

Thiazole containing schiff bases and their Cu (II) complexes

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ABSTRACT

Six metal complexes of Cu (II) metals were prepared from the heterocyclic Schiff bases and the corresponding Heterocyclic Schiff bases were prepared by refluxing of compounds such as heterocyclic amine (L_1) resacetophenone, (L_2) 2-hydroxy acetophenone, L_3 (pyrrole 2- aldehyde), L_4 (pyridine 2-aldehyde), L_5 (2- acetyl thiophene), L_6 (salicyldehyde) and L_7 (thiophene 2- aldehyde) with 2-amino, 6-sulfamyl benzothiazole. The elemental analysis data shows that the metals to ligand ratio in all Cu (II) complexes are 1:2. The structural features have been determined from IR, UV-Vis, thermal XRD spectral analysis and ESR data. All the complexes exhibit square planner geometry to Cu (II) complexes. All the synthesised ligands and their metal complexes were screened for antimicrobial activity the complexes shows enhanced activity than the ligands.

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INTRODUCTION

The condensation of primary amines with carbonyl compounds yields Schiff bases^[1,2]. Schiff bases represent an important class of compounds because they are utilized as starting materials in the synthesis of industrial products^[3]. Moreover, Schiff bases are regarded as privileged ligands^[4]. Due to their capability to form complexes with different transition metals can act as catalysts for many different reactions^[5,6]. The Schiff bases coordinate to metal ions via azomethine nitrogen and have been studied extensively^[7]. In azomethine derivatives, the C=N linkage is essential for biological activity, several azomethine has been reported to possess remarkable antibacterial, antifungal, anticancer and anti-malarial activities^[8,9].

Thiazole and its derivatives as ligands with potential sulphur and nitrogen bands are interesting and have gained special attention not only the structural

chemistry of their multifunctional coordination modes but also of their importance in medicinal and pharmaceutical field. They show biological activities including antibacterial antifungal^[10], antidiabetic^[11], antitumor^[12], antiproliferative^[13], anticancer^[14], herbicidal^[15].

Copper (II) complexes show distorted octahedral and tetrahedral symmetries due to d9 configuration (Jahn- Teller effect). The distortion is usually seen as axial elongation consistent with the lability and geometric flexibility of the complex. Therefore, typical Cu (II) complexes have square planar or square pyramidal geometries with weakly associated ligands in the axial position (s), but some copper (II) complexes possess trigonal bipyramidal geometry. The fundamental role of copper and the recognition of its complexes as important bioactive compounds *in vitro* and *in vivo* aroused an ever-increasing interest in these agents as potential drugs for therapeutic intervention in various diseases. The

vast array of information available for their bioinorganic properties and mode of action in several biological systems combined with the new opportunities offered by the flourishing technologies of medicinal chemistry, is creating an exciting scenario for the development of a novel generation of highly active drugs with minimized side effects, which could add significantly to the current clinical research and practice. A considerable number of schiff's base copper complexes have potential biological interest, being used as more or less successful models of biological compounds^[16]. Not only they have played a seminal role in the development of modern coordination chemistry, but also they can also be found at key points in the development of inorganic biochemistry, catalysis and optical materials^[17]

The complexes of copper with Schiff bases have wide applications in food industry, dye industry, analytical chemistry, catalysis, fungicidal, agrochemical, anti-inflammable activity, antiradical activities and biological activities^[18]. We were thus motivated to undertake a systematic study of preparation and characterization of Cu(II) metal complexes formed with Heterocyclic Schiff bases, prepared by refluxing of compounds such as heterocyclic amine (L₁) resacetophenone, (L₂) 2-hydroxy acetophenone, L₃ (pyrrole 2- aldehyde), L₄ (pyridine 2-aldehyde), L₅ (2- acetyl thiophene), L₆ (salicyldehyde) and L₇ (thiophene 2- aldehyde) with 2-amino, 6-sulfamyl benzothiazole and Cu halides.

EXPERIMENTAL

All the metal chelates prepared are stable to air and moisture. These are insoluble in water and in different polar and non polar organic solvents at room temperature. Some complexes are easily soluble and some are sparingly soluble in ethanol,

dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF).

The synthesized metal complexes are characterized by elemental analysis, solution conductivity, magnetic susceptibility, electronic and infrared absorption spectroscopy. They are also screened for thermo gravimetric analysis and X-ray powder diffraction analysis.

Synthesis of schiff bases

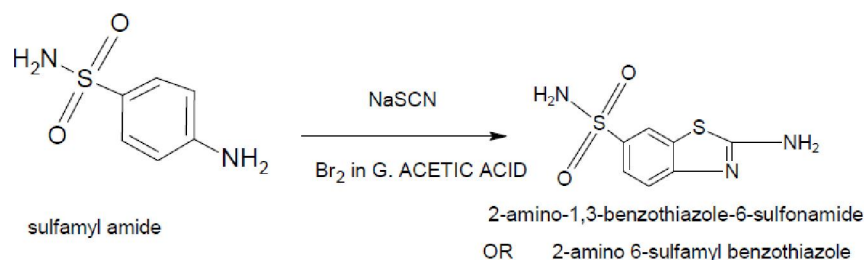
In the present work, we have reported some new Schiff bases synthesized by the condensation of 2-amino-6-sulfamyl benzothiazole and respective hydroxy ketones, aldehydes.

Synthesis of benzothiazole

Synthesis of 2-Amino-6-sufamyl-benzothiazole was carried out by the method of Rojer Adams^[19]. The method of thiocyanation and bromination was adopted. (0.1M) sulfanilamide and sodium thiocyanate (0.2M) in 100 ml glacial acetic acid are mixed together maintaining 0°C temperature. (0.2M) bromine in acetic acid (25 ml) was added to the above solution drop wise and the mixture was stirred continuously by a mechanical stirrer till the complete addition of bromine. The temperature was maintained below 10°C. The solid thus obtained after complete addition of bromine was filtered so as to remove excess of bromine and then dissolved in hot water. Again it was filtered and filtrate then treated with alkali like NaOH or KOH for the precipitation of free base. The precipitate thus obtained was filtered, washed and dried. The product was recrystallized from ethanol M.P. 105°C, Yield –40%.

Synthesis of Schiff bases

Schiff bases were synthesized by taking equimolar ethanolic solutions of heterocyclic amine and hydroxyl ketone/aldehyde in 50 ml ethanol and re-



Scheme

Full Paper

fluxing for 3-4 hours. The reaction progress was monitored by TLC. After confirming the completion of the reaction by TLC, the reaction mixture was poured on crushed ice or cold water and the solid separated was then filtered, washed with distilled water and dried, recrystallised from ethanol. The product collected was tested for $-\text{NH}_2$ group, $>\text{C}=\text{O}$ group, $-\text{SCN}$ group, $-\text{OH}$ group for the sake of the purity of the product.

Synthesis of metal complexes

For the synthesis of all Cu (II), complexes, the metal acetates were used. Ethanolic solutions of Schiff bases and respective metal acetate solutions were refluxed in the stoichiometric ratio. The precipitated solid complexes filtered, washed to remove excess base and then dried over fused CaCl_2 in vacuum desiccators.

Magnetic moment

Magnetic susceptibility of Cu (II) complexes at room temperature exhibit magnetic moment in the range 1.85 -2.20 B.M which is characteristic of spin

values for Cu (II) complexes. The values of the magnetic moment suggest the paramagnetic nature with one unpaired electron of all Cu (II) complexes indicating Square Planar geometry.

Electronic spectral analysis

For Cu(II) complexes $\text{Cu}(\text{L}_1)_2$ to $\text{Cu}(\text{L}_6)_2$ the electronic spectra showed bands in the range 34250 cm^{-1} to 42370 cm^{-1} i.e these spectral bands are observed near and above 35000 cm^{-1} can be assigned to charge transfer transitions. The bands at 34400 cm^{-1} to 37037 cm^{-1} are typically characteristic for square-planar geometry for Cu (II) complexes^[20].

IR Spectra

Ligands

All the newly synthesized six ligands show characteristic azomethine $-(\text{C}=\text{N})$ bond in the range of $1660\text{-}1600 \text{ cm}^{-1}$ ^[21] in their IR spectra. The bands in the region $3340\text{-}3450 \text{ cm}^{-1}$ ^[22] is observed which can be assigned for $-\text{OH}$ group of the ligands L_1 and L_2 . The band due to intramolecular hydrogen bonding can be assigned for the band observed at $3000 -$

TABLE 1 : Analytical data of Cu (II) complexes

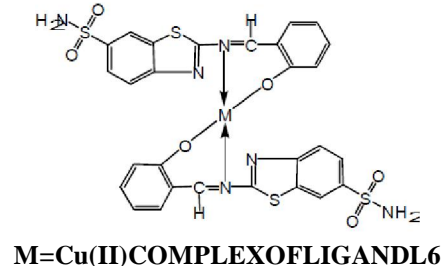
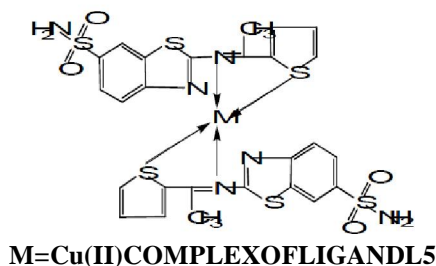
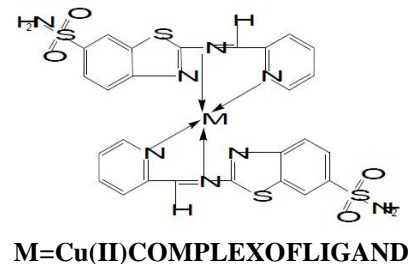
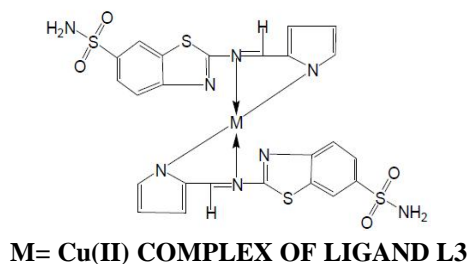
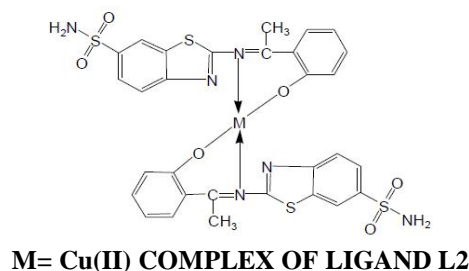
Sr. No.	Comp.	Mol. Formula	Mol. Wt.	Colour	M.P/ D.P °C	Elemental Analysis (%)				Mol.Cond. mhos cm^2	eff. B.M.
						C found (cal)	H found (cal)	N found (cal)	Metal Found (cal)		
1	L_1	$\text{C}_{15}\text{H}_{13}\text{O}_4\text{N}_3\text{S}_2$	363	Pale Gold	180	49.37 (49.58)	3.75 (3.58)	11.65 (11.57)	---	----	----
2	L_2	$\text{C}_{15}\text{H}_{13}\text{O}_3\text{N}_3\text{S}_2$	347	Vanilla	170	51.59 (51.87)	3.83 (3.74)	12.34 (12.10)	----	-----	-----
3	L_3	$\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_4\text{S}_2$	306	Pink Orange	160	46.87 (47.05)	3.47 (3.26)	18.49 (18.30)	----	-----	-----
4	L_4	$\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_4\text{S}_2$	318	Royal Yellow	165	48.98 (49.05)	3.21 (3.14)	17.77 (17.61)	----	-----	-----
5	L_5	$\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}_3\text{S}_3$	337	Stil degrain yellow	180	46.11 (46.29)	3.32 (3.26)	12.63 (12.46)	-----	-----	-----
6	L_6	$\text{C}_{14}\text{H}_{11}\text{O}_3\text{N}_3\text{S}_2$	333	Topaz	175	50.22 (50.45)	3.42 (3.30)	12.82 (12.61)	----	----	----
1	CuL_1	$\text{Cu}(\text{C}_{15}\text{H}_{13}\text{O}_4\text{N}_3\text{S}_2)_2$	789	Dark Green	280-285	45.50 (45.62)	3.70 (3.29)	10.85 (10.64)	7.28 (7.98)	55.66	1.88
2	CuL_2	$\text{Cu}(\text{C}_{15}\text{H}_{13}\text{O}_3\text{N}_3\text{S}_2)_2$	757	Forest Green	285-290	47.32 (47.55)	3.60 (3.43)	11.30 (11.09)	8.57 (8.32)	58.12	1.85
3	CuL_3	$\text{Cu}(\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_4\text{S}_2)_2$	675	Green	280	42.50 (42.66)	3.30 (2.96)	16.75 (16.59)	9.44 (9.33)	54.82	1.92
4	CuL_4	$\text{Cu}(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_4\text{S}_2)_2$	699	Drab	285-290	44.55 (44.63)	3.20 (2.86)	16.12 (16.02)	9.11 (9.01)	38.40	2.00
5	CuL_5	$\text{Cu}(\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}_3\text{S}_3)_2$	737	Apple Green	275-280	42.25 (42.33)	3.15 (2.98)	11.52 (11.39)	8.69 (8.54)	42.66	2.20
6	CuL_6	$\text{Cu}(\text{C}_{14}\text{H}_{11}\text{O}_3\text{N}_3\text{S}_2)_2$	729	Apple Green	260	46.12 (46.09)	3.30 (3.01)	11.62 (11.52)	8.72 (8.64)	50.12	1.93

TABLE 2 : Electronic spectral data of Cu (II) complexes

Complex code	$\mu_1 \text{ cm}^{-1}$	$\mu_2 \text{ cm}^{-1}$	μ_2/μ_1	Dq cm^{-1}	$\beta = \frac{B'}{R}$	LFSE (Kcal/mole)
CuL ₁	34720	42370	1.220334	765	0.553196	98.952
CuL ₂	34310	39220	1.143107	491	0.34435	97.7835
CuL ₃	35210	42020	1.193411	681	0.486846	100.3485
CuL ₄	34250	42110	1.229489	786	0.570722	97.6125
CuL ₅	34420	41840	1.215572	742	0.535443	98.097
CuL ₆	38610	41840	1.083657	323	0.222139	110.0385

TABLE 3 : ESR spectral values of Cu (II) complexes

Complex code	g_{\parallel}	g_{\perp}	g_N	G Axial symmetry parameter	μ_{eff} in B.M.
Cu(L ₁) ₂	1.878	1.803	1.828	0.621	1.88
Cu(L ₂) ₂	1.753	1.828	1.803	1.432	1.85
Cu(L ₃) ₂	1.828	1.803	1.811	0.873	1.92
Cu(L ₄) ₂	1.853	1.753	1.786	0.597	2.00
Cu(L ₅) ₂	1.803	1.853	1.836	1.336	2.20
Cu(L ₆) ₂	1.753	1.828	1.803	1.432	1.93



3100 cm^{-1} ^[23]. The band in the range of 1517-1550 cm^{-1} ^[24] is of $-(\text{C}=\text{N})$ ring stretch vibration and C-O stretching frequency of phenolic C-O-H appears in the range of 1250-1270 cm^{-1} ^[25], in ligands L₁ and L₂.

Ligand L₃ shows band at 3186 cm^{-1} ^[26] for N-H

vibration of pyrrole ring. The band at 3143 cm^{-1} ^[27] is characteristic band of 2-Pyridine nucleus of L₄. Five membered 2-substituted aromatic C-N stretch ring vibrations occurs in the range of 1460-1490 cm^{-1} ^[28]. Thiazole C-S-C vibrations in ligands appear at

Full Paper

825-860 cm^{-1} ^[29] and 740 cm^{-1} ^[30].

Metal complexes

The assignments of band frequencies for different groups in metal complexes corresponding to those considered for ligand spectra have been proposed on the basis of data available in the literature on the metal complexes of similar ligands and sensitivities of characteristic group frequencies to metal complexation.

In the IR spectra of all six metal complexes under investigation i.e Cu(II), medium to strong intensity bands appeared in the region 1660- 1630 cm^{-1} ^[31] which can be assigned to characteristic azomethine group i.e -(C=N) of all metal complexes.

It is strikingly observed for all the metal complexes compared with ligands that the band value for azomethine group has shown considerable shifting in downward or upward depending upon the intensity of coordination which indicates the involvement of azomethine nitrogen in the coordination with metal ions^[32]. This fact is well supported by the constancy of band value for -(C-N) stretch as it shows appreciable shifting in band value. IR spectral figures of respective complexes itself is the best proof for this, whereas on the other hand it is interestingly noticed that the shift in the band value for -(C=N) ring stretch is not considerable. The band value at $\sim 1550 \text{ cm}^{-1}$ shows no shift indicates non involvement of ring nitrogen in bonding. It is found that the band value absorbance in metal complexes is unchanged which strongly supports the non-involvement of thiazole nitrogen in coordination with metal ion. Further the band observed at $\sim 3450 \text{ cm}^{-1}$ ^[33] in ligand L_1 and L_2 is attributed due the presence of -(OH) (H-bond) is affected. Either it is disappeared on complexation or showed variance in frequency in downward direction which indicates the deprotonation and involvement in the coordination with transition metal ions under investigation.

The IR spectra of Cu(II) complexes show band of medium intensity at 3350-3500 cm^{-1} which can be assigned to -OH stretching due to presence of water of hydration^[34] in these complexes which is well supported and confirmed by the thermal analysis data and their respective spectral figures.

The nitrogen of the thiazole ring can be called totally lethargic and this very lethargic nature of thiazole nitrogen is well supported by the fact that the band value for -(C=N) ring 1500-1560 cm^{-1} nearly is same as observed in IR spectra of ligands and the corresponding complexes. Last but not the least the variance in the band value for -(C-N) stretch is remarkably affected due to involvement of azomethine nitrogen in coordination.

Taking into account all the above spectral facts, it can be suggested for the involvement of azomethine nitrogen along with the oxygen of -OH group of the ligands in the coordination with metal complexes.

For L_3 complexes of all six metal ions, the characteristic band at 3186 cm^{-1} due to -N-H vibration of 2-pyrrole in the ligand showed a upward shift in the band value which supports the deprotonation of -N-H (pyrrole) and bonding through nitrogen atom^[35].

In the complexes of L_4 the characteristic band at 3143 cm^{-1} for 2-pyridyl nucleus shows considerable downward shift in the band value thereby showing the pyridine nitrogen's involvement in the coordination. Thus the ligand L_3 is coordinating through thiazole ring nitrogen and pyridine ring nitrogen^[36].

The bands at 825-840 cm^{-1} and 740-756 cm^{-1} in almost all metal complexes can be assigned due to C-S-C thiazole vibrations. The appearance of non-ligand band at 555-600 cm^{-1} can be attributed to M-N band whereas the non-ligand band at 462-491 cm^{-1} can be attributed to M-O band. The appearance of these new bands of M-N and M-O vibrations supports the involvement of N and O atoms in complexation with metal ions.

The band in the region of 3200-3600 cm^{-1} for Cu(II) complexes, but it is supposed to be because of surface water (hydrated water)^[37]. Again the thermograms and thermoanalytical data supports this very fact strongly.

All ligands and complexes show the presence of SO_2 group which can be readily identified by the appearance of two strong bands in the region 1415-1300 cm^{-1} and 1200 – 1120 cm^{-1} region due to asymmetric and symmetric stretching vibrations respectively and there is no appreciable change which shows absence of bonding through $\text{-SO}_2\text{NH}_2$ group in the metal ligand bonding.

ESR study

It is observed from ESR spectrum Cu(II) complexes that there is a single line resulting in the interaction of unpaired electron present in Cu(II) nucleus. The Table reveals that the ' g_{av} ' values less than 2.3 which suggest the existence of sufficient covalent nature of metal ligand bond. Also the G values less than 4 indicates that the Cu(II) complexes are strong field ligands. As the values of $g_{||}$ and g_{\perp} are different hence all complexes show anisotropy.

The hyperfine splitting in positive amplitude and negative amplitude at respective magnetic field for each spectrum gave rise to two ' g ' values which are less than 2.3 suggests the covalent nature of complexes^[38].

X-Ray Diffraction

The diffractogram of Cu (II) complex of L_1 had twenty reflections with maxima at $2\theta = 12.78^\circ$ corresponding to d value $6.921A^\circ$ having intensity 2359 cps. Diffractogram of Cu (II) complex of L_2 had sixteen reflections with maxima at $2\theta = 12.66^\circ$ corresponding to d value $6.98641A^\circ$ having intensity 1869 cps. Diffractogram of Cu (II) complex of L_3 had twenty four reflections with maxima at $2\theta = 12.86^\circ$ corresponding to d value $6.8782A^\circ$ having intensity 3000 cps. Diffractogram of Cu (II) complex of L_4 had eighteen reflections with maxima at $2\theta = 12.86^\circ$ corresponding to d value $6.8782A^\circ$ having intensity 3433 cps. Diffractogram of Cu(II) complex of L_5 had twenty reflections with maxima at $2\theta = 12.70^\circ$ corresponding to d value $6.9645A^\circ$ having intensity 1948 cps and diffractogram of Cu(II) complex of L_6 had twenty reflections with maxima at $2\theta = 12.78^\circ$ corresponding to d value $6.921A^\circ$ having intensity 2794 cps.

Antimicrobial activity

Antifungal activity was performed by poison plate method. The medium used was Potato Dextrose Agar (Himedia). The medium was prepared and sterilized at 10 Psi in autoclave for 15 minutes. Then the compound to be tested is added to the sterile medium in aseptic condition so as to get final concentration as 1%. A plate with DMSO was prepared as blank (negative control). Similarly a plate

with 1% Grysofulvin was prepared as standard reference plate (positive control). *Aspergillus Niger*, *Penicillium Chrysogenum*, *Fusarium Moneliforme*, *Aspergillus Flavus* were selected as test fungal cultures. They were allowed to grow on slant for 48 hours so as to get profuse sporulation. 5 ml of 1:100 aqueous solution of teen 80 was added to the slant and spores were scraped with the help of nicrome wire loop to form suspension. The fungal suspension was spot inoculated on the plate's prepared using compound with the help of nicrome wire loop. The plate was incubated at room temperature for 48 hours. After incubation plates were observed for the growth of inoculated fungi. Results were recorded as a growth of fungi (no antifungal activity), reduced growth of fungi (moderate antifungal activity), and no growth of inoculated fungi (antifungal activity).

The cup plate agar diffusion method^[39, 40] was employed for determining the antibacterial activity of the newly synthesised ligands. The antibacterial activity was measured by agar cup method. Nutrient agar (Himedia) was prepared and sterilized at 15 Psi for 15 minutes in the autoclave. It was allowed to be cool below $45^\circ C$ and seeded with turbid suspension of test bacteria separately prepared from 24 hours old slant cultures. 3% incula were used every time. The bacterial culture selected where, two gram negative culture viz. *Staphylococcus aureus*, *Bacillus subtilis*. This seeded preparation was then poured in sterile Petri plate under aseptic condition and allow it to solidify. Cup of 10 mm diameter were borered in the agar plate with sterile cork borer. 100 μl of compound solution prepared in dimethyl sulphoxide (1%) was added in the cup under aseptic condition with the help of micropipette. 100 μl of DMSO was also placed in one of the cup as a blank (negative control). A standard antibiotic disk impregnated with 10 units of penicillin was also placed on the seeded nutrient agar surface as standard reference antibiotic (positive control).

The plates were kept in refrigerator for 15 minutes to allow diffusion of the compound from agar cup into the medium. Then the plates were shifted to incubator at $37^\circ C$ and incubated for 24 hours. After

TABLE 4 : Antimicrobial activity

Sr. No.	Compound	Fungal Strain				Bacterial Strain			
		An	Pc	Fm	As	Ec	St	Sa	Bs
1	L ₁	RG	-ve	RG	+ve	14	18	-ve	17
2	L ₂	+ve	RG	+ve	RG	15	24	-ve	13
3	L ₃	RG	RG	RG	+ve	20	15	12	20
4	L ₄	+ve	+ve	+ve	+ve	18	-ve	20	19
5	L ₅	+ve	RG	+ve	RG	16	-ve	16	18
6	L ₆	RG	RG	+ve	+ve	17	-ve	19	19
7	CuL ₁	RG	RG	RG	+ve	18	14	15	17
8	CuL ₂	+ve	+ve	+ve	+ve	14	14	17	18
9	CuL ₃	+ve	+ve	+ve	+ve	17	15	20	19
10	CuL ₄	RG	RG	RG	RG	18	15	22	20
11	CuL ₅	+ve	RG	-ve	+ve	16	14	18	20
12	CuL ₆	+ve	RG	-ve	+ve	13	11	17	18
13	+ve control	+ve	+ve	+ve	+ve	NA	NA	NA	NA
14	Griseofulvin	-ve	-ve	-ve	-ve	NA	NA	NA	NA
15	DMSO	NA	NA	NA	NA	-ve	-ve	-ve	-ve
16	Penicillin	NA	NA	NA	NA	13	22	36	18

Ec-E.coli, St-S.typhi, Sa- S.aureus, Bs-B.subtilis; An-A.niger, Pc-P.chrysogenum, Fm-F.moneliformae, Ca-C.albicans; -ve: No growth of fungi,+ve; Growth of fungi, RG-Reduced growth, NA-Not Applicable, Zone of inhibition was measured in mm.

incubation plates were observed for the zone of inhibition of bacterial growth around agar cup. Results were recorded by measuring the zone of inhibition in millimeters (mm) using zone reader.

CONCLUSION

The synthesized Schiff bases showed bidentate nature and gave stable transition metal complexes. All the Schiff base Cu(II) complexes under investigation are non-electrolytic in nature. The metal complexes show more potent activity than the corresponding Schiff bases. The electronic spectral data suggest that all Cu(II) complexes of ligands under study have Square planar geometry.

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