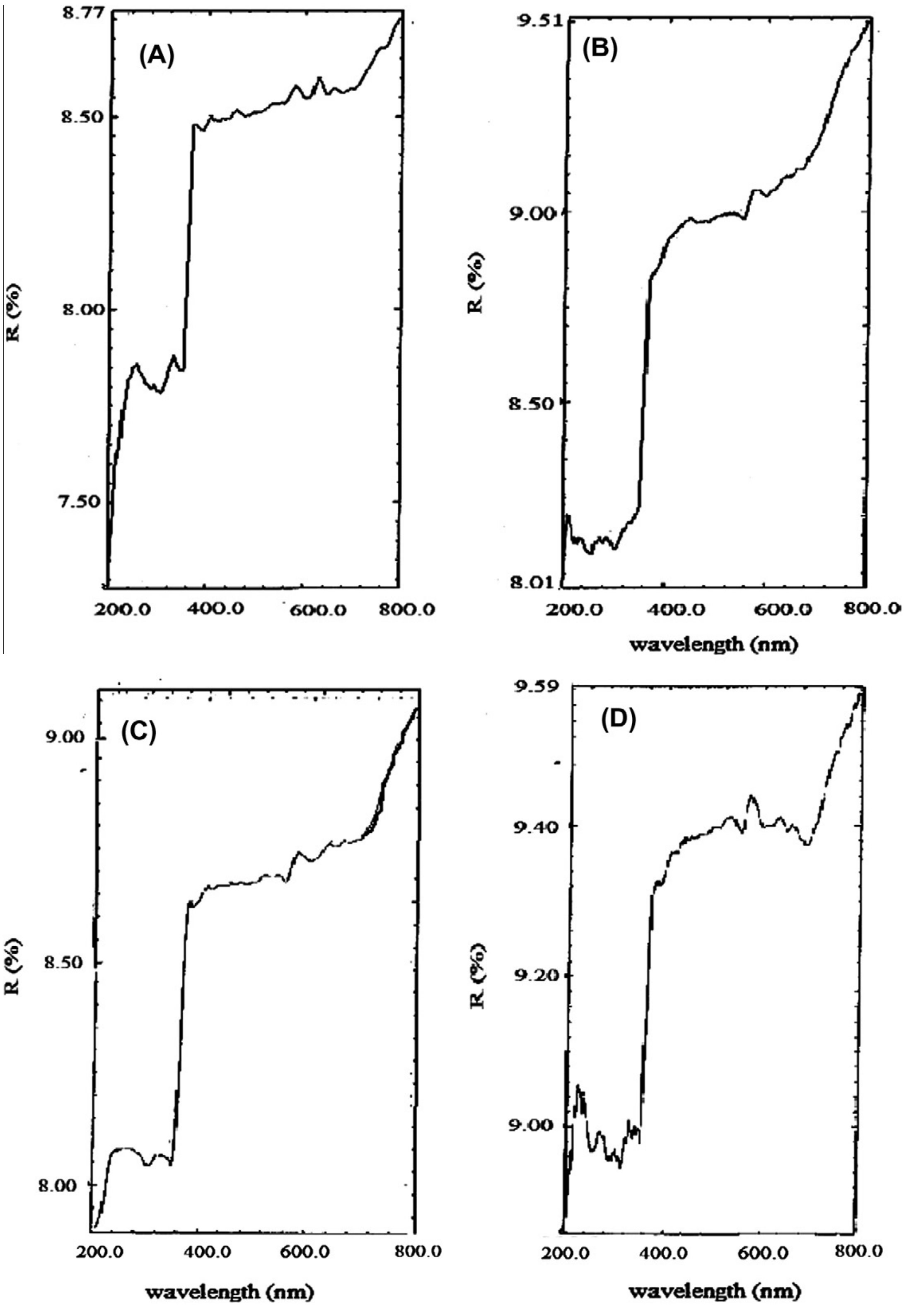


Fig. 3. Diffused reflectance spectra of (A) Mn(II), (B) Co(II), (C) Fe(III) and (D) Cu(II) complexes.

${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}(D)$ transitions, respectively [34]. The magnetic moment value is 5.42 B.M. which indicates the presence of Mn(II) complex in octahedral structure.

The electronic spectrum of the Fe(II) complex displays two absorption bands at 14,880 and 18,036 cm^{-1} which are assigned to ${}^5T_{2g} \rightarrow {}^5E_g$ transitions [33]. Also the band at 25,655 cm^{-1} is assigned to L → M charge transfer. The observed magnetic moment of 5.15 B.M. is consistent with an octahedral geometry [33]. The electronic spectrum of the Co(II) complex (Fig. 3) gives three bands at 15,289, 18,407 and 22,360 cm^{-1}. The bands observed are assigned to the transitions ${}^4T_{1g}$ (F) → ${}^4T_{2g}$ (F) (ν_1), ${}^4T_{1g}$ (F) → ${}^4A_{2g}$ (F) (ν_2) and ${}^4T_{1g}$ (F) → ${}^4T_{2g}$ (P) (ν_3), respectively, suggesting an octahedral geometry around Co(II) ion [32,40,42]. The magnetic susceptibility is found to be 5.06 B.M. indicating an octahedral geometry [25]. The region at 25,790 cm^{-1} refers to the charge transfer band.

The Ni(II) complex is found to has a room temperature magnetic moment value of 3.87 B.M.; which is in the normal range observed for octahedral Ni(II) complexes [25,33,35]. The electronic spectrum displays three bands in the solid reflectance spectrum at ν_1: 14,968 cm^{-1}: ${}^3A_{2g} \rightarrow {}^3T_{2g}$; ν_2: 17,788 cm^{-1}: ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ν_3: 21,347 cm^{-1}: ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$. The spectrum shows also a band at 24,565 cm^{-1} which may attributed to ligand to metal charge transfer. The reflectance spectrum of Cu(II) chelat (Fig. 3) consists of a shoulder band centered at 17,045 and 18,167–22,682 cm^{-1}. The magnetic moment of 2.07 B.M. falls within the range normally observed for octahedral Cu(II) complexes [25,33]. A moderately intense peak observed at 24,664 cm^{-1} is due to ligand–metal charge transfer transition. The Zn(II) complex is diamagnetic and according to the empirical formula, an octahedral geometry is proposed for this complex.

3.7. Thermal analysis (TG)

The TG data of the thermal decomposition of the complexes are shown in Table 3, Fig. 4 and Scheme 1. The thermodynamic activation parameters of decomposition processes of dehydrated complexes namely activation energy (E^*), enthalpy (ΔH^*), entropy (ΔS^*) and Gibbs free energy change of the decomposition (ΔG^*) are evaluated graphically by employing the Coats–Redfern relation [36]. The entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and the free energy change of activation (ΔG^*) were calculated. The data are summarized in Table 4. The high values of the activation energies reflect the thermal stability of the complexes. The entropy of activation is found to have negative values in all the complexes which indicate that the decomposition reactions proceed spontaneously.

The thermogram of $[CrCl_3(HL)(H_2O)]\cdot 3H_2O$ and $[CuCl_2(HL)(H_2O)]\cdot 2H_2O$ chelates show five decomposition steps within the temperature range 30–900 and 50–950 °C, respectively. The first two steps of decomposition within the temperature range 30–250 and 50–230 °C correspond to the loss of three water molecules of hydration, Cl_2, one coordinated water molecule and C_4H_9ClNO (in case of Cr(III) complex, mass loss = 51.32% (calcd. 50.62%)) and loss of two water molecules of hydration and coordination and Cl_2.(in case of Cu(II) complex, mass loss of 29.37% (calcd. 28.57%)). The energy of activation was found to be 44.40 and 78.24 (in case of Cr(III) complex) and 36.52 and 53.78 kJ mol^{-1} (in case of Cu(II) complex) for the first and second steps, respectively. The subsequent steps (230–950 °C) correspond to the removal of the organic part of the ligand leaving metal oxide as a residue. The overall weight loss amounts to 86.02% (calcd. 85.51%) and 84.26 (calcd. 84.11%) for Cr(III) and Cu(II) complexes, respectively.

The TG curves of the Mn(II), Fe(II), Co(II) and Ni(II) chelates show four stages of decomposition within the temperature range of 30–950 °C. The first step at 30–130 °C corresponds to the loss of water molecules of hydration except Fe(II) complex, it corresponds to the loss of hydrated and coordinated water molecules (30–200 °C). The subsequent three steps (2nd, 3rd and 4th) involve the loss of Cl_2 and ligand molecule. The overall weight loss amounts to 84.17% (calcd. 85.02%), 85.59% (calcd. 85.39%), 85.92% (calcd. 85.60%) and 84.97% (calcd. 85.42%) and the activation energies are 82.37–176.9, 75.98–184.2, 145.6–165.7 and 102.4–243.4 for Mn(II), Fe(II), Co(II) and Ni(II) chelates, respectively.

Based on analyses and spectral studies, tentative proposed structures of the complexes are shown in Fig. 5.

3.8. Biological activity

In testing the antibacterial activity of these compounds we used more than one test organism to increase the chance of detecting antibiotic principles in tested materials. The sensitivity of a microorganism to antibiotics and other antimicrobial agents was determined by the assay plates which incubated at 28 °C for 2 days for yeasts and at 37 °C for 1 day for bacteria. All of the tested com-

Table 3
Thermogravimetric data of HL metal complexes.

Complex	TG range (°C)	DTG$_{max}$ (°C)	n$^\#$	Mass loss Total mass loss % Found (calcd.)	Assignment	Metallic residue
$[CrCl_3(HL)(H_2O)]\cdot 3H_2O$	30–130	85	1	10.42 (10.30)	Loss of $3H_2O$	½Cr_2O_3
	130–250	219	1	40.90 (40.32)	Loss of H_2O, Cl_2 and C_4H_9ClNO	
	250–900	295, 484, 648	3	34.70 (34.89) 86.02 (85.51)	Loss of $C_8H_5N_3O_{0.5}S$	
$[MnCl_2(HL)(H_2O)_2]\cdot H_2O$	30–100	94	1	3.54 (3.80)	Loss of H_2O	MnO
	100–280	252	1	22.78 (22.57)	Loss of $2H_2O$ and Cl_2	
	280–950	500, 857	2	57.85 (58.65) 84.17 (85.02)	Loss of $C_{12}H_{14}N_4O_2S$	
$[FeCl_2(HL)(H_2O)_2]\cdot 2H_2O$	30–200	63	1	14.81 (14.60)	Loss of $4H_2O$	FeO
	200–370	272	1	32.27 (32.05)	Loss of Cl_2 and C_4H_9NO	
	370–950	504, 700	2	38.51 (38.74) 85.59 (85.39)	Loss of $C_8H_5N_3OS$	
$[CoCl_2(HL)(H_2O)_2]\cdot 3H_2O$	30–120	55	1	11.29 (10.69)	Loss of $2H_2O$	CoO
	120–320	275	1	20.92 (20.82)	Loss of $2H_2O$ and Cl_2	
	320–950	400, 690	2	53.71 (54.09) 85.92 (85.60)	Loss of $C_{12}H_{14}N_4O_2S$	
$[NiCl_2(HL)(H_2O)_2]\cdot 3H_2O$	30–130	77	1	10.69 (10.51)	Loss of $3H_2O$	NiO
	130–260	210	1	20.39 (20.82)	Loss of $2H_2O$ and Cl_2	
	260–900	386, 552	2	53.89 (54.09) 84.97 (85.42)	Loss of $C_{12}H_{14}N_4O_2S$	
$[CuCl_2(HL)(H_2O)_2]\cdot 2H_2O$	50–130	70	1	7.45 (7.19)	Loss of $2H_2O$	CuO
	130–230	185	1	21.92 (21.38)	Loss of $2H_2O$ and Cl_2	
	230–950	365, 556, 764	3	54.89 (55.54) 84.26 (84.11)	Loss of $C_{12}H_{14}N_4O_2S$	

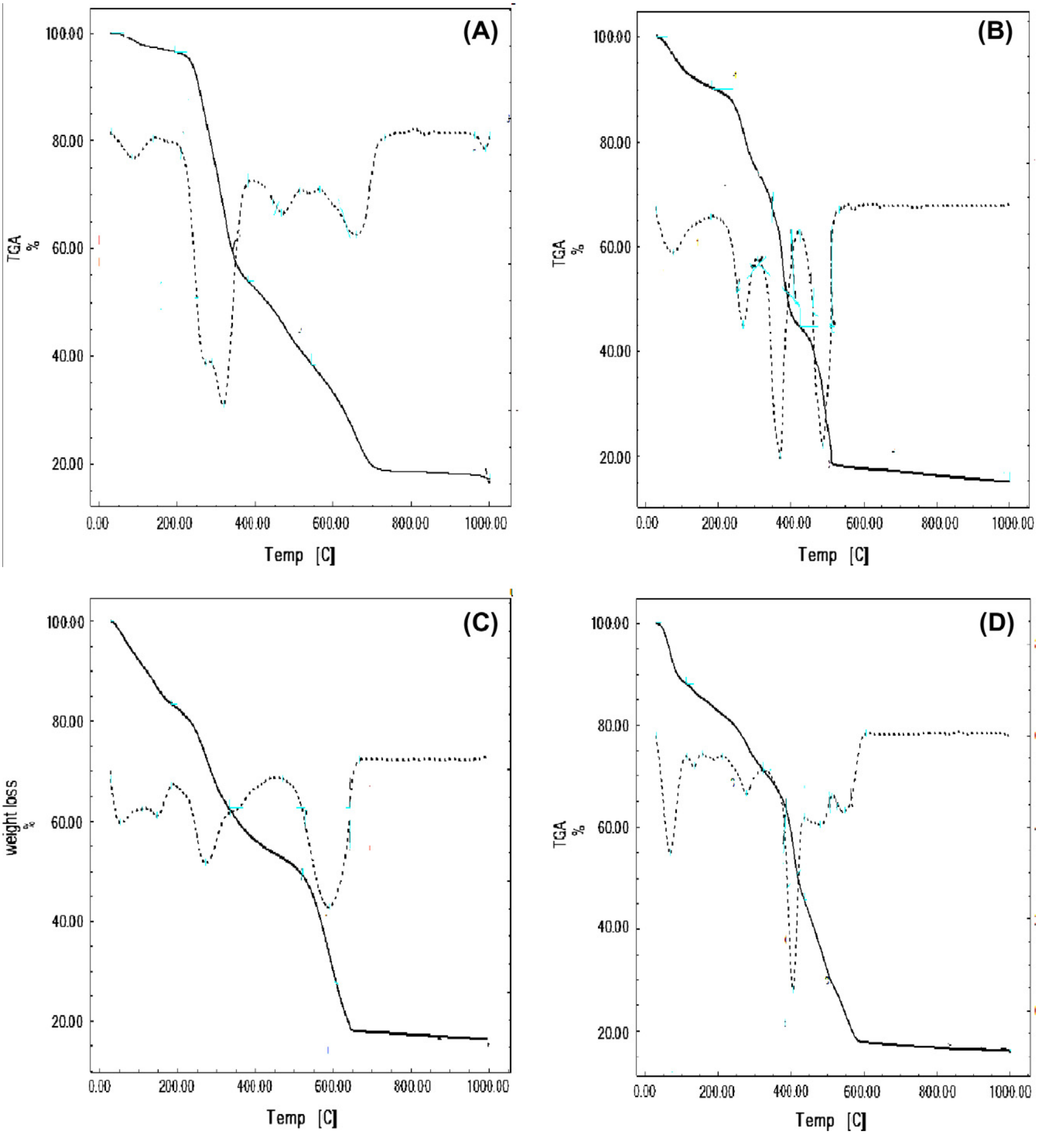


Fig. 4. Thermal analysis (TG) of (A) Mn(II), (B) Ni(II), (C) Fe(III) and (D) Co(II) complexes.

pounds showed a remarkable biological activity against different types of Gram-positive and Gram-negative bacteria and against fungi species. The data are listed in Table 5. On comparing the biological activity of the Schiff base and its metal complexes with the standard (Tetracycline, Antibacterial agent) and (Amphotricine B, Antifungal agent), it is seen that the biological activity follows the order:

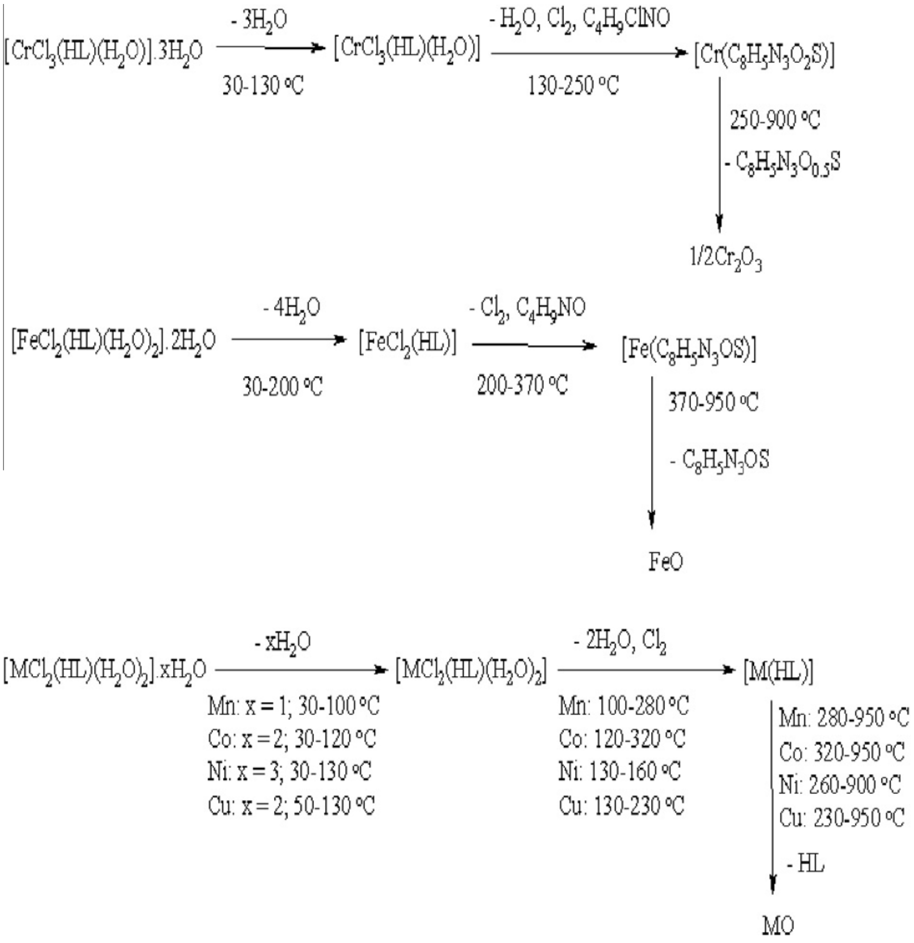
For G^- bacteria HL > Fe(II) > Ni(II) > Cu(II) > tetracycline > Mn(II) > Co(II) > Cr(III) > Zn(II) > Fe(III).

For G^+ bacteria HL > Cu(II) > Fe(II) = Ni(II) > Mn(II) > tetracycline > Co(II) > Cr(II) > Fe(III) > Zn(II).

For *Aspergillus flavus (Fungus)*: HL > amphotricine B > Cu(II) > Cr(III) > Fe(II) > Zn(II). Fe(III), Mn(II), Co(II) and Ni(II) complexes have no antifungal activity.

For *C. albicans (Fungus)*: amphotricine B > Cu(II) > Cr(III) = Co(III) > Ni(II) > Fe(II) = Mn(II) > HL > Zn(II). Fe(III) complex has no antifungal activity.

It was demonstrated that the newly prepared Schiff base and its metal complexes showed a higher effect on *E. coli* (Gram-negative bacteria) and *S. aureus* (Gram-positive bacteria). It is known that the membrane of Gram-negative bacteria is surrounded by an outer membrane containing lipopolysaccharides. The newly synthesized

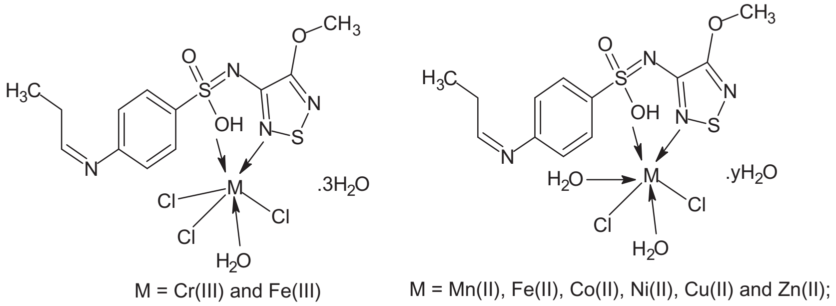


Scheme 1. Thermal decomposition scheme of metal complexes.

Table 4
Thermodynamic data of the thermal decomposition of H_2L metal complexes.

Complex	Decomp. Temp. (°C)	E^* (kJ mol^{-1})	A (s^{-1})	ΔS^* (JK^{-1}mol^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})
$[CrCl_3(HL)(H_2O)]\cdot 3H_2O$	30–100	44.40	3.67×10^8	−49.15	62.18	64.57
	130–230	78.24	4.09×10^{12}	−85.76	59.86	88.98
	230–320	119.6	5.89×10^{10}	−112.3	122.3	142.1
	400–550	182.7	2.99×10^9	−165.9	196.8	205.7
	550–800	223.5	4.05×10^7	−198.7	242.3	260.4
$[MnCl_2(HL)(H_2O)_2]\cdot H_2O$	30–110	53.25	2.87×10^8	−34.65	45.65	37.22
	140–230	82.37	4.55×10^{12}	−62.66	97.16	76.42
	240–330	132.4	6.08×10^5	−106.6	125.3	109.5
	550–700	176.9	9.34×10^7	−185.7	161.5	183.4
$[FeCl_2(HL)(H_2O)_2]\cdot 2H_2O$	30–140	22.95	5.09×10^9	−63.88	60.52	48.89
	200–310	75.98	4.68×10^6	−108.2	96.74	141.2
	450–620	137.4	8.44×10^{10}	−162.7	166.3	186.9
	620–850	184.2	1.65×10^{11}	−215.4	241.3	266.8
$[CoCl_2(HL)(H_2O)_2]\cdot 3H_2O$	30–110	63.85	6.53×10^{12}	−43.76	67.32	68.66
	150–270	145.6	3.76×10^{10}	−89.77	106.1	111.3
	300–460	187.9	7.02×10^8	−152.4	166.8	152.6
	500–720	165.7	1.98×10^9	−168.7	225.4	183.7
$[NiCl_2(HL)(H_2O)_2]\cdot 3H_2O$	30–110	51.18	4.45×10^7	−56.14	50.46	50.66
	120–280	102.4	3.19×10^{12}	−95.28	99.43	91.86
	300–520	182.9	4.56×10^{11}	−166.7	128.4	152.3
	560–720	243.4	7.21×10^7	−203.2	195.8	192.6
$[CuCl_2(HL)(H_2O)_2]\cdot 2H_2O$	50–130	36.52	1.73×10^{10}	−36.84	61.52	76.36
	130–230	53.78	4.26×10^{12}	−65.48	102.3	129.7
	230–420	79.54	5.72×10^7	−106.9	158.6	172.7
	420–660	123.2	3.28×10^{10}	−135.2	190.7	202.2
	660–950	189.6	4.66×10^8	−186.4	215.6	246.3

Schiff base and its metal complexes seem to be able to combine with the lipophilic layer in order to enhance the membrane permeability of the Gram-negative bacteria. The lipid membrane surrounding the cell favours the passage of only lipidsoluble materials; thus the lipophilicity is an important factor that controls the antimicrobial activity. Also the increase in lipophilicity enhances the penetration of



M = Cr(III) and Fe(III)   M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II);

Fig. 5. The proposed structural formulae of metal complexes.

Table 5
The antibacterial and antifungal activity of HL and its metal complexes.

Sample	Inhibition zone diameter (mm/mg sample)[a]			
	Escherichia coli (G^-)	*Staphylococcus aureus* (G^+)	*Aspergillus flavus* (Fungus)	*Candida albicans* (yeast)
HL	41	42	23	13
$[CrCl_3(HL)(H_2O)]\cdot 3H_2O$	17	18	14	16
$[MnCl_2(HL)(H_2O)_2]\cdot H_2O$	28	36	0.0	14
$[FeCl_3(HL)(H_2O)]\cdot 3H_2O$	14	15	0.0	0.0
$[FeCl_2(HL)(H_2O)_2]\cdot 2H_2O$	38	40	14	14
$[CoCl_2(HL)(H_2O)_2]\cdot 3H_2O$	25	27	0.0	16
$[NiCl_2(HL)(H_2O)_2]\cdot 3H_2O$	37	40	0.0	15
$[CuCl_2(HL)(H_2O)_2]\cdot 2H_2O$	35	41	16	18
$[ZnCl_2(HL)(H_2O)_2]$	15	13	12	12
Tetracycline (Antibacterial agent)	32	34	0.0	0.0
Amphotricine B (Antifungal agent)	0.0	0.0	17	21

+++ = Inhibition values = 16–22 mm beyond control;
++++ = Inhibition values more than 23 mm beyond control.
[a] + = Inhibition values up to 10 mm beyond control; ++ = inhibition values = 11–15 mm beyond control.

Schiff base and its metal complexes into the lipid membranes and thus restricts further growth of the organism [37–39]. This could be explained by the charge transfer interaction between the studied molecules and the lipopolysaccharide molecules which lead to the loss of permeability barrier activity of the membrane. The Schiff base and its metal complexes could enhance the antimicrobial effect on both strains probably by the sulphonic hydroxyl group [40]. The Schiff base and its metal complexes are more toxic on *S. aureus* than on *E. coli*, probably due to the sulphonic OH, OCH_3, S and CH_3CH_2CH groups, which might interact with the double membrane. This activity is related to the nature and structure of the complexes. The Cu(II), Fe(II), Ni(II), Mn(II) complexes were almost the most promising broad spectrum antimicrobial agents due to the presence of coordinated anion and O—H with higher antimicrobial activity than the other complexes [39]. From the data the inhibition zone of the metal chelates is higher than that of the ligand. Such increased activity of the metal chelates is due to the lipophilic nature of the metal ion in complexes. Furthermore, the mode of action of Schiff bases of the compounds may involve the formation of a hydrogen bond through the azomethine nitrogen atom with the active canters of all the constituents, resulting in interference with normal cell process [39,41,42].

4. Conclusion

The results of this investigation support the suggested structures of the metal complexes. It is obvious from this study that only mononuclear complexes are obtained. The IR spectral studies reveal that HL coordinated to the metal ions via enolic —OH of sulphonamide group and thiadiazole-N. The chelates are non-electrolytes. All metal cations have octahedral geometry. The thermal decomposition of the complexes as well as the thermodynamic parameters is studied. The biological activities of the Schiff base under investigation and its complexes against bacterial and fungal organisms are promising which need further and deep studies on animals and humans.

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