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FULL PAPER

Synthesis, Spectral Characterization, *in vitro* Antimicrobial and Anthelmintic Evaluations of Cu(II) Complexes with a New Schiff Base

Disha Sharma and Hosakere D. Revanasiddappa*

Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysuru 570 006, Karnataka, India

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Abstract:

Novel Schiff base ligand (*E*)-2-((3-(benzyloxypyridinylimino) methyl)-4-bromophenol (HL) was synthesized. Using this Schiff base ligand, two new copper(II) complexes, C1 and C2 were prepared. Analytical techniques such as IR, ^{1}H NMR, ^{13}C NMR, mass, UV–visible spectroscopy, molar conductivity, magnetic measurement, ESR and TGA-DTA were used to characterize the ligand HL and its copper complexes. From the ESR spectra, square planar geometry was proposed for C1 and C2. The synthesized ligand, HL along with its copper(II) complexes were subjected to test their in vitro biological efficacies against four bacterial strains Escherichia coli, Salmonella typhi, Bacillus subtilis and Staphylococcus aureus and two antifungal strains Candida albicans and Aspergillus niger. The results obtained from this work suggest that the studied metal complexes are very effective in biological activities than its ligand. The anthelmintic test of the ligand HL and copper complexes against earthworms, Pheretima posthuma are also investigated.

Keywords: anthelmintic activity; antimicrobial activity; Schiff base; electron spin resonance; thermal analysis

1. Introduction

In recent years, several Schiff base metal complexes have been widely used in diagnostics and medicine [1-4]. Metal complexes of Schiff bases are prepared easily. Both symmetrical and non-symmetrical types of Schiff bases were used as ligands for the preparation of different metal complexes [5].

In general, biological activity of the ligand is enhanced by the incorporation of the metal ion. The azomethine groups are present in various Schiff bases and the –C=N- linkage is required for biological activity [6]. N and O atoms of the Schiff base play very important role in the metal complexation and also the significant development of bioinorganic chemistry of Schiff base compounds [7-10].

In living system, the significance of metal ions is well documented. Copper is widely used as antibacterial and antifungal activity. Since few years, variety of organo copper complexes has been subjected to study their antimicrobial and antitumor activities. In general, the drug action is due to the interaction of several biomolecules and metal ions [11-21].

As the effort towards the synthesis of metal based therapeutic agents, here we report the preparation and characterization of new complex derivative of Schiff base ligand: (E)-2-((3-(bezyloxypyridinylimino) methyl)-4-bromophenol (HL). The ligand HL and its Cu(II) complexes as well as their *in vitro* bioactivity such as antimicrobial and anthelmintic properties are described here. The structure of the ligand HL is as shown in Figure 1.

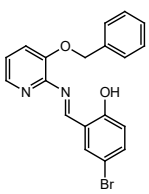


Figure 1. Structure of HL.

*Corresponding author. E-mail: hdrevanasiddappa@yahoo.com

2. Results and Discussion

The formed coloured complexes are crystalline powder, stable at ambient conditions, insoluble in water but easily soluble in organic solvents, DMF and DMSO. The stoichiometry of the complexes are 1:2 (metal:ligand) for C1 and 1:1:1 (metal:ligand:1, 10-phenanthroline) for C2; this result is in agree with the values from elemental analysis. Experimental data of HL and its C1, C2 complexes are presented in Table 1, the data are in close agreement with the probable formulae of the compounds. The molar conductance values of C1 and C2 complexes in 10^{-3} M DMSO are 17.57 and 12.53 $\Omega^{-1}cm^2mol^{-1}$, respectively, indicating that the complexes are non-electrolyte.

Table 1. Analytical and physical data of the Schiff base ligand and its metal complexes.

Compound	Molecular Formula	Melting Point (°C)	Yield (%)	Elemental analysis, Theoretical (actual)			Colour	Λ Ohm^{-1} cm^2 mol^{-1}
				(%)C	(%)H	(%)N		
HL	$C_{19}H_{15}BrN_2O_2$	128-130	87	59.55 (60.07)	3.95 (3.14)	7.31 (6.96)	Orange	—
C1	$C_{38}H_{30}Br_2CuN_4O_5$	>300	65	54.84 (55.19)	4.14 (3.77)	6.40 (7.31)	Moss Green	17.57
C2	$C_{31}H_{26}BrCuN_4O_4$	>300	72	56.24 (57.02)	3.96 (4.57)	8.46 (7.66)	Brown	12.53

2.1. Infrared spectra

The FTIR data for HL and its C1 and C2 compounds are presented in Table 2 and represented in Figure 2. A characteristic band at 3406 cm^{-1} of HL in its IR spectrum is due to its phenolic hydroxyl group. The bond formation between metal ions and phenolic hydroxyl group of HL is confirmed by an absence of band at 3406 cm^{-1} in the spectra of C1 and C2. The stretching vibration, υ (C=N) is observed at 1602 cm^{-1} due to azomethine of HL. This band is shifted to lower frequency side at 1596 and 1599 cm^{-1}, indicating the bonding between an unsaturated nitrogen donor atom of the azomethine of HL and metal ions. The band for phenolic oxygen υ (Ph–O) occurs at 1277 cm^{-1}, whereas in complexes, this band is shifted to different frequency showing very strong bands around 1241 and 1257 cm^{-1} region. The bands in the range 497-477 and 505-517 cm^{-1} provide an additional proof for M-N and M-O, respectively [22]. The IR spectra data was used to confirm the interaction of imino nitrogen and phenolic oxygen atoms.

Table 2. FTIR spectral data of the ligand [HL] and its Cu(II) metal complexes (cm^{-1}).

Compound	v(C=N) (cm^{-1})	v(Ph-O) (cm^{-1})	v(M-O) (cm^{-1})	v(M-N) (cm^{-1})
HL	1602	1277	—	—
C1	1596	1241	492	505
C2	1599	1257	477	517

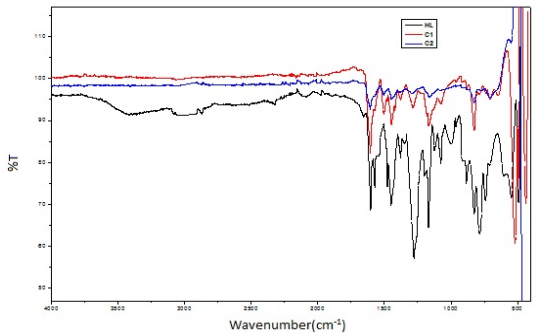


Figure 2. IR spectra of HL, C1 and C2.

2.2. Electronic Spectra and magnetic moment Studies

The electronic spectra of copper complexes C1 and C2 in DMSO were recorded in wavelength range of 800–200 nm shown in Figure 3. The UV-vis spectra of HL showed two bands at 287 and 376 nm. The first band can be attributed to π→π* transition within an aromatic ring, whereas the second band would be due to n→π* transition within -C=N group. On interaction with metal ion,

n→π* transition of new HL shifts to a longer wavelength; this reflects the complexation between ligand and metal [23]. The electronic spectra of C1 and C2 exhibit characteristic absorption peaks corresponding to square-planar geometry. There are three degenerate spin-allowed transition *viz*. $^2B_{1g} \rightarrow {}^2A_{2g}$ ($d_{x^2-y^2} \rightarrow d_{z^2}$), $^2B_{1g} \rightarrow {}^2B_{2g}$ ($d_{x^2-y^2} \rightarrow d_{xy}$) and $^2B_{1g} \rightarrow {}^2E_g$ ($d_{x^2-y^2} \rightarrow d_{xz}$, d_{yz}) for square-planar complexes with a $d_{x^2-y^2}$ ground state [24]. The complexes, C1 and C2 shows a low energy band at 517 and 535 nm which are attributed to d–d transition ($^2B_{1g} \rightarrow {}^2A_{1g}$), which strongly favors the square-planar geometry around the copper metal ion [25]. The magnetic moment value for C1 is 1.9 μB, while for C2 is 2.0 μB. These values are further confirms the square planar geometry around the Cu(II) ions in C1 and C2 [26].

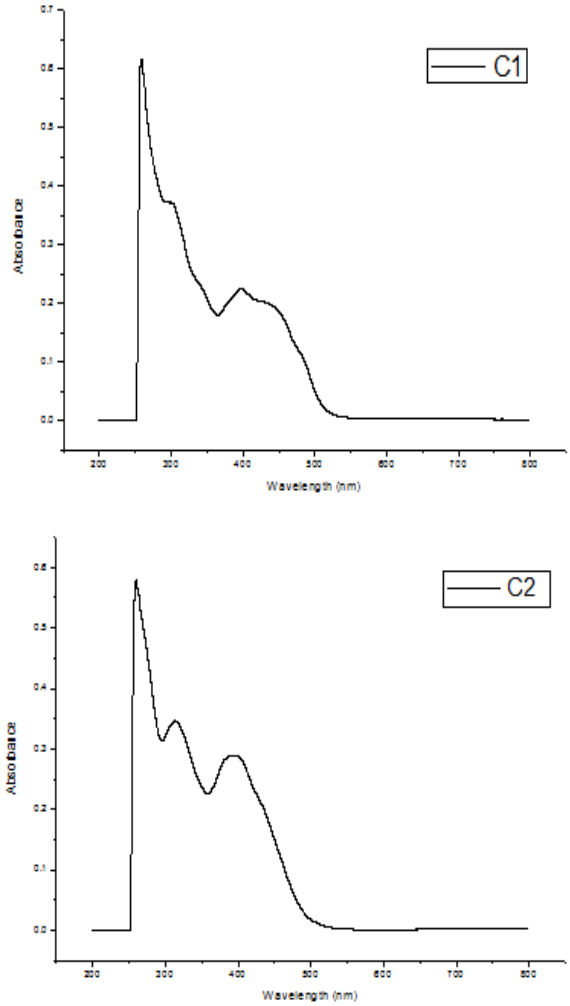


Figure 3. The Electronic spectra of complexes C1 and C2 in DMSO.

2.3. Thermal analysis

The stability of the complexes C1 and C2 was investigated using thermogravimetric analysis (TGA). In the case of C1 decomposition took place in two steps. For C1, loss of one molecule of lattice water occurs in the range of 35-90 °C with a mass loss of 9.87% (calc. 8.77%), later by the continuous mass loss of 82.58% (calc. 83.74%) occurs in the range 220-490 °C suggesting the evaporation of ligand. From the calculations, it follows that the final decomposition product can be CuO. However, for C2, loss of two molecule of lattice water took place 40-80 °C with a mass loss of 3.34% (calc. 4.74%). Later by the loss of 2 molecules of ligand from 240-390 °C with a mass loss of 59.46% (calc. 60.23%) and 1, 10-phenanthroline moiety were decomposed at 575–670 °C, with mass losses of 37.12% (calc. 36.77%) leaving behind the corresponding metal oxide respectively as depicted in Figure 4.

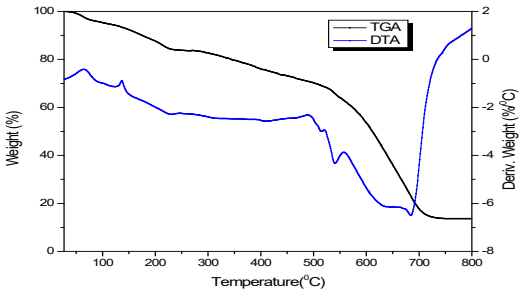


Figure 4. TGA /DTA for C2.

2.4. EPR spectra

The synthesized copper complexes are EPR active, and their EPR spectra recorded in solvent DMSO at low temperature of 77 K. The EPR spectra are given in Figure 5. The ground state of the copper complexes C1 and C2 are derived from the 'g' values. In square-planar complexes, the electrons are in $d_{x^2-y^2}$ orbitals with ground state of $^2B_{1g}$, $g_{\parallel} > g_{\perp} > 2.0023$, whereas an unpaired electron in dz^2 with ground state $^2A_{1g}$, $g_{\perp} > g_{\parallel} > 2.0023$. From the experimental values, it is clear that $g_{\parallel} > g_{\perp} > 2.0023$ and the e.s.r. parameters of the C1 and C2 are given in Table 3. The results confirm the square planar geometry of the C1 and C2. Further, it is concluded that the unpaired electron is significantly involved in $d_{x^2-y^2}$ orbital [27, 28]. This was evident from the G value, calculated from the expression:

$$G = (g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023)$$

If G is higher than 4.0, the four-fold axis is aligned parallel or misaligned slightly. If G is lower than 4.0, remarkable exchange coupling is found and an appreciable misalignment is evident. The G value for C1 is 6.71 and 7.60 for C2 is suggesting that tetragonal axis is aligned parallel and an unpaired electron is associated with $d_{x^2-y^2}$ orbital. As per the result from the spectra, the exchange coupling effects was insignificant [29]. On the basis of above facts, the proposed structure of copper complexes C1 and C2 are depicted in Figure 6.

Table 3. EPR spectral parameters for copper complexes in DMSO at 77 K.

Complex	$A_{\parallel}$	$A_{\perp}$	A_{iso}	g_{iso}	$g_{\parallel}$	$g_{\perp}$	α^2
C1	151	57	71	2.17	2.39	2.17	0.81
C2	137	48	65	2.16	2.38	2.16	0.79

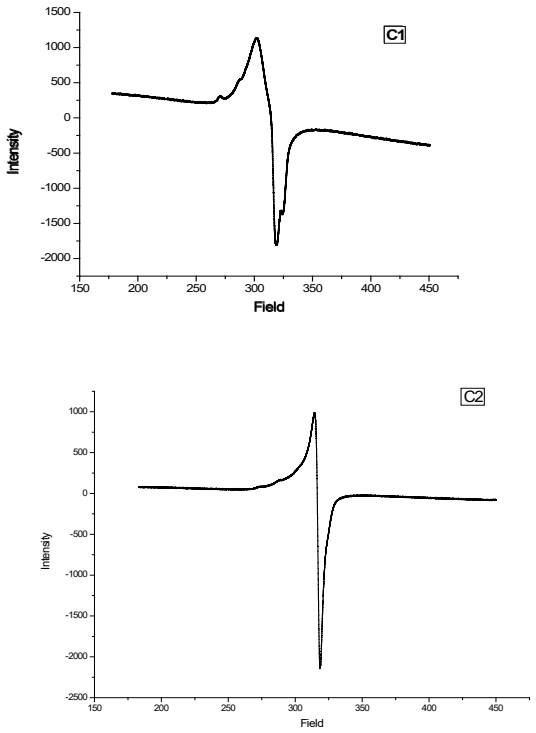
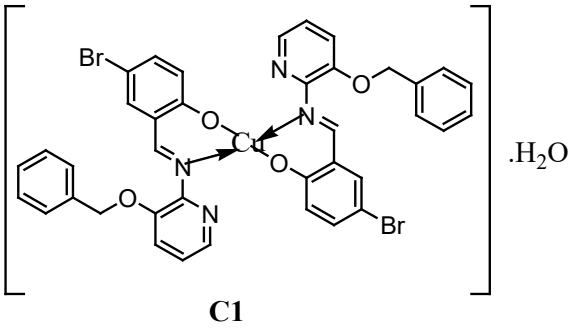


Figure 5. ESR spectrum of C1 and C2.

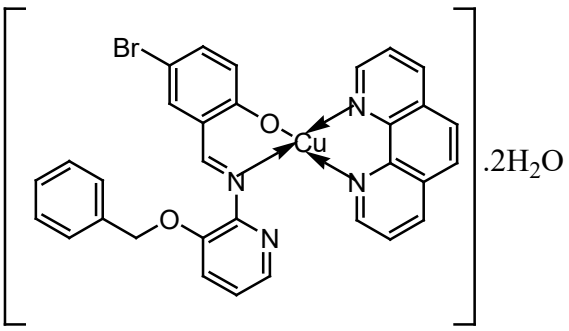
2.5. Antimicrobial activity

The results achieved from these studies are enlisted in Table 4 and Table 5. The data of the antifungal and antibacterial activity indicated that the C1 and C2 are more active than ligand, HL. Based on Overtone's and chelation theory concept, one can predict the biological activity of C1 and C2 are more than its ligand HL. The conductivity, bond length and solubility of the new complexes are also responsible for the enhanced activity [30].

The sensitivity of bacteria and fungi to the copper complexes C1 and C2 were calculated by recording the MIC (minimum inhibitory concentration). MIC is the minimum concentration of active drug at which no growth of pathogenic strains was found. Comparison of MIC values (in µg/mL) of copper complexes and standard drugs against different bacteria are presented in Table 5. C1 and C2 appeared to have broad spectrum as they exhibit mild to moderate efficacy towards most of the strains. This study reveals that these C1 and C2 complexes can further be explored as specific antimicrobial drugs due to their good activity and less toxicity of metal ion.



C1



C2

Figure 6. Proposed structure of the Schiff base complexes C1 and C2.

Table 4. Antimicrobial results of Schiff base and their corresponding copper(II) complexes.

Compound	Zone of inhibition (in mm)					
	Antibacterial				Antifungal	
	Gram-positive bacteria		Gram-negative bacteria			
	B. subtilis	*S. aureus*	*E. coli*	*S.typhi*	*C.albicans*	*A. niger*
HL	15	13	11	17	11	10
C1	27	21	29	19	17	19
C2	28	30	22	21	23	20
Gentamicin	38	33	35	26	—	—
Fluconazole	—	—	—	—	29	27

Concentration of sample =0.001g/ml of DMSO, Concentration of control drug =0.001 g/ml, (-) = No activity

Table 5. MIC [µg/ml] values for antimicrobial activity of Schiff base and its corresponding copper complexes.

Compound	Bacteria				Fungi	
	Gram-positive bacteria		Gram-negative bacteria			
	B. subtilis	*S. aureus*	*E. coli*	*S.typhi*	*C.albicans*	*A. niger*
HL	>100	>100	>100	>100	>100	>100
C1	77	69	57	62	82	71
C2	81	59	70	65	57	69
Gentamicin	37	37	37	37	—	—
Fluconazole	—	—	—	—	37	37

2.6. Anthelmintic activity

The anthelmintic activity of Cu(II) complexes C1 and C2 were performed *in vitro* using Indian adult earthworm (*Pheretima posthuma)*. The compounds are screened for activity by time taken for complete paralysis and death of worms. At higher concentration, loss of motility and mortality is more pronounced against *P. Posthuma*. The results point out that metal complexes cause paralysis and death of worms indicating that Cu(II) complexes are anthelmintic agents described in Table 6. Cu(II) complexes are found to be more active as compared to ligand and the standard drug Albendazole. The biochemical mechanism of anthelmintic action of the complexes may be due to interfering with metabolic processes, interfering with neuromuscular physiology of parasites. In general, the possible mechanism of anthelmintic action of complexes may be related to either inhibition of energy metabolism and/ or alteration in the motor activity of the parasite.

Table 6. Anthelmintic activity of the Schiff base and its metal complexes.

Compounds	2 mg/ml		10 mg/ml	
	Time taken for paralysis (min)	Time taken for death (min)	Time taken for paralysis (min)	Time taken for death (min)
Control	—	—	—	—
Albendazole	13	17	15	19
HL	9	11	12	15
C1	17	21	19	23
C2	15	20	18	25

3. Material and Methods

3.1. General

Commercially available reagents were purchased and used as such. Both phenanthroline and copper acetate (Merck Private Limited, Mumbai) were procused. Precision Digital Melting point apparatus for recording Melting point (uncorrected) and Perkin Elmer 240 CHN-analyzer for elemental analysis were used. For recording ^{1}H and ^{13}C NMR, Varian-400 MHz spectrometer with TMS (Tetra methyl silane) as a standard was utilized. Mass spectra (ESI) of the compounds were recorded using a 2010EV LCMS Shimadzu spectrometer. Perkin Elmer Spectrum with Version 10.03.09 was

used to record IR spectra of the compounds in the range 4000-400 cm^{-1}. Magnetic moments of C1 and C2 were determined using Gouy's apparatus with $Hg[Co(SCN)_4]$ as the standard. Molar conductance in ~10^{-3} M DMSO solution was recorded using an Elico Cm-180 conductometer. UV-visible spectra of the prepared complexes in the region 200-800 nm were recorded using a double beam spectrophotometer (ELICO SL 117) with 1cm quartz cuvettes. Copper(II) complexes were studied to record for their ESR spectra at 77 K under nitrogen (IIT, Mumbai) with TCNE (tetracyanoethylene) as the g-marker. Thermograms of C1 and C2 compounds were measured in nitrogen atmosphere (TGA Q50 instrument) keeping the maximum temperature at 800 °C with the heating rate at 10 °C/min.

3.2. Procedures

3.2.1. Synthesis of (E)-2-((3-(bezyloxypyridinylimino) methyl)-4-bromophenol (HL)

A new Schiff base was prepared by the condensation of equimolar amounts of 2-amino-3-benzyloxypyridine 0.002 mol and 5-bromo salicylaldehyde 0.002 mol in ethanol. 1-2 drops of acetic acid were used in the reaction mixture while reflux it for 7-8 hours at 70-80 °C. Completion of the reaction was observed by TLC. The formed product was filtered, washed and dried (using anhydrous $CaCl_2$ in a desiccators), and ethanol was used for recrystallization of the sample (Figure 7).

Ligand (HL): Orange, Yield 87%, melting point 128-130 °C. CHN found (calc.) for $C_{19}H_{15}BrN_2O_2$: C: 59.55(60.07), H: 3.95(3.14), N: 7.31(6.96); MS (m/z): 383[M^+]; Found: 385[M+2]; FTIR υ (cm^{-1}); υ (OH) 3406, υ (C=N) 1617; ^{1}H NMR (400 MHz, $CDCl_3$); 9.36(s, HC=N), 14.22(s, Ph-OH), 6.91-8.0(m, Ar–H), 5.22(-CH_2-O); ^{13}C NMR (400 MHz, $CDCl_3$); 161.816, 161.545, 148.771, 147.071, 140.203, 136.219, 135.976, 134.906, 128.706, 128.145, 126.953, 123.720, 121.459, 120.700, 119.623, 110.114, 77.293, 76.974, 76.655. UV-vis (DMSO): λmax=376 nm.

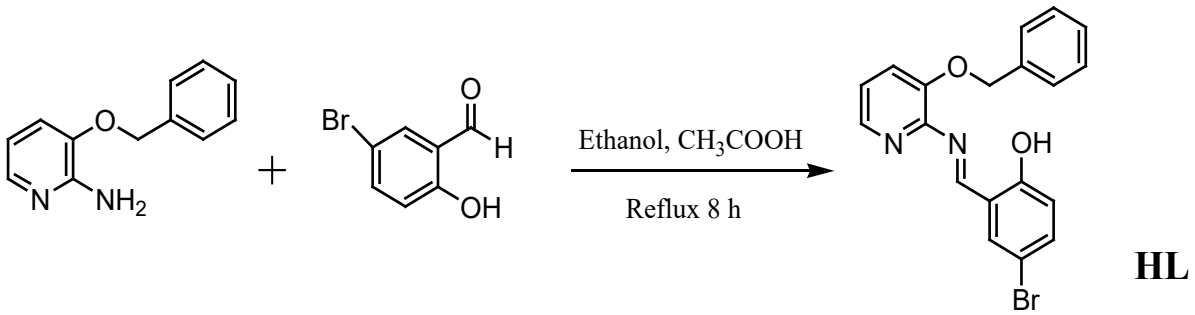


Figure 7. Schematic representation of synthesis of Schiff base ligand.

3.2.2. Synthesis of 1:2 ratio complex C1

Ethanolic solutions of copper acetate (1 mmol) and (2 mmol, 0.781 g) Schiff base ligand HL was refluxed for 7 h. The volume of the mixture was reduced on a steam bath, and the formed complex C1 was washed thoroughly with ethanol, dried under vacuum over $CaCl_2$.

3.2.3. Synthesis of 1:1:1 ratio complex C2

An ethanolic solution of phenanthroline monohydrate (Phen) (1 mmol, 0.199 g) was refluxed with copper salt (1 mmol) in ethanol under stirring for 30 min. The above solution and ethanolic solution of Schiff base ligand HL (1 mmol, 0.390 g) was added to the above reaction mixture. It was continued to reflux for 7 h on water bath. The solution was then reduced to one-third on a water bath. The formed solid complex was filtered thoroughly and washed with ethanol, dried under vacuum over $CaCl_2$. The single crystal development of the metal complexes is unsuccessful.

3.3. Crystal structure determination by X-ray crystallography

Bruker Microstar Proteum 8 diffractometer, with Cu-Kα radiation (λ=1.54178 Å) at 296 K was utilized to analyze the single crystal of HL. The crystal HL crystallizes in orthorhombic and space group Pca21 having unit dimensions a=14.240(3)

Å, b=16.090(3) Å, c=7.2170(7) Å. The ORTEP diagram was generated using the Mercury 3.8 software and is given in Figure 8. CCDC deposition number is 1585783.

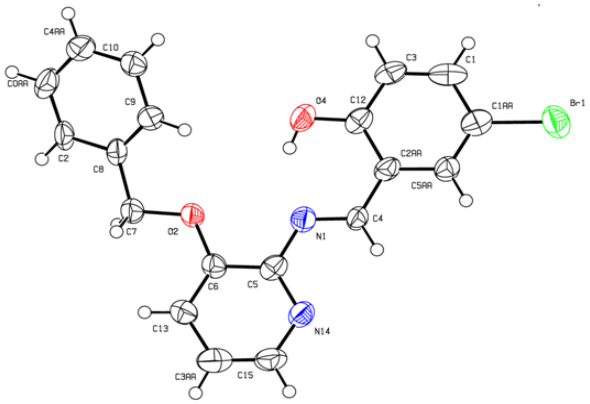


Figure 8. ORTEP view of the HL.

3.4. *In-vitro* Antimicrobial Screening

In vitro, antimicrobial study was taken on HL and its metal complexes C1 and C2 against, bacterial strains *Staphylococcus aureus* (ATCC 25923), *Bacillus subtilis* (ATCC 21332), *Escherichia coli* (ATCC 25922) and *Salmonella typhi*(19430) and fungi strains *Candida albicans* (MTCC 227) and *Aspergillus niger* (MTCC 1881) by disc diffusion experiment. Gentamicin (30µg/disc) and Fluconazole (10µg/disc) are the references for antibacterial and antifungal activities, respectively. Whatmann paper (No. 1) was used to make sterile discs with a size of 6mm diameter. They were placed on the nutrient agar medium, 100 µg of C1 and C2 in DMSO was employed on each disc by means of a micropipette. After incubation (24 hours) at 37 °C for bacteria and at 25 °C for fungi, the inhibition zone was measured in mm and compared with standard antibiotics. Triplicate measurement was made and the mean value in mm considered. DMSO was used in control experiments.

3.5. Anthelmintic Activity

An adult Indian earthworm, *Pheretima postuma* was collected for performing an anthelmintic activity of the prepared compounds. The literature method [31-33] with minor modification was followed for the assay of anthelmintic activity. After the collection of worms from local moist place, they were washed with normal saline water in order to remove all fecal matter. The prepared compounds were subjected to this study with Albendazole (2 and 10 mg/ml) as reference standard. Worms were then introduced into the Petri dishes and experimental observations were find during the time taken for paralysis and the death of worms. The time between paralysis and death was recorded in triplicate and the mean time was calculated. The death time was taken when the earthworms in hot water (50 °C).

4. Conclusions

In the present work, the Schiff base HL ligand and its copper complexes were synthesized. The metal ligand stoichiometry of these complexes is 1:2 and 1:1:1. Both complexes are non-electrolytes. Thermal behavior and IR studies of the prepared complexes illustrate the presence of lattice water molecules in the complexes. The g values $g_{\parallel} > g_{\perp} > 2.0023$ suggested that the square planar geometry of C1 and C2. *In vitro* antibacterial, antifungal and anthelmintic efficacies of Schiff base HL and its Cu(II) complexes have been screened. It is found that the Cu(II) complexes exhibit better biological activity than its Schiff base ligand.

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