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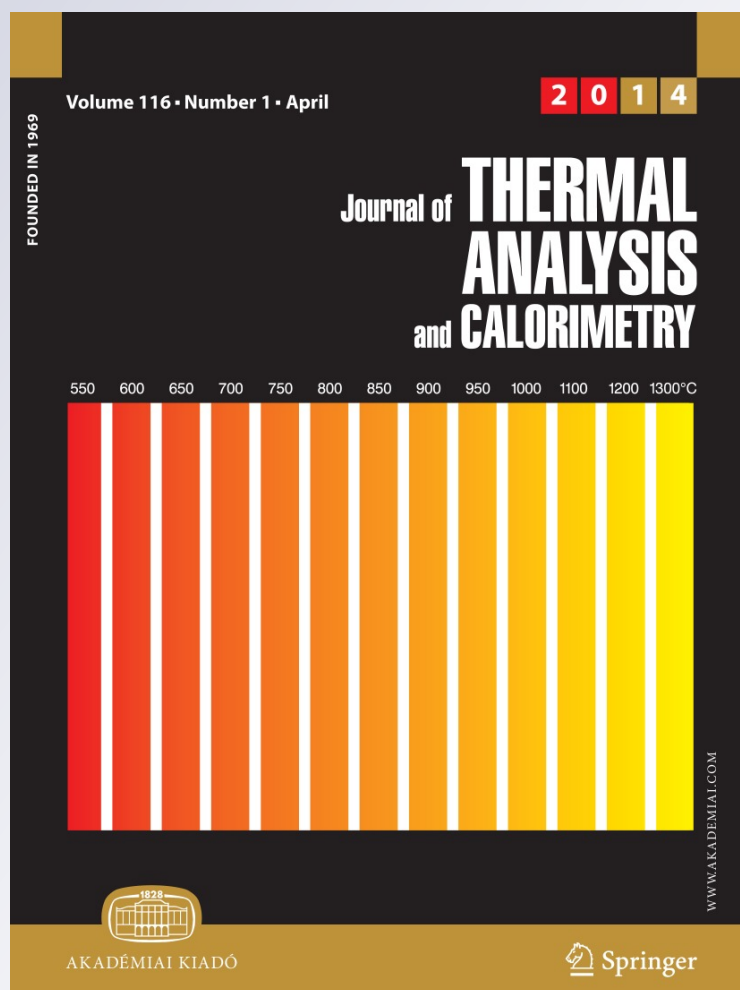
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Thermal and spectroscopic investigation of novel Schiff base, its metal complexes, and their biological activities

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Abstract The complexing behavior of H_2L ((*N,N'*Z,*N,N'E*)-*N,N'*-(ethane-1,2-diylbis(oxy)bis(2,1-phenylene)bis(methanylylidene)bis(1-hydrazinylmethanethioamide)) toward the transition metal ions namely Fe(III), Co(II), Ni(II), Cu(II), Cd(II), and Zn(II) have been examined by elemental analyses, magnetic measurements, electronic, IR, and 1H -NMR. Thermal properties and decomposition possibilities of all complexes are suggested. The interpretation of all thermal decomposition stages has been evaluated. The free ligand and its metal complexes have been tested in vitro against *Escherichia coli*, *Proteus vulgaris*, *Bacillus subtilis*, and *Staphylococcus aureus* bacteria in order to assess their antimicrobial potential. The results indicate that the metal complexes are also found to have more antimicrobial activity than the parent ligand.

Keywords Spectral studies · Transition metal complexes · Thermal analyses · Biological activity

Introduction

The coordination chemistry of macrocyclic ligands is an interesting area of study for chemists [1]. Schiff's bases have been of good importance in macrocyclic chemistry [2]. There is a continued interest in synthesizing macrocyclic complexes. The synthesis of macrocyclic complexes

have great potential applications in fundamental and applied sciences [3–5]; biochemistry, material science, catalysis, encapsulation, activation, transport, and separation phenomena, hydrometallurgy, etc. and importance in the area of inorganic chemistry [6, 7]. The development of the work of bioinorganic chemistry has been another important factor in spurring the growth in interest in macrocyclic compounds [8]. The Schiff bases ligands with oxygen and nitrogen donor atoms in their structures act as good chelating agents for the transition and non-transition metal ions [9]. Coordination compounds with metal ions, such as copper, nickel, and iron, often enhance their activities [3]. There is a continuing interest in metal complexes of Schiff's bases; because of the presence of both hard nitrogen or oxygen donor atoms in the backbones of these ligands. They readily coordinate with a wide range of transition metal ions yielding stable metal complexes, some of which have been shown to exhibit interesting physical and chemical properties [5] and potentially useful biological activities [6].

Schiff bases [6] were still regarded as one of the most potential group of chelators for facile preparations of metallo-organic hybrid materials. In the past two decades, the properties of Schiff base metal complexes stimulated much interest for their noteworthy contributions; such as material science [10], catalysis of many reactions like carboxylation, hydro formulation, oxidation, reduction, and epoxidation [11], their industrial applications [12] complexation ability toward some toxic metals [13]. The interest in Schiff base compounds as analytical reagents is increasing since they enable simple and inexpensive determinations of different organic and inorganic substances [14]. The most important step in the development of metal complexes was perhaps the preparation of a new ligand which exhibit unique properties and novel reactivity. Since, the electron

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donor and electron acceptor properties of the ligand, structural functional groups, and the position of the ligand in the coordination sphere together with the reactivity of coordination compounds may be a factor of different studies [15–20]. Schiff bases are compounds containing an azomethine group ($-\text{CH}=\text{N}$), have drawn attention for many years ago. Their metal complexes have been studied, with a variety of transition metal ions, since they frequently exhibit unusual structural properties [21].

The present study describes the chelation behavior of Schiff base derived from the condensation of 2,2'-(ethane-1,2-diylbis(oxy)) dibenzaldehyde with hydrazine carbothioamide toward some transition elements, which may help in more understanding of the mode of chelation toward metals. For this purpose, the complexes of Fe(III), Co(II), Ni(II), Cu(II), Cd(II), and Zn(II) ions with H_2L are studied in solution and in solid state. The structures of the studied complexes are elucidated using elemental analyses, IR, ^1H -NMR, solid reflectance, magnetic moment, molar conductance, and thermal analyses (TG, DTG, and DTA) measurements. The biological activity of the parent Schiff base and its metal complexes is reported.

Experimental

Materials and reagents

All chemicals used in this study were of the analytical reagent grade and of highest purity available. They included Cu(II) chloride (Sigma), Co(II) and Ni(II) chloride hexahydrates (BDH), ferric chloride hexahydrate (Prolabo), zinc chloride (Ubichem), and Cd(II) chloride (Aldrich). Organic solvents used included absolute ethyl alcohol and dimethyl formamide (DMF). These solvents were spectroscopic pure from BDH. Deionized water collected from all glass equipment was used in all preparations.

Instruments

The molar conductance of solid complexes in DMF (10^{-3} M solutions) was measured using Sybron-Barnsted conductometer (Meter-PM, $E = 3,406$). Elemental microanalyses of the separated solid chelates for C, H, N, and S were performed in the microanalytical center at Cairo University. The analyses were repeated twice to check the accuracy of the data. Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer in the region $4,000\text{--}400\text{ cm}^{-1}$ as KBr disks. The ^1H -NMR spectra were recorded with a JEOL EX-270 MHz in DMSO- d_6 as solvent, where the chemical shifts were determined relative to the solvent peaks. The diffused reflectance spectra were measured on a Shimadzu 3101 pc spectrophotometer. The molar magnetic susceptibility was

measured on powdered samples using Faraday method. The diamagnetic corrections were made by Pascal's constant and $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a calibrant. The magnetic data for the background of the sample holder were corrected. The thermal analyses (TG, DTG, and DTA) were carried out in dynamic nitrogen atmosphere (20 mL min^{-1}) with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ using Shimadzu TG-60H and DTA-60H thermal analyzers.

Synthesis of the H_2L Schiff base

30 mL of ethanol hot solution ($60\text{ }^\circ\text{C}$) of bisaldehyde (2,2'-(ethane-1,2-diylbis(oxy))dibenzaldehyde) (3 g, 0.02 mmol) was mixed with hot ethanol solution ($60\text{ }^\circ\text{C}$) of hydrazine carbothioamide (5 g, 0.02 mmol) in the same solvent. Then, ethanol–ammonia (1:1) solution was added to make the medium basic ($\sim\text{pH} = 9$) and the reaction mixture was left under reflux for 2 h. The formed solid products were separated by filtration, purified by crystallization from ethanol, washed with diethyl ether, and dried in a vacuum over anhydrous calcium chloride. The yellow Schiff base product is produced in 89 % yield.

Synthesis of metal complexes

The metal complexes of H_2L were prepared by the addition of hot solution ($60\text{ }^\circ\text{C}$) of the appropriate metal chloride in absolute ethanol (15 mL) to the hot solution ($60\text{ }^\circ\text{C}$) of the organic ligand (0.3 g H_2L) in ethanol and DMF (15 mL). The resulting mixture was heated with stirring to evaporate all the solvents to get precipitate. The precipitate was dried and weighed to calculate the yield. All the above steps were repeated for all the selected transition metal complexes.

Biological activity

The test was done using the diffusion agar technique. Spore suspension (0.5 mL , $10^{-6}\text{--}10^{-7}$ spore mL^{-1}) of each of the investigated organism was added to a sterile agar medium just before solidification, then poured into sterile Petri dishes (9 cm in diameter) and left to solidify. Using sterile cork borer (6 mm in diameter), three holes (wells) were made into each dish, and then 0.1 mL of the test compound dissolved in DMF (100 mg mL^{-1}) was poured into these holes. The dishes were incubated at $37\text{ }^\circ\text{C}$ for 48 h where clear or inhibition zones were detected around each hole. DMF (0.1 mL) was used as a control under the same conditions. By subtracting the diameter of the inhibition zone resulting with DMF from that obtained from each metal complex or the free Schiff base, antibacterial activities were calculated as a mean of three replicates. MIC₅₀ was determined and was defined as the lowest drug concentration that inhibits growth by 50 %.

Table 1 Analytical and physical data of H₂L ligand and its metal complexes

Complex	Color/% yield	MP/°C	Calcd. %/Found %			N			S	M			$\mu_{\text{eff}}/\text{BM}$	$\Delta m/\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$
			C	H		N								
H ₂ L	Pale yellow/89	230	51.20/51.90	4.27/4.84		20.67/20.18			14.10/15.40					
C ₁₈ H ₂₄ CuCl ₂ N ₆ O ₄ S ₂	Brown/85	<300	36.54/36.83	3.98/4.12		14.11/14.32			10.78/10.92				1.5	110
[Cu L 2H ₂ O]·Cl ₂														
C ₁₈ H ₂₄ ZnCl ₂ N ₆ O ₄ S ₂	White/72	<300	36.63/36.72	3.88/4.11		14.11/14.27			10.65/10.89				Dia.	115
[Zn L 2H ₂ O]·Cl ₂														
C ₁₈ H ₂₄ FeCl ₃ N ₆ O ₄ S ₂	Brown/87	284	35.22/35.17	3.84/3.93		13.45/13.67			10.32/10.43				3.8	250
[Fe L 2H ₂ O]·Cl ₃														
C ₁₈ H ₂₄ NiCl ₂ N ₆ O ₄ S ₂	Greenish yellow/93	<300	36.88/37.14	3.98/4.16		14.32/14.44			10.78/11.02				2.4	114
[Ni L 2H ₂ O]·Cl ₂														
C ₁₈ H ₂₄ CoCl ₂ N ₆ O ₄ S ₂	Brick Red/73	280	36.84/37.12	3.87/4.15		14.21/14.43			10.65/11.01				3.06	120
[Co L 2H ₂ O]·Cl ₂														
C ₁₈ H ₂₄ CdCl ₂ N ₆ O ₄ S ₂	Yellowish white/91	275	33.85/34.00	3.65/3.80		12.89/13.22			9.88/10.09				Dia.	125
[Cd L 2H ₂ O]·Cl ₂														

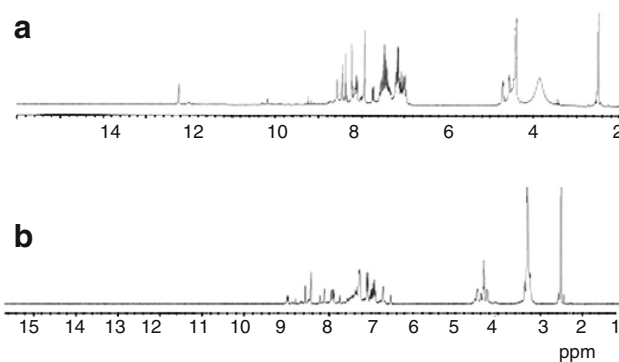


Fig. 1 The ¹H-NMR : **a** of ligand, **b** of Zn(II)-complex

Results and discussion

Characterization of metal complexes

The ligand under investigation (H₂L) is a novel Schiff base characterized by elemental analyses (Table 1) and it has a general formula (C₁₈H₂₀N₆O₂S₂) and mole mass = 416.520. Its structural formula is confirmed by ¹H-NMR (Fig. 1a).

Metal complexes were obtained through the reaction between metal ions and H₂L ligand at 1:1 (M:L) ratio. The synthesized Schiff base ligand and its complexes are very stable at room temperature. The ligand and its metals complexes are commonly soluble in DMF and DMSO. The elemental analyses, yields, melting points, of H₂L, and its metals complexes are presented in Table 1. The analytical data are compatible with the proposed stoichiometry of the complexes.

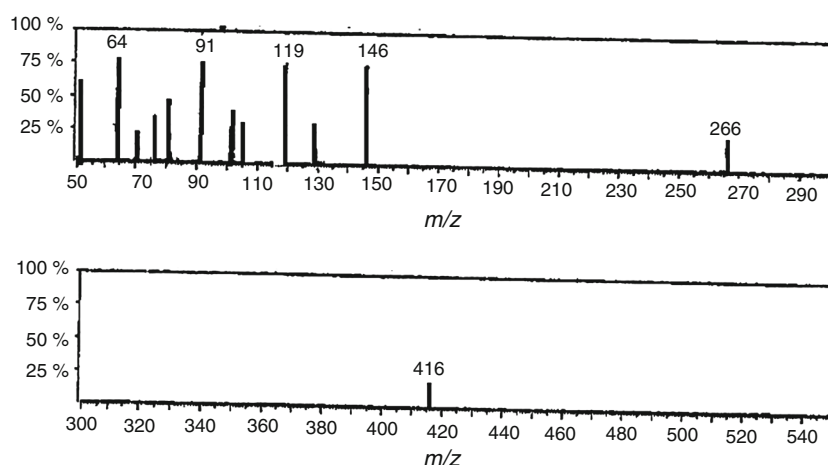
¹H-NMR

The ¹H-NMR data of H₂L ligand and its Zn(II) complex are shown in Fig. 1 as recorded in DMSO-d₆. Figure 1a of ligand shows a sharp band at 8.4 and 8.5 ppm which may be assigned to the protons of two azomethine groups (–CH=N), respectively. The NH, NH₂ signals which appears in the free ligand at 3.8 and 12.2 ppm, completely disappeared in the Zn complex (Fig. 1b) indicating that the NH and NH₂ groups are shared in chelation process. However, a singlet and multiple bands at 4.9 and 6.4–8 ppm attributed to methylene and the aromatic protons in the free H₂L ligand are shifted to down field (4.3 and 6.2–7.6 ppm) which indicates the coordination of ligand to Zn(II) ion.

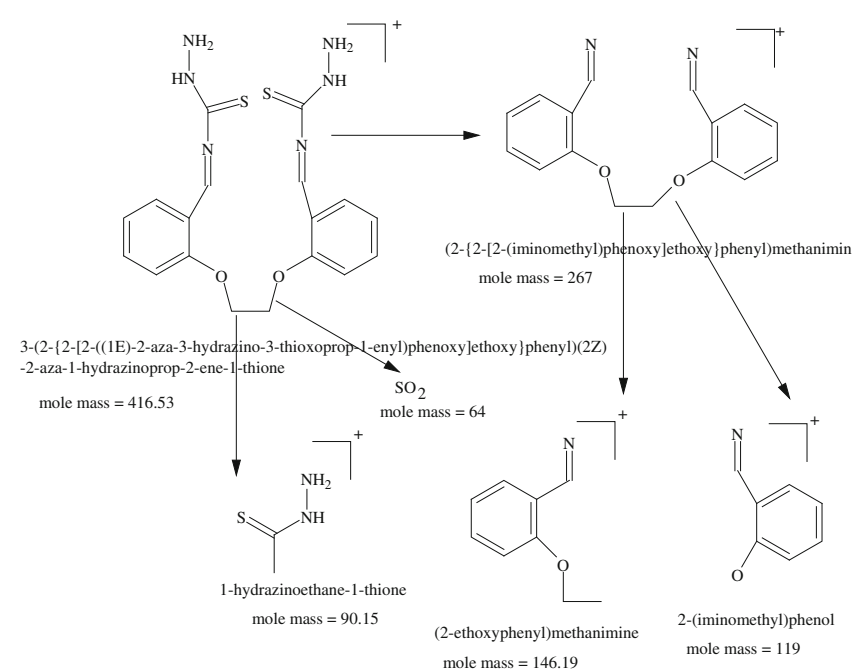
Mass spectrum of the new Schiff base ligand

The electron impact spectrum of the newly prepared H₂L ligand is recorded and investigated at 70 eV. The mass

Fig. 2 Mass spectra of ligand



Scheme 1 The proposed mass fragmentation pathways of the ligand



spectrum of the studied Schiff base (Fig. 2) shows a peak of moderate intensity (RI % = 17.9 %) at m/z = 416 (M^+) referring to the molecular ion of the ligand (mole mass = 416). It is obvious that, the molecular ion peak is in good agreement with its suggested empirical formula as indicated from elemental analyses (Table 1). It also shows the fragment ions at m/z = 64, 91, 119, 146, and 266 which may be assigned to SO_2 gas molecule, $\text{C}_2\text{H}_6\text{N}_2\text{S}$, $\text{C}_7\text{H}_5\text{NO}$, $\text{C}_9\text{H}_9\text{NO}$, and $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2$ fragments of mole masses 64, 91, 119, 146, and 266, respectively. The parent ion and the fragment ions obtained by bond cleavage in different positions in H_2L molecule are shown in Scheme 1. This scheme refers to the possible structural formulae of these fragments and their possible names using IUPAC system.

Molar conductance measurements

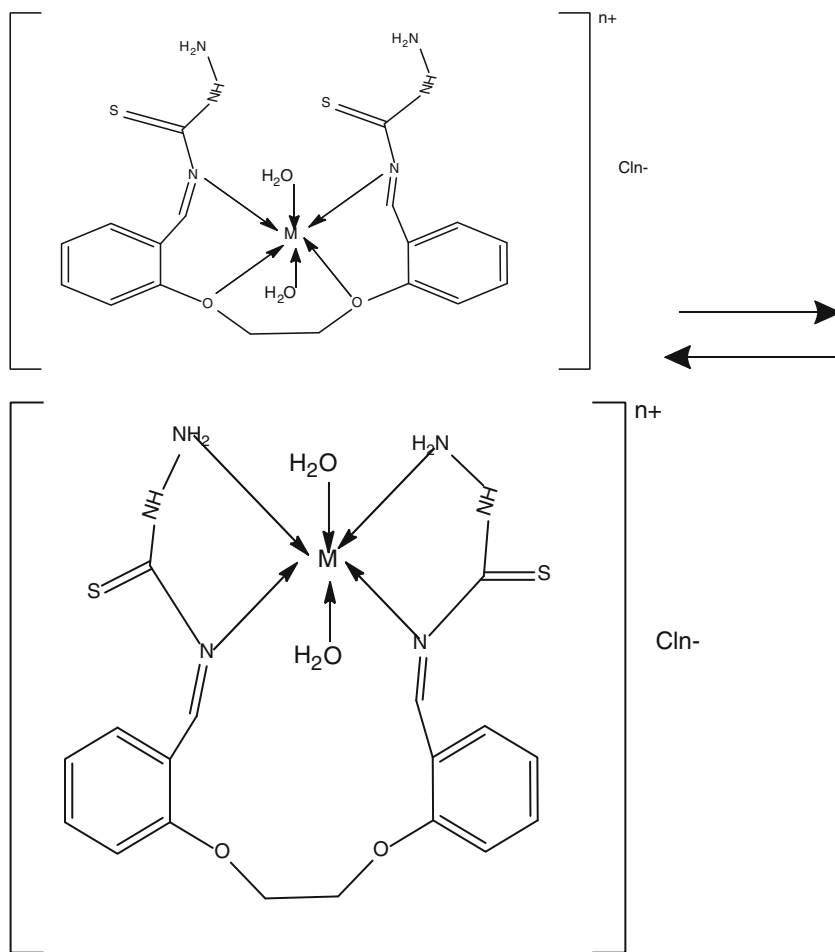
Conductivity measurements in non-aqueous solutions have been used in structural studies of metal chelates within the limits of their solubility. They provide a method of testing the degree of ionization of the complexes, the molar ions that a complex liberates in solution, the higher will be its molar conductivity and vice versa. The molar conductivities of 10^{-3} molar solutions of the metal chelates at $25 \pm 2^\circ\text{C}$ are measured and the data obtained are listed in Table 1. It is concluded from the molar conductance values ($110\text{--}125\ \Omega^{-1}\text{mol}^{-1}\text{cm}^2$) of the Co(II) , Ni(II) , Cu(II) , Cd(II) , and Zn(II) complexes with H_2L ligand are considered as 1:2 electrolytes as confirmed by the number of chloride ions given in the proposed general formulae of these complexes. In addition, $\text{Fe(III)}\text{--H}_2\text{L}$ complexes have molar

Table 2 IR data/4000–400 cm^{-1} of H_2L ligand and its metal complex

Compound	$\nu/\text{C}=\text{S}$	$\nu/\text{HC}=\text{N}_{\text{azomethine}}$	$\nu/\text{C}-\text{O}-\text{C}_{\text{ether}}$	$\nu/\text{M}-\text{O}$	$\nu/\text{M}-\text{N}$
H_2L	1686sh	1597sh	1045sh	–	–
$[\text{Fe}(\text{L})\cdot 2\text{H}_2\text{O}]\text{Cl}_3$	1655sh	1600m	1055m	529s	474s
$[\text{Co}(\text{L})\cdot 2\text{H}_2\text{O}]\text{Cl}_2$	1639sh	1610sh	1049m	520m	475s
$[\text{Ni}(\text{L})\cdot 2\text{H}_2\text{O}]\text{Cl}_2$	1692sh	1621sh	1061sh	513s	467s
$[\text{Cu}(\text{L})\cdot 2\text{H}_2\text{O}]\text{Cl}_2$	1662sh	1590sh	1049sh	513s	466s
$[\text{Zn}(\text{L})\cdot 2\text{H}_2\text{O}]\text{Cl}_2$	1659sh	1606m	1052m	524s	464s
$[\text{Cd}(\text{L})\cdot 2\text{H}_2\text{O}]\text{Cl}_2$	1670sh	1630m	1042m	530s	468s

sh Sharp, m medium, br broad, s small, w weak

Fig. 3 The proposed structure of complexes



conductance value of $250 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$, indicating their ionic nature and they are considered as 1:3 electrolytes [22].

IR spectral studies

The data of the IR spectra of 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 involve in chelation. The spectrum of free ligand showed a band in the

region $1,597\text{--}1,580 \text{cm}^{-1}$ characteristics of the azomethine stretching mode. This band was shifted toward lower/or higher frequencies in the spectra of its metal complexes ($1,590\text{--}1,689 \text{cm}^{-1}$) compared with the above Schiff base. This phenomenon appears to be due to the coordination of azomethine nitrogen to the metal ion [18, 23]. New bands are found in the spectra of complexes in the regions $513\text{--}532$, and $463\text{--}475 \text{cm}^{-1}$ which are assigned to (M–O), (M–N), and stretching vibrations, respectively. Therefore, from the IR spectra it is concluded that H_2L Schiff base is

Table 3 Thermogravimetric/TG and DTG results of ligand/H₂L and its metal complexes

Compound	TG temp range/°C	DTG _{max} /°C	n	Calcd/estim %		Assignment	Residue
				Mass loss	Total mass loss		
H ₂ L	220–282	231.46	1	21.36/22	99.95/100	-Loss of CH ₃ N ₃ S	–
	282–380	323.28	2	39.17/39		-Loss of C ₉ H ₉ NO ₂	
	400–600	579.43	3	39.42/39		-Loss of C ₈ H ₈ N ₂ S	
[Cu(L)·2H ₂ O]Cl ₂	150–280	236.09	1	12.43/12	60.46/58	-Loss of 2HCl	CuO
	280–475	311.34	2	25.89/25		-Loss of C ₂ H ₈ N ₄ S ₂	
	475–540	492.14	3	22.14/21		-Loss of C ₄ H ₆ N ₂ O ₃	
[Zn(L)·2H ₂ O]Cl ₂	120–270	130.41	1	12.39/12	60.27/58	-Loss of 2 (HCl)	ZnO
	270–460	278.98	2	25.81/24		-Loss of C ₂ H ₈ N ₄ S ₂	
	460–560	542.24	3	22.07/22		-Loss of C ₄ H ₆ N ₂ O ₃	
[Cd(L)·2H ₂ O]Cl ₂	45–100	48	1	11.47/12	55.76/56	-Loss of 2HCl	CdO
	200–300	255.56	2	9.42/10		-Loss of N ₄ H ₄	
	300–400	351.72	3	21.36/22		-Loss of C ₂ H ₄ N ₂ OS ₂	
	480–560	525.81	4	13.51/12		-Loss of C ₄ H ₆ O ₂	
[Fe(L)·2H ₂ O]Cl ₃	77–165	126.8	1	9.76/10	60.91/60	-Loss of N ₄ H ₄	1/2Fe ₂ O ₃
	165–265	230.59	2	14.47/14		-Loss of C ₂ S ₂ OH	
	265–540	465.28	3	36.68 (36)		-Loss 3HCl + C ₄ H ₁₁ N ₂ O ₂	
[Ni(L)·2H ₂ O]Cl ₂	25–75	37.68	1	10.30/10	86.75/87	-Loss of N ₄ H ₄	NiO
	240–320	286.12	2	27.65/27		-Loss of 2(HCl, CS)	
	320–439	374.96	3	48.80/50		-Loss of C ₁₆ H ₁₆ N ₂ O ₃	
[Co(L)·2H ₂ O]Cl ₂	240–340	292.72	1	25.38/26	60.88/61	-Loss of C ₂ H ₄ N ₄ S ₂	CoO
	340–400	380.24	2	15.26/15		-Loss of 2(HCl) and H ₂ O	
	400–540	495.42	3	20.24/20		-Loss of C ₄ H ₁₀ O ₂ N ₂	

n Number of decomposition steps, *calcd* theoretical percent, *estim* practical percent

tetra dentate ligand with NNOO coordination sites with 2H₂O bind to the metal. Therefore, from these data the proposed structural formulae for these complexes can be given by the proposed equilibrated forms Fig. 3.

Magnetic susceptibility and electronic spectral studies

The diffused reflectance spectral data of the complexes, position of bands, and their transitions assignments are of particular importance as they are highly dependent on the geometry of the molecule. From the diffused reflectance spectrum of the Fe(III) complex, the bands at 14,096, 18,625, and 24,585 cm⁻¹, may be assigned to the 6A_{1g} → T_{2g} (G) and 6A_{1g} → 5T_{1g} transitions in octahedral geometry of the complex [24]. The spectrum shows also a band at 27,777 cm⁻¹ which may be attributed to ligand to metal charge transfer. This geometry is further supported by its magnetic susceptibility value (3.8 BM) [24–27].

The diffused reflectance spectrum of the Cu(II) complex displayed the *d–d* transition band in the region 13,606 cm⁻¹ which is due to 2E_g → 2T_{2g} transition. This *d–d* transition band strongly favors a distorted octahedral geometry around

the metal ion. This geometry is further supported by its magnetic susceptibility value (1.5 BM) [24–27].

The spectrum of Ni(II) complex displayed three *d–d* bands at 13,150, 14,749, and 23,310 cm⁻¹. These bands correspond to 3A_{2g} (F) → 3T_{2g} (F), 3A_{2g} (F) → 3T_{1g} (F) and 3A_{2g} (F) → 3T_{1g} (P) transitions, respectively, being characteristic of an octahedral geometry. This geometry is further supported by its magnetic susceptibility value (2.4 BM) [24–27].

Diffused reflectance spectrum of Co(II) complex displayed the *d–d* transition bands in the region 15,017, 16,723, and 23,566 cm⁻¹ which are assigned to 4T_{1g} (F) → 4A_{2g} (F), 4T_{1g} (F) → 4T_{2g} (F) and 4T_{1g} (F) → 4T_{1g} (P) transitions, respectively. The transitions correspond to the octahedral geometry of the complex which is also supported by its magnetic susceptibility value (3.06 BM) [24–27].

Electronic spectra of the Zn(II) and Cd(II) complexes exhibited a sharp band of high intensity at 26,000 and 24,500 cm⁻¹, respectively, which may have been due to the ligand–metal charge transfer. The molar conductance of the complexes in DMF (10⁻³ M) are in the range over 100 Ω⁻¹ cm² mol⁻¹, indicating their electrolytic nature of

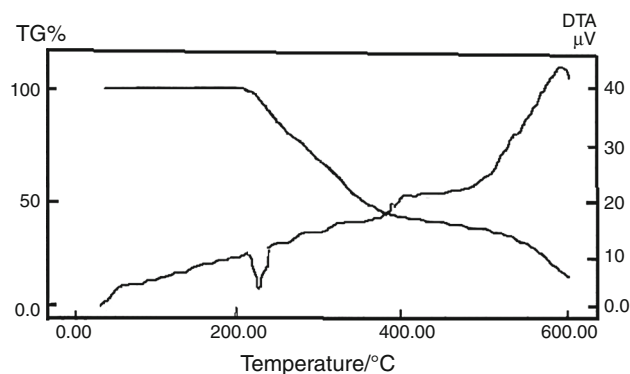


Fig. 4 Thermal analyses/TG and DTA of the ligand H_2L

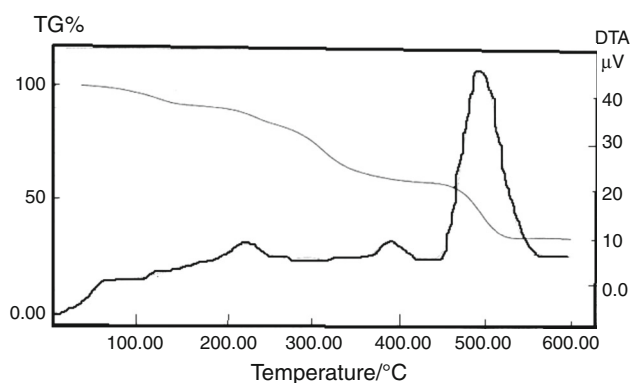


Fig. 5 Thermal analyses curves/TG and DTA of copper complex

ratio 1:2, with the exception of the Fe(III) complex of ratio 1:3 electrolyte [24–27].

Thermal analyses (TG, DTG, and DTA)

Thermal Analyses results of the Schiff base and their metalcomplexes are given in Table 3 and in Figs (4, 5).

The TG and DTA curves of the Schiff base ligand under investigation (H_2L) are given by Fig. 4. The TG curve shows that the Schiff base ligand was stable up to 220 °C (Table 3). It decomposed in three steps at temperature ranges 220–282, 282–380, and 400–600 °C and exactly at 231.46, 323.28, and 549.43 °C as given by DTG. These mass losses correspond to CH_3N_3S , $C_9H_9NO_2$, and $C_8H_8N_2S$, respectively. These data refer to the complete decomposition of this ligand as given by calculated (99.95 %) and estimated mass losses percent (100 %). The DTA curve refers to one endothermic peak over 250 °C and exothermic base shifts (at 300–400 °C) finished by vigorous exothermic peak at 570 °C. The exothermic base shifts may refer to the increase of heat capacity of the remainder parts of the ligands and final vigorous exothermic peak at 570 °C, may refer to the possible chemical rearrangements [28] occur in this ligand that given by Table 3.

The TG and DTA curves of Cu(II) complex are shown in Fig. 5. These data show that; this complex starts its decomposition at 150 °C, the mass losses occur in three steps, correspond to $2HCl$, $C_2H_8N_4S_2$, and $C_4H_6N_2O_3$ of total loss calculated = 60.46 % (estimated = 58 %). These mass losses occur in the temperature ranges 150–280, 280–475, and 475–540 °C and exactly at 136, 311, and 492 °C (DTG), respectively. The remainder part at the end of decomposition is $C_{12}H_8 + CuO$ of calculated mass loss = 39.44 % (estimated = 39 %). The DTA curve shows that most of these mass losses appear as exothermic peaks. It followed by a distinct exothermic peak at 580 °C which may refer to the possible chemical reactions and/or chemical rearrangements [28] in between the obtained fragments.

The Zn-complex starts its decomposition at 120 °C. The mass losses occur in different steps in the temperature range 120–560 °C. It corresponds to $2HCl$, $C_2H_8N_4S_2$, $C_4H_6N_2O_3$ of total loss calculated = 60.27 % (estimated = 58 %). These mass losses occur in the temperature ranges 120–270, 270–460, and 460–560 °C and exactly at 130, 278, and 542 °C (as given by DTG), respectively. The remainder part at the end of the decomposition is $C_{12}H_8 + ZnO$ of calculated mass loss = 39.62 % (estimated = 40 %). The DTA of Zn-complex shows that most of these mass losses appear as endothermic peaks and a distinct exothermic peak at 560 °C which refer to the possible chemical reactions and/or chemical rearrangements in between the obtained fragments.

The Cd-complex starts its decomposition at temperature less than 100 °C, which may refer to the less stability of this complex than both Zn and Cu complexes. The mass losses occur in four steps in the temperature range 45–560 °C. It corresponds to $2HCl$, N_4H_4 , $C_2H_4N_2OS_2$, and $C_4H_6O_2$ of the total loss calculated = 55.76 % (estimated = 56 %). These mass losses occur in the temperature ranges 45–100, 200–300, 300–400, and 480–560 °C. It exactly occurs at 48, 255, 351, and 525 °C, (DTG) respectively. The remainder part at the end of the decomposition is $C_{12}H_8 + CdO$ of calculated mass loss = 55.76 % (estimated = 56 %). The DTA data of Cd-complex show that most of these mass losses appear as endothermic peaks and two distinct exothermic peaks 450 and 550 °C may refer to the possible chemical reactions and/or chemical rearrangements in between the obtained fragments.

The Fe-complex starts its decomposition at 70 °C. The mass losses occur in three steps corresponding to mass losses $2N_2H_2$, C_2S_2H , and $3HCl + C_2H_6N_2O + C_2H_2O_2$ of total loss calculated = 60.9 % (estimated = 60 %). These mass losses occur in the temperature ranges 77–165, 165–265, and 265–540 °C and exactly at 126.6, 230.59, and 465.26 °C (DTG), respectively. The remainder part at the end of the decomposition is $C_{12}H_8 + 1/2F_2O_3$ of calculated mass loss = 40.33 % (estimated = 39 %). The

Table 4 Biological activity of ligand and its metal complexes

Sample	Inhibition zone/mm mg^{-1} sample/MIC ₅₀ /mg mL^{-1}			
	Gram negative		Gram positive	
	<i>Escherichia coli</i>	<i>Proteus vulgaris</i>	<i>Bacillus subtilis</i>	<i>Staphylococcus pyogenes</i>
H ₂ L	34	35	35	38
[Cu(H ₂ L)(H ₂ O) ₂].Cl ₂	42	44	30	28
	>100	>100	>100	>100
[Co(H ₂ L)(H ₂ O) ₂].Cl ₂	45	48	46	39
	>50	>50	>25	>50
[Fe(H ₂ L)(H ₂ O) ₂].Cl ₃	33	32	22	20
	>100	>100	>100	>100
[Ni(H ₂ L)(H ₂ O) ₂].Cl ₂	26	28	17	15
	>100	>100	>100	>100
[Cd(H ₂ L)(H ₂ O) ₂].Cl ₂	14	15	11	8
	>100	>100	>100	>100

Note: Inhibition values: 1–5 mm beyond control = +, 6–10 mm beyond control = ++, 11–15 mm beyond control = +++, >15 mm beyond control = ++++

DTA data of Fe-complex show that most of these mass losses appear as endothermic peaks. It followed by two distinct exothermic peaks at 420 and 470 °C which may refer to the possible chemical reactions and/or chemical rearrangements in between the obtained fragments.

The Ni-complex starts its decomposition at 25 °C. The mass losses occur in three steps correspond to mass losses 2N₂H₂, 2(HCl, CS), and C₁₆H₁₆N₂O₃ of total calculated mass = 86.75 % (estimated = 87 %). These mass losses occur in the temperature ranges 25–75, 240–320, and 320–429 °C and exactly at 37.5, 286 and 374 °C (DTG) respectively. The remainder part at the end of the decomposition is NiO of calculated mass loss = 12.84 % (estimated = 13 %). The DTA data of Ni-complex show that most of these mass losses appear as endothermic peaks. It followed by two distinct exothermic peaks at 380 and 480 °C which may refer to the possible chemical reactions and/or chemical rearrangements in between the obtained fragments.

The Co-complex starts its decomposition at 240 °C, which may refer to the stability of this complex than Fe and Ni complexes of the given ligand. The mass losses occur in three steps correspond to C₂H₄N₄S₂, 2HCl + H₂O, and C₄H₁₀O₂N₂ of total loss calculated = 60.88 % (estimated = 61 %). These mass losses occur in the temperature ranges 240–340, 340–400, and 400–540 °C and exactly at 292, 380, and 495 °C (DTG), respectively. The remainder part at the end of the decomposition is CoO + C₁₂H₈ of the calculated mass loss = 38.92 % (estimated = 38 %). The DTA data of Co-complex show that most of these mass losses appear as exothermic peaks. It followed by two distinct exothermic peaks at 380 and 490 °C which may refer to the possible chemical reactions and/or chemical rearrangements in between the obtained fragments.

Biological activity

Schiff bases are important class of compounds in medicinal and pharmaceutical fields. They show biological applications including antibacterial [29–33] and antitumor activities. Microbes encounter a variety of metal ions in the environment and interact with them, which is sometimes beneficial or detrimental depending on the chemical/physical nature and oxidation state of the metal ion. The microbes have the ability to bind to metal ions present in the external environment at the cell surface and to transport them into the cell for various intracellular functions. All microbes, prokaryotes or eukaryotes, were employed metal species for structural and/or catalytic functions. Antibacterial activity of the Schiff base and its metal complexes (Table 4) were tested by diffusion agar method [29–33], Streptomycin was used as a reference compound for antibacterial activities. In testing the antibacterial activity of these compounds, more than one test organism was used to increase the chance of detecting antibiotic principles in tested materials. Two Gram-positive (*Bacillus subtilis* ATTC 6051 and *Staphylococcus pyogenes* ATTC 12600) and two Gram-negative (*Escherichia coli* ATTC 11775 and *Proteus vulgaris* ATTC 13315) bacteria were used as test organisms. The antibacterial activity was evaluated by measuring the inhibition zone (mm) and MIC 50 Table (4). It is found that the Schiff-base ligand has more sensitivity for Gram-positive than Gram-negative bacteria. The activity follows the order *S. pyogenes* > *B. subtilis* > *P. vulgaris* > *E. coli*. Biological activity of the complexes are found to follow the order Co(II) > Cu(II) > Fe(III), Ni(II) > Cd(II). With respect to Gram-negative bacteria (*E. coli* and *P. vulgaris*), Co(II) complex was the most potent antibacterial element where it recorded the highest inhibition zones (45 and 48 mm),

respectively, and the lowest MIC_{50} (>50 mg mL^{-1}) in both tested bacteria. The Cu(II) complex recorded moderate inhibitory activity (42 and 44 mm) in *E. coli* and *P. vulgaris*, respectively, but recorded high MIC_{50} (>100 mg mL^{-1}) in both tested microorganisms. The parent Schiff base (H_2L), Fe(III), and Ni(II) slightly inhibited the tested two Gram negative bacteria, where inhibition zones ranging from 25 to 35 mm were recorded. Also these compounds recorded the high MIC_{50} (>100 mg mL^{-1}). Cd(II) complex has completely missed the antibacterial activity against the tested Gram-negative and Gram-positive bacteria. Regarding Gram-positive bacteria (*B. subtilis* and *S. pyogenes*), Co(II) complex was the most potent antibacterial element. It recorded the highest inhibition zones (46 and 39 mm), respectively, and the lowest MIC_{50} (>25 and >50 mg mL^{-1}), respectively. The parent Schiff base showed good inhibitory activity (35 and 38 mm) in case of *B. subtilis* and *S. pyogenes*, respectively, but recorded high MIC_{50} (>100 mg mL^{-1}) in both tested bacteria. Cu(II) complex has moderately inhibited the test organisms where inhibition zone diameters of 30 and 28 mm were recorded in *B. subtilis* and *S. pyogenes*, respectively, and recorded high MIC_{50} value > 100 mg mL^{-1} . Fe(III) and Ni(II) complexes have weakly inhibited the tested Gram-positive bacteria where inhibition zone diameters ranging from 15 to 22 mm were detected. The values were >100 mg mL^{-1} in the two tested bacteria.

Conclusions

The careful survey of this research leads to important conclusions:

1. Preparation, structure investigation, and biological importance of novel Schiff base and its metal complexes of Fe(III), Co(II), Ni(II), Cu(II), Cd(II), and Zn(II) are given. It involves elemental, spectroscopic (IR, NMR and mass spectra), and thermal data (TG and DTA). It gives structure confirmation and biological importance toward *E. coli*, *P. vulgaris*, *B. subtilis*, and *S. aureus* bacteria in order to assess their antimicrobial potential.
2. Thermal properties and thermal decomposition possibilities of all complexes are investigated. The interpretation of all thermal decomposition stages has been evaluated. This study leads to the conclusion that, these complexes thermal stability depending upon start decomposition temperature is in the following order, Co(II) 240 °C, Cu(II) 150 °C, Zn(II) 120 °C, Cd(II) 100 °C, Fe(III) 70 °C, and Ni(II) 25 °C. This start decomposition temperature depends mainly on the instability of non-coordinated terminal aliphatic parts of the ligand outside the core of coordination sphere.

The thermal stability of the remainder part of the ligand coordinated to the metal ions depending upon its decomposition temperature can be ordered as Fe(III) 470 °C, Ni(II) 480 °C, Co(II) 490 °C, Cd(II) 550 °C, Zn(II) 560 °C, and Cu(II) 580 °C. This may be related the coordination power of metal cation to this remainder part.

3. It is found that the Schiff-base ligand has more sensitivity for Gram-positive than Gram-negative bacteria. The activity follows the order *S. pyogenes* $>$ *B. subtilis* $>$ *P. vulgaris* $>$ *E. coli*. Biological activity of the complexes are found to follow the order Co(II) $>$ Cu(II) $>$ Fe(III), Ni(II) $>$ Cd(II).

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