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Synthesis, Characterization And Biological Significance of Some Novel Schiff Base Transition Metal Complexes Derived from 4-Aminoantipyrine And Dihydropyrimidine of Vanillin

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ABSTRACT

A novel series of transition metal complexes of Ni(II), Zn(II), Cd(II) and Hg(II) have been synthesized from the Schiff base derived from dihydropyrimidine derivative of vanillin (Biginelli Product) and 4-aminoantipyrine. These complexes have been characterized from their elemental analysis, melting point, molar conductance, mass, UV-Vis, IR, ^{1}H-NMR and ^{13}C-NMR spectral studies. The data show that the complexes have composition of the ML_2 type. The UV-Vis, magnetic susceptibility data of the complexes suggest a tetrahedral geometry around the central metal ion except the Ni(II) complex, which has a square planar geometry. The antimicrobial screening of the ligand and its complexes have been extensively studied on bacteria 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.

Keywords: 4-aminoantipyrine derivatives, Ni(II), Zn(II), Cd(II) and Hg(II) metal complexes, Schiff base complexes, Antimicrobial studies.

INTRODUCTION

Complexes of Schiff bases are of having great importance due to their biological, clinical and analytical applications. Schiff bases are characterized by -CH=N- (imine) group which is important in elucidating the mechanism of transimination and racemisation reactions in biological systems [1, 2]. The transition metal complexes of 4-aminoantipyine and its derivatives have been extensively examined due to their wide applications in various fields like biological, analytical and therapeutical fields [3-5]. Further they have been investigated due to their diverse biological properties like antifungal [6, 7], antibacterial [8, 9], analgesic, sedative, antipyretic, anti-inflammatory agents and DNA binding properties [10, 11]. The coordinating property of 4-aminoantipyrine has been modified to give a flexible ligand system formed by condensation with reagents like aldehydes, ketones, thiosemicarbazides and carbazides etc. Meanwhile,

Dihydropyrimidines, the products of Biginelli reaction are widely used in the pharmaceutical industry as calcium channel blockers and antihypertensive agents [12].

Literature search reveals that more attention has been given on the synthesis of Schiff base derived from 4-aminoantipyrine and several aldehydes. But less attention was found to be paid for the 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 dihydropyrimidine obtained from vanillin) and its complexes with Zn(II), Cd(II), Hg(II), and Ni(II) ions and to illustrate their geometrical structures by using different techniques and also to study their antimicrobial activity.

MATERIALS AND METHODS

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^{-1} 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. NMR spectra were recorded in $CDCl_3$ on JASCO FTNMR spectrometer using TMS as reference. The ESI mass spectra of the ligand and its complexes were recorded using Mass QTOF Micro Mass Spectrometer using nitrogen (CE8eV, CV27eV). Magnetic Susceptibility was recorded at room temperature using Lake Shore model 7410 VSM at room temperature using Std Ni as calibrate. The μ_{eff} values were corrected for the diamagnetic effect of ligand and metal. The antimicrobial activity assay was performed by agar disc diffusion method.

Synthesis of Biginelli product of Vanillin (DHPH): Vanillin (1.52g,10mmol), Ethyl acetoacetate (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 h at 50°C. The contents were then poured into ice and the solid reddish brown precipitate was filtered and recrystallised with hot aqueous ethanol (Figure 1). The product formed is dihydropyrimidone heterocycle (DHPH). The purity of the product is checked with the literal melting point of Biginelli product ~220°C (obt-225°C). The product is already synthesized well known compound.

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 were refluxed for 2 h at 50°C. The contents were then poured into ice and the solid yellow precipitate was filtered and the ligand was recrystallised with ethanol (Figure 2).

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).

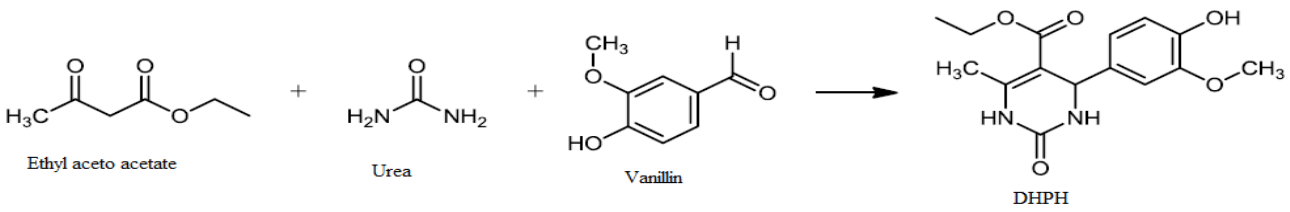


Figure 1. Synthesis of DHPH

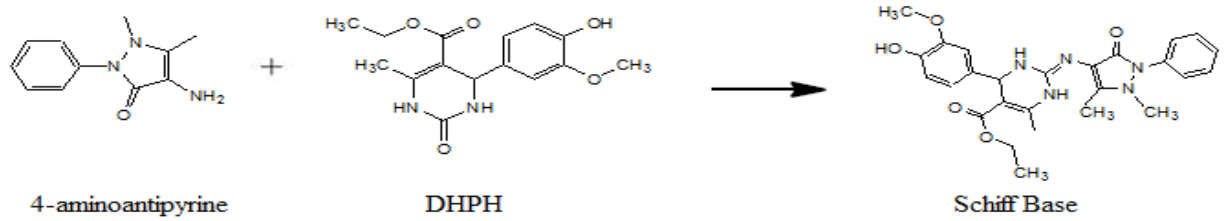


Figure 2. Synthesis of Schiff Base

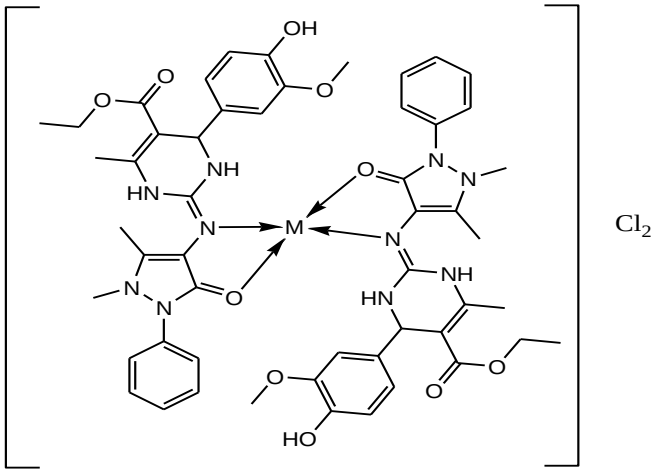


Figure 3. Proposed structure of Metal Complex

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 24h 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 [10]. 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 were 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 37ºC for 24 h. Then the antimicrobial activity was determined by measuring the diameter of zone of inhibition.

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's Dextrose agar (SDA) medium [13-15]. Then the antifungal activity was determined by measuring the diameter of zone of inhibition.

RESULTS AND DISCUSSION

The analytical data of the complexes, together with their physical properties are mentioned in Table 1. The data suggested that the complexes are in ML_2 composition in which M is Ni(II), Zn(II), Cd(II), Hg(II) and L, the Schiff base Ligand. The molar conductance data of the complexes shows that the complexes are 1:2 non electrolytes in DMSO which are in the range 1.10 -1.51 Ω^{-1} cm^2 mol^{-1} [16-18]. Also, the magnetic moments of Ni(II), Zn(II), Cd(II), Hg(II) complexes were diamagnetic. This suggested that the complexes may possess a square planar environment in Ni(II) complex and tetrahedral geometry to other complexes [19].

Electronic Spectral Analysis: The electronic absorption spectra of the Schiff base and its complexes were recorded at 300K. The UV-Vis spectrum of ligand (Fig 4(a)) exhibits two absorption peaks at 271 nm and 376 nm, which are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively [20, 21]. Electronic spectra of Ni(II) complex (Fig 4) are characterized by bands in the range of 240-570 nm. This behaviour can be assigned to $^1A_1g \rightarrow {}^1A_2g$ and $^1A_1g \rightarrow {}^1B_1g$ transitions. The presence of these transitions and absence of a band at 625 nm may confirm the square planar geometry of the complex [22, 23]. The UV spectral data values are given in table 2.

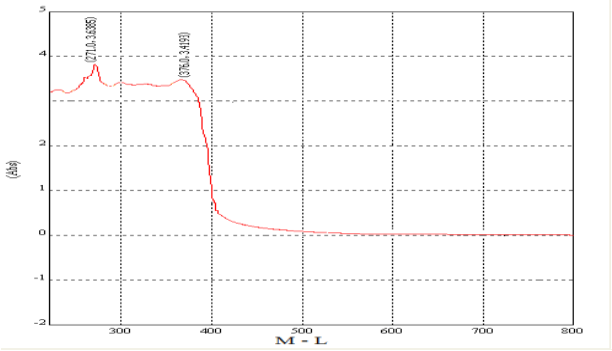


Figure 4a. UV spectra of Ligand

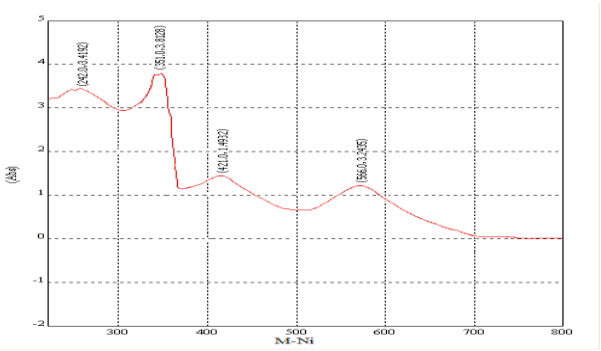


Figure 4b. UV spectra of NiL_2 complex

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	$[NiL_2]Cl_2$	1112.68	Light Brown	50	269.5	Ethanol, DMSO, $CHCl_3$	1.51	55.83 (56.13)	5.20 (5.25)	12.35 (12.59)	13.99 (14.38)	5.36 (5.27)	6.25 (6.37)
3	$[ZnL_2]Cl_2$	1119.37	Pale Brown	56	273.8	Ethanol, DMSO, $CHCl_3$	1.38	56.06 (55.80)	5.32 (5.22)	12.48 (12.51)	13.98 (14.29)	5.76 (5.84)	6.28 (6.33)
4	$[CdL_2]Cl_2$	1166.39	Dark Brown	50	276.2	Ethanol, DMSO, $CHCl_3$	1.25	52.36 (53.55)	5.11 (5.01)	12.21 (12.01)	13.68 (13.72)	9.78 (9.64)	6.16 (6.08)
5	$[HgL_2]Cl_2$	1254.57	Coffee Brown	45	278.2	Ethanol, DMSO, $CHCl_3$	1.10	49.85 (49.78)	4.45 (4.66)	11.14 (11.16)	12.68 (12.75)	15.79 (15.99)	5.45 (5.65)

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

S No.	Compound	λ_{max} (nm)	Assignments	μ_{eff} (B.M)
1	L	271 376	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	diamagnetic
2	$[NiL_2]Cl_2$	242 351 421 566	INCT INCT $^1A_1g \rightarrow {}^1A_2g$ $^1A_1g \rightarrow {}^1B_1g$	Diamagnetic
3	$[ZnL_2]Cl_2$	289 382 351	LF LF CT	Diamagnetic
4	$[CdL_2]Cl_2$	292 331 355	LF LF CT	Diamagnetic
5	$[HgL_2]Cl_2$	286 328 351	LF LF CT	Diamagnetic

The absorption spectra for Zn(II), Cd(II), Hg(II) complexes show intense bands at about 289 to 335 nm, which may be related to ligand field (INCT). The absorption peaks in the range 351-355 nm for these complexes are due to charge transfer (CT), since they belong to d^{10} configuration and they don't have d-d transition [24, 25]. On considering the position of the bands, the tetrahedral structure may be proposed for these complexes.

Infrared spectral study: The diagnostic IR frequencies of the ligand and its complexes are compiled in Table 3. The IR spectrum of free ligand (Figure 5(a)) is compared with that of complexes (Figure 5(b)) in order to determine the co-ordination sites that may have involved in chelation.

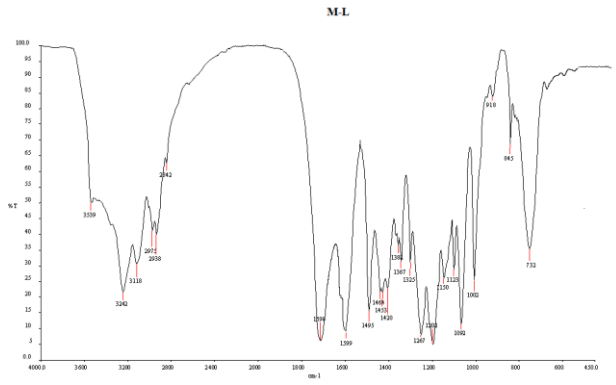


Figure 5a. IR spectra of Ligand

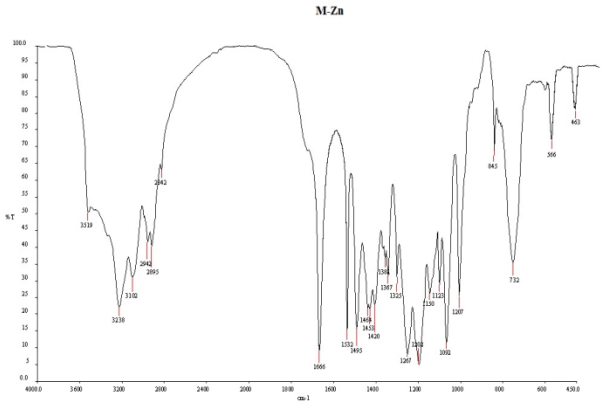


Figure 5b. IR spectra of ZnL_2 complex

Table 3. Infrared 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}
1	L	3242	3539	1202	1599	1698	-	-
2	$[NiL_2]Cl_2$	3236	3522	1202	1528	1642	468	573
3	$[ZnL_2]Cl_2$	3238	3519	1207	1532	1666	463	566
4	$[CdL_2]Cl_2$	3242	3516	1205	1533	1672	459	558
5	$[HgL_2]Cl_2$	3240	3538	1204	1548	1675	452	548

The observed band at 1599 cm^{-1} due to $\nu_{C=N}$ in free Schiff base is shifted to lower frequencies by about 30-70 cm^{-1} in the spectra of complexes which attributes to the coordination of C=N to the metal ion. A band at 1698 cm^{-1}, $\nu_{C=O}$ stretching frequency of free Schiff base which is also shifted to lower frequency ranging from 1642-1675 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 3542 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 [21]. The spectra of metal complexes also show some new bands in the regions, 452-468 cm^{-1} and 548-573 cm^{-1} which are probably due to the formation of M-O, M-N bond respectively [26, 27].

NMR Analysis: The ^1H NMR spectrum of the ligand (Figure 6a) exhibits the following signals: C_6H_5 as a multiplet at 6-8 ppm, -OH at 5.6 ppm (s), -NH at 2.2 ppm (s), -O-CH_3 at 3.89 ppm (s), -N-CH_3 at 2.37 ppm (s). The ^1H NMR spectra of complexes do not show any appreciable change as there is no proton involving in chelation.

The ^{13}C NMR spectrum (Figure 6b) shows the following signals: 115-130 ppm (aromatic carbon), 157.4 ppm (C=N), 145.4 ppm (C=O), 55.9 ppm (O-CH_3), 109.1 ppm (C-N), and shows some more peaks which confirmed the structure of ligand. There is a shift of peaks towards downfield for C=N and C=O in the case of all the complexes. This implies that azomethine N and Carbonyl O are involved in complexation with metals.

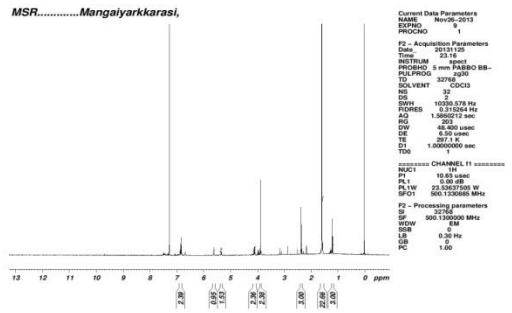


Figure 6a. ^{1}H NMR Spectra of Ligand.

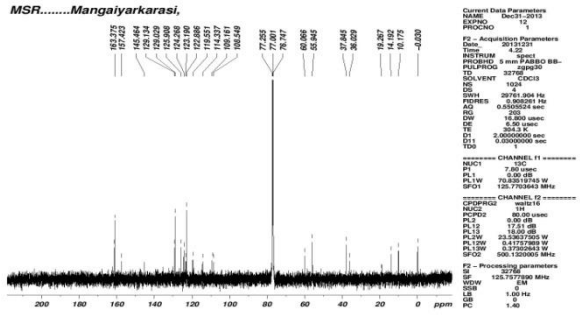


Figure 6b. ^{13}C NMR Spectra of Ligand.

Mass Analysis: The ESI mass spectra of the ligand (Figure 7a) and its metal complexes (Figure 7b) 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 Zn, Cd, Hg, Ni are observed at m/z 1119, 1166, 1254, and 1112 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.

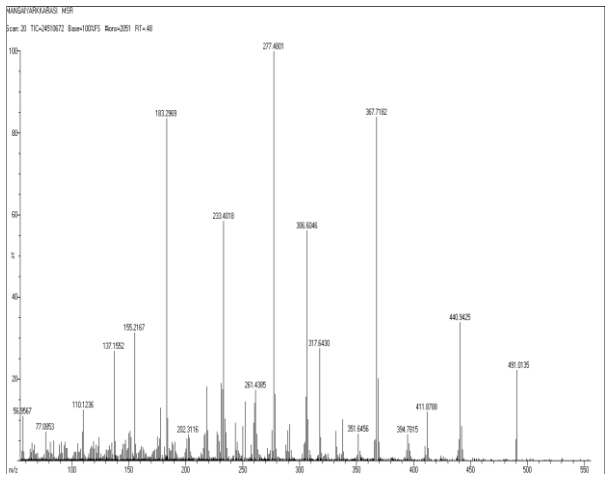


Figure 7a. Mass spectra of Ligand

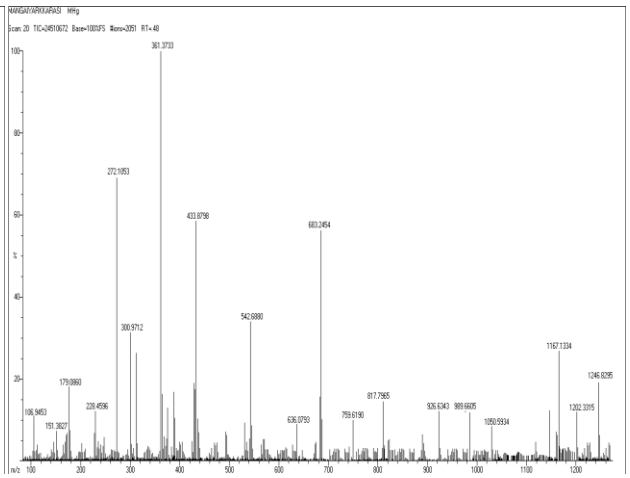


Figure 7b. Mass spectra of Hg(II) Complex

APPLICATIONS

Antimicrobial activities: The data of the antibacterial and antifungal activities of ligand and complexes are given in tables 4 and 5. The antimicrobial activity was determined by measuring the diameter of zone of inhibition (Figures 8 and 9). The data reveals that the complexes have higher inhibitory activities than the free ligand (Figure 10a and 10b). The enhancement of the activity of ligand on complexation can be explained by Overtone's Concept and Chelation Theory [28]. 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 lypophilic character of the complex and favors 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 [29, 30].

Heterocyclic compounds do play important role in regulating biological activities [31-33]. This is further evidenced when vanillin and 4-aminoantipyrine based Schiff base metal complexes shows good antibacterial activity as they contains heterocyclic group [20]. Comparatively this activity is highly enhanced for the metal complexes formed from vanillin based dihydropyrimidine heterocyclic product and 4-aminoantipyrine. The antimicrobial activity of the complexes follows the order Ni < Zn > Cd ≈ Hg, which may be due to the increasing stability of the complexes [34].

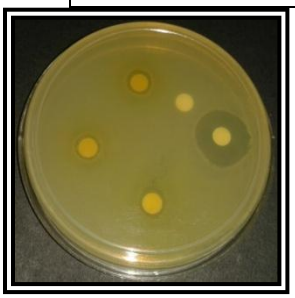
Table 4 . Antibacterial Activity Data of Ligand and Complexes

Compound / Organisms	Zone of Inhibition (mm)																
	L			NiL_2			ZnL_2			CdL_2			HgL_2			DMSO	Antibiotic (1mg/ml)
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C		
E.coli	5	3	2	8	6	6	9	7	6	8	6	4	7	6	4	--	10
Vibrio spp.	6	6	5	8	6	5	9	7	6	7	7	6	7	6	6	--	12
Staphylococcus aureus	6	5	3	7	7	6	8	6	6	7	6	5	8	6	5	--	10
Pseudomonas aeroginosa	7	6	3	8	7	7	8	7	7	7	6	4	7	7	7	--	14
Bacillus spp.	5	4	3	8	7	6	9	8	7	8	7	7	7	6	6	--	15
Vibrio parahaemolytics	7	5	4	8	8	7	8	6	5	8	7	5	7	6	5	--	13
Salmonella spp.	6	5	4	8	8	7	9	7	6	8	6	5	8	7	6	--	10
Aeromonas spp.	7	6	3	8	7	7	9	8	7	7	7	5	7	6	5	--	10
Klebsiella spp.	5	4	3	8	7	6	8	7	6	7	7	6	6	5	5	--	15
Proteus spp.	7	6	5	8	7	6	8	7	7	8	6	6	7	7	6	--	15

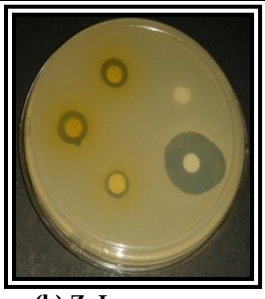
Table 5. Antifungal Activity Data of Ligand and Complexes

Compound / Organisms	Zone of Inhibition (mm)																
	L			NiL_2			ZnL_2			CdL_2			HgL_2			DMSO	Antibiotic (1mg/ml)
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C		
Candida albicans	6	5	5	7	6	5	9	7	7	8	7	6	7	6	5	--	7
Aspergillus flavus	6	5	5	7	6	6	8	7	6	7	6	6	7	7	6	--	10
Pencillium spp.	7	6	5	8	6	6	9	8	6	8	7	7	8	6	5	--	10
Aspergillus niger	5	4	4	6	5	4	7	6	6	6	6	5	6	5	5	--	5
Trichophyton	7	5	4	8	6	6	8	7	6	7	7	6	7	6	6	--	8

Note: A = 1000 µg; B= 750 µg; C= 500 µg

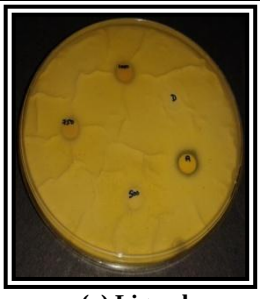


(a) Ligand



(b) ZnL_2

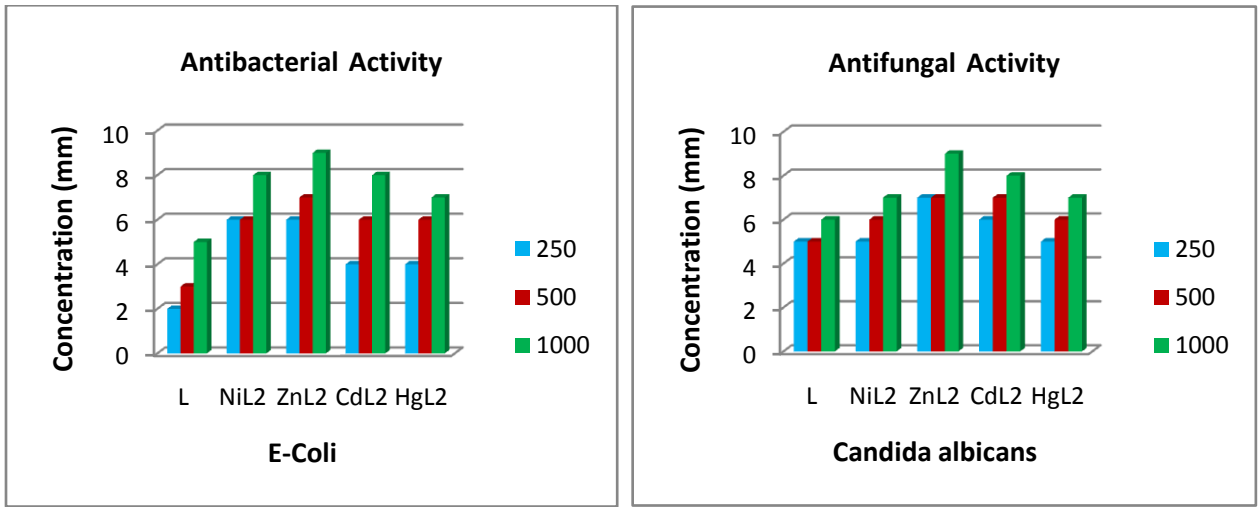
Figure 8. Antibacterial activity in E.Coli



(a) Ligand

(b) CdL_2

Figure 9. Antifungal activity in Candida albicans



(a) **(b)**

Figure 10. Activity chart **(a)** Antibacterial in E.Coli **, (b)** Antifungal in Candida albicans

CONCLUSIONS

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 Ni, Zn, Cd and Hg were also synthesized. The ligand and complexes have been characterized by FTIR, UV/Vis, ^{1}H NMR, ^{13}C NMR and ESI Mass spectra. The ligand behaved as a bidentate donor by using its carbonyl O and azomethine N as binding sites for the metals. Tetrahedral structures were proposed for all the complexes except Ni(II) which attributes square planar geometry. 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 order Ni < Zn > Cd ≈ Hg. It is hereby suggested that this ligand and its metal complexes can be used as metal based drugs.

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