



Environmentally Benign Synthesis, Structure Elucidation and Biological Studies of Indole Derived Schiff Base Complexes of Cu(II)

O.P. Putul & K.P. Srivastava*

Department of Chemistry

Jai Prakash University, Chapra (Bihar), INDIA

*Presently Principal, N.L.S.College, Jaitpur-Daudpur (Saran)

ABSTRACT

A highly efficient, environmentally benign and economical method has been used for the synthesis of indole derived four bidentate Schiff base ligands (L^1 to L^4) by condensation of 3-(2-aminoethyl) indole (tryptamine) with four different salicylaldehydes under microwave irradiation in solvent-free condition. The bivalent transition metal (Cu) complexes of synthesised ligands have been obtained in an environmentally safe microwave protocol and characterized by elemental analysis, conductivity measurements, magnetic moment and spectral analysis. The results were compared with conventional methods. The antimicrobial activity of the investigated ligands and their respective transition metal complexes clearly indicates that the complexes were found to be more active than the free ligands towards the tested microbes.

Keywords: *Tryptamine; Microwave irradiation; Schiff base; Microbial activity.*

INTRODUCTION

Due to varied biodynamic properties, indole nucleus and its derivatives occupied unique position in the chemistry of nitrogen heterocycles. The indole nucleus is present in a number of physiologically significant biologically active compounds, vis. serotonin, tryptophan, gramine, mitomycin, gliotoxin etc. [1-2]. Schiff bases have been very significant in the development of coordination chemistry due to their capability form stable complexes with the majority of the transition metals [3-6]. The Schiff base complexes have received careful attention in the field of bioinorganic chemistry due to their role in providing synthetic models for the metal-containing sites in metalloproteins and enzymes [7]. Literature survey revealed that the azomethine compounds i.e., Schiff bases not only have very good complexing ability towards metal ions but also have innumerable applications in the various fields namely pharmacy, medicine, agriculture, textiles, catalysis and polymer technology, photochemical reactions and toxins.

In recent years, environmentally benign synthetic methods have received considerable attention and some eco-friendly solvents or solvent-free protocols have been developed. Microwave-assisted reactions have gained popularity among synthetic chemists due to the drastic reduction in reaction times and minimization of secondary reactions [8]. The microwave heating has been employed as a frequent resource for improvement of classical reactions. The major benefits of performing reactions under microwave condition involved short reaction time, ease of isolation of products after easy work-up, significant rate enhancements and higher product yields as compared to reactions which run under conventional heating [9-10].

The present trend in chemical research on Schiff base complexes has gyrated towards elucidation of antibacterial and antifungal activities [11]. That is, such metal complexes may have the possibility to serve as anti-biological agents.



As a part of our continuing efforts to synthesize and characterize transition metal complexes using Schiff base ligands [12-14] under eco-friendly conditions, we now report the environmentally benign synthesis, characterization and anti-microbial activities of transition metal complexes containing Schiff bases derived from indole and aromatic aldehydes. Although, single crystal of the investigated complexes could not be isolated from any solutions; however, analytical, magnetic data and spectroscopic studies enable us to propose possible geometries of the investigated complexes.

EXPERIMENTAL SECTION

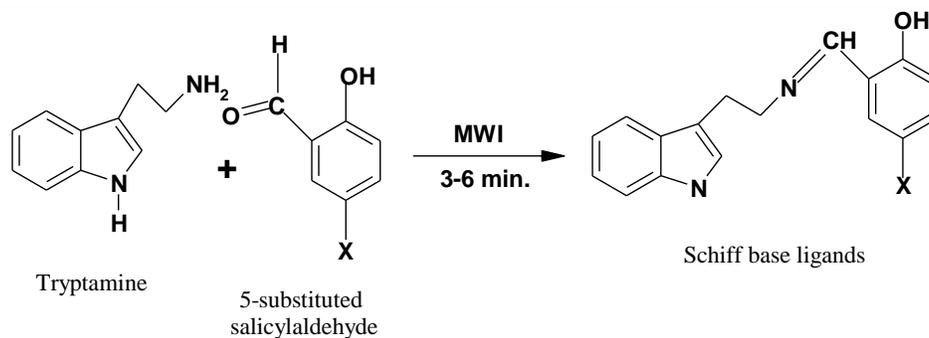
Materials and Methods

All the chemicals used for the synthesis were of analytical grade. The solvents were purified by standard methods. The melting points were measured on an Electro-thermal 9100 apparatus and are uncorrected. The conductivity measurements of the metal complexes were done in DMF bridge model PW 9501 using Philips PW 9515/10 conductivity cell. The elemental analyses were recorded on a Carlo-Ebra EA 1110 CNNO-S analyzer. The magnetic susceptibility of the investigated metal complexes was carried out by Gouy's method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ ($\chi_g = 16.44 \times 10^{-6}$) as a standard/reference. The electronic spectra in solid state as well as in solution were recorded on a Shimadzu UV-160, UV-visible spectrophotometer. The infrared spectra of the ligands and metal complexes were run as KBr discs in the range $4000\text{-}400\text{ cm}^{-1}$ on a Shimadzu Infrared Spectrophotometer. The microwave assisted syntheses were carried out in a modified microwave oven model 2001 ETB with rotating tray and a power source 230 V, at output energy of 800W and 2450 MHz frequency. A thermocouple device was used to monitor the temperature inside the vessel of the microwave oven. The microwave reactions were performed using on/off cycling to control the temperature. The progress of the reaction and purity of the products were monitored by thin layer chromatography (TLC) on pre-coated silica gel GF254 plates (E-Merck) by using appropriate solvent systems.

Synthesis of Schiff Base Ligands

Environmental friendly, economic, enhance reaction rate, less use of hazardous chemicals, low cost and better yield, and simplicity in processing and handling motivated us for solvent free synthesis of Schiff base ligands in a modified microwave oven.

An equimolar ratio of appropriate 4-substituted salicylaldehyde and tryptamine was mixed thoroughly in a grinder and the reaction mixture was taken in a 50 mL Erlenmeyer flask at ambient temperature and then irradiated in the microwave oven for the optimized time (3-5 minutes)(scheme-1). The resulting product was crystallized from ethanol and finally dried under reduced pressure over anhydrous CaCl_2 in a desiccator. The reaction was completed in a short time (3-6 min.) with better yields (80–89 %) than were obtained in the conventional method. The yield and the time required for conventional and green chemical approach have been compared and the results are reported in table-1.

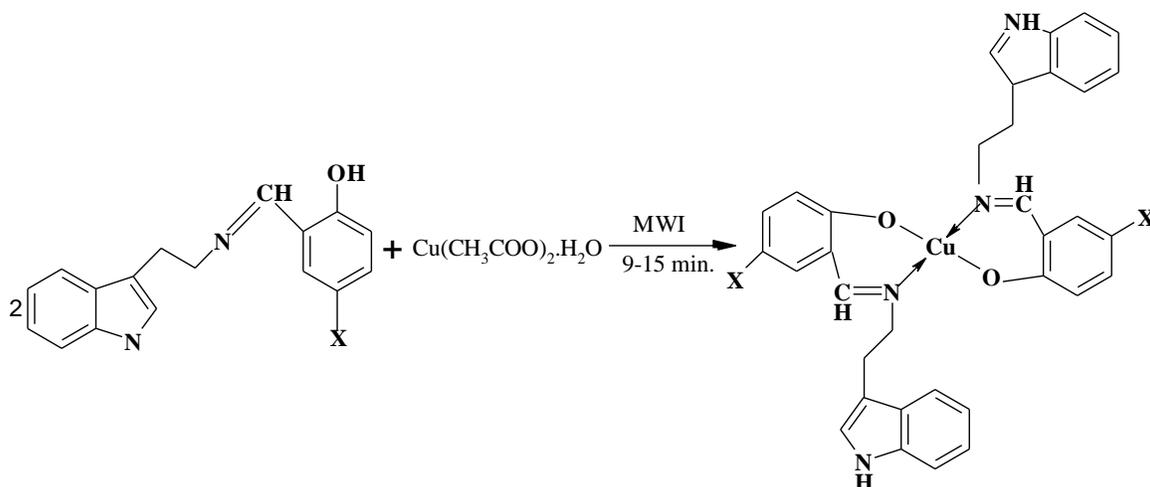


where X = H, Cl, Br & NO₂ for Ligand L¹, L², L³ & L⁴ respectively

Scheme-1: Synthesis of ligands through green chemical method

Synthesis of Metal Complexes

The desired metal complexes were prepared by adding stoichiometric (1:2, metal: ligand) ratio of hydrated metal acetate salts with ligands in a grinder and then the mixture was irradiated in the microwave oven taking 4-7 mL of dry DMF as the solvent and a few drops of triethylamine as a catalyst. The synthetic reactions were completed in a short time (9-15 min.) with better yields than were obtained by the conventional method (scheme-2). The resulting solid complexes were collected by filtration and recrystallized from DMF and washed with diethyl ether and finally dried under reduced pressure over anhydrous CaCl₂ in a desiccator. The progress of the reaction and purity of the products was monitored by TLC silica gel G (yield: 82-88%).



Scheme-2: Synthesis of metal complexes through green chemical method

Antimicrobial Activity

The antibacterial and antifungal activities of the investigated ligands [L₁-L₄] and their divalent metal complexes were performed by the disc diffusion method [15] using nutrient agar as medium for antibacterial activity and sabraoud dextrose agar medium for antifungal activity.



The in vitro antibacterial bases and their metal complexes were performed against two Gram positive bacteria namely *Staphylococcus aureus* (SA) & *Enterococcus faecalis* (EF), two Gram negative bacteria namely *Escherichia coli* (EC) & *Staphylococcus mutans* (SM) and the antifungal activity was tested against fungal strains *Candida albicans* (CA) & *Aspergillus niger* (AN). The chloramphenicol was used as a standard reference in the case of bacteria while griseofulvin was used as a standard for antifungal reference of the same concentration under identical conditions [16]. The tested compounds were dissolved in DMSO (no inhibition activity) to get concentration of 1 mg/mL. The sterile disks were soaked in test compounds and carefully placed on incubated agar surface. The petridishes were incubated for 24 hours at 37°C in the case of bacteria and for 48 hours at 37°C in case of fungi. Finally, the zone of inhibition was carefully measured. Each test was performed in triplicate in individual experiments and the average is reported (Table-5).

RESULTS AND DISCUSSION

All the microwave irradiated synthesized complexes are coloured, solid and stable towards air and moisture at room temperature. They do not possess sharp melting points and decompose on heating at higher temperature than 300°C. The investigated complexes are not soluble in common organic solvents. The micro-analytical data suggest that the composition of all the investigated metal complexes corresponds to 1:2 (metal:ligand) stoichiometry. The observed molar conductance values ($0.65 - 5.87 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) are too low to account for any dissociation of the complexes in DMF at room temperature., indicating their non-electrolytic nature [17].

It was observed that the synthetic reactions were completed in a short time with higher yields in the microwave assisted synthetic procedure compared to the conventional thermal method. This is because of the enhanced homogeneity of reaction mixture by the rotation of reaction platform tray in the microwave oven. The comparative results obtained by microwave assisted synthesis versus conventional thermal method shows that synthetic reactions which required 2-3 h by conventional method completed within 4-15 min. by the microwave irradiation technique and yields have been improved from 45-61% to 80-89%. The comparative results of conventional and green chemical methods, analytical data of the investigated complexes together with their physical properties consistent with proposed molecular formula are presented in table-1.

**Table-1**

The comparative results of conventional and microwave methods, analytical and physical data of the compounds under investigation

Compounds (Colour)	Reaction Time CM (MM)	Yield (%) CM (MM)	Mol. Weight	Melting point (in K)	Elemental analysis Calculated (Found) %			μ_{eff} (BM)	Conductance (ohm ⁻¹ cm ² mol ⁻¹)
					C	H	N		
C ₁₇ H ₁₆ N ₂ O Light yellow L ¹ H	2h (5m)	64 (87)	264.32	373	77.17 (76.99)	6.05 (6.04)	10.59 (10.23)	--	--
C ₁₇ H ₁₅ N ₂ O Cl Yellow L ² H	2h (3m)	67 (89)	298.77	383	68.34 (68.26)	5.06 (4.96)	9.38 (9.16)	--	--
C ₁₇ H ₁₅ N ₂ OBr Yellow L ³ H	3h (4m)	66 (88)	359.22	408	56.78 (56.82)	4.17 (4.20)	7.79 (7.82)	--	--
C ₁₇ H ₁₅ N ₃ O ₃ Light yellow L ⁴ H	3h (9m)	54 (82)	309.32	443	66.01 (65.97)	4.89 (4.79)	13.58 (13.6)	--	--
[Cu(L ¹) ₂] Brown	2.5h (12m)	56 (82)	590.18	487	69.13 (69.50)	5.08 (5.46)	9.48 (9.34)	1.76	3.10
[Cu(L ²) ₂] Pale green	2.5h (10m)	59 (84)	687.13	463	61.90 (61.78)	4.25 (4.32)	8.49 (8.52)	1.67	2.35
[Cu(L ³) ₂] Green	2.5h (9m)	61 (88)	777.58	511	52.47 (52.51)	3.60 (3.58)	7.20 (7.18)	1.69	0.65
[Cu(L ⁴) ₂] Green	2.5h (15m)	45 (83)	680.18	537	59.98 (59.62)	4.11 (4.32)	12.35 (12.17)	1.74	0.47

IR Spectral Studies

The data of the IR spectra of investigated Schiff base ligands and their metal complexes are listed in **Table-2**. The IR spectra of the complexes were compared with those of the free ligand in order to determine the involvement of coordination sites in chelation. Characteristic peaks in the spectra of the ligand and complexes were considered and compared. The FT-IR spectra of the investigated complexes contained all the absorption bands from the ligands and some new absorption bands indicative of coordination of the ligands with metal ion through N & O.

Table-2
Observed IR bands (cm⁻¹) of Ligands and their Cu-complexes

Compound	$\nu(\text{N-H})$	$\nu(\text{O-H})$	$\nu(\text{C-H})$ aliphatic	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{C-H})$ out of plane	$\nu(\text{M-O})$	$\nu(\text{M-N})$
L ¹ H	3420	3025	2936	1630	1281	746	--	--
L ² H	3434	3054	2919	1630	1281	746	--	--
L ³ H	3446	3057	2932	1627	1286	746	--	--
L ⁴ H	3360	--	2929	1647	1301	741	--	--
[Cu(L ¹) ₂]	3424	--	2901	1623	1326	743	579	427
[Cu(L ²) ₂]	3431	--	2913	1622	1324	739	453	421
[Cu(L ³) ₂]	3438	--	2919	1618	1336	736	455	421
[Cu(L ⁴) ₂]	3399	--	2913	1619	1301	739	553	446



On comparing the IR spectra of the ligand precursor, salicylaldehyde and the ligand itself, the absence of the characteristic aldehydic carbonyl group stretching band near 1700 cm^{-1} , and the appearance of the azomethine -C=N band at 1630 cm^{-1} indicating the formation of the Schiff bases. The broad band at $3049\text{-}2857\text{ cm}^{-1}$ could be attributed to the intra-molecular hydrogen-bonded O-H group [58]. The hydrogen bond arises between the azomethine nitrogen atom and the proton of the hydroxyl group [21]. The sharp band at 3420 cm^{-1} is due to the N-H stretching of the indole group. The C-O phenolic band appears at 1281 cm^{-1} , and the strong band at 746 cm^{-1} is attributed to the C-H out- of- plane aromatic bend.

In the case of Cu-complexes, it is clear that the hydroxyl band at 3049 cm^{-1} of the ligands was disappeared indicating deprotonation of the ligands, and confirming coordination of the phenolic oxygen atom to the metal [59]. This fact can also be supported further by the shifting of the C-O stretching band with respect to the same band in the free ligand. The azomethine stretching band in the free ligand shifts from 1630 cm^{-1} to 1623 cm^{-1} in the complex. This supports the participation of the azomethine nitrogen atom in coordinate bond to the metal center.

A new bands at 596 cm^{-1} and 489 cm^{-1} could be assigned to vibrations associated with Cu-O, and Cu-N bonds respectively [21,61].

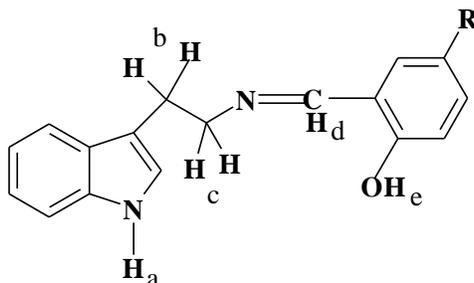
The comparison of the IR spectra of the ligand and its copper complex illustrates, principally, coordination to the copper centre is in two ways. The band appearing at 1614 cm^{-1} due to the azomethine linkage in the ligand is shifted to lower frequency by 20 cm^{-1} in the complex. This proves azomethine nitrogen interaction with the metal ion. A broad band centered at 3055 cm^{-1} assigned to O-H in the Schiff base was no longer found in the spectra of the metal complex. Instead, appearance of strong band at 1315 cm^{-1} due to C-O stretching vibration was observed, indicating deprotonation and coordination of the hydroxyl oxygen to the copper ion and the ligand acts as a bidentate ligand. Further conclusive evidence of the coordination pattern was provided by the appearance of weak intensity bands at 593 cm^{-1} and 490 cm^{-1} assignable to Cu-O and Cu-N vibrations respectively.

Thus, IR spectral data suggest monobasic bidentate N,O ligational behaviour of all the ligands.

NMR Spectral Studies

The NMR (^1H & ^{13}C) spectral studies of ligands aids the complete assignment of chemical shifts of protons directly attached to carbon and in turn confirms the formation of Schiff bases. The numbering scheme for the assignment of carbons and corresponding protons for ligands is given in Figure-1. The ^1H NMR spectra of all the ligands L^1 were recorded in d^6 -

DMSO with chemical shifts expressed in ppm using tetramethylsilane (TMS) as internal standard was given in table-3.



where R = H, Cl, Br & NO₂ in ligands L¹H, L²H, L³H and L⁴H respectively

Figure-1: Numbering of H-atoms in ligands L¹H, L²H, L³H and L⁴H

Table-4
Observed ¹H NMR spectra of the ligands and their Cu-complexes:

Compounds	H _a	H _b	H _c	H _d	H _e	H _{aromatic}
L ¹ H	10.79(s)	3.03(t)	3.85(t)	8.43(s)	--	6.81-7.32(m)
L ² H	10.80(s)	3.03(t)	3.85(t)	8.45(s)	--	6.82-7.42(m)
L ³ H	10.81(s)	3.03(t)	3.85(t)	8.44(s)	--	6.82-7.41(m)
L ⁴ H	10.89(s)	3.10(t)	3.90(t)	8.59(s)	--	6.52-7.98(m)
Cu-complexes	No clear spectra					

The indolic proton H_a appears as a singlet at 10.79-10.89 ppm, integration due to one proton. This position may be overlapping with the hydroxyl O-H proton when deuterated chloroform were used as a solvent [21] due to the effect of intra-molecular hydrogen bonding with the azomethine nitrogen atom [63]. The aliphatic (-CH₂-) protons H_b resonate as a triplet at 3.03-3.10 ppm and the other (-CH₂-) protons of the tryptamine moiety H_c also resonate as a triplet at higher frequency 3.85-3.90 ppm. The aldehydic proton H_d resonates as a singlet down field at 8.43-3.59 ppm, and the aromatic protons appears in the range 6.81 – 7.32 ppm as a multiplet integration indicates 9 protons altogether in L¹ but 6.52-7.98 ppm for other three ligands L², L³ & L⁴ respectively indicates 8 protons altogether due to the presence of substituents compared to the previous unsubstituted ligand L¹. The peaks at 2.50 and ≈ 3.40 ppm are solvent peaks.

No ¹H NMR spectra was detected for Cu complexes of the ligands because they are paramagnetic in solution.

**Electronic Spectral Studies & Magnetic Properties**

Electronic spectra of ligands and their complexes were recorded in order to assign the plausible geometry around the metal ions. The electronic spectra of all the compounds in DMF were scanned in the region 200-1000 nm.

The electronic spectra of the respective ligands and their copper complexes with their tentative assignments are given in table-4.

Table-4

Compounds	λ_{\max} (nm)	Assignments
L ¹ H	314	n - π^*
	291	π - π^* (chelate ring)
	283	π - π^* (chelate ring)
	267	π - π^* (indole group)
[Cu(L ¹) ₂]	365	CT, n - π^*
	283	π - π^*
	275	π - π^*
L ² H	420	n - π^*
	326	π - π^* (chelate ring)
	284	π - π^* (chelate ring)
	265	π - π^* (indole group)
[Cu(L ²) ₂]	373	CT, n - π^*
	293	π - π^* (ligand)
	260	π - π^* (ligand)
L ³ H	416	n - π^*
	323	π - π^* (chelate ring)
	281	π - π^* (chelate ring)
	261	π - π^* (indole group)
[Cu(L ³) ₂]	370	CT, n - π^*
	286	π - π^* (ligand)
	254	π - π^* (ligand)
L ⁴ H	420	n - π^*
	368	π - π^* (chelate ring)
	260	π - π^* (indole group)
[Cu(L ⁴) ₂]	383	CT, n - π^*
	261	π - π^* (ligand)

The spectra of the ligands show 4-3 absorption maxima. The intense bands at 316-420 nm could be attributed to n - π^* . The intensity of this band have been increased because of the additive effect of the two isolated chromophores (-CH=N-) and the chloro, bromo or nitro group in the fifth position of the benzene ring [69]. The band at 291-368 nm is due to π - π^* transition of the chelate ring. A bathochromic shift of this band in relation to the 314 nm band of L¹ ligand is due to the increased ketonic character of the phenolic C-O bond caused by the effect of electron withdrawal of the nitro group. The band at 260-265 nm could be assigned to π - π^* transition associated with the indole group.

The copper complex electronic spectra in DMSO shows bands at 365-383 nm, 261-293 nm and a weak band at 254-267 nm. The band at 365-383 nm is ascribed to the charge transfer between the metal and the ligand, while the band at 261-293 and 254-267 nm can be attributed to $\pi - \pi^*$ transition of the ligand. Also the ligand field d-d transition is not seen in the spectra, perhaps due to comparatively low molar absorptivity coefficient associated with this transition. The electronic spectra of investigated Cu(II) complexes with all the ligands are consistent with the *square planar geometry* [26]. The magnetic moment value observed for all the complexes supports the electronic transitions. An effective magnetic moment of 1.67-1.76BM observed for Cu(II) complexes is close to 1.73 BM expected for discrete magnetically non-coupled spin only value for Cu(II) ion [27].

In conclusion, the copper atom lies on a centre of inversion. It is N,O-chelated by the deprotonated Schiff base ligands in a square-planar coordination environment.

Proposed Structures

On the basis of the above observations, it is tentatively suggested that Cu(II) investigated complexes show square planar geometry [Figure-2] in which the ligands act as bidentate ligands.

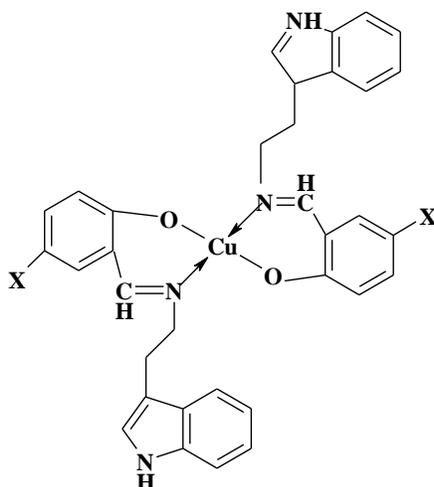


Figure-2: Proposed structures for investigated Cu(II) complexes

Anti-Microbial Activity

The difference in anti-microbial activities of the investigated complexes and ligands were studied and the results are presented in table-5.

A comparative study of MIC (Minimum Inhibitory Concentration) values of the ligands and their complexes (Table-5) indicates that the metal complexes generally have a better activity than the free ligands. Such an increased activity of the metal complexes is probably due to the greater lipophilic nature of the complexes which can be explained based on chelating theory



[36]. The antimicrobial results evidently show that the activity of the ligands has enhanced on coordination to the metal ion.

The antimicrobial activity reveals that the compounds exhibited better activity against the bacterial strains tested. The bacterium, *Staphylococcus Aureus* (SA) is found to be most susceptible one. Similarly, *Candida Albicans* (CA) is most susceptible among the fungal strains. From the *in vitro* antimicrobial assay, it is thus found that the tested compounds possess excellent antimicrobial activities even when compared with the standards used.

Table-5

In vitro Antimicrobial Activity of the ligands and their Cu-complexes (in $\mu\text{g mL}^{-1}$)

Compound	MIC($\mu\text{g/mL}$)					
	Bacteria				Fungi	
	Gram positive		Gram negative			
	SA	EF	EC	SM	CA	AN
L ¹ H	11	10	9	14	15	18
L ² H	9	8	12	9	16	13
L ³ H	8	11	15	11	10	13
L ⁴ H	7	9	13	9	16	15
[Cu(L ¹) ₂]	6	5	7	5	7	10
[Cu(L ²) ₂]	7	4	5	8	11	10
[Cu(L ³) ₂]	5	8	7	9	10	12
[Cu(L ⁴) ₂]	6	8	6	7	9	11
Chloramphenicol	0.25	1.5	2.3	1.7	3.2	3.5
Griseofulvin	--	--	--	--	8	11

CONCLUSIONS

Metal complexes of these ligands with Cu(II) have been obtained with good stoichiometric yields. Spectroscopic studies revealed that copper complexes adopt slightly distorted square planar geometry through coordination of the copper ion to phenolate oxygen and azomethine nitrogen atoms of two molecules of the Schiff base. Antimicrobial data suggests that the metal complexes are better antibacterial and antifungal agents as compared to their ligands.

In conclusion, this paper describes a simple, proficient and green approach for the synthesis of ligands and their Cu(II) complexes in green solvent media under MWI as green methodology. Present methodology offers very attractive features such as simple experimental procedure, higher yields and economic viability, when compared with other method as well as with other methodologies and solvents, and will have wide scope in organic/inorganic syntheses.

ACKNOWLEDGEMENTS

One of the authors (O.P. Putul) is thankful to Prof. U.S. Yadav, Dean, Faculty of Science, J.P. University, Chapra, Bihar for his kind cooperation and suggestion during the completion of his research project.



Conflicts of interest

The authors declare no conflict of interest.

REFERENCES

1. R.J.Sundberg; *The Chemistry of Indoles*, Academic Press, New York, **1970**, 10-50.
2. A. Bayer; *Chem. Ber.* **1880**, 13, 2254.
3. D.E.Fenton; *Chem.Soc. Rev.* **1988**, 17, 69-90.
4. S.R.Collinson and D.E.Fenton; *Coord. Chem. Rev.* **1996**, 148, 19-40.
5. P.A.Vigato and S.Tamburini; *Coord. Chem. Rev.* **2004**, 248, 1717-2128.
6. P.G.Cozzi; *Chem.Soc. Rev.* **2004**, 33, 410-421.
7. W.Radecka-Paryzek, V.Patroniak and J.Lisowski; *Coord. Chem. Rev.* **2005**, 249, 2156-2175.
8. N.E.Leadbeater; *Microwave Heating as a Tool for Sustainable Chemistry*, CRC Press, Boca Raton, Florida, USA, **2011**.
9. S.Caddick; *Microwave Assisted Organic Reactions, Tetrahedron*, **1995**, 51, 10403-10432
10. G.Majetic and K. Wheless; *In Microwave-enhanced Chemistry: H. M. Kinsington and S.J.Haswell, Eds, American Chemical Society; Washington, DC, 1997*, 455.
11. M.P.Sathisha, V.K.Revankar and K.S.R. Pai; *Metal Based Drugs*, **2008**, 1-11.
12. K.P.Srivastava, Sunil Kumar Singh and Bir Prakash Mishra; *Der Pharma Chemica*, **2015**, 7 (1), 121-127.
13. K.P.Srivastava and Anuradha Singh; *IOSR-Journal of Applied Chemistry*, **2016**, 9, 11 (III), 01-06.
14. K.P.Srivastava and Anuradha Singh; *Journal of Applicable Chemistry*, **2017**, 6 (4), 599-606.
15. D.Greenwood, R.Snack, J.Peurther, *Medical Microbiology: A guide to microbial infections: Pathogenesis, immunity, laboratory diagnosis and control*, 15th edn., **1997**.
16. R.Vijayalakshmi, M.Kanthimathi, V.Subramanian, B.U.Nair, *Biochem, Biophys, Acta.* **2000**, 1475, 157-164.
17. W.J.Geary, *Coord. Chem. Rev.*, **1971**, 7, 81.
18. S.G. Gruber, C.M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, **1968**, 30, 1805.
19. M.G. Martin Reyes, P. Gili, P. Martin Zarza, A. Medina and M.C Diaz; *Inorg Chim.*



- Acta*, 1986, 116, 153.
20. G.C. Peroy, *J. Inorg. Nucl. Chem.*, 1975, 37, 2071.
21. H. Dong; *J. Organometallic Chem.*, 2005, 690, 3714.
22. D. M. Adams, *Metal-ligand and related vibrations*, Edward Arnold, London, 1967, pp 248 & 284
23. S.A Abdel-Latif, H.B. Hassib, Y.A. Issa, *Spectrochim. Acta*, Part A, 2007, 67, 950-957.
24. G. D. Christian, *Analytical Chemistry*, 3rd edition, John Wiley and sons, New York, 1980
25. C. Biswas, S. Chattopadhyay, M. G. B. Drew, A. Ghosh, *Polyhedron*, 2007, 26, 4411.
26. R. Gup, B. Kırkan, *Spectrochim. Acta Part A*, 2005, 62, 1188.
27. K.P.Srivastava, O.P. Putul, Nagendra Kumar, *Der Pharma Chemica*, 2016, 8(3):105-116.