

Synthesis, characterization, and biological activity of Schiff bases metal complexes

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Abstract

The new Schiff base 1-[(2-{1-[(dicyclohexylamino)-methyl]-1H-indol-3-yl}-ethylimino)-methyl]naphthalen-2-ol (HL) was prepared from 1-[[2-(1H-Indol-3-yl)-ethylimino] methyl]-naphthalen-2-ol and dicyclohexyl amine. From this Schiff base, monomeric complexes $[M(L)_n(H_2O)_2Cl_2]$ with $M = Cr, Fe, Mn, Cd,$ and Hg were synthesized and characterized based on elemental analysis (EA), FT-IR, mass (MS), UV-visible, thermal analysis, magnetic moment, and molar conductance. The results showed that the geometrical structures were octahedral geometries for the Cr(III) and Fe(III) complexes, square planar for Pd(II) complex, and tetrahedral for Mn(II), Cd(II), and Hg(II) complexes. Kinetic parameters such as ΔE^* , ΔH^* , ΔG^* , and K of the thermal decomposition stages were calculated from the TGA curves using Coats-Redfern method. Additionally, density functional theory (DFT) was applied for calculations of both electronic structure and spectroscopic properties of synthesized Schiff base and its complexes. The analysis of electrostatic potential (EPS) maps correlates well with the computed energies providing on the dominant electrostatic nature of N-H...O interactions. The biological activities had been tested in vitro against *Staphylococcus aureus*, *Pseudomonas aeruginosa*, as well as fungi like *Penicillium expansum*, *Fusarium graminearum*, *Macrophomina phaseolina*, and *Candida albicans* bacteria in order to assess their antimicrobial potential.

KEYWORDS

biological activity, molecular orbital calculation, Schiff base, thermal analysis

1 | INTRODUCTION

Schiff bases and their complexes are considered as privileged class of compounds due to their biochemical synthesis, electrochemical analysis, anti-fungal, antiviral, anti-malarial, anti-inflammatory, as well as, catalytic activities.^[1,2] Schiff bases are also of interest in industrial fields and as a corrosion inhibitor, thermostable materials, as well as, powerful ligands in the formation of coordination compounds.^[3] Recently, Al Zoubi and co-workers have reported the synthesis and structural characterization of Schiff bases and their complexes

derived from different amines.^[4] These compounds exhibit antimicrobial activity against several Gram-positive and Gram-negative bacteria.

Schiff bases continue to occupy as vital ligands in metal coordination chemistry, even almost a century since their discovery. Schiff's bases^[5] were still regarded as one of the most potential groups of organic compounds for facile preparations of metallo-organic hybrid materials and their role in organic synthesis. Moreover, there is a continued interest in synthesizing macrocyclic ligands^[6,7] because of their potential applications in various fields. In addition, the properties of Schiff base stimulated much interest for

their noteworthy contributions to single molecule-based magnetism, material science, and catalysis of many reactions like carbonization, oxidation, reduction,^[8] and binding and release of metal ions carried out by facilitated transport membranes. Schiff's bases had been considered among the most widely used organic compounds in different aspects. These compounds had been used for industrial purposes such as pigments, catalysts in several reactions such as polymerization reaction reduction of thionyl chloride of ketone, and oxidation of organic compound intermediates in organic synthesis and as polymer stabilizers.^[9] Schiff's bases considered as an important class of compounds in both the medical, pharmaceutical, and biological fields. They were also found to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, antiinflammatory, antiviral, and antipyretic properties.^[10–13]

In continuation of our interest on Schiff bases and their complexes,^[14] in the present work, we report the synthesis and spectroscopic studies as well as thermal investigation of novel Mannich-Schiff based ligand 1-[(2-{1-[(dicyclohexylamino)-methyl]-1H-indol-3-yl}-ethylimino)-methyl]-naphthalen-2-ol (HL) and its complexes. Moreover, the measurements were complemented with quantum chemical calculations based on DFT methods.

2 | EXPERIMENTAL

2.1 | Materials and methods

All chemicals were purchased from commercial sources and were used without further purifications (CaCl₂, CrCl₃·6H₂O, MnCl₂·4H₂O, FeCl₃·2H₂O, PdCl₂, CdCl₂·2H₂O, HgCl₂, 2-hydroxy-naphthalene-1-carbaldehyde, dicyclohexyl amine, 2-(1H-Indol-3-yl)-ethylamine, DMSO, CH₃OH, and C₂H₅OH from Merck).

2.2 | Physical measurements

All reagents were commercially available and used without further purification. Solvents were distilled from appropriate drying agents immediately prior to use. Elemental analyses (C, H, and N) were performed using a Perkin-Elmer C.H.N 2400 elemental analyzer. The content of metal ions was calculated gravimetrically as metal oxides. Molar conductance measurements of the ligand and its complexes with 10⁻³ mol/L in DMSO were carried out using Jenway 4010 conductivity meter. Magnetic measurements were carried out on a Sherwood Scientific magnetic balance using the Gouy method. Electron impact (70 eV) mass spectra were recorded on a Finnegan-MAT model 8430 GC-MS-DS spectrometer. The UV-vis spectra were obtained in DMF solution (10⁻³ M) for the ligand

and their metal complexes with a Jenway 6405 spectrophotometer using 1-cm quartz cell, in the range 200–900 nm. IR spectra (4000–400 cm⁻¹) were recorded as KBr pellets on a Bruker FT-IR spectrophotometer. ¹H-NMR spectra were acquired in DMSO-d₆ Solution using a Bruker AMX 400 MHz spectrometer with tetramethylsilane (TMS) as an internal standard for ¹H NMR analysis, and thermal analysis studies of the ligand and complexes were performed on a Perkin-Elmer Pyris Diamond DTA/TG thermal system under nitrogen atmosphere at a heating rate of 10C/min from 25 to 700°C.

2.3 | Synthesis of Schiff base Mannich (HL)

2.3.1 | Preparation of 1-[[2-(1H-Indol-3-yl)-ethylimino] methyl]-naphthalen-2-ol (A)

This compound was synthesized by condensation of 2-hydroxy-naphthalene-1-carbaldehyde (0.01 mmol) and 2-(1H-Indol-3-yl)-ethylamine (mmol) in ethanol solution. The mixture was stirred and refluxed at 85°C during 3 hours, and the progress was followed by TLC. On completion, the reaction mixture was cooled, and the product formed was isolated by filtration and washed with cool ethanol. The solid was re-crystallized from hot ethanol and dried under vacuum.

Preparation of 1-[(2-{1-[(dicyclohexylamino)-methyl]-1H-indol-3-yl}-ethylimino)-methyl]-naphthalen-2-ol (HL)

Schiff base (10 mmol) was mixed with dicyclohexyl amine (10 mmol), and formaldehyde (37% v/v) was added to it. The solution mixture was stirred thoroughly for approximately 3 hours with occasional cooling. Then, this mixture was kept in the refrigerator for 12 hours, and gradually a precipitate was separated in small amounts. To this suspension, an excess of petroleum ether was added, followed by scratching the walls of the beaker with a glass rod. All the precipitate suspension were suddenly solidified and settled down. This was filtered, washed well with 15 mL of petroleum ether and dried. The crude product was recrystallized from ethanol. The molecular formula, molecular weight, melting point, yield, and elemental analysis (EA) are shown in (Table 1). ¹H-NMR (DMSO, ppm): 9.08 (s, -CH=N, 1H), 7.18 to 7.99 (m, arom-10H), 5.99(s,-OH, 1H), 3.1 (m, CH₂ cyclo, 20H), 4.49 (s, CH₂, 2H), 2.69 (t, CH₂, 4H), (2.5, DMSO).

2.4 | Synthesis of Schiff base Mannich complexes

Schiff base complexes were prepared by the drop wise addition of the respective hydrated metal chloride

TABLE 1 Analytical and physical data of the ligand and its complexes

Compounds	Formula m. wt	Color	m. p °C	Yield%	Elemental analysis, found / Calc.%				
					C	H	N	M	Cl
HL	C ₃₄ H ₄₁ N ₃ O 507.71	Orange	188-190	88	81.21 80.43	7.99 8.14	7.97 8.28		
[Mn (L) (H ₂ O) ₂]Cl	C ₃₄ H ₄₄ N ₃ O ₃ ClMn 633.12	Light yellow	232d	69	63.66 64.50	7.62 7.00	7.18 6.64	10.01 8.68	6.27 5.60
[Pd (L) (H ₂ O) ₂]Cl	C ₃₄ H ₄₄ N ₃ O ₃ ClPd 684.60	Red-brown	210d	60	60.74 59.65	5.78 6.48	7.97 6.14	14.07 15.54	5.79 5.18
[Cd (L) (H ₂ O) ₂]Cl	C ₃₄ H ₄₄ N ₃ O ₃ ClCd 690.60	Light brown	194d	81	60.86 59.13	7.29 6.42	7.55 6.08	17.31 16.28	5.87 5.13
[Hg (L) (H ₂ O) ₂]Cl	C ₃₄ H ₄₄ N ₃ O ₃ ClHg 778.77	Light brown	182d	77	54.33 52.44	5.93 5.69	7.04 5.40	23.98 25.76	5.51 4.55
[Cr(L)(H ₂ O) ₂ Cl ₂]	C ₃₄ H ₄₄ N ₃ O ₃ Cl ₂ Cr 665.63	Dark green	215d	82	62.78 61.35	5.31 6.66	7.49 6.31	8.76 7.81	13.05 10.65
[Fe(L)(H ₂ O) ₂ Cl ₂]	C ₃₄ H ₄₄ N ₃ O ₃ Cl ₂ Fe 669.48	Red-brown	217d	73	61.14 61.00	5.77 6.62	7.45 6.28	10.05 8.34	9.97 10.59

d = decompose.

(VOSO₄·H₂O, CrCl₃·6H₂O, MnCl₂·4H₂O, FeCl₃·2H₂O, and PdCl₂) (1 mmol) dissolved in 20 mL of distilled water to an ethanolic solution (20 mL) of the ligand L1 (0.295 g, 1 mmol) with stirring, and the stirring was continued for 1-1.5 hours at room temperature. The solid was collected by filtration and washed with absolute ethanol and then recrystallized from a methanol-chloroform (1:3 v/v). The colored complexes so obtained were dried under vacuum over CaCl₂. Elemental analysis data, colors, and yields for the complexes are given in Table 1.

2.5 | Microbiological investigations

All the metal complexes, ligand, and metal salts were screened against *Staphylococcus aureus* (gram positive) and *Pseudomonas aeruginosa* (gram negative) bacteria as well fungi like *Penicillium expansum*, *Fusarium graminearum*, *Macrophomina phaseolina*, and *Candida albicans*, by using the wall agar diffusion method using solvent (DMSO); the concentration of the compounds in this exposure was (10⁻³ M) by using disc sensitivity test. This method involves the exposure of the zone inhibition towards the diffusion of micro-organism on an agar plate. The plates were incubated for 24 and 48 hours of bacteria and fungi respectively at 37°C.

2.6 | Programs used in theoretical calculation

Hyper Chem-8 program is a sophisticated molecular modeler, editor, and powerful computational package that are known for its quality, flexibility, and ease of use, uniting 2D visualization and animation with quantum chemical

calculations, molecular mechanics, and dynamics. In the present work, parameterization method 3 (PM3) was used for the calculation of the heat of formation and binding energy for all metal complexes. The PM3 and AMBER are more popular than other semiempirical methods because of the availability of algorithms, and these are more accurate than other methods.^[14] It has parameterized primarily for organic molecules and selected transition metals.^[15,16]

2.7 | The thermal analysis

From the TGA curves recorded for the successive steps in the decomposition process of this ligand and its complexes, it was possible to determine the following characteristic thermal parameters for each reaction step: Initial point temperature of decomposition (Ti): the point at which TG curve starts deviating from its base line. Final point temperature of decomposition (Tf): the point at which TG curve returns to its base line. Peak temperature, ie, temperature of maximum rate of weight loss (TDTG): the point obtained from the intersection of tangents to the peak of TG curve. The mass loss at the decomposition step (Dm): it is the amount of mass that extends from the point T_i up to the reaction end point T_f on the TG curve, ie, the magnitude of the ordinate of a TG curve. The material released at each step of the decomposition is identified by attributing the mass loss (Dm) at a given step to the component of similar weight calculated from the molecular formula of the investigated complexes, comparing that with the literature of relevant compounds considering their temperature. This may assist identifying the mechanism of reaction in the decomposition steps taking place

in the complexes under study. Activation energy (E) of the composition step: the integral method used is the Coats-Redfern equation,^[17] for reaction order $n - 1$ or $n = 1$, which when linearized for a correctly chosen n yields the activation energy from the slope;

$$\text{Log} \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \text{Log} \left[\left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{2.303RT} \text{ for } n \neq 1$$

$$\text{Log} \left[\frac{-\log(1-\alpha)}{T^2} \right] = \text{Log} \left[\frac{ZR}{qE_a} \left(1 - \frac{2RE}{E_a} \right) \right] - \frac{E_a}{2.303RT} \text{ for } n = 1$$

$\Delta S^* = 2.303 R [\log(Ah/K T_{\max})]$, $\Delta H^* = E - RT_{\max}$, $\Delta G^* = \Delta H^* - T_{\max} \Delta S^*$. Where α = fraction of weight loss, T = temperature (K), n = order of reaction, A or Z = pre-exponential factor, R = molar gas constant, E = activation energy, and q = heating rate. Order of reaction (n): it is the one for which a plot of the Coats-Redfern expression gives the best straight line among various trial values of n that are examined relative to that estimated by the Horowitz-Metzger method.^[18,19]

3 | RESULTS AND DISCUSSION

Chemistry: Schiff base was prepared in good yield by refluxing of 1-[[2-(1H-Indol-3-yl)-ethylimino] methyl]-naphthalen-2-ol and dicyclohexyl amine in ethanol solution as shown in Scheme 1. The ligand was characterized by EA (Table 1), IR (Table 2), UV-vis (Table 3), and mass spectroscopy. This compound was further used in the complexation reaction via the use of the following metal chloride salts: $\text{VOSO}_4 \cdot \text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$, and PdCl_2 . The ligand with its monomeric complexes, formed in solution, was isolated pure from ethanol in very good yield, and they are of various colors. However, in ethanol solution, deprotonation of the ligand occurs facilitating the formation of the complexes $[\text{M}(\text{II}) (\text{L}) (\text{H}_2\text{O})_2] \text{Cl}$ with $\text{M}(\text{II}) = \text{Mn}, \text{Pd}, \text{Cd}, \text{and Hg}$, and $[\text{M}(\text{III}) (\text{L}) (\text{H}_2\text{O})_2 \text{Cl}_2]$ with $\text{M}(\text{III}) = \text{Cr}$ and Fe are reported (Scheme 1). These complexes are air-stable solids, soluble in DMF and DMSO, sparingly soluble in MeOH, CHCl_3 , CH_2Cl_2 and not soluble in other common organic solvents. The microanalysis (CHN) was found to be in good agreement with the proposed molecular formulae.

3.1 | Infrared spectra

The FT-IR spectral data of the ligand (HL) and its complexes were characterized at 3462, 3035, 2960, 2905, and 1673 cm^{-1} due to the $\nu(\text{OH})$ phenol, $\nu(\text{CH})$ aromatic, $\nu(\text{CH})$ aliphatic, $\nu(\text{CH})$ aldehyde, and $\nu(\text{C} = \text{N})$ functional groups, respectively, for the ligand.^[20] The IR spectra of the complexes exhibited ligand bands with the appropriate

shifts due to complex formation.^[21] The $\nu(\text{C} = \text{N})$ bands of the ligand were observed at (1660-1644) cm^{-1} , and these bands were shifted to the lower frequencies by 29-13 cm^{-1} in the spectra of the complexes. This finding indicated that the ligand was coordinated with the metal ions through the OH phenol group and C = N azomethine group atoms, respectively. At lower frequency, the complexes exhibited bands around 523-459 cm^{-1} due to the $\nu(\text{M}-\text{N})$ and exhibited bands around 467-411 cm^{-1} due to the $\nu(\text{M}-\text{O})$ for complexes and new bands in complexes around 3562-3547 cm^{-1} and 874-828 cm^{-1} due to the $\nu(\text{H}_2\text{O})$ and $\delta(\text{H}_2\text{O})$. These results indicated that the ligand was coordinated with the metal ion through the H_2O atom.^[22,23]

3.2 | Mass spectrum

3.2.1 | Synthesis of L

The electron impact spectrum of the ligand (HL) confirms the probable formula by showing a peak at 507 m/z, corresponding to Schiff base moiety $[(\text{C}_{34}\text{H}_{41}\text{N}_3\text{O})]$, calculated atomic mass 507.71]. The series of peaks in the range of 491, 353, and 142 m/z may be assigned to various fragments. Their intensity gives an idea of the stability of fragments.

3.2.2 | Synthesis of Cr(III) complex

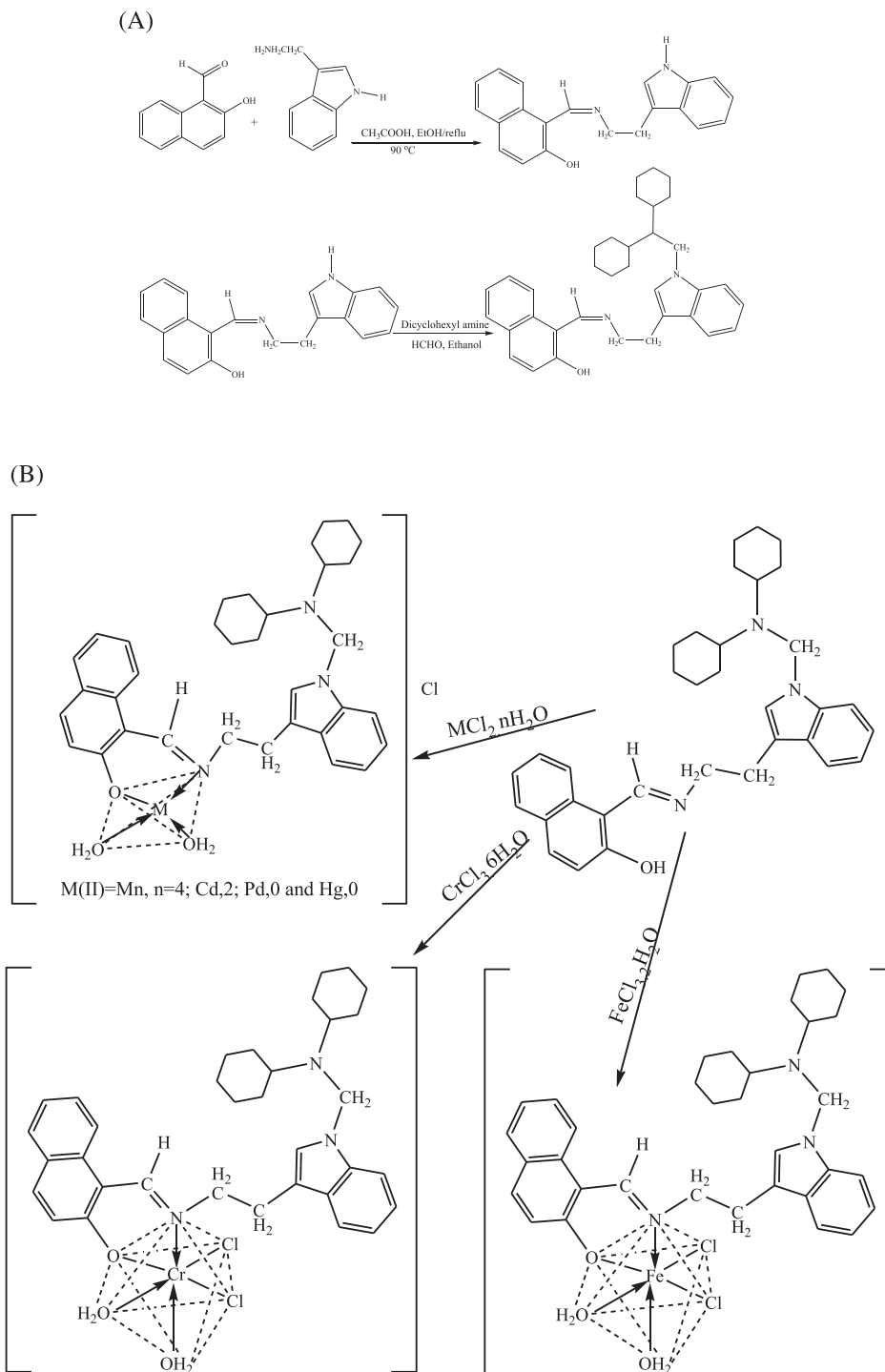
The electron impact spectrum of $[\text{Cr} (\text{L}) (\text{H}_2\text{O})_2 \text{Cl}_2]$ confirms the probable formula by showing a peak at 665 m/z, corresponding to complex moiety $[(\text{C}_{34}\text{H}_{44}\text{N}_3\text{O}_3\text{Cl}_2 \text{Cr})]$, calculated atomic mass 665.63]. The series of peaks in the range of 629 and 365 m/z may be assigned to various fragments.

3.2.3 | Synthesis of Cu (II) complex

The electron impact spectrum of $[\text{Fe} (\text{L}) (\text{H}_2\text{O})_2 \text{Cl}_2]$ confirms the probable formula by showing a peak at 669 m/z, corresponding to complex moiety $[(\text{C}_{34}\text{H}_{44}\text{N}_3\text{O}_3\text{Cl}_2\text{Fe})]$, calculated atomic mass 669.48]. The series of peaks in the range of 633, 562.5, 337.5, and 225 m/z may be assigned to various fragments.

3.2.4 | Synthesis of Mn(II) complex

The electron impact spectrum of $[\text{Mn}(\text{L})(\text{H}_2\text{O})_2] \text{Cl}$ confirms the probable formula by showing a peak at 597.5 m/z, corresponding to complex moiety $[(\text{C}_{34}\text{H}_{44}\text{N}_3\text{O}_3\text{Mn})]$, calculated atomic mass 597.67]. The series of peaks in the range of 561, 367, 171, and 196 m/z may be assigned to various fragments.



SCHEME 1 Synthesis route of the proposed structures of (A) ligand and (B) its metal complexes

3.3 | Electronic absorption spectra, magnetic moments, and conductivity measurements

The electronic spectrum at the ligand (HL) exhibits intense absorption at 282 and 330 nm attributed to $\pi \rightarrow \pi^*$, the 348 nm attributed to $n \rightarrow \pi^*$.

The electronic spectra of the $Cr^{(III)}$ and $Fe^{(III)}$ complexes with ligand exhibit 3 and 1 absorption band at 535, 645, and 905 nm and 462 nm which is attributed to ${}^4A_2g \rightarrow {}^3T_1g$ p, ${}^4A_2g \rightarrow {}^3T_1g$ pF, and ${}^4A_2g \rightarrow {}^3T_2g$ F, respectively, and ${}^5T_2g \rightarrow {}^5E_g$, respectively. Furthermore, the magnetic moment of the $Cr^{(III)}$ (d3) and $Fe^{(III)}$ (d5) complexes was found to be 3.05 and 5.01 B.M., respectively. The Complexes with the μ_{eff}

TABLE 2 FTIR spectral data (wavenumber ν) cm^{-1} for the ligand and its complexes

Compounds	$\nu(\text{OH})$	$\nu(\text{CH})$ aromatic	$\nu(\text{CH})$ aliphatic	$\nu(\text{CH})$ aldehyde	$\nu(\text{C} = \text{N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	H_2O rocking
HL	3462	3035	2960	2905	1673	-	-	
[Mn (L) (H ₂ O) ₂]Cl	-	3044	2958	2909	1660	511	445	3547 874
[Pd (L) (H ₂ O) ₂]Cl	-	3051	2945	2941	1649	523	433	3562 870
[Cd (L) (H ₂ O) ₂]Cl	-	3077	2965	2919	1658	509	467	3557 828
[Hg (L) (H ₂ O) ₂]Cl	-	3033	2977	2923	1651	487	440	3549 829
[Cr(L)(H ₂ O) ₂ Cl ₂]	-	3046	2951	2916	1644	521	436	3555 848
[Fe(L)(H ₂ O) ₂ Cl ₂]	-	3044	2974	2898	1659	459	411	3569 837

TABLE 3 Electronic data and molar conductivity for the metal complexes

Complexes	λ Nm	Assignment	Ω ohm ⁻¹ cm ² mol ⁻¹	μ_{eff} B.M.	Suggested formula
[Mn (L) (H ₂ O) ₂]Cl	418 568	⁶ A ₁ → ⁴ T ₂ (G) ⁶ A ₁ → ⁴ T ₁ (G)	78	5.11	Tetrahedral
[Pd (L) (H ₂ O) ₂]Cl	493 765	¹ A _{1g} → ¹ B _{1g} ¹ A _{1g} → ¹ A _{2g}	76	Diamagnetic	Square planer
[Cd (L) (H ₂ O) ₂]Cl	395	C.T	88	Diamagnetic	Tetrahedral
[Hg (L) (H ₂ O) ₂]Cl	385	C. T	86	Diamagnetic	Tetrahedral
[Cr(L)(H ₂ O) ₂ Cl ₂]	535 645 905	⁴ A _{2g} → ³ T _{1g} p, ⁴ A _{2g} → ³ T _{1g} pF ⁴ A _{2g} → ³ T _{2g} F	21	5.01	Octahedral
[Fe(L)(H ₂ O) ₂ Cl ₂]	409 462	C. T ⁵ T _{2g} → ⁵ E _g	15	3.05	Octahedral

value (Table 3) have an octahedral geometry around the central metal.

The electronic spectrum of Pd(II) complex showed 2 broad peaks at 493 and 765 nm assigned to ¹A_{1g} → ¹B_{1g} and ¹A_{1g} → ¹A_{2g}, suggesting a square planar geometry.

The electronic spectrum of Mn(II) complex showed 2 broad peaks at 418 and 568 nm assigned to ⁶A₁ → ⁴T₂(G) and ⁶A₁ → ⁴T₁(G), respectively.^[31,32] Finally, the absorption bands of the Cd(II) and Hg(II) complexes exhibited charge transfer at 385 and 395 nm, respectively. This is because of the electronic configuration and the diamagnetic of these complexes which confirmed the absence of any d-d electronic transition. Furthermore, the magnetic moment of the Mn^(II)(d⁵) complex was found to be 5.11 B.M., and the Cd and Hg complexes were found to be diamagnetic. All the above mentioned data correspond to a tetrahedral geometry.^[24] All the absorption bands

were fully assigned in Table 3. The molar conductivity value of the complexes was consistent with 1:1 electrolytes of all complexes and non-electrolytes for Cr^(III) and Fe^(III) complexes. Refer to Scheme 1 for proposed structures of metal complexes.^[31,25]

3.4 | Study complexes in gas stat (theoretical studies)

3.4.1 | Electrostatic potentials

Electron distribution governs the electrostatic potential of the molecules. The electrostatic potential (EP) describes the interaction of energy of the molecular system with a positive point charge. EP is useful for finding sites of reaction in a molecule; positively charged species tend to attack a molecule where the electrostatic potential is

strongly negative (electrophonic attack).^[26] The EP of the free ligand (HL) was calculated and plotted as 2D contour to investigate the reactive sites of the molecules (Figure 1). Also, one can interpret the stereochemistry and rates of many reactions involving “soft” electrophiles and nucleophiles in terms of the properties of frontier orbital (HOMO, highest occupied molecular orbital) and (LUMO, lowest unoccupied molecules). The results of calculations show that the LUMO of metal ions prefer to react with the HOMO of 2 donor atoms with the nitrogen of azomethane and oxygen of the hydroxyl group for free ligand (HL).

3.4.2 | Optimized energies

The program Hyperchem-8 was used for the semi-empirical and molecular mechanics calculations. The heat of formation (ΔH_f°) and binding energy (ΔE_b) for free ligand and their metal complexes were calculated (Table 4).

3.4.3 | Optimized vibrational spectra for ligand (HL)

The vibrational spectra of the free ligand and their metal complexes have been calculated (Table 5). The

theoretically calculated wavenumbers for this ligand showed that some deviations from the experimental values are generally acceptable in theoretical calculations.^[27] The most diagnostic calculated vibrational frequencies were chosen for the assignment of ligand (HL) and metal complexes which are included in (Table 5). and their respective experimental vibrational modes are shown as well (Table 2). The results obtained for the theoretical calculations of the frequencies agreed well with those obtained for the experimental values (Table 2).

3.4.4 | Bond length measurements for the (HL) and their metal complexes

Calculation of parameters has optimized bond lengths of the free ligand (HL) and their metal complexes by applying the semi-empirical (PM3) at geometry optimization ($0.001 \text{ K.Cal.mol}^{-1}$), to give excellent agreement with the experimental data^[28,29] as shown in Table 6.

3.4.5 | Theoretical electronic spectra for the metal complexes

The electronic spectra of the metal complexes have been calculated, and the wavenumber of these compounds showed some deviations from the experimental values as

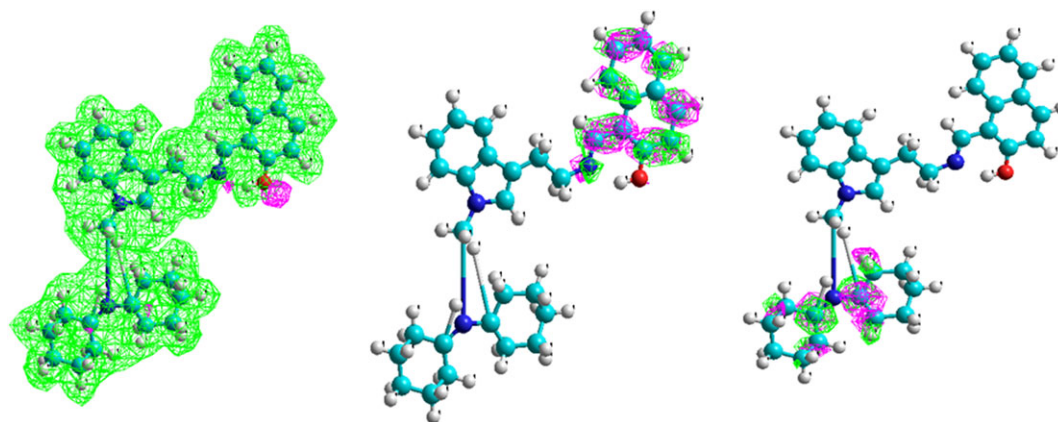


FIGURE 1 Electrostatic potential (HOMO and LUMO) as 2D contours for (HL)

TABLE 4 Conformation energetic (in KJ.mol^{-1}) for Naringin and its metal complexes

Compounds	ΔE_{tot}	ΔH_f°	ΔE_b	Dipole (Debyes)
HL	-125392.57133	102.2404773	-8242.7605227	4.581
[Mn (L) (H ₂ O) ₂]Cl	-122628.72311	2115.401668	-986.4163316	4.648
[Cr(L)(H ₂ O) ₂ Cl ₂]	-135141.76535	1781.34446	-4482.78009	3.106
[Cd (L) (H ₂ O) ₂]Cl	-194751.1675	1742.1165	-5998.176532	5.112
[Fe(L)(H ₂ O) ₂ Cl ₂]	-20848.11537	1553.5667	-6859.1997001	5.142
[Pd (L) (H ₂ O) ₂]Cl	-1096.463316 (Amber)			8.120
[Hg (L) (H ₂ O) ₂]Cl	-3757.82801 (Amber)			4.451

TABLE 5 Comparison between the experimental and theoretical vibrational frequencies (cm^{-1}) for free ligand (HL) metal complexes

Compounds	ν C = N	ν M-N	ν M-O	H ₂ O rocking			
HL	1677 ^a	1673 ^b	-	-	-	-	-
[Mn (L) (H ₂ O) ₂]Cl	1653 ^a	1660 ^b	505 ^a	511 ^b	491 ^a	445 ^b	882 ^a 874 ^b
[Pd (L) (H ₂ O) ₂]Cl	1655 ^a	1649 ^b	563 ^a	523 ^b	465 ^a	433 ^b	850 ^a 870 ^b
[Cd (L) (H ₂ O) ₂]Cl	1640 ^a	1658 ^b	546 ^a	509 ^b	501 ^a	467 ^b	836 ^a 828 ^b
[Hg (L) (H ₂ O) ₂]Cl	1645 ^a	1651 ^b	435 ^a	487 ^b	495 ^a	440 ^b	835 ^a 829 ^b
[Cr(L)(H ₂ O) ₂ Cl ₂]	1640 ^a	1644 ^b	581 ^a	521 ^b	488 ^a	436 ^b	855 ^a 848 ^b
[Fe(L)(H ₂ O) ₂ Cl ₂]	1644 ^a	1659 ^b	477 ^a	459 ^b	488 ^a	411 ^b	853 ^a 837 ^b

Where

^aTheoretical frequency.

^bExperimental frequency.

TABLE 6 Selected bond lengths (\AA) for (E) ligand and their metal complexes

Compounds	C = N	C-O	M-N	M-O	M-Cl
HL	1.347	1.363	-	-	-
[Mn (L) (H ₂ O) ₂]Cl	1.450	1.354	1.689	1.944	1.889
[Pd (L) (H ₂ O) ₂]Cl	1.449	1.360	1.690	1.946	1.978
[Cd (L) (H ₂ O) ₂]Cl	1.441	1.355	1.689	1.944	1.899
[Hg (L) (H ₂ O) ₂]Cl	1.441	1.355	1.691	1.945	1.898
[Cr(L)(H ₂ O) ₂ Cl ₂]	1.352	1.351	1.690	1.946	1.954
[Fe(L)(H ₂ O) ₂ Cl ₂]	1.351	1.358	1.689	1.946	1.954

shown in Table 7. These deviations in the theoretical calculation are generally acceptable due to couplings between the electronic spectra modes and the approximation that each normal mode of the electronic spectra interacts independently with electronic spectra beam.^[30]

^[33,34] The most diagnostic calculated electronic spectra were chosen for the assignment of the metal complexes. Experimental electronic modes are shown in Table 3. All the theoretical electronic spectra of all compounds were calculated by using the semi-empirical (PM3) method at geometry optimization (0.01 K.Cal.Mol⁻¹) and the comparison between the experimental data and theoretical data of the electronic spectra for metal complexes in Table 7.

3.4.6 | Optimized geometries of HL and their complexes

All theoretically probable structures of free ligand and their complexes have been calculated by PM3 method in gas phase to search for the most probable model building the stable structure (Figure 2).

TABLE 7 Comparison between experimental and theoretical of the electronic spectra for complexes

Complexes	Maximum absorption (nm)	Band assignment	Suggested geometry	
[Mn (L) (H ₂ O) ₂]Cl	577 ^a 624 ^a	6A ₁ → 4T ₂ (G) 6A ₁ → 4T ₁ (G)	Tetrahedral	
[Pd (L) (H ₂ O) ₂]Cl	557 ^a 687 ^a	493 ^b 765 ^b	1A _{1g} → 1B _{1g} 1A _{1g} → 1A _{2g}	Tetrahedral
[Cd (L) (H ₂ O) ₂]Cl	453 ^a	395 ^b	C.T	Tetrahedral
[Hg (L) (H ₂ O) ₂]Cl	485 ^a	385 ^b	C. T	Tetrahedral
[Cr(L)(H ₂ O) ₂ Cl ₂]	457 ^a 687 ^a 876 ^a	535 ^b 645 ^b 905 ^b	4A _{2g} → 3T _{1g} p, 4A _{2g} → 3T _{1g} pF 4A _{2g} → 3T _{2g} F	Octahedral
[Fe(L)(H ₂ O) ₂ Cl ₂]	492 ^a 590 ^a	409 ^b 462 ^b	C. T 5T _{2g} → 5E _g	Octahedral

Where

^aTheoretical frequency.

^bExperimental frequency

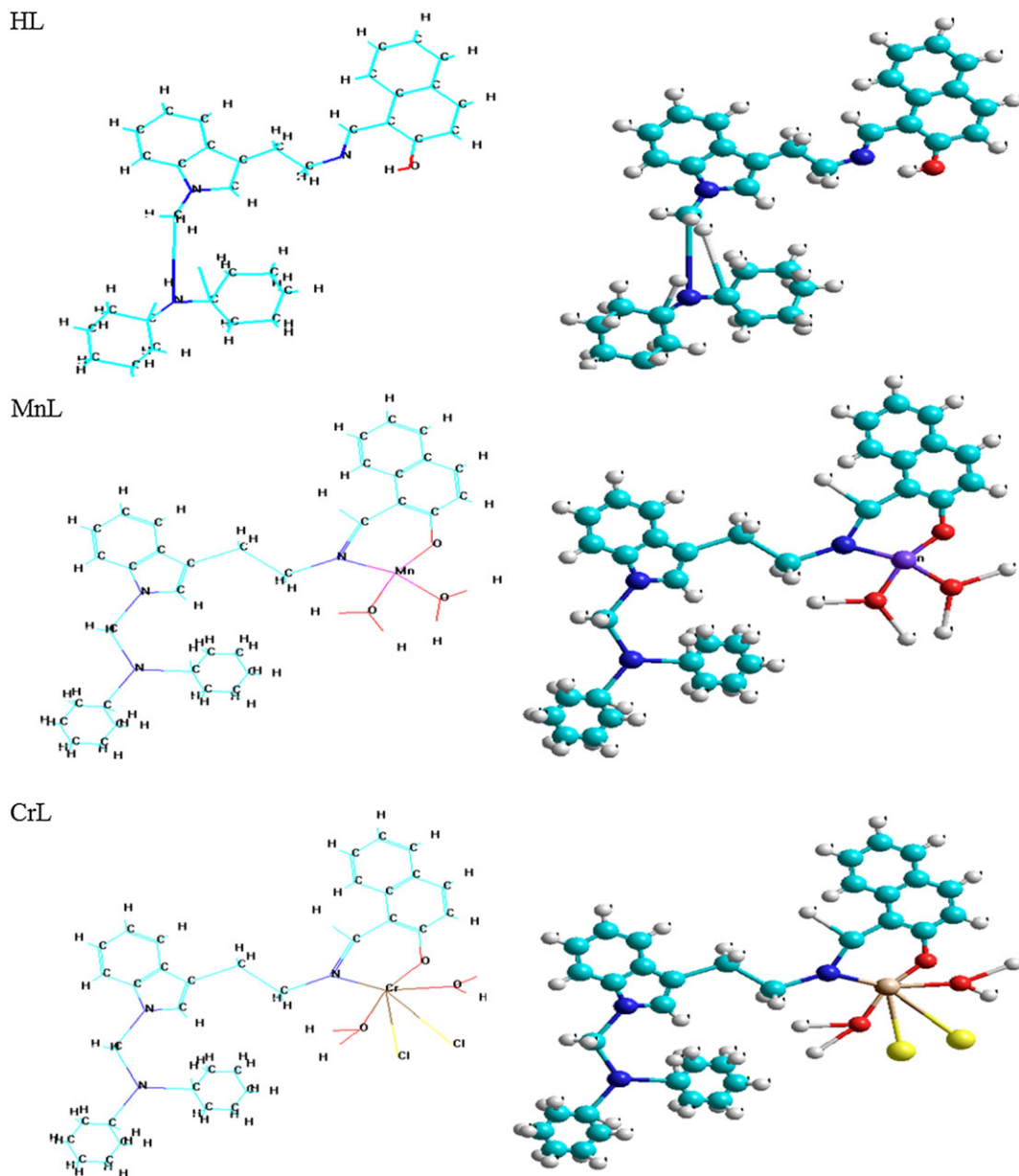


FIGURE 2 Conformational structure of (HL) and their metal complexes

3.5 | Thermal analysis

Thermal analysis was utilized to examine thermal behavior of Schiff base and its complexes. The thermograms have been carried out in the range of 25–700°C at a heating rate of 10°C/min in a nitrogen atmosphere; they showed an agreement in weight loss between their results obtained from the thermal decomposition and the calculated values, which supports the results of elemental analysis and confirms the suggested formulae as shown in Table 8.

Therefore, Schiff base showed a common general behavior as the first step ($C_{34}H_{41}N_3O$) was loss of $C_{12}H_{16}N_3$ moiety followed by the other parts of the ligand; the final step of the thermolysis reactions of the complexes was found to give the metal oxide; see Table 9.

(HL)- $C_{34}H_{41}N_3O$ [99.34%Found (100%Cal)]
 (199.1–313.7°C) $\rightarrow C_{12}H_{16}N_3$ [29.8%Found (29.53%Cal)]
 (313.7–589.3°C) $\rightarrow C_{22}H_{25}N_2O$ [69.54%Found (70.47%Cal)]

(CrL)- $C_{34}H_{44}N_3O_3CrCl_2$ [89.011%Found (89.542%Cal)]
 (33.5–139.8°C) $\rightarrow 2H_2O$ [4.163%Found (5.408%Cal)]
 (139.8–389.7°C) $\rightarrow 2Cl + C_{13}H_{23}N$ [40.794%Found (39.515%Cal)]
 (389.7–698.4°C) $\rightarrow C_{21}H_{17}N_2$ [44.054%Found (44.619%Cal)]

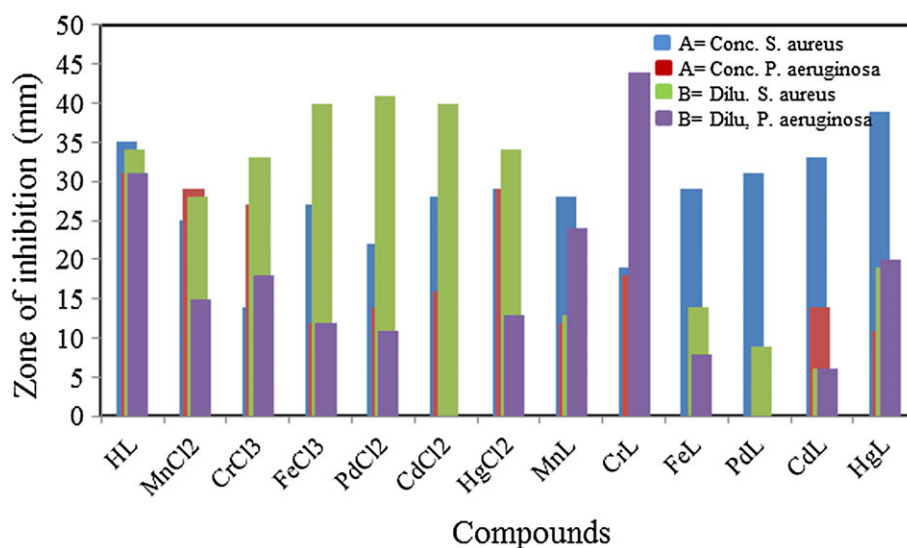
(MnL)- $C_{34}H_{44}N_3O_3MnCl$ [84.644%Found (83.08%Cal)]
 (35.5–118.9°C) $\rightarrow 2H_2O$ [4.981%Found (5.686%Cal)]
 (118.9–304°C) $\rightarrow C_{15}H_{10}Cl$ [29.612%Found (30.168%Cal)]
 (304–689.5°C) $\rightarrow C_{10}H_{30}N_3$ [50.051%Found (47.226%Cal)]

TABLE 8 Thermal analysis data of some metal complexes of HL

Com.	TG range (°C)	DTG max (°C)	% estimated (calculated)		Assignment
			Mass loss	Total mass loss	
HL	199.1-313.7	287.9	29.8(29.53)	99.34	C ₁₂ H ₁₆ N
	313.7-589.3	524.4	69.54(70.47)	(100)	C ₂₂ H ₂₅ N ₂ O
CrL	33.5-139.8	71.12	4.163(5.408)	89.011	2H ₂ O
	139.8-389.7	288	40.794(39.515)	(89.542)	C ₁₃ H ₂₃ NCl ₂
	389.7-698.4	504	44.054(44.619)		C ₂₁ H ₁₇ N ₂ CrO ⁺
MnL	35.5- 118.9	89.5	4.981 (5.686)	84.644	2H ₂ O
	118.9- 304	235	29.612 (30.168)	(83.08)	C ₁₅ H ₁₉ N ₂ Cl
	304- 689.5	482	50.051 (47.226)		C ₂₂ H ₂₁ N MnO

TABLE 9 Thermodynamic data of the thermal decomposition of ligand and their complexes

Sam	T range (°C)	n	R ²	Tmax (K)	Ea (kJ mol ⁻¹)	ΔH* (kJ mol ⁻¹)	A (s ⁻¹ × 10 ⁷)	ΔS* (J mol ⁻¹ K ⁻¹)	ΔG* (kJ mol ⁻¹)	K × 10 ⁻⁷
HL	199.1-313.7	1	0.997	287.9	10.160737	5.70751	3.661	-104.996	61.946	9.09510
HL	313.7-589.3	1	0.998	524.4	13.851965	13.1808	7.791	-102.075	95.086	6.45457
CrL	33.5-139.8	0.9	0.995	71.12	6.16778	3.79795	2.4383	-89.589	41.4703	6.2516
CrL	139.8-389.7	0.9	0.991	288	10.4435	4.1547	5.4487	-88.137	68.8081	0.19629
CrL	389.7-698.4	0.9	0.991	504	14.46375	8.4279	6.5654	-87.93	85.4412	0.44099
MnL	35.5-118.9	0.9	0.998	89.5	8.209644	3.357	2.82715	-118.68	49.8031	0.11652
MnL	118.9-304	0.9	0.989	235	13.4215	5.4185	13.0333	-108.2493	77.8435	0.23090
MnL	304-689.5	0.9	0.997	482	17.1548	7.957	15.97571	-79.445	107.4027	0.55368

**FIGURE 3** The antibacterial activity of compounds against *S. aureus* and *P. aeruginosa*

3.6 | Antimicrobial activity of ligand and all complexes

The biology activity of the Schiff and its complexes was studied against *S aureus*, *P aeruginosa*, as well as fungi like *P expansum*, *F graminearum*, *M phaseolina*, and *C albicans* bacteria. The results observed are tabulated (Figures 5, 6). The results were compared with the

standard sample (DMSO). Schiff base activity exhibited antibacterial against *S aureus* and *P aeruginosa*, but activity was found to be lower than the metal complexes and salt metals. Schiff base also exhibited antibacterial activity against *S aureus* and *P aeruginosa* but activity high in complexes and metal salts as shown in Figure 3. Ligand which did not exhibit antifungal activity but exhibited activity was in some metal complexes and salts metals as

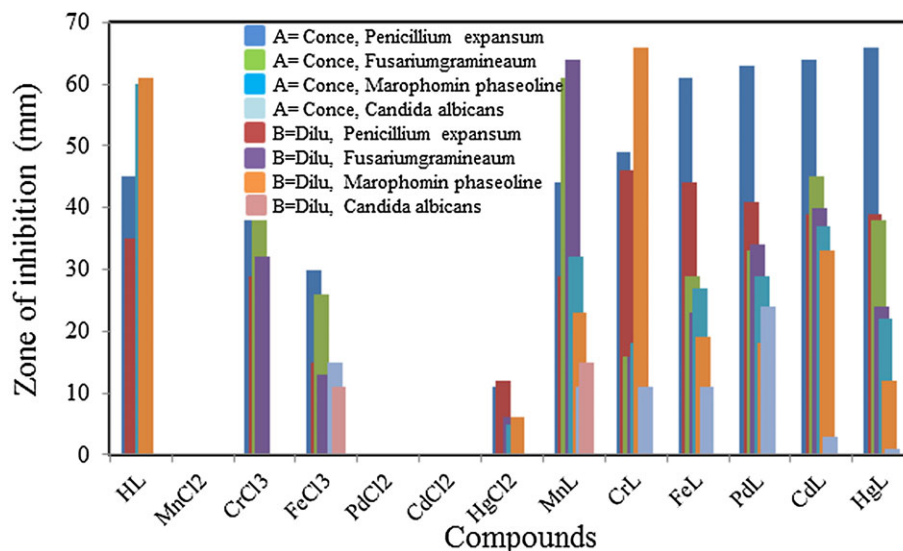


FIGURE 4 The antibacterial activity of compounds against *P expansum* and *F graminearum*

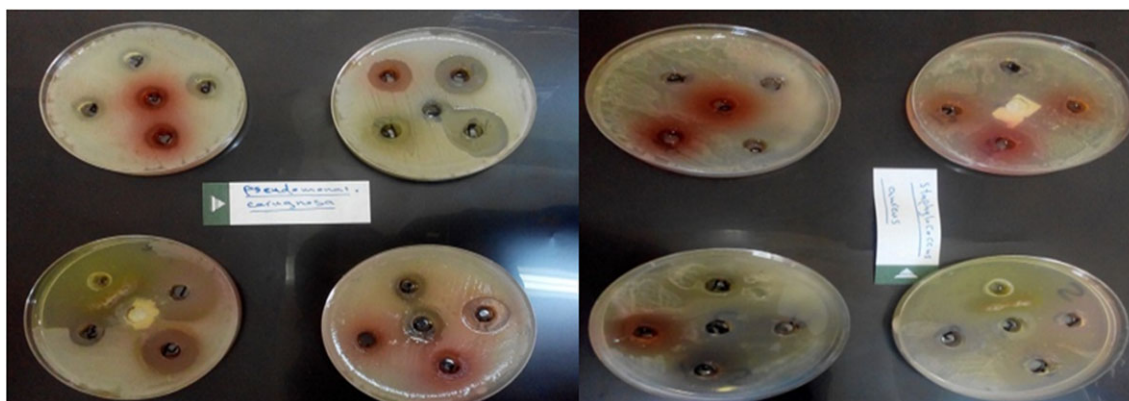


FIGURE 5 Effect of the ligand complexes towards the *Staphylococcus aureus* and *Pseudomonas aeruginosa*

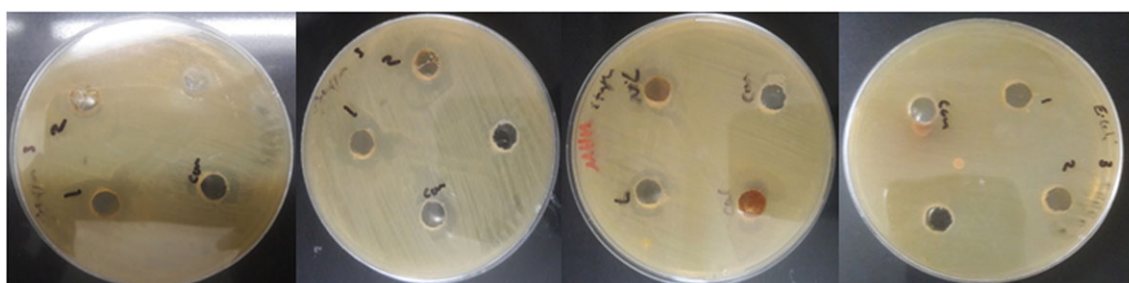


FIGURE 6 Effect of the ligand and complexes towards the *Penicillium expansum*

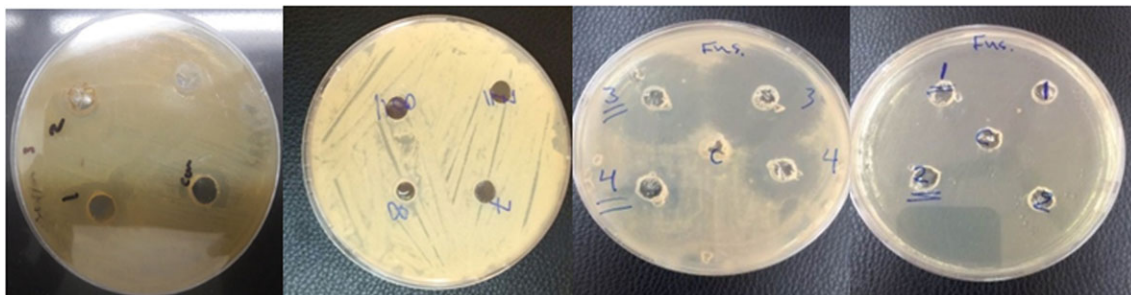


FIGURE 7 Effect of the ligand and complexes towards the *Fusarium graminearum*

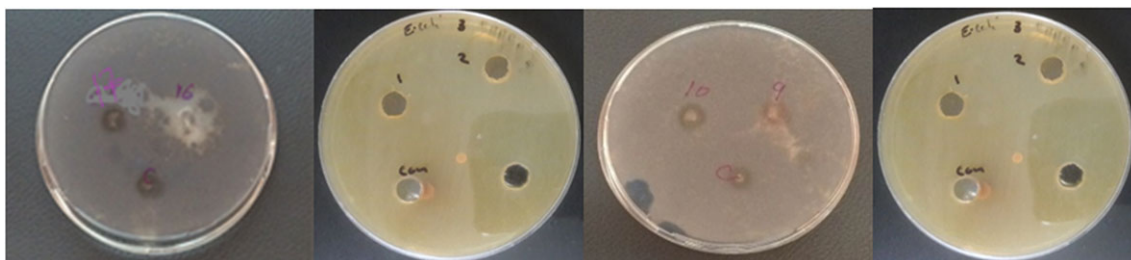


FIGURE 8 Effect of the ligand and complexes towards the *Macrophomina phaseolina*

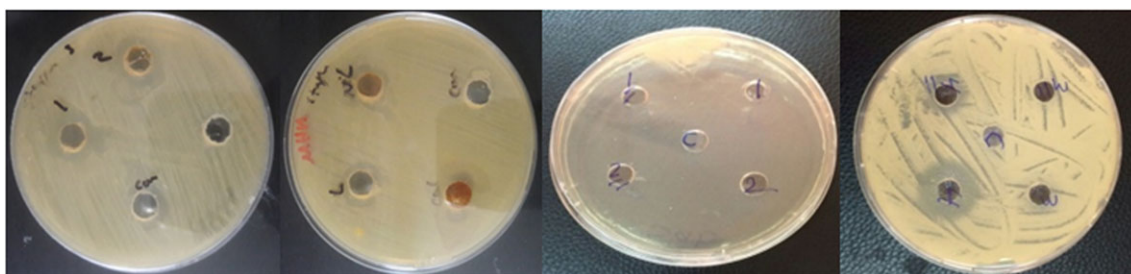


FIGURE 9 Effect of the ligand and complexes towards the *Candida albican*

shown in Figure 3, which exhibited CrL and FeL complex activity lower compared with salts of Cr and Fe against *P expansum* and *F graminearum*. The HL and some salt metals exhibit antifungal strong activity against *P expansum* and *C albicans*, by not exhibiting antifungal activity against *F graminearum* and *M phaseolina* as compared with the antimicrobial activity with some mixed ligand metal complexes which exhibited antifungal activity more than ligand as shown in (Figure 3). An influence of the central ion of the some complexes in the antibacterial activity strong against *F.graminearum* and *M. phaseolina* shows that the complexes have an enhanced activity compared to the ligand itself (Figure 4). Figures 5–9 show compounds exhibiting bioactivity against 2 kinds of bacteria and 4 kinds of fungal.

4 | CONCLUSION

This article involved preparation of Schiff base, and their complexes were characterized by elemental, spectroscopic

(FT-IR, ^1H NMR, mass), thermal techniques, magnetic moment, and molar conductance. Their structures were confirmed by comparative studies between practical techniques and theoretical molecule orbital calculations. The thermodynamic parameters, such as ΔE^* , ΔH^* , ΔS^* , ΔG^* , and K were calculated from the TGA curve using Coats-Red fern method. Antibacterial activity of Schiff base and its complexes were tested by diffusion agar method. DMSO was used as a reference compound for antibacterial activates. They were found to be biologically active complexes.

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How to cite this article: Al Zoubi W, Al-Hamdani AAS, Ahmed SD, Ko YG. Synthesis, characterization, and biological activity of Schiff bases metal complexes. *J Phys Org Chem.* 2018;31: e3752. <https://doi.org/10.1002/poc.3752>