

Green and Efficient Synthesis, Characterization and Anti-Bacterial Activity of Copper (II) Complexes with Unsymmetrical Bidentate Schiff Base Ligands

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Abstract: A rapid, efficient, clean and environmentally benign exclusive synthesis of Schiff bases as new ligands and their complexes with Cu(II) have been developed using condensation of salicylaldehyde and amoxicillin (L^1), cephalixin (L^2), sulphamethoxazole (L^3) and trimethoprim (L^4) efficiently in analcoholic suspension medium using alkali catalyst with excellent yields under microwaves irradiation. This method provides several advantages such as environmental friendliness, simple work-up procedure, short reaction times, non-hazardous and excellent yield of products. The results are compared with conventional methods for their yield and reaction time. The Schiff base ligands and the complexes were characterized by micro-analytical, thermo-gravimetric, magnetic and spectroscopic studies. All the Schiff bases were bidentate (NO donor) ligands. Salicylidene sulphamethoxazole-Cu(II) monohydrate was five co-ordinate whereas all other complexes were found to be six co-ordinate dihydrates and ML_2 [1:2 (metal: ligand) ratio] type. The complexes are coloured and stable in air. All the complexes under investigation possess antibacterial activity. The antibacterial activity showed the following trend:

$Cu(II)$ -complexes > Schiff base ligands > parent drugs.

Keywords: Microwave irradiation; Schiff bases; Coordination compounds; Antibacterial activity; Copper

I. Introduction

As environmental consciousness in chemical research and industry has increased, efficient, economic and clean procedures have received increased attention in recent years. The development of a simple and effective method, using an environmentally friendly approach as well as an economical process is in great demand in coordination chemistry. Recent advances in technology have now made microwave energy a more efficient means of heating reactions. Chemical transformations that took hours, or even days, to complete their organic reaction, can now be accomplished in minutes. Microwave irradiation is well known to promote the synthesis of a variety of organic and inorganic compounds, where chemical reactions are accelerated because of selective absorption of microwave by polar molecules [1-5].

Schiff base ligands have been widely studied in the field of coordination chemistry mainly due to their facile syntheses, easily availability, electronic properties and good solubility in common solvents and they easily form stable complexes with most transition metal ions [6-11]. A large number of Schiff bases and their metal complexes have been found to possess important biological and catalytic activity. Due to their great flexibility and diverse structural aspects, a wide range of Schiff bases have been synthesized conventionally and their complexation behavior was studied. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species and were investigated for antifungal, antimicrobial, antibacterial, anti-inflammatory, anti-convulsant, anticancer activities [12-16].

Copper is the third most abundant and essential metallic element which has a biological role in sustaining life and has antibacterial property. A trace quantity of copper is required by all living organisms to maintain their proper cellular functions [17].

Application of green and sustainable chemistry protocols has seen enormous surge in recent times for the development of novel and eco-friendly methodologies towards the synthesis of valuable synthetic scaffolds and drug intermediates. Microwave syntheses of coordination and organometallic compounds are presented by relatively a small number of reports in the available literature in comparison with inorganic and organic synthesis. Prompted by the above mentioned biological and multifunctional activities of Schiff bases and their metal complexes as well as the utility of microwave irradiation in inorganic syntheses, in continuation of our efforts to synthesize novel heterocyclic molecules of biological importance [18-19], we envisaged a mild base mediated synthesis of some new Schiff bases of salicylaldehyde with amoxicillin (L^1H), cephalixin (L^2H), sulphamethoxazole (L^3H) and trimethoprim (L^4H) using alcoholic medium as a recyclable eco-friendly solvent under microwave irradiation without using any non-ecofriendly organic solvents and the products were isolated

simply by crystallization. We report the eco-friendly and efficient synthesis, structural characterization and antibacterial activities of synthesized new ligands and their complexes with Cu(II) ion in this research article.

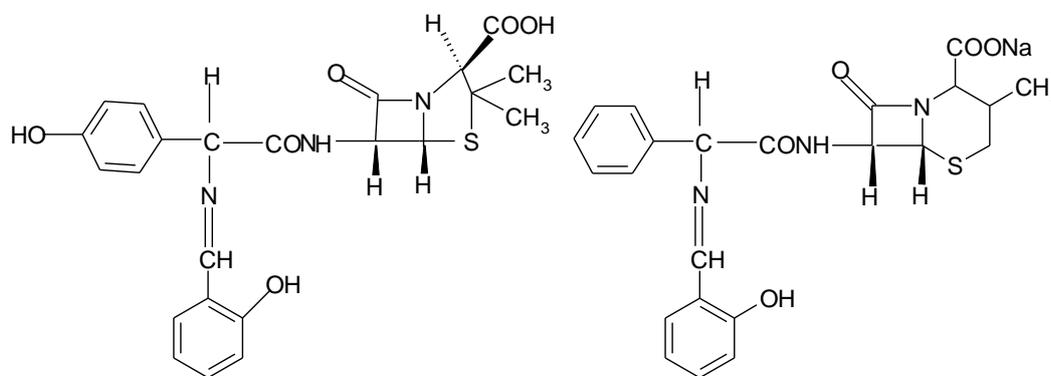
II. Experimental Section

Materials & Methods

All the used chemicals and solvents were of Anal R grade. All the reagents used for the preparation of the Schiff bases were obtained from Sigma Aldrich. Metal salts were obtained from Loba Chemie and original drugs were obtained from Glaxo SmithKline, India and were used without further purification. Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. All compounds were analysed satisfactorily for C, H and N using Carl-Ebra 1106 elemental analyser in micro analytical laboratory. Thin layer chromatography (TLC) was carried out on silica gel plates (Fluka-Kieselgel, 0.2 mm thickness) and the plates were scanned under 254 nm ultraviolet light. Magnetic susceptibility measurements of the metal complexes in the solid state were determined by a Gouy balance at room temperature. Electronic spectra (in DMSO solvent) in the UV-Visible range were recorded on Perkin Elmer Lambda-2B-spectrophotometer. Molar conductance measurements were conducted using 10^{-3} M solution of the complexes in DMSO on Elico-CM 82 Conductivity Bridge at room temperature. Magnetic susceptibility measurements were carried out on a Gouy balance at room temperature using mercuric tetrathiocyanato cobaltate(II) as the calibrant. Diamagnetic corrections were applied in compliance with Pascal's constant [20]. FT-IR spectra were recorded in KBr medium and Nujol mull techniques on a Perkin Elmer RX1 spectrophotometer in wave number region $4000-400\text{ cm}^{-1}$. The X-band EPR spectra were recorded in powder and solution (in DMF) forms on a Varian E-112 spectrometer at room temperature operating at the X-band region at a microwave frequency of 9.44GHz. The g values of investigated complexes were determined by the use of Kneubuhl approximation [21]. Thermogravimetric analysis was carried out under atmospheric condition with a heating rate $10^{\circ}\text{C min}^{-1}$ on TGA Q500 universal V4.5A TA instrument from ambient to 773K. The solid state electrical conductivity has been measured by impedance spectroscopic method using HIOKI 3532-50 LCR Hitester at fixed frequency 1 KHz in the temperature range of 298-473 K. Microwave assisted synthesis were carried out in open glass vessel on a modified microwave oven model 2001 ETB with rotating tray and a power source 230 V, microwave energy output 800 W and microwave frequency 2450 MHz. A thermocouple used to monitor the temperature inside the vessel of the microwave. The microwave reactions were performed using on/off cycling to control the temperature. Completion of reaction was monitored by performing TLC and melting point.

Synthesis of Ligands

The equimolar (1:1) ratio of methanolic solution of drug and methanolic solution of salicylaldehyde were mixed thoroughly and 0.1% methanolic KOH was added to adjust the pH of the solution within 7-8 and was then irradiated in the microwave oven by taking 3-4 ml solution. The reaction was completed in a short time (1-2 min) with higher yields showing clear coloured solution. The Schiff base ligands were isolated by crystallization after volume reduction by evaporation. The crystalline products were dried under vacuum or reduce pressure under anhydrous CaCl_2 and kept in a desiccator till further use. The progress of the reaction and purity of the products were monitored by TLC using silica gel G (yield: 75-89%).



L^1H = Salicylideneamoxicillin

L^2H = Salicylidenecephalexin

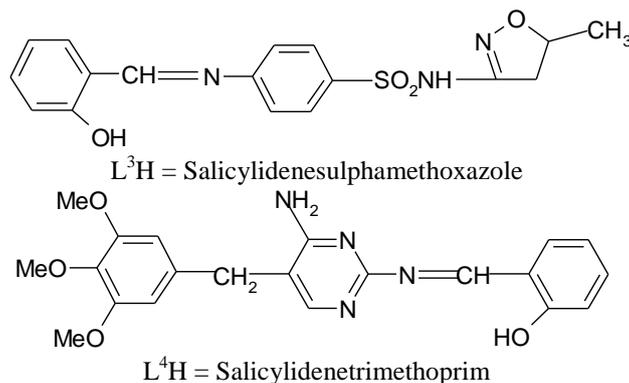
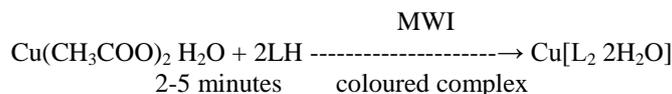


Figure-1: Structure Formulae of the investigated ligands

Synthesis of metal complexes

The methanolic solution of ligand and the metal salt were mixed thoroughly in 1:2 (metal : ligand) ratio and 0.1% methanolic KOH was added to adjust the pH of the solution within 7-8 and was then irradiated in the microwave oven by taking 3-4 ml solution. The reaction was completed in a short time (2-5 min.) with higher yields. The resulting coloured product was then recrystallized with methanol and ether and finally dried under reduced pressure over anhydrous CaCl₂ in a desiccator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 78.6-88.4%) (**Scheme-1**).



Scheme-1: Synthesis of metal complexes

Biological Evaluation

The *in vitro* biological activity of the investigated Schiff base ligands (L¹H –L⁴H) and their metal complexes was tested against three bacteria *Escherichia coli*, *P.aeruginosa* and *Staphylococcus aureus* by disc diffusion method [22] using nutrient agar as medium and streptomycin as control. The minimum inhibitory concentration was determined using the disc diffusion technique [23].

III. Results And Discussion

As a result of microwave assisted synthesis, it was observed that the reaction was completed in a short time with higher yields compared to the conventional method. In the microwave method homogeneity of reaction mixture was increased by the rotating of reaction platform tray. The confirmation of the results was also checked by the repeating of the synthesis process. Comparative study results obtained by microwave assisted synthesis; versus conventional heating method is that some reactions which required 2-3 h. by conventional method, was completed within 2-5 min. by the microwave irradiation technique, yields have been improved from 35-48% to 73-85%.

All the metal 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 high temperature (at about >563K). The complexes are insoluble in common organic solvents but soluble in DMF and DMSO. The comparative results of conventional and microwave methods, analytical data of the compounds, together with their physical properties are consistent with proposed molecular formula are given in **Table-1**. The microanalytical data suggest that the composition of all the metal complexes corresponds to 1:2 (metal: ligand) stoichiometry and have one or two water molecules i.e. hydrated. The observed molar conductance values (2.9 – 21.55 ohm⁻¹cm²mole⁻¹) are too low to account for any dissociation of the complexes in DMF at room temperature, indicating non-electrolytic nature of the complexes [24].

Table-1
The comparative results of conventional and microwave methods, analytical and physical data of the compounds

Compounds (Colour)	Reaction Time	Yield (%)	Elemental analysis Found (Calculated) %				Decomposition Point (°C)	Conductance (ohm ⁻¹ cm ² mol ⁻¹)
	CM (MM)	CM (MM)	C	H	N	Cu		
L ¹ H=Salicylideneamoxicillin (Orange)	0.5 (1.5)	39 (75)	58.07 (58.9)	5.13 (5.05)	8.76 (9.05)	--	194	16.5
L ² H=Salicylidenecephalexin (Yellow-orange)	0.5 (2.0)	45 (83)	60.84 (61.5)	4.92 (5.30)	9.19 (9.25)	--	193	21.5
L ³ H=Salicylidenesulphamethoxazole (Pale yellow)	0.5 (2.0)	42 (80)	57.04 (57.0)	4.26 (4.30)	11.12 (11.35)	--	197	4.0
L ⁴ H=Salicylidenetrimethoprim (Yellowish-green)	0.5 (3.0)	48 (89)	64.25 (64.0)	5.70 (5.60)	14.10 (14.4)	--	190	12.5
Cu-L ¹ 2H ₂ O complex Dark brown	2-3 (3.0)	35 (73)	53.11 (53.3)	4.41 (4.5)	8.02 (8.2)	6.23 (6.15)	196	12.8
Cu-L ² 2H ₂ O complex Brown	2-3 (3.0)	40 (79)	54.93 (55.2)	4.50 (4.6)	8.16 (8.25)	6.41 (6.35)	290	9.1
Cu-L ³ H ₂ O complex Dark yellow	2-3 (3.0)	45 (85)	51.54 (51.4)	3.63 (3.5)	10.72 (10.8)	8.09 (8.15)	231	2.9
Cu-L ⁴ 2H ₂ O complex Yellow green	2-3 (3.0)	41 (83)	56.70 (56.8)	5.19 (5.25)	12.67 (12.7)	7.22 (7.3)	230	10.4

CM = Conventional method, time in hours; MM = Microwave method, time in minutes

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 and O. The spectra of these complexes exhibited a broad band around 3380-3500 cm⁻¹ which is assigned to water molecules, ν(OH), associated with the complexes. The coordinated water exhibited, in addition to these modes, the ρ_r(H₂O), rocking near 892, 840 cm⁻¹, ρ_w(H₂O), wagging near 530-550 cm⁻¹[25]. The FT-IR spectra of all the ligands contained a band at 1619-1632 cm⁻¹, ν(C=N), which shifted slightly to a higher value in all the complexes suggesting that the ligands are coordinated through -C=N- [26]. The absorption due to carboxylic group did not change in the spectra of complexes indicating that the carboxylic groups are not involved in coordination with the metal ion. New absorption bands, ν(MN) and ν(MO), appeared at 435-460 cm⁻¹ and 335-355 cm⁻¹ respectively, in the spectra of the investigated complexes indicating coordination of the ligands through N and O.

The important bands along with their assignments are listed in **table-2**. The assignments were made by comparison with related Schiff base complexes[27-28].

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

Compound	ν(O-H)	ν(C=N)	ρ _r (H ₂ O)	ρ _w (H ₂ O)	δ (CO)	π (CO)	ν(M-N)	ν(M-O)
Salicylideneamoxicillin	3540	1615	892, 840	544	750	560	----	----
Salicylidenecephalexin	3500	1610	880, 845	540	740	575	----	----
Salicylidenesulphamethoxazole	3520	1625	885, 850	535	----	----	----	----
Salicylidenetrimethoprim	3480	1625	890, 845	545	----	----	----	----
Cu-L ¹ 2H ₂ O complex	3480	1630	885, 840	540	750	555	440	335
Cu-L ² 2H ₂ O complex	3472	1630	885, 845	545	750	580	438	335
Cu-L ³ H ₂ O complex	3380	1620	875, 841	535	----	----	455	345
Cu-L ⁴ 2H ₂ O complex	3475	1625	885, 850	545	----	----	442	345

Electronic Spectral Studies

The electronic absorption spectra show that when drug substances and salicylaldehyde were mixed together, the imine formation occurred which was indicated by colouration of the solution and development of an absorption band in the visible region [29].

In these spectra, there is an intense band at 240-294 nm which is assigned to a $\pi-\pi^*$ transition originating in the phenyl ring [30]. The bands in the 325-370 nm range, by analogy with LM, are attributed to a $\pi-\pi^*$ transition originating in the $-\text{CH}=\text{N}-$ chromophore. The low-energy broad absorption band in the range of 641-672 nm in the spectra of the investigated complexes arises from a d-d transition. The position of this is consistent with a distorted square-planar geometry [31]. The important electronic spectral bands along with their assignments of the isolated ligands and the complexes under investigation are listed in **table-3**.

Magnetic Moment Studies

The magnetic moments of the complexes under investigation were observed as expected and given in **table-3**. The complexes showed μ_{eff} values in the range of 1.97 – 2.32 B.M., indicative of one unpaired electron per Cu(II) ion suggesting that these investigated complexes had structures within the range consistent to mononuclear spin-free distorted octahedral geometry [32].

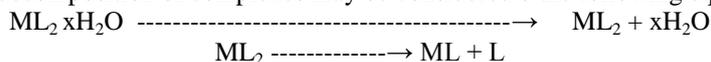
Table-3
Electronic spectral bands, magnetic moments and proposed geometry of the Cu(II) complexes

Compound	nm ($\epsilon, \text{cm}^2 \text{mol}^{-1}$)		Magnetic moments μ (BM)	Proposed geometry of complexes
	Ligand bands	d-d bands		
Salicylideneamoxicillin	220(20469), 240(18896), 350(4284)	----	----	----
Salicylidenecephalexin	210(21760), 250(15756)	----	----	----
Salicylidenesulphamethoxazole	210(7375), 270(4473)	----	----	----
Salicylidenetrimehoprim	210(15261), 90(3261)	----	----	----
Cu-L ¹ 2H ₂ O complex	220(7000), 241(6440), 352(1464)	650(635)	2.22	Octahedral
Cu-L ² 2H ₂ O complex	210(7444), 252(5389)	641(629)	2.17	Octahedral
Cu-L ³ H ₂ O complex	214(2565), 272(1526)	652(105)	1.97	Square-pyramidal
Cu-L ⁴ 2H ₂ O complex	212(2563), 293(1144)	662(485)	2.13	Octahedral

Thermo-analytical Studies

The thermal decomposition reactions of investigated complexes have been studied in N₂ atmosphere using TG and DTA techniques. Thermal decomposition curves (TG & DTA) are shown in **figure-1**, while the TG weight loss data and DTA peak temperatures are presented in **table-4**.

The complexes begin to lose weight around 353K show the presence of moisture and around 393K suggesting the presence of coordinated water; it is the dehydration stage which water molecules are eliminated. There was a weight loss equivalent to one water molecule in case of salicylidene sulphamethoxazole-Cu(II) and two water molecules in the case of other complexes around 393 K showing that the water is coordinated. From 473 to 773 K a sharp decrease in weight indicated a loss of one of the Schiff base ligands from the complexes. In general the thermal decomposition of complexes may be considered by the following equation:



The DTA curves show different peaks in the range of 483-663K. The first (endothermic) peak in the range of 483-503K corresponds to the loss of water molecules. The second (exothermic) peak in these complexes in the range of 643-648K is assigned to the loss of one of the Schiff base ligands.

Table-4
Thermal analysis data of the Cu(II) complexes

Complexes	Temperature range (°C)	Stage	TG Wt. Loss, % Found	DTA Temp. Peak, (°C)	Evolved Moiety	
					Formula	Mass calculated %
Cu-L ¹ 2H ₂ O complex	100-200	1	3.74	168.41(Exo)	2H ₂ O	3.79
	200-500	2	44.71	388.72(Exo)	Ligand	46.82
Cu-L ² 2H ₂ O complex	100-200	1	3.73	222.66(Endo)	2H ₂ O	3.62
	200-500	2	45.92	375.00(Exo)	Ligand	46.70
Cu-L ³ H ₂ O complex	50-250	1	2.32	239.06(Endo)	H ₂ O	2.40
	250-500	2	45.36	468.75(Endo)	Ligand	45.90
Cu-L ⁴ 2H ₂ O complex	50-100	1	4.27	93.05(Exo)	2H ₂ O	4.83
	100-500	2	45.82	373.67(Exo)	Ligand	46.26

ESR Studies

The EPR parameters of the investigated complexes are given in **table-5**. There was a general correspondence between the powder and solution spectra; however, the g_{\parallel} region was well resolved in the solution. The spectra were indicative of rhombic distortion from axial symmetry. Owing to coordination of two kinds of atoms (O & N) with the metal ion, the spectra were characteristic of magnetically dilute systems with Cu(II) ions in the $d_{x^2-y^2}$ ground state ($g_{\parallel} > g_{\perp} > g_e$). The hyperfines as a result of nitrogen ($I=1$) were visible on the main absorption line g_{\perp} , confirming the coordination through N. On the basis of the experimental evidence thus these synthesized complexes were characterized as five- or six- coordinates with fifth or sixth position occupied by one or two water molecules, respectively.

Table-5
ESR parameters of the Cu(II) complexes

Complexes	Solid		Solution		
	g_{\parallel}	g_{\perp}	g_{\parallel}	g_{\perp}	$ A_{\parallel}(Cu) $
Cu-L ¹ .2H ₂ O complex	2.15	2.06	2.261	2.020	16.21
Cu-L ² .2H ₂ O complex	2.18	2.07	2.285	2.024	16.48
Cu-L ³ .H ₂ O complex	2.20	2.05	2.284	2.017 2.026	16.00
Cu-L ⁴ .2H ₂ O complex	2.21	2.06	2.273	2.0273	16.01

Proposed Structures

On the basis of the above observations, it is tentatively suggested that Cu(II) investigated complexes show an octahedral geometry [**Figure-2, 3 & 4**] in which the Schiff bases act as bidentate [N & O donor] ligands.

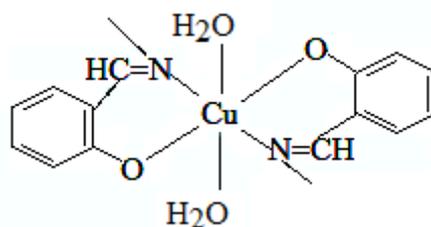


Figure-2: Proposed octahedral structure of Cu-L¹.2H₂O and Cu-L².2H₂O complexes

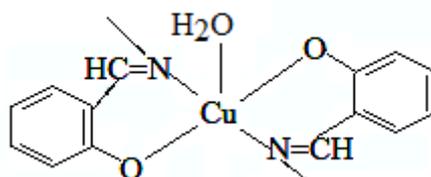


Figure-3: Proposed square-pyramidal structure of Cu-L³.H₂O complex

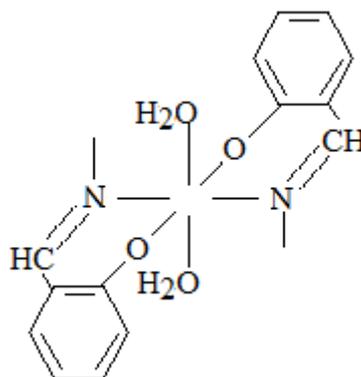
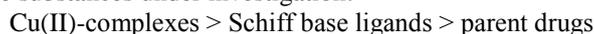


Figure-4: Proposed octahedral structure of Cu-L⁴.2H₂O complex

Anti-bacterial Activity

The difference in anti-bacterial activities of the investigated complexes, ligands and their parent drugs were studied and the results are presented in **table-6**. The cursory view of the data indicates the following trend in antibacterial activity of the substances under investigation:



All the Cu(II)-complexes and Schiff base ligands under investigation were more active than the parent drugs against *E. coli* and *S. aureus*. All the Cu(II)-complexes with the Schiff bases derived from cephalixin showed substantially enhanced activity against *P.aeruginosa* as compared with the parent drug.

Table-6
Minimum inhibitory concentrations of investigated ligands, their Cu-complexes and the parent drugs (in µgmL⁻¹)

Compound	MICs (in µgmL ⁻¹)		
	<i>E.coli</i>	<i>S.aureus</i>	<i>P.aeruginos</i>
Amoxicillin	95	13	>300
Cephalexin Sodium	99	10	>300
Sulphamethoxazole	100	65	>300
Trimethoprim	0.5	0.7	>300
Salicylideneamoxicillin	73	10	>300
Salicylidenecephalexin	51	5.5	>300
Salicylidenesulphamethoxazole	76	46	>300
Salicylidenetrimethoprim	0.4	0.5	>300
Cu-L ¹ 2H ₂ O complex	8.5	5.3	>200
Cu-L ² 2H ₂ O complex	5.8	2.5	>150
Cu-L ³ H ₂ O complex	8.4	5.2	>200
Cu-L ⁴ 2H ₂ O complex	0.1	0.1	>200

IV. Conclusion

In this report, we described coordination chemistry of unsymmetrical Schiff bases as new ligands and their complexes with Cu(II) which have been synthesized using condensation of salicylaldehyde and amoxicillin (L¹), cephalixin (L²), sulphamethoxazole (L³) and trimethoprim (L⁴) efficiently in an alcoholic suspension medium using alkali catalyst with excellent yields under microwaves irradiation and characterized by various physicochemical and spectral analyses. In the result of microwave assisted synthesis, it has been observed that the reaction time decreased from hours to minutes and availability of the product within better yields compared to the classical method. The synthesized Schiff base ligands coordinated with the Cu(II) ion in a bidentate manner through the phenolic oxygen and azomethine nitrogen. The ¹H-NMR data suggest that both the Schiff base ligand deprotonated after complexation. The thermal data show degradation pattern of the complexes. Thermo-gravimetric studied of the complexes also helped to characterize the complexes. Antimicrobial data suggests that the metal complexes are better antibacterial agents as compared to their ligands. The compounds also inhibit the growth of bacteria to a greater extent as the concentration is increased.

In conclusion, we have described here an efficient and environmentally benign synthesis of Schiff base ligands and their corresponding Cu(II) complexes under microwave irradiation using water and methanol as solvents. Further, this method is simple, mild and ecofriendly from green chemistry point of view.

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