

**Elaborated studies on Schiff base homo-binuclear Cu(II) and Co(II) complexes,
spectral, thermal, P-XRD and biocidal studies**

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Abstract

A homo-binuclear Cu(II) and Co(II) complexes were synthesized using a Schiff base ligand derived by condensation of 2,6-diaminopyridine and glyoxal. The reasonable geometry of the Schiff base and its binucleating metal complexes were examined by means of elemental and thermal analyses, molar conductance, ¹HNMR, UV-Vis, IR, ESR, P-XRD and mass spectra. The ligand behaved as a polydentate, coordinating through the nitrogen atom of the azomethine group, a nearest nitrogen atom of the pyridine group and the oxygen atom of a glyoxal group. From the spectral studies, a six coordinate environment around the metal dimers was confirmed. The binuclear nature of the metal complexes was assessed from their magnetic susceptibility values. Both of the Schiff base and its metal complexes were also tested for their in vitro antimicrobial activities against some bacterial and fungal strains. Schiff base and the metal complexes were also investigated for its cytotoxic effect against human breast cancer (MCF7) cell lines.

Keywords: Cu(II) and Co(II) complexes, spectral, thermal, P-XRD, biocidal

1. Introduction:

Heterocyclic based Schiff base metal complexes have been studied extensively due to their chelating capability, structural flexibility, interesting electrical as well as the magnetic properties [1] and also found interest in the context of bioinorganic chemistry [2-4]. Currently, they are extensively being used for their hopeful applications in the treatment of several diseases, several chemicals and photochemical reactions [5,6] as well as in numerous industrial applications of science and technology. Schiff base metal complexes resultant from pyridine derivatives with some transition metals such as Cu(II), Co(II), Ni(II) and Zn(II) exhibited important biological statement including antimicrobial, antibacterial, antifungal and anticancer activitie antidiabetic, antioxidant, hypocholesterolemic, antihelminthic, antibacterial, appetizer, hepatoprotective, anticancer and anxiolytic activitiess [7-15]. On the other hand, Schiff base metal complexes also proposed as good acid base indicators [16] and as reservoir sensors [17] because of the color strengthening properties which accompany deprotonation. More than a few Schiff base ligands derived from pyridine derivatives and their metal complexes have also been found to inhibit the growth of tumor cells. Based on the foregoing attentions, we were initiating a line of research on the coordination chemistry of Schiff base compounds. In earlier work, we have designated the Schiff base complexes formed from the reactions of 2,6-diaminopyridine and benzil.[18] In extension of these studies, presently we have reported the synthesis, spectroscopic and biological studies of homo-binuclear Cu(II) and Co(II) Schiff base metal complexes derived from 2,6-diaminopyridine and glyoxal bearing NNNO donor sets.

2. Materials and Method

2.1 Reagents and chemicals

The chemicals such as 2,6-diaminopyridine and glyoxal were getting from Sigma Aldrich and used without further purification. The metal salts were obtained from Merck with analytical grade. All other reagents and solvents were purchased from commercial sources of analytical grade and used as received.

2.2. Physical measurements

The melting/decomposition points were determined by using Technico Melting point apparatus. The FT-IR spectra using KBr were recorded by JASCO/FT-IR 410 spectrometer in the range of 4000-400 cm^{-1} . UV-Vis spectral studies were shown on a Perkin Elmer Lambda-25 spectrophotometer using DMSO as solvent in the range of 200-800 nm. The conductivity measurements of the metal complexes were performed in $\sim 10^{-3}\text{M}$ DMSO solutions working a Digital/TDS conductivity meter(MK509). The ^1H NMR measurements were studied using a bruker spectrometer. The mass spectrometry measurements were recorded using JEOL GC Mate II (EI) spectrometer. Powder X-ray diffraction analysis was done using RIGAKUMINI FLEX II. Antimicrobial screening of the Schiff base ligand and its metal complexes were performed using the agar-well diffusion method. Thermogravimetric analysis was carried out on a PerkinElmer thermal analyzer.

2.3. Synthesis of Schiff base ligand and its metal complexes

2.3.1. Synthesis of Schiff base ligand

The Schiff base were prepared by the hot ethanolic solution of 2,6-diaminopyridine (0.22 g, 2 mmol) was mixed with a ethanolic solution of glyoxal (0.18 ml, 3 mmol) with constant stirring for 3 hours. The color of the reaction mixture was changed to brown color. It was filtered off and washed several times with ethanol and then dried in vacuum.

2.3.2. Synthesis of binuclear Cu(II) and Co(II) complexes

Cu(II) and Co(II) metal complexes of the Schiff base (HL) were produced by template method. An equimolar amount of a hot aqueous solution of the metal chloride (Cu(II) and Co(II)) was added slowly into the hot solution of the Schiff base ligand (L) which was dissolved in DMF. The reaction mixture was refluxed for 4 h, the formation colour precipitate was filtered off then washed with ethanol and left to dry in vacuum.

2.3.3. Antimicrobial activity

The *in vitro* antimicrobial activities of the free Schiff base ligand and its binuclear metal complexes were tested against the gram +ve and gram -ve bacteria in Mueller Hinton-Agar medium. The screening activity of the synthesized compounds was performed using standard disc diffusion method. The MIC of the Schiff base ligand and its metal complexes were determined using the different bacteria and compared with standard antibiotics. The concentration of the drug solution was maintained to be 200 µg/ml in DMSO. The well (8 mm diameter) was filled with the test solution and the plates were inoculated at 37°C for 48 h. During this time, the growth of the inoculated microorganisms was affected and then the inhibition zones developed on the plates were measured.

3. Result and Discussion

3.1 Elemental Analysis

The experimental percentages of C, H, N, O and Cl in the synthesized compounds, colours, yield percentage, molar conductivities and magnetic moments were presented in Table 1. The analytical data were reliable with the proposed molecular formula. The synthesized Schiff base ligand was soluble in DMF, CHCl₃, CH₂Cl₂, DMSO and CH₃CN but insoluble H₂O, EtOH and MeOH. The metal complexes were stable in air, soluble in DMF, DMSO and

insoluble CH_2Cl_2 , CHCl_3 , and CH_3CN . The low molar conductance value predicts the complexes were non-electrolytic in nature.

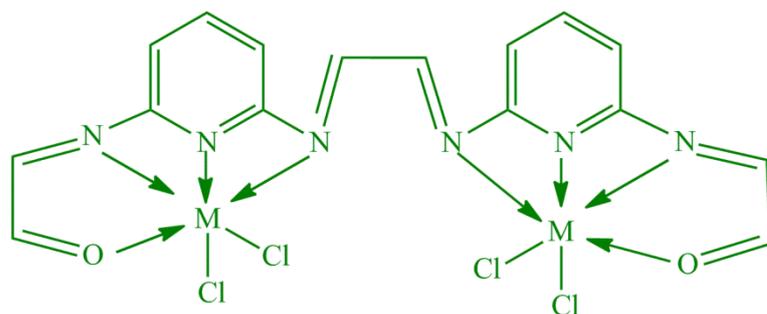


Figure 1. The structure of homo-binuclear Schiff base metal complexes(M-Cu(II) and Co(II))

Table 1. Analytical and physical data of the Schiff bases and their their binuclear metal chelates.

Compounds	Colour	Yield (%)	Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	Magnetic moment μ_{eff} B.M	Elemental analysis found (calculated) (%)					
					C	H	N	O	M	Cl
Ligand (HL)	Brown	78	-	-	60.00 (59.94)	3.78 (3.74)	26.24 (26.22)	9.99 (9.99)	-	-
CuHL	Black	76	38	1.78	32.62 (32.59)	2.05 (2.04)	14.26 (14.26)	5.43 (5.43)	21.57 (22.00)	24.07 (24.03)
CoHL	Brown	64	42	4.70	33.13 (33.10)	2.09 (2.04)	14.49 (14.48)	5.52 (5.52)	20.32 (20.35)	24.25 (24.41)

3.2 IR spectra

The significant infrared peaks were summarized in Table 2 and Figure 2a-b. The IR spectra of the metal complexes were related with the free Schiff base with the intention of determine the connection of coordination sites in chelation. The IR spectra shows the peak of $\nu(\text{C}=\text{N})$

in the region 1601 cm^{-1} representing the Schiff base functional group[19]. The shift of sharp peaks of $\nu(\text{C}=\text{N})$ was usually observed to lower frequencies upon complexation. The free Schiff base shows the bands at 1442 and 766 cm^{-1} , these bands were shifted in the region of 1434 - 1442 cm^{-1} and 766 - 781 cm^{-1} on complexation, approving the pyridine nitrogen atom likewise involving in the coordination sphere of the metal complexes.[20] The band at 1726 cm^{-1} exhibit a stretching vibration of $\nu(\text{C}=\text{O})$ present in free Schiff base. On complexation this band was shifted in the lower region of 1628 - 1652 cm^{-1} , respectively. [21] Additional indication for metal ions coordination through the oxygen, nitrogen and chlorine atoms is the appearance of the new $\nu(\text{M}-\text{O})$, $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{Cl})$ bands in the region of 612 - 614 cm^{-1} , 487 - 494 cm^{-1} , and 335 - 364 cm^{-1} respectively, these results were good agreement with earlier reports[22,23].

Table 2: IR Spectrum of Schiff base and its metal complexes

Compounds	$\nu(\text{C}=\text{N})$ (cm^{-1})	$\nu(\text{C}=\text{O})$ (cm^{-1})	Pyridine ring			ν ($\text{M}-\text{O}$) (cm^{-1})	ν ($\text{M}-\text{N}$) (cm^{-1})	ν ($\text{M}-\text{Cl}$) (cm^{-1})
			Deformations					
			<i>In Plane</i>	<i>Out of plane</i>				
Ligand(HL)	1601	1726	1442	766	-	-	-	
CuHL	1581	1628	1434	781	612	487	335	
CoHL	1578	1652	1438	776	614	494	364	

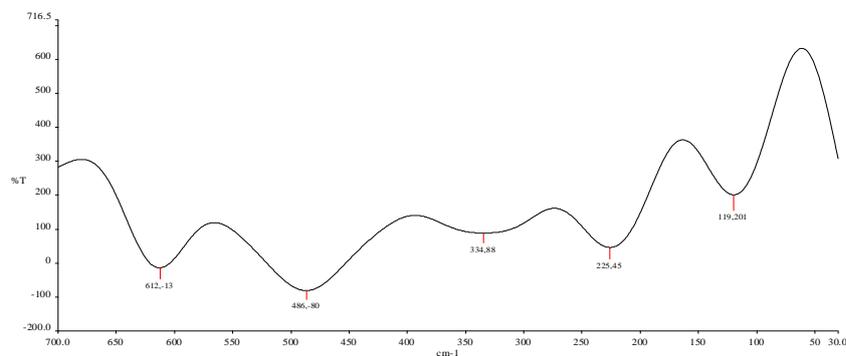


Figure 2a. Far IR for Cu(II) complex

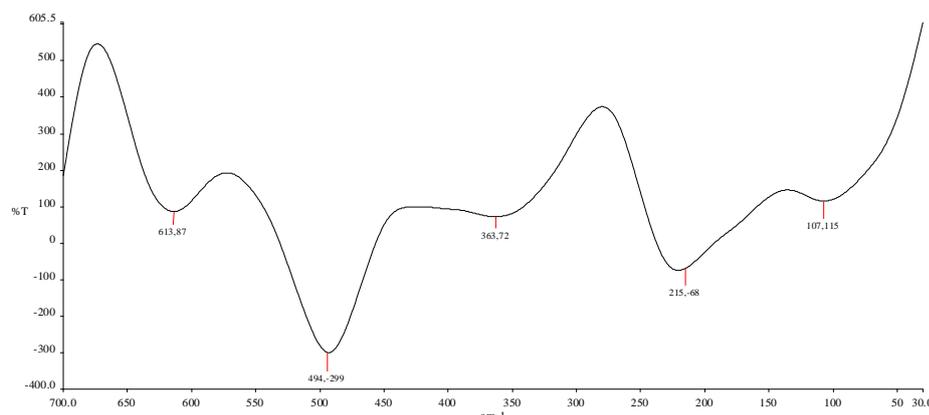


Figure 2b. Far IR for Co(II) complex

3.3 Electronic spectral studies

The UV-Vis spectral data of the Schiff base and its metal complexes were listed in Table 3. The free Schiff base ligand shows absorption bands at 303 and 372 nm, demonstrate the $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transitions respectively. On complexation these bands were shifted in the region of 318-324 nm and 386-398 nm. Cu(II) complex exhibits the broad band casing the range of 690-712 nm corresponds to ${}^2E_g \rightarrow {}^2T_{2g}$ transition and the magnetic moment value (1.78 B.M.) favours the distorted octahedral geometry [24]. The spectrum of Co(II) complex exhibit the two bands at 548 and 472 nm are related to the transitions ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ respectively signifying the octahedral geometry and the value(4.7 B.M.) of magnetic moment showed the complex was paramagnetic and three unpaired electrons consistent to a high spin of this geometry[25].

Table 3: UV Spectrum of Schiff base and its metal complexes

Compounds	$\pi \rightarrow \pi^*(\text{nm})$	$n \rightarrow \pi^*(\text{nm})$	d-d transition	Geometry of the complex
Ligand(HL)	303	372	-	-
CuHL	318	386	690, 712	distorted octahedral
CoHL	324	398	472, 548	octahedral

3.4. Thermal analysis

The thermal studies of Schiff base metal complexes were implementing of TG and DTG analysis with the view to give more perception into the structure of the metal complexes shown in figure 3 [26]. Table 4 provides the complete thermal decomposition data for the Cu(II) and Co(II) complexes. The Cu(II) complex showed that it decomposed in two thermal

steps. The first decomposition peak befallen in the range of 70-223°C with a weight loss of 24.07 % (23.81 % calc.). The percentage loss was reliable with the rejection of four chlorine atoms. In the second decomposition peak arose in the range 223-698°C with a weight loss of 54.36 % (53.57 % calc.) might be associated with the loss of HL leaving 2Cu (21.56 %) as the metallic residue. The thermogram of Co(II) exhibited three decomposition steps. The first decomposition step appeared in the range 68-139°C with a loss of 12.27 % (12.05 % calc.) indicating the loss of 2 chlorine atoms. The second step was occurred in the temperature range of 139-304°C, with a net mass loss of 12.27 % (12.53 % calc.) due to the elimination remain two chlorine atoms in the molecule. The third decomposition step occurred in the 304-684°C range, which was assigned to the loss of Schiff base ligand. The metallic residue persisted at the end of decomposition was assigned as 2Co (20.39%).

Table 4. The thermodynamic data of the thermal decompositions of metal complexes.

Complex	Temperature range/°C	Mass loss (%)		Loss moiety	Peak assignment due to loss moiety
		found	calc.		
[Cu ₂ LCl ₄]	70-223	24.07	23.81	4Cl	[Cu ₂ L]
	223-698	54.36	53.57	L	[Cu ₂]
[Co ₂ LCl ₄]	68-139	12.27	12.05	2Cl	[Co ₂ LCl ₂]
	139-304	12.27	12.53	2Cl	[Co ₂ L]
	304-684	55.43	55.46	L	[Co ₂]

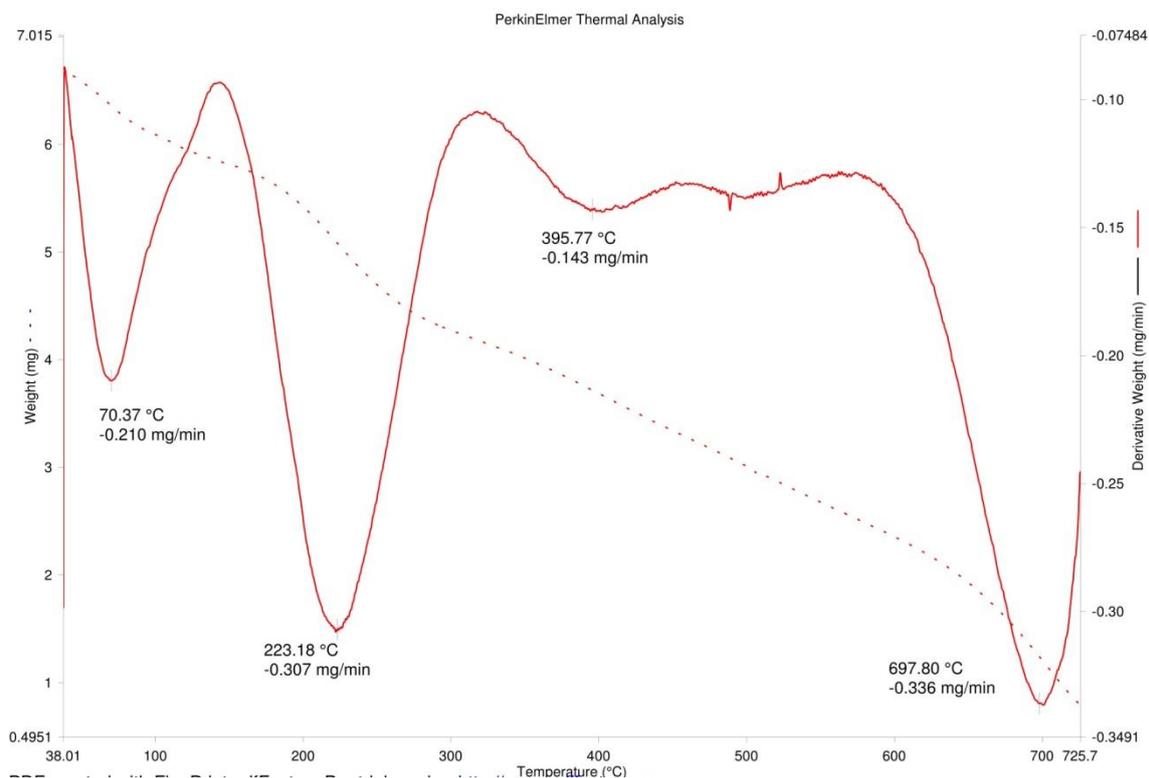


Figure 3. TG/DTA curve for Cu(II) complex

3.5. Mass spectroscopy

Mass spectrometry is an active method for analysis of molar weight and structure of the Schiff base ligand and metal complexes. The mass spectrum of the Schiff base (HL) revealed a molecular ion peak at m/z 320 (Figure. 4) Which was approved the proposed formulae and its geometry. The ligand also indicated a series of ion peaks at 264, 209, 133 and 78 referred to the several fragments such as $[C_{14}H_{10}N_5O]^+$, $[C_{12}H_9N_4]^+$, $[C_7H_5N_2O]^+$ and $[C_5H_4N]^+$ respectively, whichever contributes an indication of the stabilities of fragments and may perhaps be helped to decide molecular formula.

3.6. 1H NMR spectra

1H NMR spectra of the free Schiff base were recorded in DMSO solution indicated that they are NMR active. The ligand established a multiple within the range 7–7.6 ppm, which

allotted to aromatic protons. The imine protons (-CH=N-) were occurring as a singlet at 8.1 ppm. The ligand also showed a singlet peak at 9.6 ppm, belonging to the aldehydic protons.

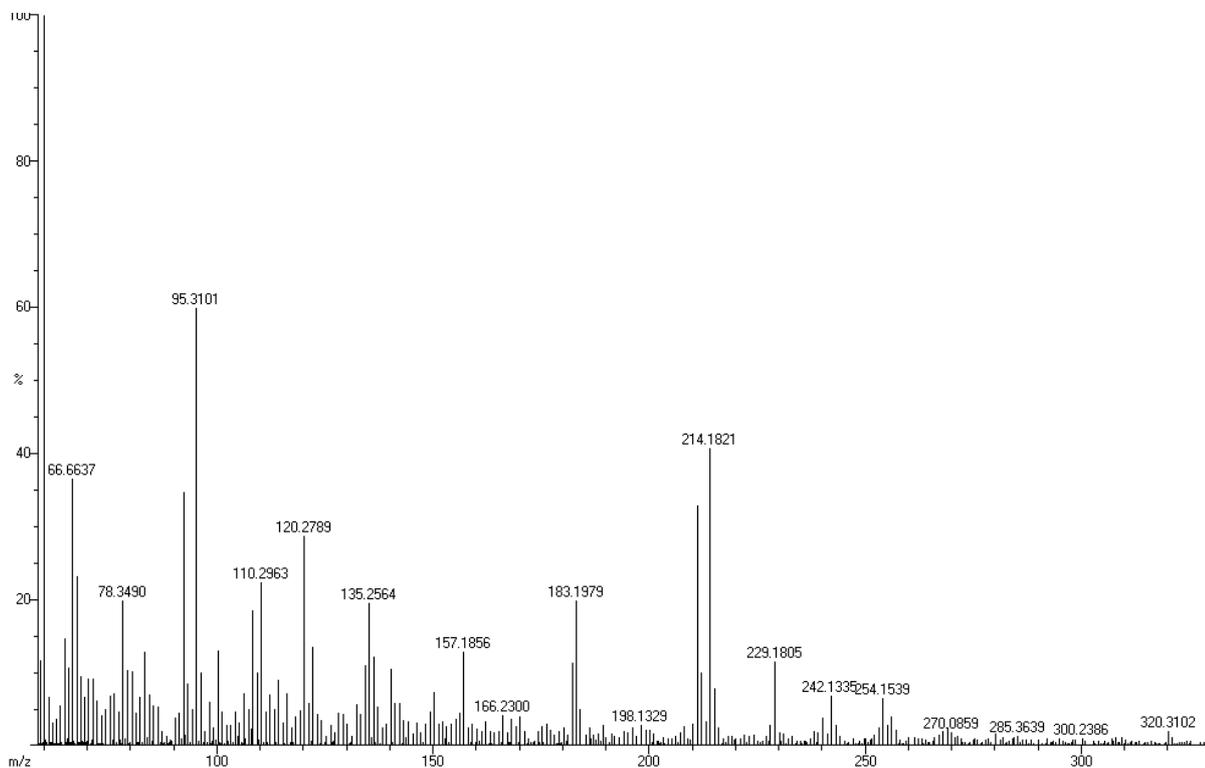


Figure 4. Mass spectrum of Schiff base ligand

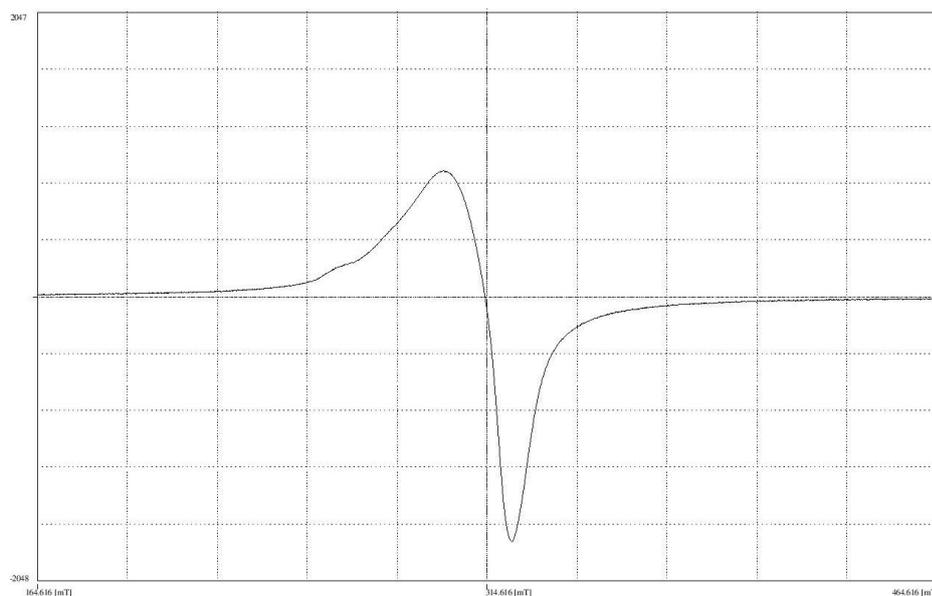


Figure 5. ESR spectrum of Cu(II) complex

3.7. ESR Spectra

The X-band EPR spectrum of Cu(II) complex were recorded at 9.21 GHz frequency under the magnetic field strength 3127 G at room temperature (298 K) and shown in figure 5. The g_{\parallel} and g_{\perp} values were determined from EPR spectra and g_{av} values were calculated. Analysis of the EPR spectrum of the Cu(II) complex gives g_{\parallel} 2.19, g_{\perp} 2.03 and g_{av} 2.08. The tendency $g_{\parallel} > g_{\perp} > 2.002$ perceived for the complex under study designates that the unpaired electron is localized in the dx^2-y^2 orbital of the Cu(II) ion. Consequently, the EPR value supports octahedral geometry for the Cu(II) complex.[27]

3.8. Powder X-ray Diffraction

Though the newly synthesized Cu(II) complex were soluble in some polar organic solvents like DMSO and DMF, crystals that are suitable for single crystal studies are not obtained. The P-XRD pattern of the Cu(II) complex scanned in the range $10-80^{\circ}$ at wavelength 1.54 \AA . The diffractogram and related data illustrate the 2θ value for each peak, relative intensity and inter-planar spacing (d-values). The Cu(II) complex displayed a five reflections with maxima at $2\theta = 27.06^{\circ}$ corresponding to d value 3.29 \AA [28]. The d-spacing has been calculated by using Bragg's equation, $n\lambda=2d \sin \theta$. The unit cell calculations have been calculated and $h^2 + k^2 + l^2$ values were determined. The $h^2 + k^2 + l^2$ values of Cu(II) complex were 1, 3, 4, 6, and 10. The calculated lattice parameter for Cu(II) complex was $a=b=c= 6.658$. It was witnessed that the presence of forbidden number 7, 15 indicates that the Cu(II) complex may belong to hexagonal or tetragonal systems (figure 6).

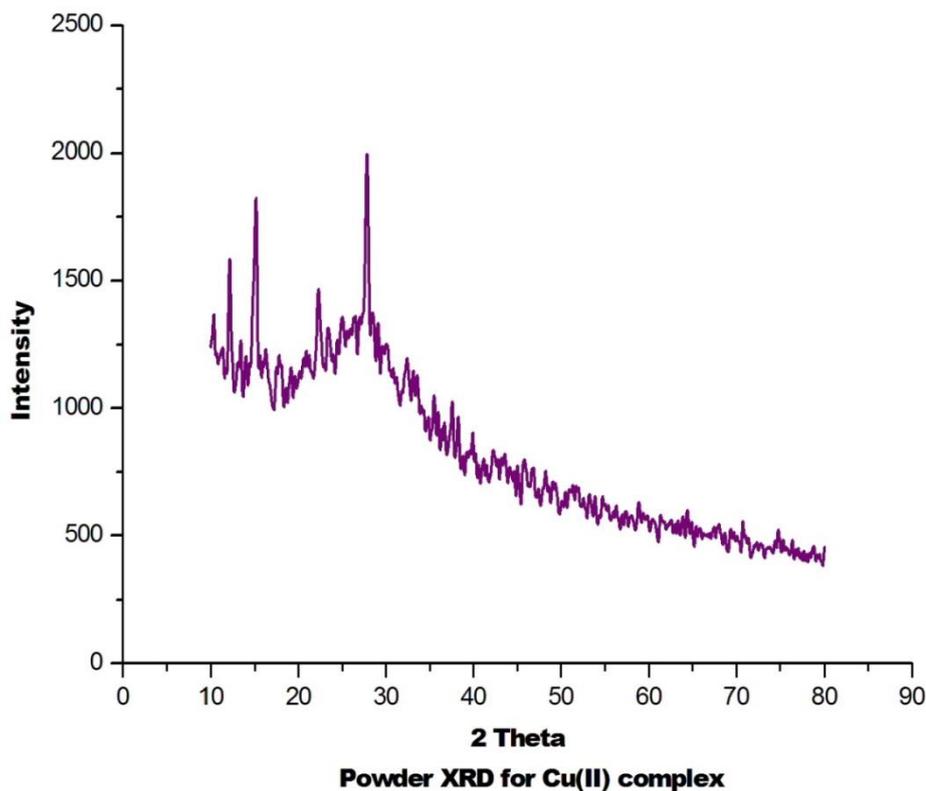


Figure 6. P-XRD for Cu(II) complex

3.9. The antimicrobial activity

The screening effect of the free Schiff base ligand and their metal complexes against four bacteria (*S. aureus*, *B. Suptiles*, *K. Pneumonia* and *E. Coli*) and two fungi was tested by the agar well-diffusion method with standard drug. Furthermost of the reported complexes showed enhanced biological activity towards bacteria with respect to that of the free ligands (Figure. 7). This enhancement in the activity can be clarified on the basis of chelation theory [29]. On comparing the antimicrobial of the ligand and their metal complexes with the standard ciprofloxacin (antibacterial agent) and griseofulvin (antifungal agent), it was resolved that:

- (1) The antimicrobial activity of ligands were sufficient in comparison with the standard used.

(2) The antibacterial and antifungal activity of Cu(II) complex has higher activity in comparison with their corresponding ligand.

(3) The Co(II) complex also have similar activity in comparison with the ligand.

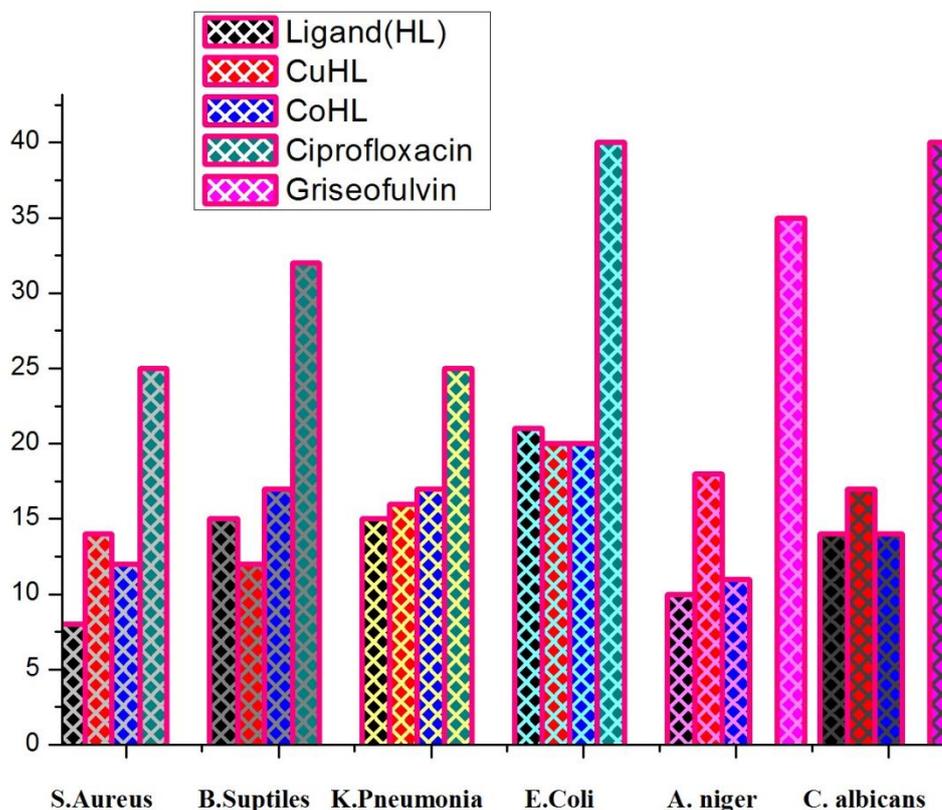


Figure 7. Antimicrobial activity of Schiff base and its metal complexes

4. Conclusion

In summary, the work described elaborate the synthesis and spectroscopic characterization of Cu(II) and Co(II) complexes with a new Schiff base ligand prepared by condensation of 2,6-diaminopyridine with glyoxal. The Schiff metal complexes were characterized using various physiochemical methods. The Schiff base ligand acts as a polydentate ligand and the metal complexes show octahedral geometry. Their low molar conductance values confirm that non-electrolytes. Thermal analysis measurements exhibited a high thermal stability of the complexes. P-XRD revealed that the Cu(II) complex were nano crystal in nature and the

Co(II) complex were amorphous. The Schiff base ligand and their metal complexes are found to possess considerable antimicrobial activity. The Cu(II) complex has high antimicrobial activity than others.

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