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RESEARCH ARTICLE

SYNTHESIS, SPECTRAL CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF SOME NOVEL SCHIFF BASE METAL COMPLEXES OF VANILLIN BASED DIHYDROPYRIMIDONE HETEROCYCLIC PRODUCT AND 4-AMINOANTIPYRINE

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ABSTRACT

A series of novel metal complexes of general formula $[ML_2]Cl_2$ and $[CrL_2Cl_2]Cl$ where M is Cu(II), Co(II) and L is a Schiff base formed by condensation of dihydropyrimidone derivative of vanillin (Biginelli Product) and 4-aminoantipyrine have been prepared and characterized by analytical, spectral, magnetic and conductance measurements. Magnetic measurements and electronic spectral studies suggest an octahedral structure for the Cr(III) complex and square planar geometry for Cu(II) and Co(II) complexes. The data show that the complexes have composition of the ML_2 type. The antimicrobial screening of the ligand and its complexes have been extensively studied on bacterias like *E.coli, Vibrio spp., Staphylococcus aureus, Pseudomonas aeroginosa, Bacillus spp., Vibrio parahaemolytics, Salmonella spp., Aeromonas spp., Klebsiella spp., Proteus spp.* and fungi such as *Candida albicans, Aspergillus flavus, Pencillium spp., Aspergillus niger, Trichophyton.* The results also indicate that the metal complexes are better antimicrobial agents as compared to the Parent Schiff base ligand and Biginelli product.

INTRODUCTION

During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors[1-4]. Schiff base complexes of transition metals have played prominent role in the development of co-ordination chemistry[5]. Schiff bases are considered as "Privileged ligands", because they are easily prepared by the condensation between aldehydes and amines. Among these derivatives, 4-aminoantipyrine is a remarkable reagent due to its importance in biological, pharmacological, clinical and analytical applications[6,7]. In particular, heterocyclic Schiff base ligands containing 'N' and 'O' as donors could be applied variously. They have been of great importance due to their synthetic flexibility, selectivity and sensitivity towards the metal ion. The heterocyclic ring containing S, N and O import special biological activity to these Schiff bases and their metal complexes[8]. In addition, when the Schiff base is formed by condensation of 4-aminoantipyrine with dihydropyrimidones of vanillin, additional heterocyclic ring is included. This could also enhance the activity of complex.

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Meanwhile the dihydropyrimidones, the products of Biginelli reaction are widely applicable in the field of pharmaceutics as calcium channel blockers and antihypertensive agents[9]. Literature search reveals that more research work has been carried out so far on the synthesis of Schiff base derived from 4-aminoantipyrine and several aldehydes. But less attention was found to be paid for synthesis of Schiff base derived from dihydropyrimidone heterocycle and 4-aminoantipyrine. Bearing all the above aspects, the present paper therefore aims to prepare a Schiff base (derived from the reaction of 4-AAP and dihydropyrimidone obtained from vanillin) and its complexes with Cu(II), Co(II) and Cr(III) ions and to illustrate their geometrical structures by using different techniques and also to study their antimicrobial activity.

MATERIALS

All the chemicals used were of analytical reagent grade purchased from Aldrich, Fischer etc. Commercial solvents were distilled and used for synthesis.

METHODS

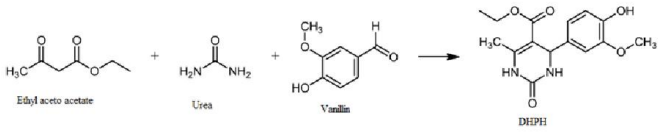
Elemental analysis for carbon, hydrogen and nitrogen were carried out using Perkin Elmer 240C elemental analyzer. Molar conductance measurements were carried out with 10^{-3}

mol/L solutions of the complexes in DMSO at room temperature using ELICO-CM 180. Infrared spectral studies were carried out using KBr discs on a JASCO FTIR/4000 spectrophotometer. The electronic spectra were recorded on JASCO UV spectra from 200-800 nm. The ESI mass spectra of the ligand and its complexes were recorded using Mass QTOF micromass spectrometer using nitrogen (CE8eV, CV27eV). Magnetic Susceptibilities were recorded at room temperature using Lake Shore model 7410 VSM at room temperature using Std Ni as calibrate. The antimicrobial activity assay was performed by agar disc diffusion method. The Electron paramagnetic resonance (EPR) spectra for all the complexes were recorded by using a Bruker EMX EPR instrument at 300 K.

Synthesis of Biginelli product of Vanillin (DHPH)

Vanillin (1.52g, 10mmol), Ethylacetoacetate (1.95 g, 15 mmol), Urea (0.6 g, 10 mmol) and 5 ml of HCl/ethanol were refluxed in a 25 ml RB flask for 1.5 hrs at 50°C. The contents were then poured into ice and the solid reddish brown precipitate was filtered and recrystallised with hot aqueous ethanol (Scheme 1). The product formed is dihydropyrimidone heterocyclic product (DHPH). The purity of the product was checked with the literal melting point of biginelli product ~220°C (obt-225°C). The product is already synthesized well known compound.

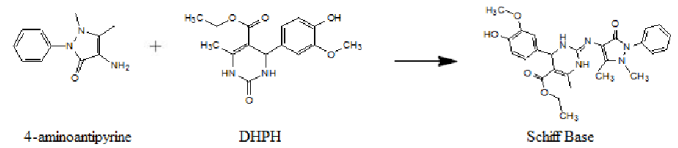
Scheme 1 Synthesis of DHPH



Synthesis of Schiff base ligand (L)

An ethanolic solution of 4-aminoantipyrine (2.033 g, 10 mmol) was added to DHPH (3.08 g, 10 mmol) dissolved in 40 ml ethanol and was refluxed for 2 hrs at 50°C. The contents were then poured into ice and the solid yellow precipitate was filtered and the ligand was recrystallised with ethanol (Scheme 2).

Scheme 2 Synthesis of Schiff Base



Synthesis of Complexes (ML_2)

A solution of metal (II) chloride in ethanol (10 mmol) was refluxed with an ethanolic solution of the Schiff base (20 mmol, 9.82 g) in 1:2 ratios. The solution was then reduced to one-third on a water bath. The precipitated solid complex was filtered, washed and recrystallised with ethanol (Figure 3).

Antibacterial activity assay

Stock cultures were maintained at 4°C on Nutrient agar Slant. Active cultures for experiments were prepared by transferring a loop full of culture from the stock cultures into the test tubes containing nutrient broth, that were incubated for 24hrs at 37ºC. The assay was performed by agar disc diffusion method. Antibacterial activity of extracts was determined by disc diffusion method on Muller Hinton agar (MHA) medium. Muller Hinton Agar (MHA) medium is poured into the petriplate. After the medium was solidified, the inoculums were spread on the solid plates with sterile swab moistened with the bacterial suspension (*Staphylococcus aureus, Salmonella spp., E.coli, Vibrio spp., Pseudomonas aeroginosa, Vibrio parahaemolytics, Aeromonas spp., Klebsiella spp., Proteus spp.,and Bacillus spp.,*). The disc was placed in MHA plates and 20 µl of the samples (Concentration: 1000 µg, 750 µg and 500 µg) were placed in the disc. The plates were incubated at 37°C for 24 hrs. Then the antimicrobial activity was determined by measuring the diameter of zone of inhibition.

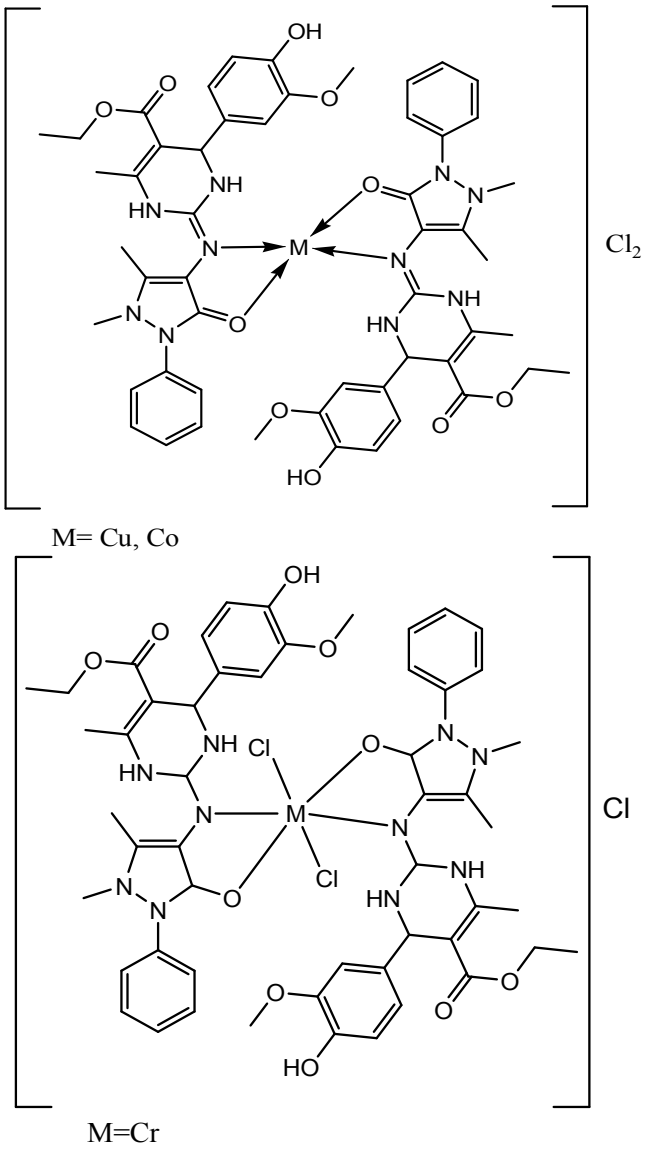


Figure 3. Proposed Structures of Metal Complexes

Antifungal activity Assay

Stock cultures were maintained at 4°C on Sabouraud Dextrose agar Slant. The assay was performed by agar disc diffusion method. Antifungal activity of the extracts was determined by

disc diffusion method as explained above on Sabouraud Dextrose agar (SDA) medium. Then the antifungal activity was determined by measuring the diameter of zone of inhibition.

RESULTS AND DISCUSSION

The colour, percentage yield, molar conductance, analytical data and melting point of complexes are presented in Table 1. The data from complexes correspond well with general formula ML_2, where M= Co(II), Cu(II), Cr(III), and L= $C_{26}H_{29}N_5O_5$. The molar conductance values of the complexes show that the chelates are 1:2 non electrolytes[10-12] in DMSO, which are in the range 1.42-1.86 Ω^{-1} cm^2 mol^{-1}.

Table 1. Analytical Data and Physical Properties of Ligand and Complexes

S No.	Compound	Mol.Wt.	Colour	Yield %	M.Pt (°C)	Solubility	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$)	Elemental Analysis % Found(Calc.)					
								C	H	N	O	M	Cl
1	$C_{26}H_{29}N_5O_5$= L	491.22	Pale Yellow	60	248.5	Ethanol, DMSO, $CHCl_3$	--	63.27 (63.53)	5.29 (5.95)	14.98 (14.27)	16.44 (16.27)	--	--
2	$[CrL_2Cl_2]Cl$	1160.50	Brown	56	261.2	Ethanol, DMSO, $CHCl_3$	1.86	54.85 (54.96)	5.65 (5.61)	12.07 (12.12)	13.79 (13.72)	4.48 (4.44)	9.16 (9.18)
3	$[CoL_2]Cl_2$	1112.68	Brown	52	267.3	Ethanol, DMSO, $CHCl_3$	1.59	56.12 (56.13)	5.25 (5.26)	12.59 (12.56)	14.38 (14.38)	5.30 (5.27)	6.37 (6.40)
4	$[CuL_2]Cl_2$	1117.53	Dark Brown	56	272.1	Ethanol, DMSO, $CHCl_3$	1.42	55.89 (55.80)	5.23 (5.22)	12.53 (12.51)	14.32 (14.29)	5.69 (5.74)	6.34 (6.33)

Electronic Spectra and Magnetic measurements

The Electronic Spectra were recorded in DMSO. In the spectrum of the ligand (Figure 4a), the bands in the range 271nm and 376 nm are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively[13]. During the formation of complexes, these bands are slightly altered in their range due to the metal co-ordination with the ligand[14] (Table 2).

Table 2. Electronic Absorption Spectral Data of the Ligand and Complexes

S No.	Compound	λ_{max} (nm)	Assignments	μ_{eff} (B.M)
1	L	271	$\pi \rightarrow \pi^*$	-
		376	$n \rightarrow \pi^*$	
2	$[CrL_2Cl_2]Cl$	289	INCT	3.84
		324	$^4A_2g(F) \rightarrow {}^4T_1g(P)$	
		402	$^4A_2g(F) \rightarrow {}^4T_1g(F)$	
		542	$^4A_2g(F) \rightarrow {}^4T_2g(F)$	
3	$[CoL_2]Cl_2$	280	INCT	2.10
		352	INCT	
		521	$^2A_1g \rightarrow {}^2B_1g$ $^2A_1g \rightarrow {}^2Eg$	
		562		
4	$[CuL_2]Cl_2$	286	INCT	1.87
		336	INCT	
		532	$^2B_1g \rightarrow {}^2Eg$ $^2B_1g \rightarrow {}^2A_1g$	
		620		

Cu(II) complex

At room temperature, the magnetic moment of Cu(II) complex at 1.75 B.M corresponds to one unpaired electron[15,16]. The UV spectrum of Cu(II) chelate exhibits bands at 532 & 620 nm which are assigned to $^2B_1g \rightarrow {}^2Eg$ and $^2B_1g \rightarrow {}^2A_1g$ transitions respectively[15]. This confirms the square planar configuration. The magnetic moment value and the ligand field parameters are consistent with square planar configuration.

Co(II) complex

The magnetic moment of Co(II) complexes is found to be 2.18 B.M. This suggests a low spin square planar geometry. This is due to mixing of ^2A_2g with ^2A_1g ground term on account of spin orbit coupling, so that magnetic moment of Cobalt complex goes above the spin value of 1.73 B.M[17]. In addition, the electronic spectra of Co(II) complex are characterized by bands in the range 280-560 nm (Figure 4b). This behaviour can be assigned to $^2A_1g \rightarrow {}^2B_1g$ and $^2A_1g \rightarrow {}^2Eg$ transitions[18]. This supports the square planar geometry to the complex.

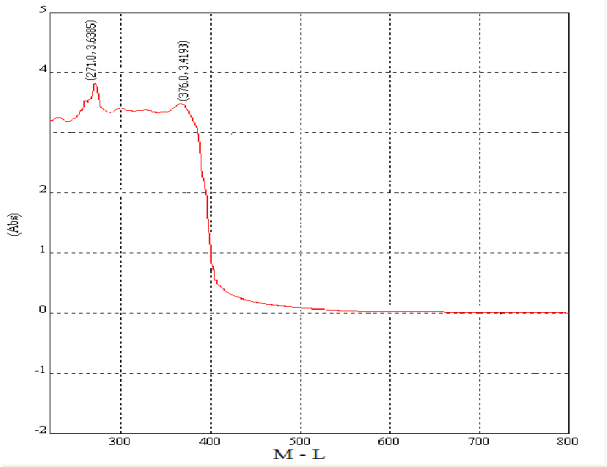


Figure 4a. UV Spectra of Ligand

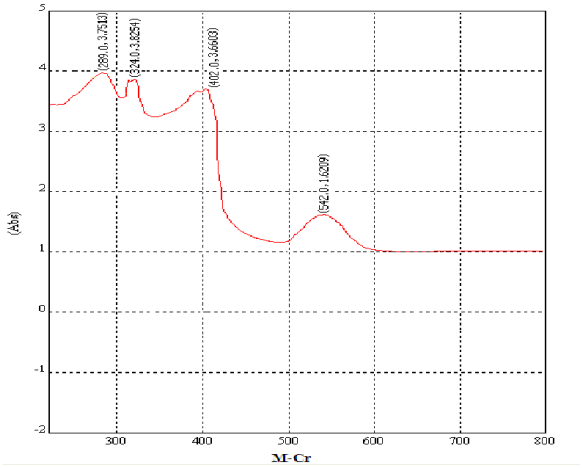


Figure 4b. UV Spectra of Cr(III) complex

Cr(III) complex

The electronic spectral data of Cr(III) complex shows bands at 542, 402 & 289 nm, which are assigned to $^4A_2g(F) \rightarrow {}^4T_2g(F)$, $^4A_2g(F) \rightarrow {}^4T_1g(F)$, $^4A_2g(F) \rightarrow {}^4T_1g(P)$ transitions respectively[19]. This may confirm an octahedral geometry around the metal complex. The magnetic moment value also supports the geometry. The magnetic moment of 3.81BM is slightly less than 3.88 BM, the spin only of octahedral complexes due to small spin orbit coupling constant[20].

IR Spectra

The diagnostic IR frequencies of the ligand and its complexes are compiled in Table 3. The IR spectrum of free ligand is compared with that of complexes (Figure.5a & 5b) in order to determine the co-ordination sites that may have involved in chelation. The observed band at 1599 cm^{-1} due to $\nu_{C=N}$ in free Schiff base is shifted to lower frequencies by about 70 cm^{-1} in the spectra of complexes which attributes to the coordination of C=N to the metal ion[21]. A band at 1698 cm^{-1}, $\nu_{C=O}$ stretching frequency of free Schiff base which is also shifted to lower frequency ranging from 1635-1649 cm^{-1} in all the metal complexes, suggests the co-ordination of ligand to metal ion via the C=O group. The phenolic -OH stretching which appears as a strong band in free ligand at 3242 cm^{-1} and a band at 3539 cm^{-1} due to ν_{N-H} do not undergo any change in the spectra of the complexes. It reveals that phenolic –OH group and the N-H group do not involve in the bond formation with metals[22]. The spectra of metal complexes also show some new bands in the regions, 465-478 cm^{-1} and 571-590 cm^{-1} which are probably due to the formation of M-N, M-O bond respectively[21,23]. The spectra of Cr(III) complex shows an extra band at 396 cm^{-1} which attributes to M-Cl bond[24].

Table 3. Infrared Spectral Data of Ligand and Complexes (cm^{-1})

S No	Compound	ν_{OH}	ν_{N-H}	ν_{O-CH3}	$\nu_{C=N}$	$\nu_{C=0}$	ν_{M-N}	ν_{M-O}	ν_{M-Cl}
1	L	3242	3539	1202	1599	1698	-	-	-
2	$[CrL_2Cl_2]Cl$	3249	3516	1205	1519	1638	478	593	396
3	$[CoL_2]Cl_2$	3253	3502	1206	1531	1649	465	571	-
4	$[CuL_2]Cl_2$	3241	3498	1207	1525	1640	473	585	-

EPR analysis

The X-band ESR spectrum of powder Cu(II) complex were recorded at room temperature using DPPH as reference standard. The ESR studies of paramagnetic transition metal (II) complexes yield information about the distribution of the unpaired electron. The ESR spectrum of Cu complex (Figure 6) at 300 K shows one intense absorption band in high field region and its isotropic tumbling motion of the molecules gives the value of $g_{\|}$ (2.272) > $g_{\perp}$ (2.055). This is due to the unpaired electron lies in $d_{x^2-y^2}$ orbital with ^2B_1g as ground state. This supports the geometry as square planar[25]. Also, g|| > g⊥ > 2 supports that the system is axially symmetric. The value of G provides whether the exchange interaction is negligible or not. The spectrum of Cu complex gives the value of G (5.117) greater than 4 and hence the tetragonal axes are aligned parallel or slightly misaligned and hence the exchange interaction is negligible[23].

Mass Spectra

The ESI mass spectra of the ligand and its metal complexes were used to compare the stoichiometric composition. The Schiff base ligand shows a molecular ion peak at m/z 491. The molecular ion peaks for complexes of Co, Cu, Cr are observed at m/z 1112, 1117, 1160 respectively which were in good agreement with the molecular weight of the proposed structures. This clearly coincides with the stoichiometry of metal chelates as ML_2 type.

Antimicrobial activities

The data of the antibacterial and antifungal activities of ligand and complexes are given in Table 4 & 5. The antimicrobial activity was determined by measuring the diameter of zone of inhibition (Figure 7 & 8). The data reveals that the complexes have higher inhibitory activities than the free ligand (Figure 9a & 9b). The enhancement of the activity of ligand on complexation can be explained by Overtone's Concept and Chelation Theory[26]. This theory states that chelation reduces the polarity of the metal atom by the partial sharing of its positive charge with donor groups and possible π- electron delocalization over the whole ring. This results in increasing lipophilic character of the complex and favours the permeation of the complex through the lipid layer of cell membrane. The complex blocks the metal binding sites in the enzymes of microorganisms. Consequently the complex disturbs the metabolism pathways in cell, resulting in the extinction of microorganisms. The mode of action of the compounds may involve formation of a hydrogen bond through the azomethine group (>C=N–) with the active centers of various cellular constituents, resulting in interference with normal cellular processes[27,28]. Heterocyclic compounds do play important role in regulating biological activities[29-31]. This is further evidenced when vanillin and 4-aminoantipyrine based Schiff base metal complexes show good antibacterial activity as they contain heterocyclic group[13]. Comparatively this activity is highly enhanced for the metal complexes formed from vanillin based dihydropyrimidone heterocyclic product and 4-aminoantipyrine. The antimicrobial activity of the complexes follows the order $Co^{2+} < Cu^{2+} < Cr^{3+}$, which may be due to the increasing stability of the complexes[32].

Conclusion

The potentiation of antimicrobial activity of ligand by metal chelation has been studied. A Schiff base ligand [2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)-4-(4-hydroxy-3-methoxy-phenyl)-6-methyl-1, 2, 3, 4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester] has been synthesized from biginelli product of vanillin and 4-aminoantipyrine. Its divalent metal complexes of Cu, Co, Cr were also synthesized. The structural interpretations of these complexes have been done from FTIR, UV/Vis, EPR and ESI Mass spectra. The ligand behaved as a bidendate donor by using its carbonyl O and azomethine N as binding sites for the metals. Square planar structure was proposed for Cu(II) and Co(II) complexes and an octahedral geometry was predicted to Cr(III) complex. The ligand showed low activity against some microbes but the complexes were remarkably more active against the bacteria and fungi species. The activity is in the

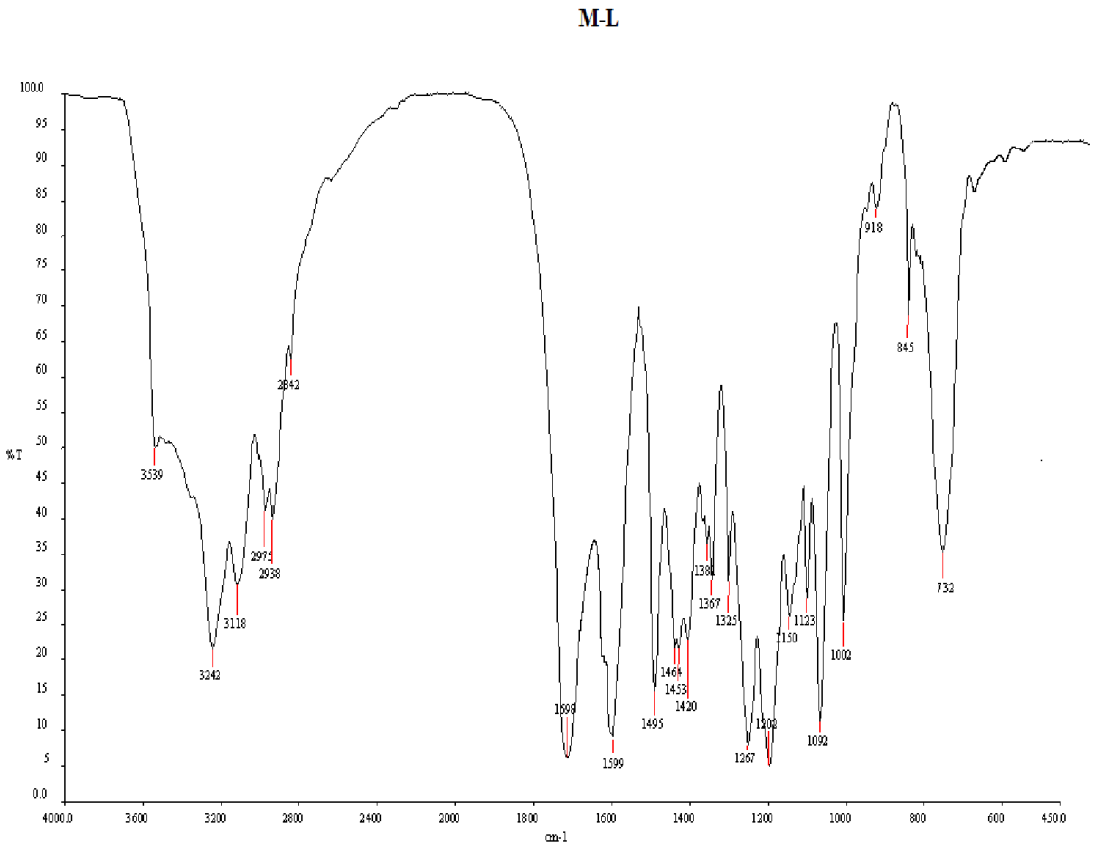


Figure 5a. IR Spectra of Ligand

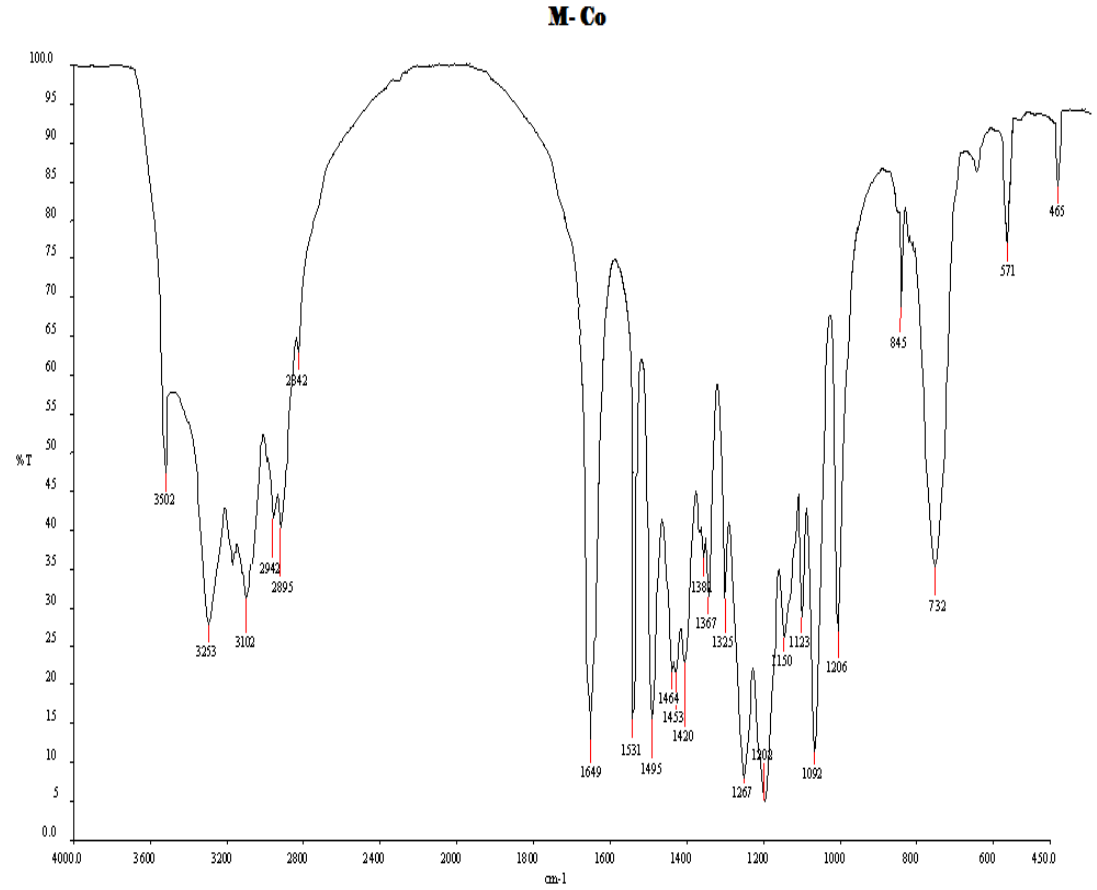


Figure 5b. IR Spectra of Co(II) complex

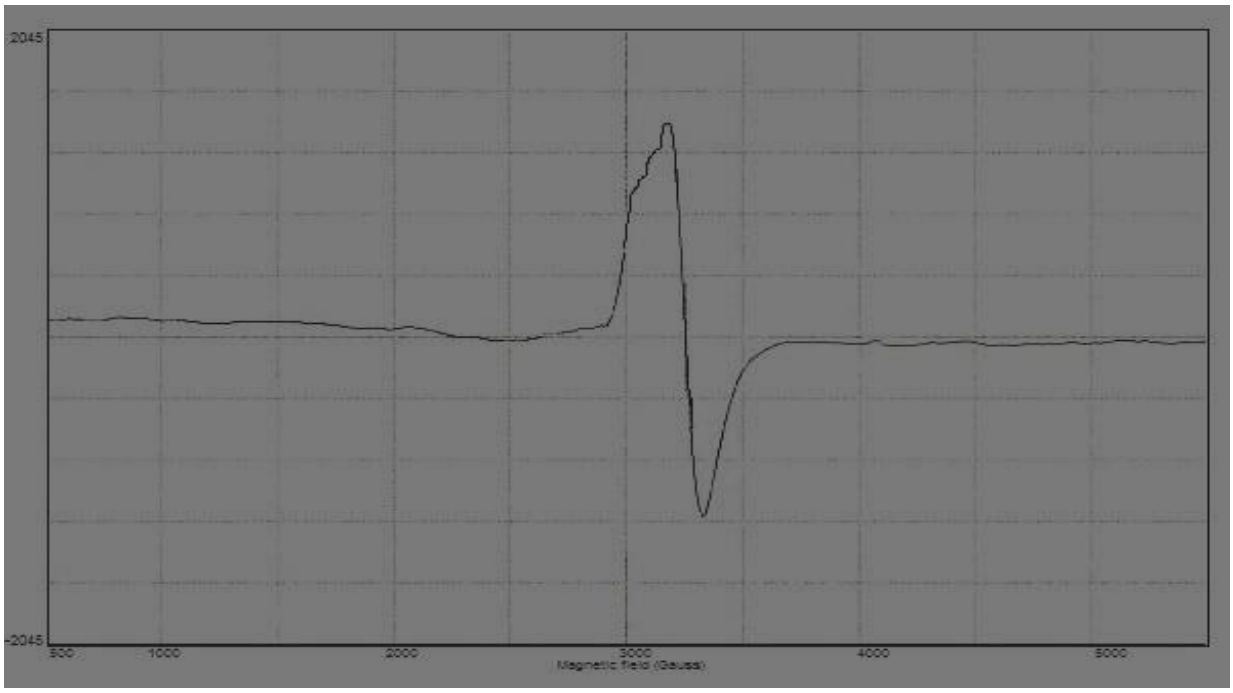
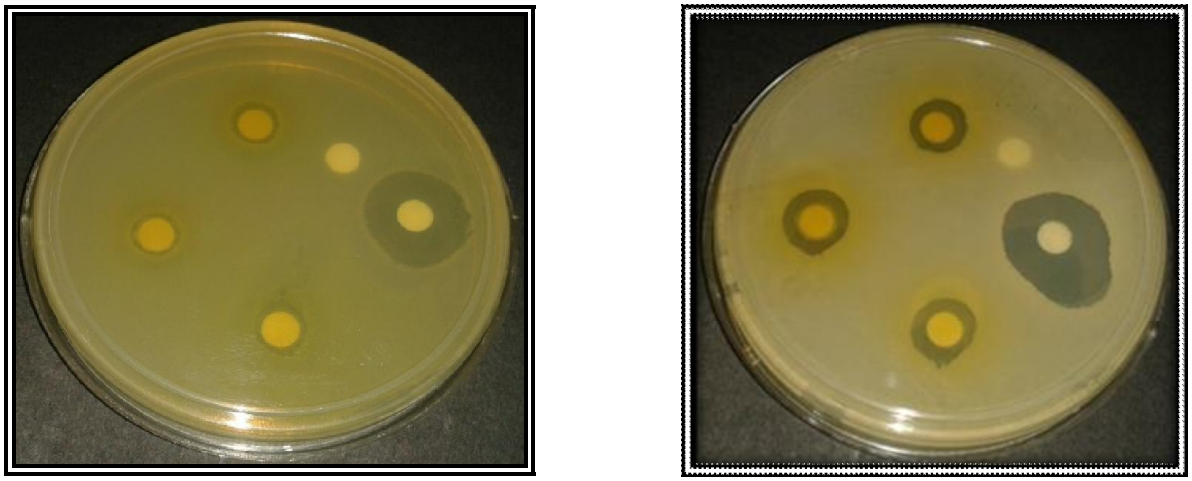
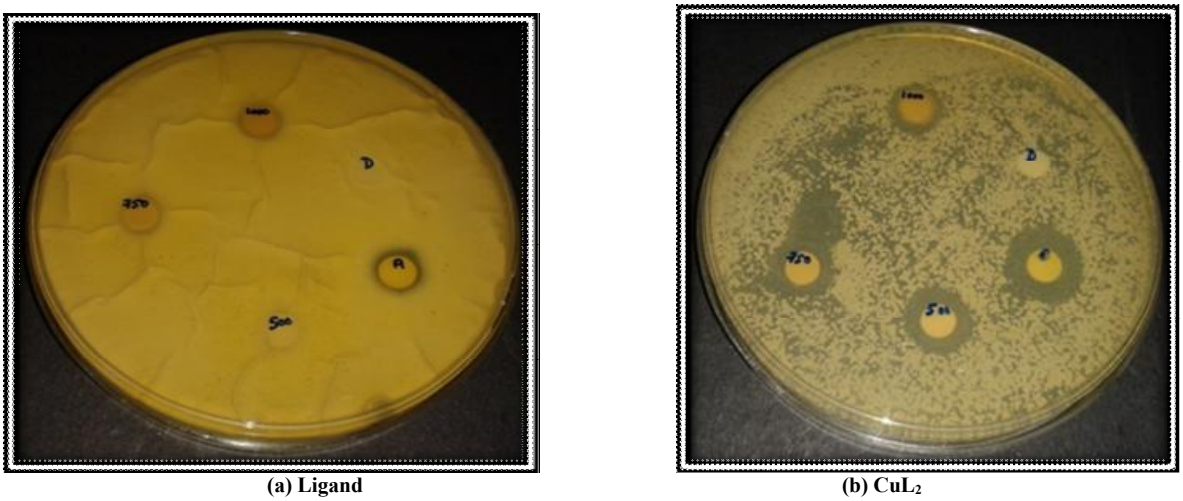


Figure 6. EPR Spectra of CuL_2



(a) Ligand **(b) CuL_2**

Figure 7. Antibacterial Activity in *Pseudomonas aeroginosa*



(a) Ligand **(b) CuL_2**

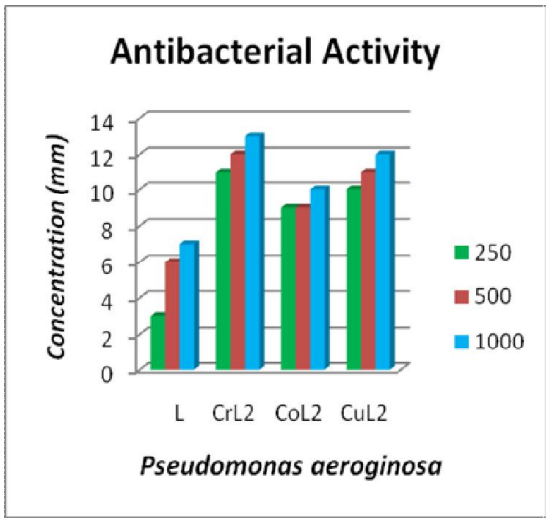
Figure 8. Antifungal Activity in *Aspergillus flavus*

Table 4. Antibacterial Activity Data of Ligand and Complexes

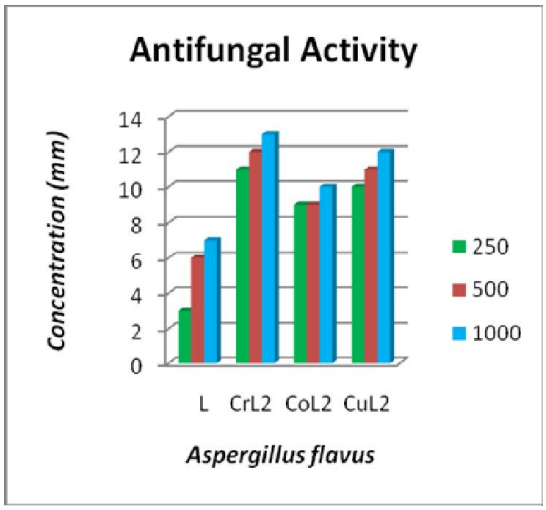
Compound Organisms	Zone of Inhibition (mm)													
	L			CrL_2			CoL_2			CuL_2			DMSO	Antibiotic (1mg/ml)
	A	B	C	A	B	C	A	B	C	A	B	C		
E.coli	5	3	2	10	10	9	8	7	7	9	9	8	--	10
Vibrio spp.	6	6	5	12	11	11	8	6	6	11	10	10	--	12
Staphylococcus aureus	6	5	3	10	9	8	9	8	7	9	8	8	--	10
Pseudomonas aeroginosa	7	6	3	13	12	11	10	9	9	12	11	10	--	14
Bacillus spp.	5	4	3	15	14	13	12	11	9	13	12	11	--	15
Vibrio parahaemolytics	7	5	4	13	12	11	11	9	8	11	10	8	--	13
Salmonella spp.	6	5	4	10	9	9	9	7	7	9	8	7	--	10
Aeromonas spp.	7	6	3	10	9	9	9	8	6	9	8	8	--	10
Klebsiella spp.	5	4	3	14	13	13	12	10	8	12	10	10	--	15
Proteus spp.	7	6	5	14	13	12	11	10	10	13	10	9	--	15

Table 5. Antifungal Activity Data of Ligand and Complexes

Compound Organisms	Zone of Inhibition (mm)													
	L			CrL_2			CoL_2			CuL_2			DMSO	Antibiotic (1mg/ml)
	A	B	C	A	B	C	A	B	C	A	B	C		
Candida albicans	6	5	5	7	7	6	7	6	5	7	6	6	--	7
Aspergillus flavus	6	5	5	10	9	9	8	7	5	9	8	8	--	10
Pencillium spp.	7	6	5	10	9	9	8	8	6	9	8	7	--	10
Aspergillus niger	5	4	4	5	5	4	4	3	2	5	4	4	--	5
Trichophyton	7	5	4	8	8	7	7	6	6	8	8	7	--	8



(a) Antibacterial in Pseudomonas aeroginosa



(b) Antifungal in Aspergillus flavus

Figure 9. Activity Charts

order Co < Cu < Cr. It is hereby suggested that this ligand and its metal complexes can be used as metal based drugs.

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