

Chemical and Biological Characterization of Newly Synthesized Drug Based Metal Complexes

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Abstract

The wide utilization of the anti-infection agents brought about the serious therapeutic issue of medication protection and general wellbeing concern. Synthesis of new antibiotics having more antibacterial activity has turned into an imperative errand to adapt to tranquilize protection issues. For this purpose, Synthesis of novel Schiff base ligand was done with a series of copper (II), cobalt (II), zinc (II), nickel (II), manganese (II), iron (II) complexes. The ligand and metal complexes were characterized by using different instruments like FT-IR, ¹H NMR, ¹³C NMR, Mass, Atomic absorption spectroscopy, Elemental analyzer, UV-visible Spectrophotometer, Evans balance and Conductivity meter. The synthesized ligand and transition metal complexes were tested against various bacteria and fungi. These studies demonstrated the enhanced activity of metal complexes against reported microbes when compared with free Schiff base ligand.

Introduction

The rise of safe human pathogens is a noteworthy issue in current antimicrobial treatment, urging endeavors to synthesize new drugs. Metal complexes were observed to be especially valuable in this issue, as contributing in drug designing. Schiff bases have assumed an extraordinary part in metal coordination science because of stability under different type of reaction i.e. reductive and oxidative conditions and to the way that they are fringe amongst soft and hard Lewis bases [1].

Schiff bases have been reported by Hugo Schiff. It is prepared by condensation of primary amines with carbonyl compounds. Schiff base sustain azomethine or imine ($-C = N$) group which coordinated with transition metal ions [2]. Schiff base ligands and their transition metal complexes have been studied extensively because of their wide use and applications in different fields.

Many drugs have improved pharmacological properties when forms Schiff base metal complexes. The Schiff base metal chelate have gained attention in fields like medicine and pharmaceutical because of wide spectrum of biological activities such as anti-inflammatory drugs, antimicrobial, antifungal, antispasmodic, tuberculosis, anti-cancer, anthelmintic, antioxidant and so forth [3-10].

Schiff bases include have a wide variety of applications in organic and inorganic chemistry. Aside from biological activities, Schiff bases are additionally utilized as catalysts, [11-13] dyes and pigments, [14,15] polymers [16,17] and corrosion inhibitors [18-20]. Schiff base assumed an impact part in the improvement of coordination science and were included as key point in the advancement of inorganic biochemistry and optical materials [21].

The metal complexes of Schiff base derived from different drugs are good antibacterial and antifungal agents. So present work has endeavored to broaden the extent of derivatization by giving more adaptability through Schiff base ligand. Here we report preparation, characterization and biological studies of new Schiff base transition metal complexes obtained from sulphadoxine and 2-hydroxybenzaldehyde

Materials and Methods

Pure chemicals and solvent were used throughout the studies. Sulphadoxine and 2-hydroxybenzaldehyde were taken from BDH while other chemicals and solvent were purchased from Alfa Aesar.

Microanalysis was performed utilizing normal strategies. Metals were assessed by atomic absorption spectroscopy. Basic investigation was resolved on a CE-440 Elemental analyzer, FT-IR spectra were recorded with a Perkin Elmer Spectrum-100 spectrometer utilizing KBr plates. ^1H NMR, ^{13}C NMR spectra were measured on a Jeol ECS 400 spectrometer. Mass spectra were measured with the assistance of Thermo Scientific Exactive TM Plus Orbitrap spectrometer. Thermogravimetric examination for the buildings were completed on a SDT-Q600 instrument. Magnetic moments were estimated using Evans balance with anhydrous calcium chloride. Electronic absorption spectra of all the complexes were recorded on a Shimadzu-1800 spectrophotometer. Jenway-4510 conductivity meter was used for conductance measurement of the complexes by using DMSO (10^{-3} mol L^{-1}) as a solvent.

Preparation of Schiff Base Ligand

2.0mmole of sulphadoxine was dissolved in 2ml (1N) sodium hydroxide. To this ethanolic solution of 2-hydroxybenzaldehyde (2.0 mmole) was added and refluxed for one hour. After this ligand was collected by crystallization. The crystalline product was washed with alcohol, dried under vacuum and kept in a desiccator for further use.

Preparation of Schiff Base Metal Complexes

Preparation of copper (II), cobalt (II), zinc (II), nickel (II), manganese (II), iron (II) complexes were done by using the same protocol as described in literature. The salts and ligand were dissolved in ethanol separately and combine with 2:1 proportion. The reaction mixture was then refluxed for 1h. After preparation, the colored precipitate of Schiff base ligand was filtered off, washed with water, ethyl alcohol and dried under reduced pressure at room temperature.

Biological Assay

In vitro antimicrobial and antifungal tests were estimated by agar well diffusion method [22]. The antimicrobial activities of synthesized compounds were investigated against *Escherichia coli*, *Enterobacter aerogenes*, *Staphylococcus aureus*, *Bacillus pumilus*, *Klebsiella oxytoca* and *Clostridium butyrium*. *Mucor* and *Aspergillus niger* were used for antifungal studies.

Results

The results obtained after characterization are reported as below:

Synthesis of *N*-4-(2-hydroxybenzylideneamino) - (5,6-dimethoxy-4-pyrimidine) benzene sulfonamide.

Yield 70% (yellow). m. p. 218-220°C. IR (KBr, cm⁻¹) 3442 (OH), 1617 (HC=N azomethine), 1570 (C=N-pyrimidine), 1151(O=S=O), 1082 (C-N).

Anal. Calcd. For C₁₉H₁₈N₄O₅S (414.45); Calcd: C,55.01; H, 4.34; N, 13.51; Found: C,55.09; H, 4.25; N, 13.43%.

¹H NMR (DMSO-D₆, δ ppm) 10.21 (NH), 8.93 (-CH=N), 7.81-6.94 (phenyl) 3.57-3.70 (OCH₃); ¹³C NMR (DMSO-D₆, δ ppm) 164.5 (-CH=N), 146.2 (C-S=O), 112.4-160.8 (phenyl), 58.3-58.8 (OCH₃). MS (EI); m/z (%) = 415.4501 [M⁺].

Copper (II) Complex of Ligand

Yield 79% (Green). m. p. (decomp.) 265-268°C. IR (KBr, cm⁻¹) 3250 (OH), 1614 (HC=N azomethine), 1581 (C=N- pyrimidine), 1153 (O=S=O), 430 (M-N), 383 (M-O).

UV (DMSO) λ_{max} (cm⁻¹) 16611, 24630; B.M (1.90μ_{eff}); molar conductance (147μS cm⁻¹). Anal. Calcd. For C₃₈H₃₆N₈O₁₀S₂Cu (928.44); Calcd: C,49.11; H 3.87; N, 12.06; Co, 6.84 Found: C,49.22; H 3.89; N, 12.15; Cu, 6.92%.

Cobalt (II) Complex of Ligand

Yield 75% (Pink). m. p. (decomp.) 279-282°C. IR (KBr, cm^{-1}) 3460 (OH), 1615 (HC=N azomethine), 1582 (C=N- pyrimidine), 1197 (O=S=O), 481 (M-N), 345 (M-O).

UV (DMSO) λ_{max} (cm^{-1}) 17668, 25575; B.M (4.26 μ_{eff}); molar conductance (110 $\mu\text{S cm}^{-1}$). Anal. Calcd. For $\text{C}_{38}\text{H}_{36}\text{N}_8\text{O}_{10}\text{S}_2\text{Co}$ (923.83); Calcd: C,49.35; H 3.89; N, 12.12; Co, 6.37 Found: C,49.22; H 3.89; N, 12.15; Co, 6.92%.

Zinc (II) Complex of Ligand

Yield 73% (Orange) M. p. (decomp.) 269-272°C. IR (KBr, cm^{-1}) 3378 (OH), 1612 (HC=N azomethine), 1573 (C=N- pyrimidine), 1182 (O=S=O), 454 (M-N), 340 (M-O).

UV (DMSO) λ_{max} (cm^{-1}) 29325; Diamagnetic; molar conductance (119 $\mu\text{S cm}^{-1}$). Anal. Calcd. For $\text{C}_{38}\text{H}_{36}\text{N}_8\text{O}_{10}\text{S}_2\text{Zn}$ (930.28); Calcd: C,49.01; H 3.86; N, 12.03; Zn, 7.02 Found: C, 50.49; H 3.37; N,12.11; Zn,7.19%.

Nickle (II) Complex of Ligand

Yield 72% (Dirty Green) M. p. (decomp.) 262-266°C. IR (KBr, cm^{-1}) 3310 (OH), 1618 (HC=N azomethine), 1581 (C=N- pyrimidine), 1113 (O=S=O), 456 (M-N), 378 (M-O).

UV (DMSO) λ_{max} (cm^{-1}) 16122, 25000; B.M (2.96 μ_{eff}); molar conductance (89 $\mu\text{S cm}^{-1}$). Anal. Calcd. For $\text{C}_{38}\text{H}_{36}\text{N}_8\text{O}_{10}\text{S}_2\text{Ni}$ (923.59); Calcd: C, 49.37; H 3.89; N,12.12; Ni, 6.35 Found: C,50.01; H 3.55; N,12.23; Ni, 6.77%.

Manganese (II) Complex of Ligand

Yield 71% (Brown) M. p. (decomp.) 277-279°C. IR (KBr, cm^{-1}) 3255 (OH), 1614 (HC=N azomethine), 1581 (C=N- pyrimidine), 1155 (O=S=O), 433 (M-N), 342 (M-O).

UV (DMSO) λ_{max} (cm^{-1}) 17889, 23696; B.M (5.36 μ_{eff}); molar conductance (90 $\mu\text{S cm}^{-1}$). Anal. Calcd. For $\text{C}_{38}\text{H}_{36}\text{N}_8\text{O}_{10}\text{S}_2\text{Mn}$ (919.83); Calcd: C,49.57; H 3.91; N, 12.17; Mn, 5.97 Found: C,49.66; H 3.97; N, 12.22; Mn, 5.94%.

Iron (II) Complex of Ligand

Yield 75% (Reddish brown) M. p. (decomp.) 279-283°C. IR (KBr, cm^{-1}) 3236 (OH), 1624 (HC=N azomethine), 1581 (C=N- pyrimidine), 1151 (O=S=O), 475 (M-N), 362 (M-O).

UV (DMSO) λ_{max} (cm^{-1}) 28409, 31250; B.M (5.81 μ_{eff}); molar conductance (102 $\mu\text{S cm}^{-1}$). Anal. Calcd. For $\text{C}_{38}\text{H}_{36}\text{N}_8\text{O}_{10}\text{S}_2\text{Fe}$ (920.74); Calcd: C, 49.52; H 3.90; N, 12.16; Fe, 6.06 Found: C,51.03; H 3.98; N, 12.31; Fe,6.53%.

Discussion

The synthesis of ligand was accomplished by refluxing the sulphadoxine and 2-hydroxybenzaldehyde in a molar ratio 1:1 in ethanol as reported in literature. The metal complexes of ligand were prepared using metal chloride and ligand in a 2:1 molar ratio as shown in scheme1.

The structure elucidation of Schiff base and complexes was done with Elemental analyzer, FT-IR, ^1H NMR, ^{13}C NMR Mass spectroscopy, Thermo-gravimetric analysis and micro-analytical data. All the metal complexes are amorphous solids and have decomposition point. They are insoluble in water, organic solvents, partially soluble in acetone and completely soluble in DMF and DMSO. Molar conductance value ($75\text{--}144\mu\text{S cm}^{-1}$) point out the electrolytic nature of metal complexes. The structure of synthesized Schiff base ligand along with metal complexes were investigated by different techniques.

Spectroscopic Studies

The important infrared spectral bands of the synthesized Schiff base ligand were compared with the spectra reported in the literature on similar systems. FT-IR spectra of the ligand showed the absence of bands of carbonyl and amino and a new band appeared at $\sim 1617\text{ cm}^{-1}$ assigned to the azomethine ($\text{HC}=\text{N}$) linkage. This suggested that amino and aldehyde moieties of the starting reagents have been converted into their corresponding Schiff base.

^1H NMR and ^{13}C NMR Spectra were taken in d_6 -DMSO. The peaks of all the proton and carbon atoms were fixed in their expected region. The NMR spectra of Schiff base ligand was confirmed the absence of aldehyde peak at δ 9-10 and presence of azomethine at δ 8.93. ^{13}C NMR spectra also verify azomethine peak at δ 164.5.

FT-IR Spectra

The metal ligand bond was verified by comparing the FT-IR spectra of the Schiff base ligand with metal (II) complexes. The FT-IR spectra predicted all the absorption bands of the Schiff base ligand and some new bands at specific frequency confirmed the modes of absorption and the completion of the ligands with the metal ions through nitrogen and oxygen. The azomethine group of ligand was shifted to value $1614\text{--}1624\text{cm}^{-1}$ in all the complexes thus suggested the coordination of metal to ligand bond through azomethine ($\text{HC}=\text{N}$). Absorption bands of the sulfonamides moiety in the synthesized ligand and in metal complexes have same frequency. Further definitive proof of the coordination of the Schiff base with the metal ions were confirmed by the appearance new bands at $430\text{--}481$ and $340\text{--}383\text{cm}^{-1}$ designate to the metal nitrogen (M-N) and metal-oxygen (M-O) extending vibrations, individually [23]. These bands were not present in the spectra of the free ligand, therefore affirming the presence of O and N in coordination

Electronic Spectra and Magnetic Susceptibility

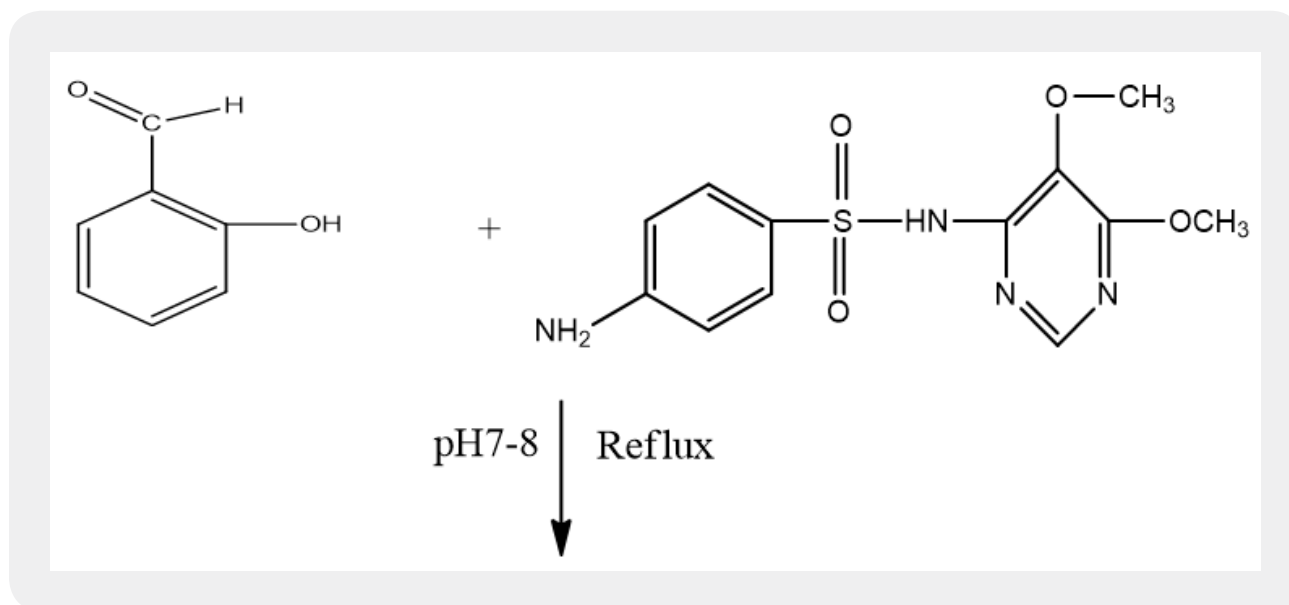
The studies of electronic absorption spectra of transition metal(II) complexes were recorded in DMSO. 10^{-3}M solutions of each complex was prepared and spectra were recorded in the range $2000\text{--}10000\text{cm}^{-1}$ at room temperature.

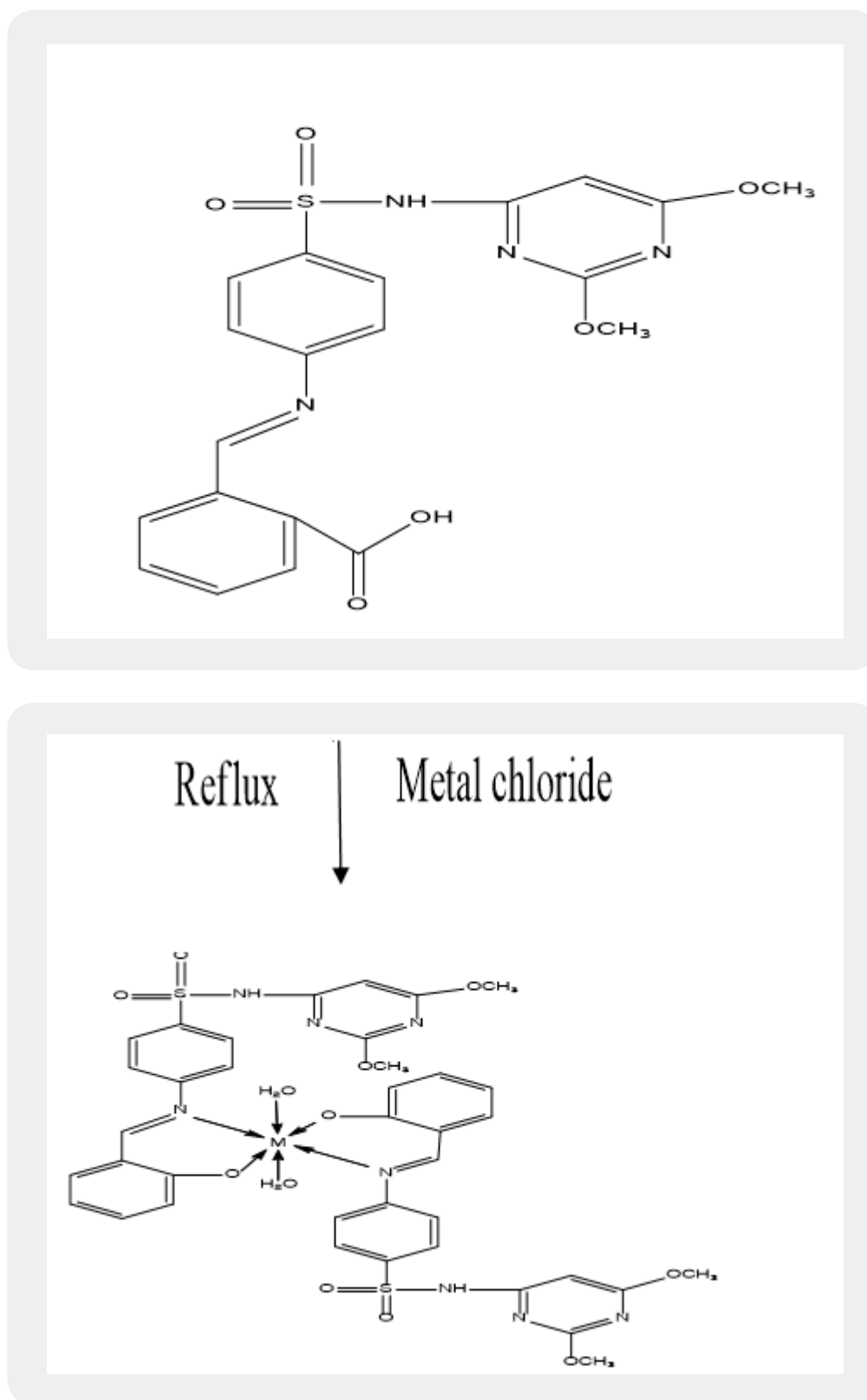
Table 1: UV-Visible assignment of metal complexes

Sr. No.	Metal complexes	λ_{\max} (cm ⁻¹)	Tentative assignment	B.M (μ_{eff})
1	[Cu(L-H) ₂ (H ₂ O) ₂]	16611, 24630	² B _{1g} → ² A _{1g}	1.90
2	[Co(L-H) ₂ (H ₂ O) ₂]	17688, 25575	⁴ T _{1g} (F) → ⁴ T _{2g} (F) ⁴ T _{1g} (F) → ⁴ T _{1g} (P)	4.26
3	[Zn(L-H) ₂ (H ₂ O) ₂]	29325	ligand → metal	Diamagnetic
4	[Ni(L-H) ₂ (H ₂ O) ₂]	16122, 25000	³ A _{2g} (F) → ³ T _{1g} (F) ³ A _{2g} (F) → ³ T _{1g} (P)	2.96
5	[Mn(L-H) ₂ (H ₂ O) ₂]	17889, 23696	⁶ A _{1g} → ⁴ A _{1g} (G) ⁶ A _{1g} → ⁴ A _{1g} , 4E _g	5.36
6	[Fe(L-H) ₂ (H ₂ O) ₂]	28409, 31250	³ A _{2g} (F) → ³ T _{1g} (P) ⁵ T _{2g} → ⁵ E _g	5.81

The electronic absorption spectra of metal complexes showed bands at specific wavelength which supports octahedral geometry as shown in table 1. Also, the magnetic moment value for all the complexes suggests the octahedral geometry.

The spectrum of Zn(II) complex exhibited only one band which was assigned to a ligand → metal charge transfer. The zinc (II) complex of ligand was observed to be diamagnetic obviously and in this manner, its magnetic properties could not be calculated [24-25].





Scheme 1: Proposed scheme for the synthesis of Schiff base ligand and metal(II) complexes

Thermal Studies

Thermogravimetric analyses (TGA) for the transition metal complexes were done from room temperature to 1000°C. Calculated and found mass losses are shown in Table below.

Table 2: Thermal Analysis Data of the Metal(II) Complexes of ligand

NO	Metal Chelates	Temperature Range(°C)	Mass Loss % Found (Calculated)	Assignment
1	[Cu(L-H) ₂ (H ₂ O) ₂]	110-238 238-520	3.44(3.87) 45.13(44.63)	Loss of 2H ₂ O Loss of L ₁
2	[Co(L-H) ₂ (H ₂ O) ₂]	105-250 250-552	2.89(3.89) 45.00(44.86)	Loss of 2H ₂ O Loss of L ₁
3	[Zn(L-H) ₂ (H ₂ O) ₂]	115-240 240-545	4.14(3.86) 44.86(44.55)	Loss of 2H ₂ O Loss of L ₁
4	[Ni(L-H) ₂ (H ₂ O) ₂]	120-235 235-565	3.78(3.86) 45.21(44.87)	Loss of 2H ₂ O Loss of L ₁
5	[Mn(L-H) ₂ (H ₂ O) ₂]	108-245 245-540	4.33(3.91) 45.11(45.05)	Loss of 2H ₂ O Loss of L ₁
6	[Fe(L-H) ₂ (H ₂ O) ₂]	120-250 250-560	4.24(3.90) 45.33(45.01)	Loss of 2H ₂ O Loss of L ₁

Biological Activity

Antimicrobial and Anti-Inflammatory Activities

Antimicrobial and antifungal activity of all the synthesized transition metal complexes and Schiff base ligand were tested against *Escherichia coli*, *Enterobacter aerogenes*, *Staphylococcus aureus*, *Bacillus pumilus*, *Klebsiella oxytoca*, *Clostridium butyrium*, *Mucor* and *Aspergillus niger* by using Ager well method. The results showed enhanced activity when coordinated with transition metals. It was reported previously that metal complexes suppressed the microorganism growth and involved in blocking the proteins. Presently, various bacterial strains

(*E. Coli*, *E. Aerogenes*, *S. Aureus*, *B. Pumilus*, *K. Oxytoa*, and *C. Butyrium*) and fungal strains (*A. Niger* and *Mucor*) were used to investigate the inhibitory effects of newly synthesized schiff base metal complexes. All compounds were found to be significantly active against bacterial and fungal strains when compared with ligand and reference drug. No significant different was found between reference drug and ligand for their antimicrobial activities. Metal complexes easily penetrate into the lipid membrane and block the enzymes in the microorganism. Metal complexes convert the super coiled DNA to open chain and cleave the DNA in the presence H_2O_2 [26-27].

Metal complexes	<i>E. coli</i> (mm)	<i>E. aerogenes</i> (mm)	<i>S. aureus</i> (mm)	<i>B. pumilus</i> (mm)	<i>K. Oxytoca</i> (mm)	<i>C. butyrium</i> (mm)	<i>A. niger</i> (mm)	<i>Mucor</i> (mm)
[Cu(LH) ₂ (H ₂ O) ₂]	29	19	30	19	19	27	18	22
[Co(LH) ₂ (H ₂ O) ₂]	22	15	24	14	15	22	13	15
[Zn(LH) ₂ (H ₂ O) ₂]	28	19	31	21	20	28	16	20
[Ni(LH) ₂ (H ₂ O) ₂]	26	15	32	17	17	25	13	15
[Mn(LH) ₂ (H ₂ O) ₂]	25	13	25	20	16	23	12	12
[Fe(L-H) ₂ (H ₂ O) ₂]	21	12	21	19	14	20	10	11

Conclusion

The results got after investigation demonstrate that after derivatization the antibacterial activities were enhanced against chosen bacterial strains. The metal complexes additionally demonstrate action against aspergillus niger and mucor though parent drug and ligand showed no antifungal activity. These observations, in accordance with different studies, prescribe that metal based drugs have potential as therapeutics.

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