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RESEARCH ARTICLE

Ultrasonic assisted preparation of some new zinc complexes of a new tetradentate Schiff base ligand: thermal analyses data, antimicrobial and DNA cleavage potential

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Abstract

A new tetradentate Schiff base ligand (L) (L = obtained by condensation reaction between triethylenetetraamine and (E)-3-(2-nitrophenyl)acrylaldehyde) and some of its zinc (II) complexes formulated as $ZnLX_2$ in which X = halide/ pseudohalide were synthesized and characterized by some physical and spectral techniques such as infra-red (IR), nuclear magnetic resonance (NMR), UV-Visible, microanalyses, and conductivity measurements. Among the complexes, zinc chloride, iodide, and nitrate complexes were also prepared as nanostructure powder under sonication conditions confirmed by x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive x-ray analysis (EDAX). Moreover, zinc oxide nanoparticles were prepared by direct thermolysis of nanopowder of ZnLI₂ complex under air atmosphere. Moreover, the thermal behaviors of the compounds were studied based on thermogravimetric (TG)/differential thermal gravimetric (DTG)/differential thermal analyses (DTA) analyses data under nitrogen atmosphere. Furthermore, antibacterial/antifungal activities of the ligand and its zinc complexes were screened by the well diffusion method against some bacteria and funguses. Ultimately, the DNA cleavage potential of the compounds was evaluated by gel electrophoresis technique.

KEYWORDS

antimicrobial, DNA cleavage, sonochemistry, tetradentate Schiff base, thermal, zinc complex, ZnO

1 | INTRODUCTION

Schiff bases with their azomethine group are an important class of ligands in coordination chemistry and were first reported by an Italian chemist, Hugo Schiff by condensation process of a primary amine with a carbonyl compound.^[1] In fact, they are the compounds that the oxygen atom of carbonyl group (C=O) of a ketone or aldehyde is substituted by the nitrogen of the primary amine.^[2] The azomethine group has played an important role in these compounds as chelating ligands in main group and transition metal coordination chemistry.^[3–5] The azomethine group, planarity of the π -bonding orbitals and electrons from the attached electronegative atoms afford them the great opportunity for coordination to metal ions.^[6] Study of the coordination chemistry of transition metal with different types of the ligands has been increased by the current developments

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in the fields of bioinorganic chemistry, medicine, dve, and industry.^[7-10] The sustained attempts in the study of the Schiff base complexes with several transition metals generally in (II) oxidation states arises from the ease of their preparation, high stability, versatility, and good solubility in common solvents.^[11,12] Moreover, Schiff base complexes have some properties like photochromic, catalytic activity in hydrogenation of olefins,^[13] antioxidant,^[14] anticancer, antifungal,^[15] antibacterial,^[16] DNA cleavage systems,^[17] antiinflammatory,^[18] OLED applications,^[19] transistors,^[20] lasers,^[21] and oxygen storage potential.^[22] Binding of Schiff base compounds to metal ions depends on the structural nature of them such as presence of the heteroatoms of oxygen, nitrogen, and sulfur; or the existence of unsaturated bonds.^[23-26] On the other hand, it is worth mentioning that zinc is the second most plentiful metal in organisms and the only metal which emerges in all six enzyme classes.^[27] Besides, it is known that Zn is essential for structure and function of a large number of macromolecules and over 300 enzymatic reactions.^[28] The spherical d¹⁰ configuration of metal ion of Zn²⁺ leads to a flexible coordination environment so that geometries of these complexes can change from tetrahedral to octahedral (tetrahedral/square planar, pyramidal/trigonal bipyramidal, and trigonal prismatic/ octahedral).^[29-33] In recent years, considerable attention has been drawn to the nanostructure compounds.^[34-40] The size and shape of materials influence the chemical and physical properties especially due to their large surface-to-volume ratio. Therefore, conventional methods have been replaced by modern sonochemical methods in the synthesis of nano-structured coordination compounds.^[41-44]

Though literature contains various symmetrical and unsymmetrical tetradentate Schiff bases and chelates,^[45] to the best of our knowledge, long-chain tetradentate Schiff base ligand entitled (N²E, N²'E)-N¹, N¹'-(ethane-1, 2-diyl)bis(N2-((E)-3-(2-nitrophenyl)allylidene)ethane-1,2diamine) and its zinc complexes have not been presented yet. Therefore, herein, in continuation of our previous studies on bidendate, tridendate, and tetradendate donor Schiff bases,^[46-49] synthesis of a novel N₄ Schiff base ligand and its bulk/nanostructure Zn (II) complexes is described. Ligand and its complexes were characterized by using different spectral and physical techniques. Also, their biological properties and DNA cleavage potentials are reported. Moreover, the thermal behaviors of the compounds were studied. Thus, some kinetics activation parameters of the complexes at various thermal decomposition steps were evaluated based on thermograms. Finally, zinc iodide complex was used as a precursor for preparation of nanostructured zinc oxide.

2 | EXPERIMENTAL

2.1 | Materials

All the reagents and solvents such as (E)-3-(2-nitrophenyl) acrylaldehyde, N1-(2-(2-aminoethylamino)ethyl)ethane-1, 2-diamine, zinc salts, methanol, dimethyl sulfoxide- d_6 (DMSO-d6), potassium bromide, and other used chemicals were provided by the Aldrich and Merck chemical companies and were used without any further purification. Zinc (II) thiocyanate and azide salts were prepared according to the previous published procedure.^[50]

2.2 | Instrumentation

Melting points (m.p.) or decomposition temperatures (°C) of the ligand and its complexes were recorded by the Kruss instrument. The fourier transform infra-red (FT/IR) spectra of all compounds were recorded based on potassium bromide disks on a JASCO- Fourier transform FT/IR-680 spectrometer in the range of $4000-400 \text{ cm}^{-1}$. UV-Visible spectra of the compounds were obtained in dimethylformamide (DMF) by use of a JASCO-V570 spectrophotometer in the range of 200 to 800 nm. Molar conductances of the Schiff base ligand and its complexes $(1.0 \times 10^{-3} \text{ M in DMF})$ solution) were determined using a Metrohm 712 conductometer at 298 K. ¹H and ¹³C NMR spectra were run on a Brucker DPX FT-NMR-400 spectrometer in DMSO-d₆ using tetramethylsilane (TMS) as internal standard at room temperature. Elemental analyses (C, N, and H) data were performed using a CHNS-932 (Leco) elemental analyzer. Thermo-gravimetric analyses (TGA) were done by a Perkin-Elmer Pyris model under N_2 atmosphere with a heating rate of $20^{\circ}C/min^{-1}$ from ambient temperature up to 900°C. X-ray powder diffraction (XRD) patterns were conducted on an analytical model X' Pert Pro focus diffractometer with Cu-Ka radiation ($\lambda = 1.5418$ Å). SEM images were taken by a Hitachi S-1460 field emission SEM using alternating current voltage of 20 kV. An ultrasonic bath (Tecno-Gasz SPA, Parma, Italy) with frequency of 40 kHz and 130 W was handled for the sonochemical synthesis of the compounds. In biological tests, the nutrient agar (Merck, Germany) was used for preparing nutrient plates, while Mueller Hinton broth (Scharlab) was used as a liquid culture media. Escherichia coli (ATCC 25922), Pseudomonas aeruginosa (ATCC 9027), Staphylococcus aureus (ATCC 6538), and Bacillus subtilis (ATCC 6633) were selected for antibacterial studies and Candida albicans and Aspergillus oryzae were chosen for antifungal tests.

2.3 | Synthesis of tetradentate Schiff base ligand (L)

An ethanolic solution of N1-(2-(2-aminoethylamino) ethyl)ethane-1,2-diamine (1 mmol. in 5 ml) was dropwisely added to an ethanolic solution of (E)-3-(2-nitrophenyl)acrylaldehyde (2 mmol, in 5 ml) under intense stirring for 5 h at room temperature. The reaction progress was monitored by thin layyer chromatography (TLC). A brownish solution was obtained after mentioned time. Evaporation of solvent led to a brown precipitate. Recrystallization from ethanol/dichloromethane (1:1) solvent mixture afforded Schiff base orangish powder (yield, 77%; m.p., 147–150°C).

2.4 | Synthesis of zinc (II) complexes

The zinc complexes were synthesized by gradually addition of ethanolic solution of the fresh Schiff base ligand (1 mmol in 5 ml) to an ethanolic solution of zinc halide and/or pseudohalide salt (1 mmol in10 ml) under vigorous stirring for 2–4 h at ambient temperature similar to our previous report.^[38] The precipitated complexes were filtered, washed twice with cold ethanol, and dried under vacuum. Tables 1–4 contain some important physical and spectral data (FT-IR, UV–Visible, ¹H, and ¹³C NMR) of the ligand and its zinc complexes based on Scheme 1:

2.5 | Sonochemical synthesis of nanostructured zinc complexes

An ethanolic solution of zinc salts (1 mmol in 10 ml) was placed in an ultrasonic bath. Then, a solution containing 1 mmol of Schiff base ligand in 10 ml was gradually added to zinc salt solution. The reaction mixture was kept in the ultrasonic bath for 1 h. The resulting precipitates were collected from the solution by filtration and then washed with ethanol twice and dried at room temperature.

Compounds	Color	Melting (decomposition) points/°C	Yield, %	С %	Elemental analysis, Experimental (Calculated)% N%	$\frac{\Lambda_{\rm M}/\Omega^{-1}}{\rm cm^2 mol^{-1}}$ H%	
Ligand	Brown	147–150	70	61.9 (62.1)	17.8 (18.1)	6.2 (6.1)	19.40
ZnLCl ₂	Cream	248-250	85	46.8 (47.9)	13.7 (13.9)	4.5 (4.7)	20.50
ZnLBr ₂	Yellow	183–185	63	42.1 (41.7)	11.9 (12.1)	4.2 (4.0)	10.23
ZnLI ₂	Yellow	177–179	61	36.5 (36.7)	10.9 (10.7)	3.8 (3.6)	19.50
ZnL (NO ₃) ₂	Cream	224–227	83	43.8 (44.0)	17.3 (17.1)	4.1 (4.3)	20.60
ZnL (NCS) ₂	Cream	140–143	75	48.4 (48.3)	17.4 (17.3)	4.5 (4.3)	19.50
ZnL(N ₃) ₂	Orange	150–154	60	49.7 (49.9)	27.5 (27.3)	4.7 (4.6)	20.20
$ZnL (ClO_4)_2$	Orange	203–107	65	39.7 (39.6)	11.7 (11.5)	3.7 (3.6)	20.70

TABLE 1 Some analytical and physical data of the tetradentate Schiff base ligand (L) and its zinc coordination compounds

TABLE 2 IR frequencies (cm⁻¹) and electronic (nm) spectral data of the Schiff base ligand (L) and its zinc (II) complexes

Compound	ν NH amine	ν CH alkene	ν CH aliph.	ν CH imine	ν (SCN/ N ₃ / NO ₃ /ClO ₄)	ν (C=N)	ν (C=C)	ν (C-N)	ν (NO ₂)	ν (M-N)	λ _(nm)
Ligand	3432	3066	2923	2850, 2801	-	1633	1459, 1442	1160	1523, 1346	-	267, 319
ZnLCl ₂	3478	3070	2927	2835, 2802	-	1639	1451, 1446	1127	1523, 1346	441	269, 323
ZnLBr ₂	3454	3080	2930	2851, 2862	-	1635	1463, 1439	1171	1524, 1346	430	272, 336
$ZnLI_2$	3471	3071	2922	2837, 2800	-	1639	1450, 1441	1172	1523, 1346	446	268, 325
$ZnL (NO_3)_2$	3451	3178	2931	2877, 2801	1343, 1569	1635	1469, 1442	1172	1527, 1342	431	271, 327
ZnL (NCS) ₂	3455	3081	2927	2886, 2856	2075	1635	1461, 1440	1172	1523, 1346	428	269, 321
$ZnL(N_3)_2$	3394	3088	2927	2889, 2877	2059	1635	1460, 1442	1160	1523, 1346	408	272, 324
$ZnL (ClO_4)_2$	3502	3089	2927	2890, 2877	1087	1639	1460, 1454	1087	1523, 1346	408	270, 324

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TABLE 3 ¹HNMR spectral data of ligand and its zinc-Schiff base complexes in DMSO-d₆

Compound	¹ H NMR data (δ , ppm)
Ligand	8.17 (d, $2H_{dd'}$, $J = 8.5$ Hz), 8.03 (d, $2H_{gg'}$, $J = 7.8$ Hz), 7.96 (t, $2H_{ii'}$, $J = 7.8$ Hz), 7.76 (t, $2H_{hh'}$, $J = 8.0$ Hz), 7.63 (d, $2H_{jj'}$, $J = 8.0$ Hz), 7.36 (d, $2H_{ff'}$, $J = 15.5$ Hz), 6.95 (d d, $2H_{ee'}$, $J_1 = 15.3$ Hz, $J_2 = 8.2$ Hz), 3.60–3.57 (m, $4H_{cc'}$), 3.20 (s, $2H_{NH}$), 1.26 (m, $4H_{bb'}$), 0.88 (s, $4H_{aa'}$)
ZnLCl ₂	8.41 (d, $2H_{dd'}$, $J = 9.0$ Hz), 8.09 (d, $2H_{gg'}$, $J = 8.4$ Hz), 7.83 (d, $2H_{jj'}$, $J = 7.9$ Hz), 7.66 (t, $4H_{ii',hh'}$, $J = 8.0$ Hz), 7.64 (d, $2H_{ff'}$, $J = 16.0$ Hz), 7.02 (d d, $2H_{ee'}$, $J_1 = 15.7$ Hz, $J_2 = 9.1$ Hz), 3.80–3.77 (m, $6H_{cc',NH}$), 2.84 (s, $4H_{aa'}$), 2.76 (m, $4H_{bb'}$)
ZnLBr ₂	8.42 (d, $2H_{dd'}$, $J = 9.1$ Hz), 8.10 (d, $2H_{gg'}$, $J = 7.8$ Hz), 7.83 (m, $4H_{hh',jj'}$), 7.69 (t, $2H_{ii'}$, $J = 8.6$ Hz), 7.65 (d, $2H_{ff'}$, $J = 16.0$ Hz), 7.07 (d d, $2H_{ee'}$, $J = 15.7$ Hz, $J_2 = 9.1$ Hz), 3.79 (t, $4H_{cc'}$, $J = 5.5$ Hz), 2.88 (bs, $6H_{aa',NH}$), 2.77 (t, $4H_{bb'}$, $J = 6.0$ Hz)
ZnLI ₂	8.28 (d, $2H_{dd'}$, $J = 8.4$ Hz), 8.06 (d, $2H_{gg'}$, $J = 8.1$ Hz), 7.91 (d, $2H_{jj'}$, $J = 8.0$ Hz), 7.80 (t, $2H_{ii'}$, $J = 7.6$ Hz), 7.65 (t, $2H_{hh'}$, $J = 7.7$ Hz), 7.49 (d, $2H_{ff'}$, $J = 15.9$ Hz), 7.05 (dd, $2H_{ee'}$, $J_1 = 15.8$ Hz, $J_2 = 8.8$ Hz), 3.69 (b s, $4H_{cc'}$), 2.64 (m, $10H_{bb',aa',NH}$)
ZnL (NO ₃) ₂	8.64 (d, $2H_{dd'}$, $J = 9.3$ Hz), 8.13 (d, $2H_g$, $J = 8.9$ Hz), 8.08 (d, $2H_{jj'}$, $J = 7.2$ Hz), 7.74 (d, $2H_{ff'}$, $J = 15.7$ Hz), 7.61 (t, $2H_{ii'}$, $J = 7.6$ Hz), 7.46 (t, $2H_{hh'}$, $J = 9.6$ Hz), 7.00 (d d, $1H_e$, $J_1 = 15.2$ Hz, $J_2 = 8.8$ Hz), 6.96 (dd, $1H_{e'}$, $J_1 = 14.9$ Hz, $J_2 = 6.6$ Hz), 4.33 (s, $2H_{NH}$), 3.85–3.64 (m, $4H_{CC'}$), 3.19–3.08 (m, $4H_{bb'}$), 2.69–2.63 (m, $4H_{aa'}$)
ZnL(N ₃) ₂	8.63 (d, $2H_{dd'}$, $J = 9.3$ Hz), 8.07 (d, $4H_{gg',jj'}$, $J = 8.0$ Hz), 7.73 (m, $4H_{ii',hh'}$), 7.38 (d, $2H_{ff'}$, $J = 16.0$ Hz), 7.06–6.97 (m, $2H_{ee'}$), 3.84–3.79 (m, $4H_{cc'}$), 3.61 (s, $2H_{NH}$), 2.82–2.68 (m, $8H_{bb',aa'}$)
ZnL (ClO ₄) ₂	8.60 (d, $2H_{dd'}$, $J = 9.1$ Hz), 8.13 (d, $2H_{gg'}$, $J = 8.0$ Hz), 7.81–7.68 (m, $2H_{jj',ii'}$), 7.65–7.59 (m, $2H_{hh'}$), 7.39 (d, $2H_{ff'}$, $J = 15.8$ Hz), 6.86 (dd, $2H_{ee'}$, $J_1 = 15.8$ Hz, $J_2 = 7.6$ Hz), 4.15–4.13 (m, $2H_{NH}$), 3.69 (s, $4H_{cc'}$), 2.96 (s, $4H_{bb'}$), 2.86 (s, $4H_{aa'}$)

TABLE 4 ¹³C NMR spectral data of ligand and its zinc-Schiff base complexes in DMSO-d₆

Compound ¹²	³ C NMR data (δ, ppm)
Ligand	$163.15 (C_{4,4'}), 148.24 (C_{8,8'}), 134.01 (C_{6,6'}), 133.01 (C_{11,11'}), 130.66 (C_{7,7'}), 130.35 (C_{10,10'}), 129.16 (C_{12,12'}), 128.89 (C_{9,9'}), 125.01 (C_{5,5'}), 67.87 (C_{3,3'}), 53.13 (C_{1,1'}), 50.84 (C_{2,2'})$
ZnLCl ₂	$167.90 (C_{4,4'}), 148.47 (C_{8,8'}), 134.56 (C_{6,6'}), 131.33 (C_{11,11'}), 131.19 (C_{7,7'}), 130.46 (C_{10,10'}), 129.84 (C_{12,12'}), 128.89 (C_{9,9'}), 125.31 (C_{5,5'}), 58.52 (C_{3,3'}), 56.06 (C_{1,1'}), 53.12 (C_{2,2'})$
ZnLBr ₂ ZnLI ₂	167.02 (C _{4,4'}), 148.48 (C _{8,8'}), 134.55 (C _{6,6'}), 132.12 (C _{11,11'}), 131.19 (C _{7,7'}), 130.77 (C _{10,10'}), 129.80 (C _{12,12'}), 128.83 (C _{9,9'}), 125.32 (C _{5,5'}), 58.54 (C _{3,3'}), 55.58 (C _{1,1'}), 53.12 (C _{2,2'}) 165.03 (C _{4,4'}), 148.48 (C _{8,8'}), 134.31 (C _{6,6'}), 132.60 (C _{11,11'}), 132.15 (C _{7,7'}), 130.77 (C _{10,10'}), 130.50 (C _{12,12'}), 128.87 (C _{9,9'}), 125.17 (C _{5,5'}), 58.58 (C _{3,3'}), 56.70 (C _{1,1'}), 53.19 (C _{2,2'})
ZnL (NO ₃) ₂	$169.52 (C_{4,4'}), 148.30 (C_{8,8'}), 134.26 (C_{6,6'}), 132.60 (C_{11,11'}), 132.15 (C_{7,7'}), 131.54 (C_{10,10'}), 129.93 (C_{12,12'}), 129.81 (C_{9,9'}), 125.29 (C_{5,5'}), 57.61 (C_{3,3'}), 47.62 (C_{1,1'}), 46.15 (C_{2,2'})$
$ZnL (ClO_4)_2$	$167.44 (C_{4,4'}), 147.85 (C_{8,8'}), 134.46 (C_{6,6'}), 132.59 (C_{11,11'}), 132.14 (C_{7,7'}), 130.65 (C_{10,10'}), 129.81 (C_{12,12'}), 129.15 (C_{9,9'}), 125.31 (C_{5,5'}), 57.27 (C_{3,3'}), 47.66 (C_{1,1'}), 45.92 (C_{2,2'})$



SCHEME 1 The proposed structure for tetradentate $[N_4]$ donor Schiff base ligand (a) and its complexes, $ZnLX_2$ wherein $X = Cl^-$, Br^- , I^- , NO_3^- , SCN^- , N_3^- , and ClO_4^- (b)

2.6 | Synthesis of nanostructure ZnO

Nanostructure zinc iodide complex (0.6 g) was heated to 500°C in a static atmosphere of air for about 4 h. The obtained white powder was washed with a little amount of acetone solvent to remove organic impurity and then was dried at room temperature to obtain nanostructured zinc oxide as product in 68% yield. The nanostructured ZnO were identified by XRD, SEM, and EDAX methods.

2.7 | Antimicrobial activities

The antibacterial activity of the ligand and its complexes were studied against four bacterial species including two Gram-negative bacteria of E. coli and P. aeruginosa and two Gram-positive bacteria of S. aureus and B. subtilis and also two fungi such as A. orvzae and C. albicans by well diffusion method. Assessments of biological agents were evaluated in three concentrations (50, 25, and 12.5 mg cm⁻³) of Schiff bases ligand and its zinc complexes dissolved in DMSO solvent in the sample tubes. A blank test demonstrated that the DMSO had no remarkable effect against above microorganisms strains.^[50] The bacterial and fungal cultures were grown on sterilized nutrient agar (NA); Sabouraud dextrose agar (SDA) were saturated and solidified into each petri plate, respectively. Incubation of the microorganisms in Muller-Hinton broth medium was done at 37°C for 24 h, and their enriched cultures were prepared. According to well diffusion method, after solidification of the agar gel, a sterile glass spreader was used so that 0.1 ml of suspension of the previously mentioned microorganism was swabbed on to particular petri plates and based on our previous reports.[51]

2.8 | Determination of minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC)

MIC is defined as the lowest concentration required arresting the growth of the bacteria at the end of 24 h at 37° C of incubation. The MICs were measured by using the serial dilution technique. MBC is the lowest concentration from which the bacteria do not grow when transferred to fresh medium. MBCs were determined by sub-culturing a loop full of broth dilution MIC tests to Muller–Hinton agar medium on the plate and then incubated at 37° C for 24 h.

2.9 | DNA cleavage test

The DNA cleavage potential of the Schiff base ligand and its zinc complexes in the presence of hydrogen peroxide (H_2O_2) as an oxidant was monitored by agarose gel electrophoresis method. The extraction of DNA as a substrate was performed according to our previous report.^[39] For DNA cleavage test, the electrophoresis experiment was performed by incubation of the samples containing $(4 \mu l)$ of the solution that was prepared by dissolving of 5 mg of each compound in 1 ml of DMSO and 4 µl of the extracted DNA. The mixtures were incubated at 37°C for 2 h. After incubation, the trial samples were mixed with bromophenol blue dye and along with the standard DNA (alone), the mix of DNA and H₂O₂, and ladder were loaded carefully into the wells. Gel electrophoresis was performed at constant voltage 100 V for about 30 min. Then resulting bands of DNA cleavage observed under UV light and then photographed.

3 | RESULTS AND DISCUSSION

3.1 | Physical and analytical data

Physical and analytical data of the tetradentate Schiff base ligand and its zinc complexes have been summarized in Table 1. The suggested structures of the compounds as shown in Scheme 1 were confirmed by using spectroscopic and physical techniques according to other literature survey. The elemental analyses data suggest a general formula of $ZnLX_2$ [L = Schiff base ligand and X = chloride, bromide, iodide, nitrate, thiocynate, azide, and perchlorate] for the complexes as shown in (Scheme 1). The ligand melts at the range of 147–150°C, while the decomposition temperatures of the complexes were found in the range of 140-250°C. These coordination compounds are non-soluble in water and many common organic solvents such as alcohols but are soluble/ low soluble in solvents like DMF and DMSO. The yields of ligand and metal complexes were obtained in 70% and 60% to 85%, respectively. All zinc complexes are colored solids, non-sensitive to moisture, stable at ambient temperature, and decomposable on heating. The molar conductivities of the compounds in DMF (10^{-3} M) were evaluated in the range of 19.4 to 20.7 cm² Ω^{-1} mol⁻¹ which well confirm their non-electrolytic nature at room temperature.^[52] The low molar conductivities indicate that the halide/pseudohalide ions and Schiff base ligand have been bonded to the zinc ion in an inner-sphere coordination mode. Moreover, according to these data, the maximum dissociation in DMF solution is related to zinc perchlorate complex that may be due to steric effect of perchlorate ions during the coordination with respect to other X anions.

3.2 | FT/IR spectra

The IR spectral data of the free ligand and its zinc coordination compounds were recorded in the range of 4000–400 cm⁻¹. Figure 1 depicts FT/IR spectra of ligand, ZnLCl₂ and ZnL (NCS)₂ complexes as typical ones. Table 2 summarizes some important vibrational frequencies of the zinc complexes as compared with free Schiff base ligand. In IR spectrum of the free ligand, the absence of functional group vibration at 1685 cm^{-1} for (-C=O) of the aldehyde and stretching vibrations of - NH_2 group of amine at 3285 cm⁻¹, and appearance of a new strong vibration peak at 1633 cm⁻¹ assigned to azomethine stretching frequency, ν (C=N), well support the formation of the Schiff base ligand.^[37,38,50] This vibration peak shifts towards higher frequencies at 1635–1639 cm⁻¹in the zinc complexes. It is to be noted that in many Schiff base complexes^[53-55] the stretching frequency of iminic (-C=N) shift to lower frequencies after coordination attributing to the π -back bonding of metal (d¹⁰) to π^* of azomethine bond of ligand.^[56] But according to the other literature^[57,58] –C=N stretching vibration in some Schiff base complexes shift to higher frequencies that can be explained based on a limitation in resonance of π -electrons during the ligand structure due to coordination of azomethine nitrogen to metal center according to our previous report.^[53] The sharp peaks

appearing at 1523 and 1346 cm⁻¹ of ligand spectrum are safely assigned to the asymmetric (asym) and symmetric stretching (sym) of $-NO_2$ groups. As shown, in the zinc complexes spectra these strong peaks change a few wavenumbers. Very strong signals at 2075, 2059, and 1087 cm⁻¹ in the IR spectra of the complexes ZnL (NCS)₂ and ZnL(N₃)₂ ZnL (ClO₄)₂ are safely assigned to the coordinated *N*-NCS⁻, N₃⁻, and ClO₄⁻ ions, respectively.^[59] Finally, vibrational signals in all zinc complexes spectra at the range of 408–446 cm⁻¹ that are not present in the free ligand that well were assigned to the existence of Zn–N bonds confirming coordination of ligand to zinc ion center.^[16]

3.3 | UV-visible spectra

Electronic spectral data of the ligand and its zinc (II) coordination compounds in DMF solvent $(10^{-5} \text{ mol } \text{L}^{-1})$ were recorded in the range of 200–500 nm at room temperature (Table 2). In the UV-visible spectrum of the free Schiff base ligand, a distinct and a shoulder absorption band appear. These bands are observed at 267 and 319 nm, respectively, that are attributed to π - π * transition of benzene rings, an olefin moieties, and imine groups.^[51,60] In all title zinc complexes spectra, these bands have a red shift to longer wavelengths by 2-8 nm confirming well binding of the ligand to zinc ion center. Zinc (II) complexes do not show any d-d electronic transition because of its completely filled d¹⁰ transition. The electronic spectra of the Schiff base and its zinc complexes are shown in Figure 2.



FIGURE 1 Infrared spectra of (a) ligand, (b) ZnLCl₂, and (c) ZnL (NCS)₂ complexes



FIGURE 2 Electronic spectra of the ligand and its zinc (II) complexes

3.4 | NMR spectra

In continuation of FT/IR and UV–visible spectral analyses, the ligand and its zinc complexes were subjected to ¹H and ¹³C NMR spectroscopy. The spectral data have been tabulated as Tables 3 and 4. The ¹H and ¹³C NMR spectra of the ligand and zinc iodide complex are observed in Figure 3 as typical ones. A comparative assignment of the NMR signals of the complexes with respect to the free ligand based on Scheme 1 can well confirm their formation in current conditions. Characteristic signal of the Schiff base ligand assigned to azomethine protons of **dd**' appearing as a doublet at 8.17 ppm. In the complexes spectra, the signals in the range of 8.28–8.60 ppm can be safely attributed to the azomethine group protons. This is a powerful evidence indicating coordination of azomethine Schiff base to zinc center. The aromatic signals of the free ligand protons of gg' and jj' as doublet and also ii' and hh' as triplet peaks are found at 8.03, 7.63, 7.96, and 7.76 ppm, respectively. These signals are smoothly upfielded or downfielded after coordination of ligand to metal center and appeared in the range of 8.06-8.13, 7.61-8.08, 7.66-7.80, and 7.46-7.83 ppm, respectively. The olefinic protons of **ff'** and **ee'** in the free ligand structure are observed as doublet of doublet and doublet peaks at 7.36 and 6.95 ppm that shift to the downfielded regions of 7.38-7.74 and 6.86-7.07 ppm after coordination of the ligand, respectively. Aliphatic hydrogens signals of cc', bb', and aa' are found at 3.60-3.57, 1.26, and 0.88 ppm as multiple or broad singlet signals. These signals are downfielded and appeared in the regions of 3.64-3.8, 2.68-3.19, and 2.63-2.88 ppm in the zinc complexes spectra. Finally amine protons(-NH groups) peak



FIGURE 3 The HNMR spectra of ligand (a) and zinc iodide complex (b)

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appears at 3.2 ppm that notably is downfielded and observed in the region of 3.46–3.92 ppm due to coordination of amine nitrogen atoms of free ligand to zinc ion. Along with ¹H NMR, assignment and comparison of ¹³C NMR spectral data (as Table 4) confirmed synthesis of the ligand and its complexes. The azomethine carbons ($C_{4,4'}$) peak as characteristic carbon signal of free ligand appears at 163.15 ppm. This signal shifts to weak fields in the range of 165.03–167.90 ppm in the complexes spectra due to binding of azomethine groups to zinc ion. Other aromatic, alkenic and aliphatic carbon signals in the complexes spectra with downfielding or upfielding shift with respect to free ligand as found in Table 4 are in agreement with suggested structure in Scheme 1.



FIGURE 4 X-ray powder diffraction patterns of (a) ZnLCl₂, (b) ZnLI₂, and (c) ZnL (NO₃)₂

3.5 | XRD analysis

For preparation of the zinc complexes in nanostructure format, the synthetic procedure was run under sonochemical conditions in an ultrasonic bath. XRD



FIGURE 5 The scanning electron microscopic images of (a) ZnLCl₂, (b) ZnLI₂, and (c) ZnL (NO₃)₂ complexes

pattern of the synthesized complexes of zinc chloride, iodide and nitrate are shown in Figure 4. The diffraction intensities were recorded in 2θ angles from 10° to 80° . The expanding of the peaks in the XRD patterns indicates that the products have nano scale dimensions. The observed pattern for the zinc chloride matches with the reference of JCPDS File with No = 96-152-8213 with the highest intensity in 2θ rang of 13.01° , for the zinc iodide complex matches with the reference (JCPDS No. 96-900-9138) with the highest intensity in 2θ rang of 13.48° and finally for the zinc nitrate complex matches with the reference (JCPDS No. 96-210-7051) with the highest intensity in 2θ rang of 11.61°. Also, the average sizes of nanostructured ZnL Cl₂, ZnLI₂, and ZnL (NO₃)₂ estimated by using the Debye–Scherrer equation $(D = k\lambda/\beta\cos\theta)^{[61]}$ were 6.05, 4.33, and 5.77 nm, respectively.

3.6 | SEM and EDAX of the titled compounds

The morphology, structure and size distribution of nanostructured zinc chloride, iodide, and nitrate complexes



FIGURE 6 EDAX analysis data of (a) ZnLCl₂, (b) ZnLl₂, and (c) ZnL (NO₃)₂ complex

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were investigated by SEM technique. The SEM images in Figure 5 show that the morphology of the zinc chloride, iodide and nitrate complexes are sheet shape in the solid state with the average size of about 20-40 nm in dimension. A size evaluation on SEM images indicates that the nanostructure sizes of the zinc complexes are agreement with the calculated sizes based on XRD data using Scherrer's equation.

The EDAX of nanostructured zinc chloride, iodide, and nitrate complexes showed the presence of carbon, nitrogen, and zinc as the elementary components (Figure 6).

Characterization of zinc oxide 3.7 nanoparticles

Zinc iodide complex was used as precursor for preparation of zinc oxide nanoparticles. For this mean a difinite amount of zinc iodide complex was heated to 500°C for about 4 h, and then the residual material was characterized by XRD as shown in Figure 7. The crystal planes of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), and (2 0 0) are corresponded to the hexagonal phase of ZnO, with the lattice parameters (a = b = 0.3250 nm, c = 0.5207 nm, and z = 2), which are close to the reported values, (JCPDS cards number 96-210-7060).^[48] From the Debye-Scherrer equation, the crystallite size of the prepared ZnO nanoparticles was calculated to be about 10.11 nm. Finally, the SEM image of prepared zinc oxide nanoparticles shows agglomerated and non-uniform spherical particles with diameters of nano-dimension (Figure 8). Finally, nanoparticles of zinc oxide were characterized by energy-dispersive X-ray diffraction (EDX), as shown in Figure 9. Zinc and oxygen atoms were elementary components in the structure of ZnO nanoparticles with the highest percentage.



102)

100)

(002)

1200

1000

800

600 400

Intensity

from calcination of zinc iodide complex



FIGURE 8 SEM image of zinc oxide nanoparticles prepared by calcination of zinc iodide complex

Thermal investigation (TG/DTA) 3.8

In order to study the thermal stabilities and existence of water molecules inside or outside of the Schiff base ligand and its zinc (II) coordination complexes lattice, thermo-gravimetric (TG) and differential thermal analyses (DTA) were carried out under N2 atmosphere from ambient temperature to 900°C at the heating rate of 20°C/min. Figure 10a-h present TG/differential thermal gravimetric (DTG)/DTA diagrams of the ligand and its zinc complexes, and Tables 5 and 6 summarize all TG data including the thermal decomposition steps, temperature range, mass loss (%), proposed lost segment, final residues, and kinetic activation parameters of each thermal decomposition steps of the ligand and its zinc complexes. No weight loss was observed under 200°C



FIGURE 9 EDAX pattern of zinc oxide nanoparticles prepared by calcination of zinc iodide complex



FIGURE 10 Thermo-gravimetric/differential thermal gravimetric (TG/DTG) plots of (a) Schiff base ligand, (b) ZnLCl₂, (c) ZnLBr₂, (d) ZnLI₂, (e) ZnL (NO₃)₂, (f) ZnL (NCS)₂, (g) ZnL(N₃)₂, and (h) Zn (ClO₄)₂ complexes

confirming absence of water molecules in their structures. The Schiff base ligand loses almost whole of its mass during one step in the temperature range of $72-580^{\circ}$ C (more than 95.8%). On the other hand,

regarding suggested structure in Scheme 1, the zinc complexes have quite different thermal behavior. As a typical model, a proposed decomposition pathway for ZnLBr₂ complex is exhibited in Scheme 2. On heating the ZnLBr₂

Compound	Temperature range/ °C	Mass loss[found (calculated)]/ %	DTG peak/ °C	Proposed segment	Final residue
Ligand	72–580	95.8 (96.3)	326.1	$C_{24}H_{28}N_6O_4$	-
ZnLCl ₂	120-303	13.6 (14.9)	245.0	N_2O_4	0.35Zn
	303-416	7.9. (7.3)	365.4	$C_{10}H_4$	
	416-632	27.4 (26.1)	588.6	$C_{12}H_{12}N_2$	
	632–754	39.4 (38.8)	722.3	$C_{2}H_{6}Cl_{2}N_{2}Zn_{0.75}$	
ZnLBr ₂	72-376	31.3 (30.8)	486.0	$C_{12}H_6N_2O_4$	0.2Zn
	376-881	66.2 (67.6)	902.2	$C_{12}H_{22}Br_2N_2Zn_{0,8}$	
ZnLI ₂	124–388	18.0 (17.9)	308.5	$C_4 H_2 N_2 O_4$	0.25Zn
	388–588	32.4 (32.3)	548.1	$C_{20}H_{26}N_4$	
	588–790	44.1 (44.6)	662.9	$I_2 Zn_{0.75}$	
$ZnL (NO_3)_2$	132–319	49.0 (48.8)	216.7	$C_{18}H_{10}N_{2}O_{4}$	0.75Zn
	319–610	35.0 (36.5)	480.8	$C_{6}H_{18}N_{6}O_{6}Zn_{0.25}$	
ZnL (NCS) ₂	110-471	36.8 (37.5)	286.2	$C_{12}H_4N_2O_4$	Zn
	471–759	45.2 (46.3)	615.4	$C_{14}H_{24}N_6S_2$	
$ZnL(N_3)_2$	123–387	27.5 (26.8)	257.23	$C_6N_2O_4$	0.9Zn
	387-473	15.2 (14.3)	430.8	$C_{12}H_{12}N_2$	
	473–617	35.5 (36.5)	545.6	$C_6H_{16}N_8Zn_{0.1}$	
$ZnL (ClO_4)_2$	62–260	20.8 (19.4)	161.38	$C_4 H_2 N_2 O_4$	0.35Zn
	260-575	48.4 (49.6)	418.2	$C_{14}H_{10}Cl_{2}N_{2}O_{8}$	
	575-859	15.9 (16.4)	717.5	$C_6H_{16}N_2Zn_{0.75}$	

TABLE 5 Thermal analysis data of the Schiff base and zinc complexes including temperature range, mass loss, differential thermal gravimetric peak (DTG), proposed segment, and final residual

TABLE 6 Thermo-kinetic parameters of the thermal decomposition steps for the Schiff base ligand and its zinc complexes

	Decomposition					
Compound	step (°C)	E^{*} (kJ mol ⁻¹)	$A^{*}(s^{-1})$	ΔS^* (kJ mol ⁻¹ K ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔG^* (kJ mol ⁻¹)
Ligand	72–580	139.36	5.72×10^{11}	-2.56×10^{1}	134.38	1.50×10^2
$ZnLCl_2$	120-303	56.15	2.04×10^2	-2.05×10^{2}	51.84	1.58×10^2
	303-416	33.75	1.21×10^{-1}	-2.69×10^{2}	28.44	2.00×10^{2}
	416-632	33.69	5.71×10^{-3}	-2.97×10^{2}	26.52	2.82×10^2
	632–754	110.34	1.03×10^{-3}	-1.97×10^{2}	102.06	2.98×10^2
ZnLBr ₂	52-376	8.40	1.55×10^{-3}	-3.03×10^{2}	4.36	1.52×10^2
	376-881	18.63	3.08×10^{-4}	-3.21×10^{2}	11.12	3.01×10^{2}
$ZnLI_2$	124–388	45.95	4.56	-2.38×10^{2}	41.11	1.79×10^2
	388-588	65.42	7.80	-2.36×10^{2}	58.59	2.53×10^{2}
	588-790	48.23	4.31×10^{-2}	-2.81×10^{-2}	40.44	3.03×10^{2}
$ZnL(NO_3)_2$	132–319	89.49	7.43×10^{7}	-9.84×10^{1}	85.42	1.34×10^2
	319–610	17.32	6.42×10^{7}	-3.13×10^{2}	11.42	2.34×10^2
ZnL (NCS) $_2$	110–471	28.56	2.28×10^{-2}	-2.82×10^{2}	23.91	1.81×10^2
	471–759	58.95	4.35×10^{-1}	-2.61×10^{2}	51.56	2.83×10^2
$ZnL(N_3)_2$	123-387	13.82	8.42×10^{-4}	-3.09×10^{2}	9.41	1.73×10^{2}
	387-473	28.54	1.12×10^{-2}	-2.89×10^{2}	22.69	2.26×10^2
	473–617	45.95	1.14×10^{-1}	-2.71×10^{2}	39.14	2.61×10^{2}

Compound	Decomposition step (°C)	<i>E</i> [*] (kJ mol ⁻¹)	A * (s ⁻¹)	ΔS^* (kJ mol ⁻¹ K ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔG^* (kJ mol ⁻¹)
$ZnL (ClO_4)_2$	62–260	42.88	5.06×10^1	-2.15×10^{2}	39.27	1.33×10^{2}
	260-575	39.30	2.51×10^{-1}	-2.63×10^{2}	33.65	2.16×10^2
	575-859	24.62	5.61×10^4	-1.70×10^{2}	16.38	1.58×10^2



Trace amount of Zn

SCHEME 2 The proposed decomposition pathway for ZnLBr₂ complex

complex, the first decomposition step was occurred in the temperature range of 72°C to 376°C that may be assigned to the loss of C12H6N2O4 fragment with mass loss of 31.3% (calculated 30.8%). The second step of decomposition within the temperature range of 376°C to 881°C is attributed to the loss of suggested C12H22Br2N2Zn08 fragment with mass loss of 66.2% (calculated 67.6%). Some trace amount of zinc metal is suggested to be as final residue. ZnLI₂, ZnL(N₃)₂ and ZnL (ClO₄)₂ complexes are decomposed via three consecutive steps. Other compleses are decomposed as: ZnLCl₂ via four steps, and ZnL (NCS)₂ and ZnL (NO₃)₂ within two thermal steps. Similar to ZnLBr₂, Other complexes left out zinc or trace amount of zinc as final residual. The suggested segments eliminated from the complexes structures via thermal decompositions have been collected in Tables 5. Furthermore, thermo-kinetic parameters of decomposition processes of the compounds such as activation energy (ΔE^*), entropy of activation (ΔS^*), enthalpy of activation (ΔH^*), Arrhenius constant (A), and Gibbs free energy change of decomposition (ΔG^*) were evaluated graphically by use

of the Coats-Redfern relation^[62], and calculated data have been tabulated as Table 6. An overall view shows that the values of the activation energies are high, suggesting suitable thermal stability of the ligand and its zinc complexes. The lowest value of activation energy (8.4 kJ/mol) is related to the first thermal step of ZnLBr₂, while the highest value (139.36 kJ/mol) was evaluated for the first thermal step of the ligand. The positive values of ΔH^* in the range of 4.36 to 134.38 kJ/mol reflect the endothermic character of all thermal decomposition steps, and the positive values of the Gibbs free energy of activation (ΔG^*) in the range of (1.33 to 3.03) $\times 10^2$ kJ/mol revealed the non-spontaneous nature of thermal decomposition processes. Ultimately, the negative ΔS^* values for the compounds indicate diversity of degree of disorder during the thermal decomposition steps.^[63]

3.9 | In vitro antibacterial activity

The biological tests of the ligand and its zinc complexes by well diffusion method were assayed against E. coli and P. aeruginosa as Gram-negative bacteria and S. aureus and B. subtilis as Gram-positive bacteria. The compounds were prepared at 50, 25, and 12.5 mg/ml concentrations in DMSO solvent. Zone diameter of inhibition from the growth (mm) obtained from the experiments as antibacterial activities have been tabulated as Table 7 and depicted as column plots in Figure 11. All data of the antimicrobial results confirmed that coordination of ligand to zinc ion in all of the complexes leads to an increase in their biological activities that it can be explained on the basis of Overtones and Tweedy's concepts.^[64,65] This achievement is in agreement with some other previous studies showing metal complexes have higher activities against microorganisms than free Schiff base ligand. Based on data in Table 7, ZnL (NO₃)₂ complex is the most active compound against S. aureus and E. coli in concentration of 50 mg/ml. Other compounds showed nearly similar activity against S. aureus and E. coli. At this concentration, ZnL (NCS)₂ has minimum bactericidal effect against S. aureus and B. subtilis, whereas ZnL (ClO₄)₂ and ZnLCl₂ complexes showed maximum efficiency against B. subtilis and Pseudomons

TABLE 7Antibacterial activities of the ligand and its zinc complexes as diameter of zone of inhibition (mm) around the well againstbacteria

Gram-positive							Gram-negative					
Compound	Bacillu	s subtili	s	Staphyl	ococcus ai	ureus	Pseudon	nonas aeru	ginosa	Escherichia coli		li
	12.5 ^a	25 ^a	50 ^a	12.5 ^a	25 ^a	50 ^a	12.5 ^a	25 ^a	50 ^a	12.5 ^a	25^{a}	50 ^a
Ligand	10	13	20	9	11	20	4	5	5	8	10	10
ZnLCl ₂	10	18	22	19	19	20	7	8	13	9	12	14
ZnLBr ₂	15	19	23	18	18	23	5	5	12	10	11	11
$ZnLI_2$	16	19	20	15	20	21	5	5	6	10	11	12
$ZnL(NO_3)_2$	16	20	20	18	19	26	6	7	8	9	16	20
ZnL (NCS) ₂	13	18	19	15	16	19	4	4	5	11	11	14.2
$ZnL(N_3)_2$	9	10	21	20	21	22	5	6	6	12	15	16
$ZnL (ClO_4)_2$	11	17	25	15	16	20	2	3	4	9	10	18
DMSO		-	-		-	-	-	-	-	-	-	-

^aRefers to concentrations of the compound in mg/mL for well filling.





aureus, respectively. The lowest activity against all bacteria strains is related to free ligand. In the case of *Escherichia coli*, the antibacterial activity can be ordered as ZnL $(NO_3)_2 > ZnL (ClO_4)_2 > ZnL(N_3)_2 > ZnL (NCS)_2 > ZnLCl_2 > ZnLI_2 > ZnLBr_2 > Ligand at concentration of 50 mg/mL. It is to be noted that, against selected microorganisms, the complexes showed lower but acceptable values as compared with standard drugs including amoxicillin, penicillin, and cephalexin.^[48]$

In addition to the above bioassay, the MIC and MBC tests of all the compounds against all of bacteria

were performed, and the data have been compiled in Table 8. MIC and MBC values were obtained in the ranges of 2500–4.88 µg/ml for four types of bacteria. In fact, the samples with lower MIC and MBC display better antibacterial activity. According to the results of the antibacterial screening, $ZnL(N_3)_2$ with MIC value of 4.88 µg /ml and MBC 9.76 µg/ml against *E. coli* showed a better inhibitory effect than other compounds. ZnL (NO₃)₂ complex with MIC value of 39.06 µg/mL and MBC 78.12 µg/mL was more effective towards *P. aeruginosa* with respect to others. Among the zinc

TABLE 8 MIC and MBC values of the Schiff base ligand and its zinc complexes for inhibition from the growth in µg/mL

	Bacillus	subtilis	Staphyloc	occus aureus	Pseudomonas aeruginosa		Escherichia coli	
Compound	MIC	MBC	MIC	MBC	MIC	MBC	MIC	MBC
Ligand	625	1250	312.5	625	625	1250	312.5	625
ZnLCl ₂	78.1	156.2	78.1	156.2	39	78.1	78.1	156.2
ZnLBr ₂	78.1	156.2	19.5	39	156.2	312.5	156.2	312.5
ZnLI ₂	156.2	312.5	39	67.1	156.2	312.5	78.1	156.2
$ZnL (NO_3)_2$	39	78.1	9.7	19.5	78.1	156.2	39	78.1
ZnL (NCS) ₂	156.2	312.5	156.2	312.5	78.1	156.2	78.1	156.2
$ZnL(N_3)_2$	19.5	39	39	78.1	156.2	312.5	4.8	9.7
$ZnL (ClO_4)_2$	156.2	312.5	78.1	156.2	625	1250	9.7	19.5

complexes, $ZnL(N_3)_2$ showed the highest inhibitory effect with MIC and MBC values of 19.53 and 39.06 µg/mL against *B. subtilis*. Finally, ZnL (NO₃)₂ with MIC value of 9.76 µg/mL and MBC 19.53 µg/mL showed the most activity against *S. aureus* among the zinc complexes.

3.10 | In vitro antifungal activity

The in vitro antifungal studies of the free Schiff base ligand and its Zn (II) complexes were carried out against *C. albicans* and *A. orayzea* fungal strains. The bioassay resulting data as the diameter of inhibition zone from the growth (in mm), which was measured by using the well diffusion method, have been compiled in Table 9 and graphed as shown in Figure 11. Similar to the previous section, the results showed that the antifungal activity of ligand at the considered concentrations was very weak with respect to zinc complexes. ZnLCl₂ and ZnL (NCS)₂

TABLE 9 Antifungal activities of the ligand and its zinc complexes as diameter of zone of inhibition (mm) around the well against two fungi

	Candida albicans			Aspergillus niger			
Compound	12.5 ^a	25 ^a	50 ^a	12.5	25	50	
Ligand	4	4	5	4	5	5	
ZnLCl ₂	19	26	30	5	6	7	
ZnLBr ₂	12	15	17	7	9	10	
ZnLI ₂	19	20	21	8	9	11	
$ZnL (NO_3)_2$	19	25	25	5	5	8	
ZnL (NCS) ₂	10	13	15	6	7	18	
$ZnL(N_3)_2$	4	5	8	5	5	9	
$ZnL (ClO_4)_2$	4	6	9	4	4	6	

^aRefers to concentrations of the compound in mg/mL for well filling.

complexes showed excellent antifungal activities against C. albicans and A. orayzea, respectively. The general order of antifungal activities of compounds at concentration of 50 mg/mL against C. albicans is as follows: $ZnLCl_2 > ZnL (NO_3)_2 > ZnLI_2 > ZnLBr_2 > ZnL$ $(NCS)_2 > ZnL (ClO_4)_2 > ZnL(N_3)_2 > ligand and at the$ same concentration for A. orayzea is ZnL $(NCS)_2 > ZnLI_2 > ZnLBr_2 > ZnL(N_3)_2 >$ ZnL $(NO_3)_2 > ZnLCl_2 > ZnL (ClO_4)_2 > ligand.$ In this work, similar to many previous reports,^[47,48] binding of ligand to metal ion increases antifungal properties. In fact, after coordination of nitrogen donor sites of Schiff base ligand to zinc ion center, due to overlap of Schiff base ligand and metal ion valence orbitals, the positive charge of metal and π -electron delocalization in ligand are reduced and significantly lead to reduction of the polarity of the metal ion as well as an increase in the lipophilic character of the metal ion facilitating more diffusion of complex into cell membranes and also more effective blocking of the metal coordination sites of the enzymes of the bacteria and/or fungi,^[48] leading to stop of biochemical functions and then their death.

3.11 | DNA cleavage potential

The DNA cleavage ability of the free ligand and its zinc complexes were examined via investigation of their interactions with extracted DNA of *E. coli* using agarose gel electrophoresis method. The results of the interaction of compounds with DNA have been shown in Figure 12. According to this method, DNA transfers under the influence of the electrical field on agarose gel. These changes are illustrated in the gel electrophoresis by the intensity of the bands. Lanes A to G refer to the mixture of DNA with ZnLCl₂, ZnLBr₂, ZnLl₂, ZnL (NO₃)₂, ZnL (NCS)₂, Zn(N₃)₂, and ZnL (ClO₄)₂, respectively. Lanes La, P, H, and L are attributed to ladder, the control DNA 16 of 17 WILEY Journal of Physical Organic Chemistry



FIGURE 12 Gel

electrophoresis photograph for DNA cleavage activities of free ligand and its zinc coordination compounds. Lanes A to G: ZnLCl₂, ZnLBr₂, ZnLI₂, ZnL (NO₃)₂, ZnL (NCS)₂, ZnL(N₃)₂, and ZnL (ClO₄)₂, respectively, lane La: ladder, lane P: (DNA alone), lane H: (DNA + H₂O₂) and lane L: (free ligand+ DNA)

(DNA alone), the mixture of DNA and H₂O₂ and free ligand plus DNA, respectively. If any compound behaves similarly to H₂O₂, it is suggested to be a good cleaver agent, while the appearance of DNA band similar to lane P indicates the lack of cleavage potential for the compound. As shown in Figure 12, lanes A (ZnLCl₂), B (ZnLBr₂) and C ZnLI₂ correspond to the completely degraded DNA so that the DNA band is not observed (as compared with lanes P and La). According to Figure 12, it is obvious that complex of ZnL (NCS)₂ (lane E) has moderate activity for DNA cleavage but ZnL $(NO_3)_2$ complex and ZnL $(ClO_4)_2$ (lanes D and E) are better than other complexes to cleave DNA. $ZnL(N_3)_2$ complex (lane F) has the least activity for DNA cleavage. It is worth mentioning that the free Schiff base ligand has partial potential for the DNA cleavage as compared to its zinc complexes. The higher activity of the zinc complexes may be due to their efficient DNA binding ability via coordination of donor sites of DNA to the central metal ion leading to more deformations of DNA by them.

4 | CONCLUSIONS

In this study, the synthesis and characterization of a novel N_4 -Schiff base ligand and its zinc (II) complexes with general formula of ZnLX₂ were described. Six coordination number with octahedral geometry are suggested for them. Molar conductivity measurements indicated molecular character for the complexes. Some zinc complexes were prepared as nanostructured compounds and then were used as precursor for synthesis of zinc oxide nanoparticles via direct calcination at 500°C under air atmosphere. XRD and SEM/EDX confirmed their nanostructure. Thermo-gravimetric analyses (TG/DTG) of the ligand and its zinc complexes showed that they are decomposed via one to four thermal steps and leave out some trace of zinc metal as residual. Moreover, some thermo-kinetics activation parameters such as ΔG^* , ΔH^* , ΔS^* , A, and E^* were calculated using Coats–Redfern relation. High values of activation energy confirmed the thermal stability of the compounds. Positive values of ΔH^* and ΔG^* at all steps suggest the endothermic character of decomposition of compounds. Finally, the antimicrobial activities of the titled compounds were revealed that free ligand has lower activity than zinc complexes. The DNA cleavage studies of the compounds were more efficient as compared with free ligand.

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