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Synthesis, Characterization Biological Activities of Some Transition metal complexes with Coumarin Schiff base

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***Abstract*— The new type complex ML, where M = Cu(II), Co(II), Ni(II) and Mn(II) and M'L, where M' = Zn(II), Cd(II) and Hg(II)] with the ligand Schiff base L = N-(1-(4-hydroxy-2-oxo-2H-chromen-3yl)ethylideneisonicotinohydrazide, (HCEIH) has been synthesized and characterized. Their characterizations are done by elemental analysis, IR, NMR, conductivity measurements, ESR and X-ray powder diffraction studies. On the basis of spectral studies, complexes of Ni(II), Mn(II), Cu(II), and Co(II)complexes shows octahedral geometry, where as the complexes Cd(II), Zn(II), and Hg(II) complexes shows tetrahedral geometry. The Schiff base ligand and its metal complexes treated for their antimicrobial activity verses selected fungi and bacteria using couplet method.**

***Index Terms* — Schiff Base; Elemental Analysis; Biological activity.**

I. INTRODUCTION

Coordination chemistry of major important in the stability and chemistry of mixed ligands is studied by the concept of coordination compounds.Schiff base are used as substrate in the preparations of a number of industrial and biologically active compounds *via* closure, cycloaddition and replacement reactions. Schiff base are also known to have biological activities such as antibacterial, antifungal, antitumor and antioxidant activities. Schiff base have also been employed as ligands for complexation of metal ion[1]. The literature survey shows that work has been carried out on the lanthanide metal complexes of Schiff base derived from 8-formyl 7-hydroxy-4-metyl -2H-chromen-2-one and the Schiff base derived from 4-hydroxy-3-(1-ethyl)chromen-2-one[2]. The less work seems to have been carried out on the metal complex of Schiff base derived from the 4-hydroxy 3-(1-ethyl) chromen-2-one3. Hence, it was thought worthfull to prepare new coumarin ligand (HCEIH) and its metal (II) complexes.

II. EXPERIMENTAL STUDY

All the reagents used were of analytical grade and used without any further purification

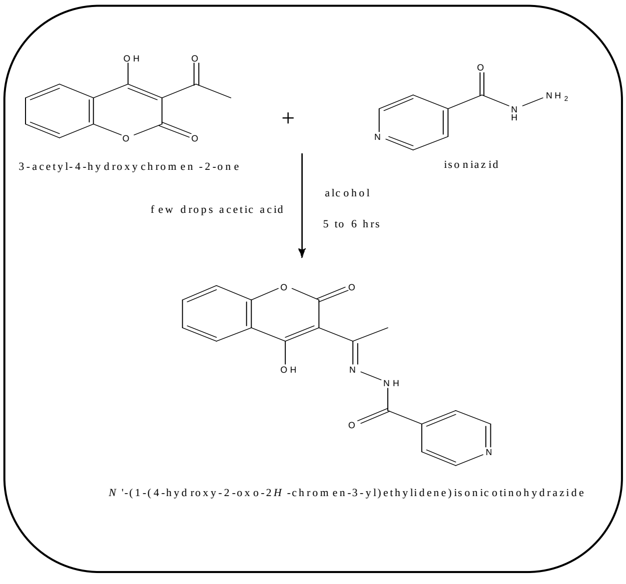
Synthesis of Ligand:

2.1 Synthesis of 3-acetyl-4-hydroxychromen-2-one (AHC):

4-hydroxy chromen-2-one (3g), in acetic acid (16 ml) phosphorus oxychloride (5.6 ml) added. The whole mixture was reflux for 30 minutes and then cool, collect the precipitate and recrystallized from ethanol. White needles of 3-acetyl-4-hydroxy-chromen-2-one obtained. Yield: 90%, M.P: 134-36°C.

2.2. Synthesis of N-(1-(4-hydroxy-2-oxo-2H-chromen-3yl) ethylideneisonicotinohydrazide (HCEIH) :

The ligandSchiff base prepared by the condensation of 3-acetyl-4-hydroxy-chromen-2-one (AHC) (0.1mol) and isoniazid (0.1mol) in ethanol. Refluxed for 5-6 hours on water bath in presence of few drops of acetic acid. The mixture was cooled to the room temperature, after cooling; the product was recrystallized from ethanol. The purity of the ligand checked by M.P. and TLC, Yield: 85%, M.P: 272°C.



2.3 Preparation of complexes:

The respective metal chlorides 0.01mole in ethanol (15 ml) was added to the hot solution of the Schiff base ligand (HCEIH)0.01 mole in ethanol (35 ml),and reaction mixture was then treated with sodium acetate (0.5 g) and the reflux was continue for 2 hrs. The resulting mixture was then decomposed by pouring to distilled water (80 – 100 ml), the coloured complex separated out and collected by filtration, washed with distilled water, and then with hot ethanol finally dried in vacuum over unhydrous calcium chloride. Elemental analysis data is shown in Table 1. All the complexes were analysis for their metal and chloride contents by standards method.

Table – 1: Analytical data, magnetic susceptibility, molar conductance of the ligand (HCEIH) and its metal (II) complexes.

Ligand / complex	Colour	Mol. Wt.	M.P (°C)	Yield (%)	Found /Calculated %					Molar conductance Ohm^{-1}cm^2 mol^{-1}
					M	C	H	N	Cl	
$C_{17}H_{13}N_3O_4$	Pale Yellow	323.30	272	85	-	63.16 (63.12)	4.05 (4.09)	13.00 (13.02)	-	-
$[Cu(C_{34}H_{24}N_6O_8)]$	Green	708.10	310	70	8.97 (8.12)	57.67 (57.62)	3.42 (3.39)	11.87 (11.83)	-	20
$[Co(C_{34}H_{24}N_6O_8)]$	Brown	703.52	324	74	8.38 (8.42)	58.05 (58.10)	2.76 (2.79)	11.95 (11.98)	-	22
$[Ni(C_{34}H_{24}N_6O_8)]$	Yellow	703.28	318	67	8.35 (8.39)	58.07 (58.12)	3.44 (3.48)	11.95 (11.97)	-	19
$[Mn(C_{34}H_{24}N_6O_8)]$	Buff	699.53	330	65	7.85 (7.88)	58.38 (58.44)	3.46 (3.49)	12.01 (12.07)	-	24
$[Zn(C_{17}H_{12}N_3O_4Cl)]$	Yellow	438.19	296	68	14.93 (14.97)	49.34 (49.38)	3.45 (3.49)	9.59 (9.63)	8.09 (8.13)	16
$[Cd(C_{17}H_{12}N_3O_4Cl)]$	Dark Yellow	485.84	326	70	23.17 (23.21)	44.56 (44.51)	3.12 (3.15)	8.66 (8.72)	7.31 (7.36)	18
$[Hg(C_{17}H_{12}N_3O_4Cl)]$	Yellow	573.37	320	74	34.98 (35.02)	37.71 (37.76)	2.64 (2.68)	7.33 (7.38)	6.18 (6.23)	27

III. PHYSICAL MEASUREMENTS

Infrared spectra of the Schiff base ligand and its metal (II) complexes in KBr pellets were recorded in the spectral range 4000–300cm^{-1} with perkin Elmer spectrum one FT-IR spectrometer. ^{1}H-NMR spectra were recorded on Brukerav–300 NMR spectrometer, using TMS as internal standard and $CDCl_3$ as a solvent.ESR spectra were recorded on JES-FA Series.The magnetic susceptibility measured on Gouy balance at room temperature using $HgCo(SCN)_4$as calibrant. The molarconductances of the complexes were measured on an ELICO-CM-82-conductivity in DMF solution at concentration 10^{-3}M. X-ray powder diffraction was recorded on Rigaku X-ray diffractometer. Calf thymus DNA (CT-DNA) at Bio-Genics, Research and Training Centre in Biotechnology, Hubli (Karnataka).

IV. RESULTS AND DISCUSSION

The analytical data and physical properties showed that, Schiff base ligand and its metal complexes arecolored and very stable. All the metal complexes were sparingly soluble in common organic solvents and completely soluble in DMF, $CDCL_3$ and DMSO. The molar conductance values of metal complexes measures in DMF solution fall in the range (16-27 Ohm^{-1}cm^2 mol^{-1}) indicating the non-electrolytic nature[4].The conductance values shows that the complexes well agreement with 1:1 metal to ligand stoichiometry with empirical formula [M(L)(Cl)] for Zn(II), Cd(II) and Hg(II) and 1:2 with empirical formula $(M(L)_2)$ for Co(II), Cu(II), Ni(II) and Mn(II) complexes are given in the Table-1.

4.1. Infrared spectra:

The significant IR spectral data of Schiff base ligandN-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl)ethyidene) isonicotinohydrazide (HCEIH) and its metal complexes were presented in Table-2 and Figures 1 to 3. The Schiff base (HCEIH) exhibited a broad band due to the phenolic ν(OH) in the region 3350-3330 cm^{-1}. Comparison with the spectra of the Schiff base ligand, all the metal complexes shows disappearance of broad band due to the phenolic ν(OH) indicating the deprotonation and involvement of phenolic oxygen in chelation[5]. The band due ν(C=N) group is appeared in the region 1598–1590 cm^{-1} shows the shift to lower wave numbers indicating the involvement of azomethine nitrogen coordinated to the metal ion[6]. The band due to ν(NH) which was shifted from 12 to 31 cm^{-1} in all metal complexes. A medium to high intensity band appeared in the region 1708-

1685 cm^{-1} due to ν(C=O) shows the involvement of carboxyl group of coumarin ring (C=O) in complexation with metal ion[7] and 1308-1314 cm^{-1} due to phenolic ν(C-O) indicates the coordination of phenolic oxygen via deprotonation[8] as shown in figure 2 and 3. The low frequency skeletal vibrations due to M–O and M–N stretching provide direct evidence for complexation. The new bands appeared in the region of 548-520 cm^{-1} and 466 - 450 cm^{-1} in the spectra of the complexes are assigned to stretching frequencies of ν(M–O) and ν(M-N) bonds respectively[9]. The bands due to ν(M-Cl) were observed in region 320 -325 cm^{-1} and these are characteristic of chloride atom in Zn(II), Cd(II) and Hg(II) complexes and is further confirmed by quantitative chloride estimation.

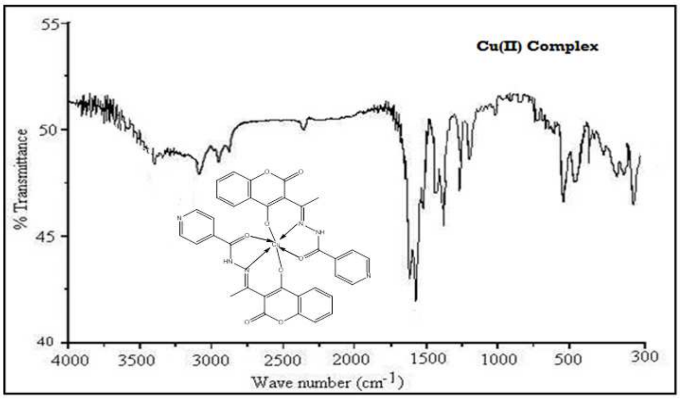


Fig. 2 IR spectrum of [Cu($C_{34}H_{24}N_6O_8$)]Complex

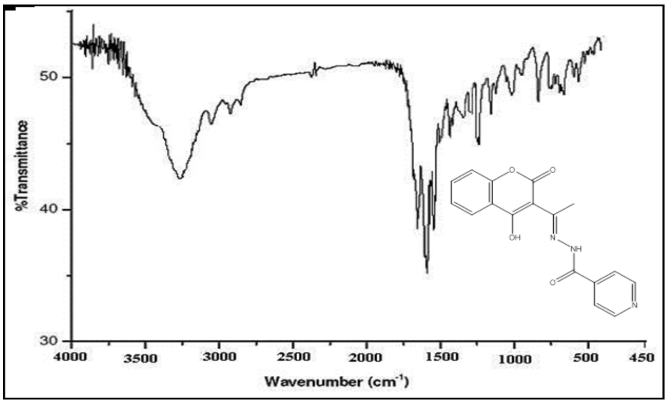


Fig. 1 IR spectrum of ligand (HCEIH)

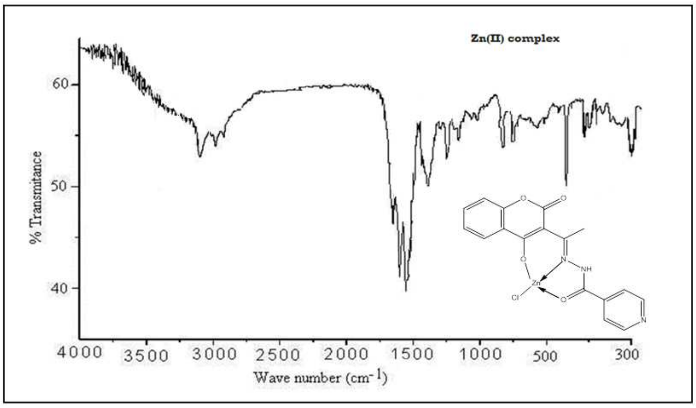


Fig. 3 IR spectrum [Zn($C_{17}H_{12}N_3O_4Cl$)] complex

Table – 2: Important spectral IR bands of the ligand (HCEIH) and its metal(II) complexes (cm^{-1})

Ligand / complex	υ_{OH} (Strech)	υ_{NH} (strech)	$\upsilon_{C=0}$	$\upsilon_{C=N}$ (strech)	υ_{C-O-C}	Phenolic υ_{C-O}	υ_{M-O}	υ_{M-N}	υ_{M-Cl}
$C_{17}H_{13}N_3O_4$	3340	3000	1620	1600	1296	1270	-	-	-
[Cu($C_{34}H_{24}N_6O_8$)]	-	2950	1616	1596	1300	1262	546	468	-
[Co($C_{34}H_{24}N_6O_8$)]	-	2992	1614	1590	1302	1259	523	465	-
[Ni($C_{34}H_{24}N_6O_8$)]	-	2997	1610	1594	1304	1256	523	461	-
[Mn($C_{34}H_{24}N_6O_8$)]	-	2993	1607	1598	1309	1255	525	458	-
[Zn($C_{17}H_{12}N_3O_4Cl$)]	-	2991	1604	1595	1305	1258	523	454	319
[Cd($C_{17}H_{12}N_3O_4Cl$)]	-	2996	1602	1591	1306	1264	521	451	322
[Hg($C_{17}H_{12}N_3O_4Cl$)]	-	2998	1604	1590	1304	1267	522	450	324

4.2 ^{1}H NMR Spectra:

The chemical shift of different types of protons in the ^{1}H NMR spectra of the Schiff base N-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl)ethyidene)isonicotinohydrazide (HCEIH) and its Zn(II) complex were recorded in $CDCl_3$ using TMS as a internal standard. The Schiff base exhibited signals at δ 10.54 ppm (s, 1H) due to phenolic-OH which is completely disappearance in the spectra of Zn(II) on the formation of Zn-O bond indicating that the phenolate group is coordinated to the metal ion through oxygen after deprotonation[10], The ligand (HCEIH) shows signal at δ (11.54) (s, 1H) was assigned to the amide proton (-CONH-), which is found to be shifted down field in the region at δ 11.72 in the Zn(II) complex indicating the coordination of the oxygen of –CONH- with metal ion[11], the signal at δ 8.31 ppm (s, 1H) was assigned to azomethine proton (-CH=N), which is shifted to downfield in the region of δ 8.43 ppm supporting the coordination azomethine nitrogen with metal ion[12], in addition the signals at δ 2.52 ppm (s, 3H) and δ 2.55 ppm (s,3H) were assigned to -CH_3 protons which are shifted to downfield in the region of δ 2.62 ppm and The aromatic protons at δ(6.87-8.12) (m, 8H) shifted downfield in their respective complexes. Thus, the ^{1}H-NMR spectral observations shows the assigned geometry, as shown in Figures 4 and 5.

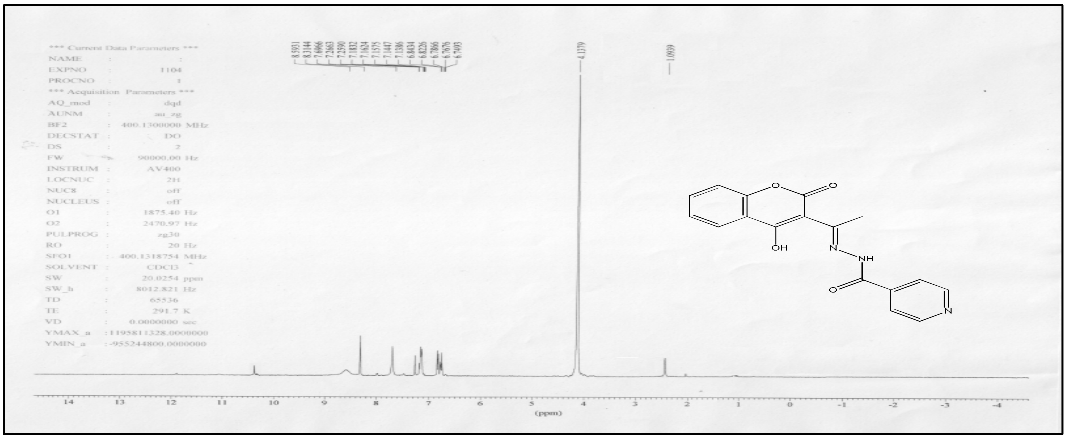


Fig. 4^{1}H NMR spectrum of ligand(HCEIH)

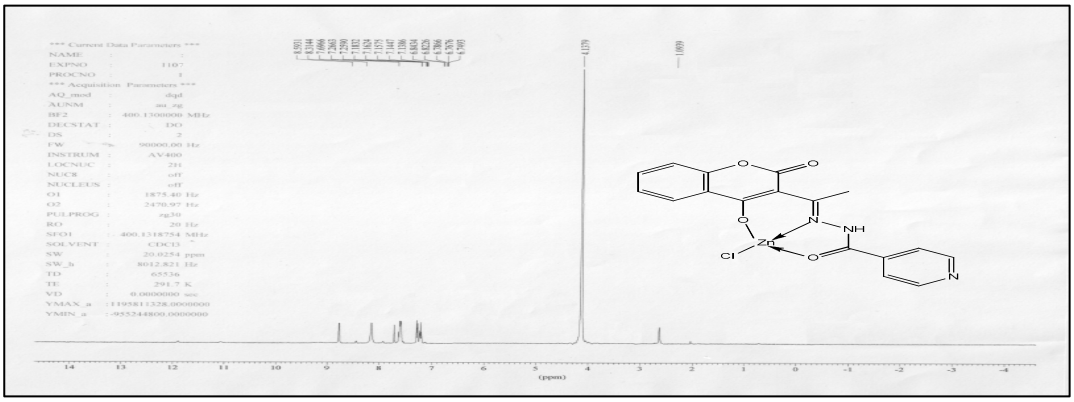


Fig. 5^{1}H NMR spectrum of [Zn($C_{17}H_{12}N_3O_4Cl$)] complex

Table – 3: ESR spectral data of [Cu($C_{34}H_{24}N_6O_8$)]complex

g_{II}	$g_{\perp}$	g_{av}	g_{iso}	G
2.18	2.04	2.08	2.13	4.71

4.3. ESR Spectra

The ESR spectra of Cu(II) complex were recorded as polycrystalline sample at room temperature, as shown in Figure 6. The value of$g_{\parallel}$and $g_{\perp}$were calculated and presented in Table-3. The 'g' value averaged to overall distortion which was measure the exchange inter action between copper centers in polycrystalline solid has calculated. According to Hathway[13], if G value is greater than 4, the exchange interaction is negligible, while the G value less than 4 indicates the considerable exchange interaction between metal ions in the solid complex.

In a majority of Cu(II) copper complexes, the formal ground state is almost a pure d_{x2-y2} as revealed by spectra with $g_{\parallel}>g_{\perp}$[14.] In the present study the Cu(II) complex shows G > 4 indicating the exchange interaction is negligible in solid complex, thus it shows that the Cu(II) complex is mononuclear in nature. From the spin Hamiltonian parameters of Cu(II) ion in the present case it is found that$g_{\parallel}> g_{\perp}$ which indicate that Cu^{+2} ion are present in the octahedral site with tetragonal distortion.

4.4. X-ray Powder Diffraction Studies

X-ray powder diffraction pattern for Ni(II) complex has characterized with a view to find the type of crystal system. The XRD data given the Table-4 and Figure 7.The diffractogram of Ni(II) complex consists of ten reflections in the range of 13-70 (2θ value) with maxima at 2θ=15.62A^o.The inter planar spacing (d) has been calculated from the position of intense peaks using Bragg's equation $n\lambda=2d\sin\theta$; where λ = 1.54056A^0, the observed and calculated values of d and are quite consistent as shown in Table-4. The unit cell calculations have been carried out for the cubic system, the set of $h^2 + k^2 + l^2$ values of the complex were found to be 1,2,3, 5, 6, 7, 9,10 and 12 which corresponds to the planes and presence of forbidden number 7 confirms the hexagonal. From the above results the unit cell constants for hexagonal system were found to be a=b=c =6.754 A^0 for the Ni(II) complex of the ligand the complex showed broad peak indicates amorphous nature[15-17].

Table – 4: Powder X-ray diffraction data of [Ni($C_{34}H_{24}N_6O_8$)] complex

2θ	**θ**	**sinθ**	**sin^{2}θ**	**h^2+k^2+l^2 (a)**	**h^2+k^2+l^2 (b)**	**h k l**	**d-spacing**		**Relative intensity (%)**	**a (A°)**
							Cal.	**Abs**		
13.48	6.74	0.117	0.013	1.3	1	1 0 0	6.58	6.55	19.01	6.75
15.62	7.81	0.135	0.018	2.2	2	1 1 0	5.70	5.68	100	6.80
19.84	9.92	0.172	0.029	2.8	3	1 1 1	4.47	4.49	43.97	6.72
26.78	13.39	0.231	0.053	4.2	4	2 2 0	3.33	3.35	22.39	6.68
28.25	14.12	0.243	0.060	4.7	5	2 1 0	3.16	3.14	33.01	6.72
30.63	15.31	0.264	0.068	5.6	6	2 1 1	2.91	2.93	7.11	6.83
35.52	17.76	0.305	0.093	7.1	7	-	2.45	2.43	21.84	6.64
58.29	29.14	0.486	0.236	9.2	9	2 2 1	1.58	1.56	25.15	6.58
65.35	32.67	0.539	0.290	10.7	11	3 1 1	1.42	1.44	32.66	6.67
70.48	35.24	0.577	0.332	11.8	12	2 2 2	1.33	1.35	12.93	6.55

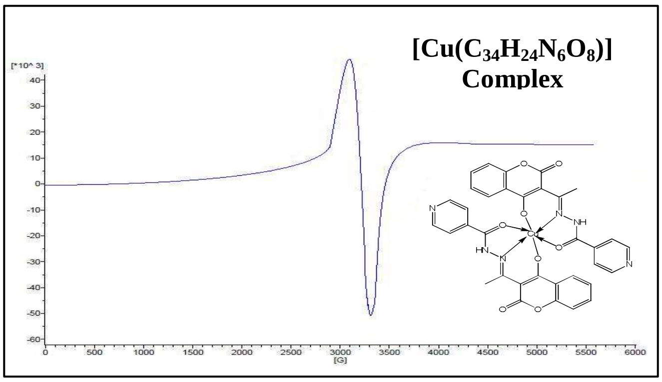


Fig. 6 ESR Spectrum Cu(II) Complex

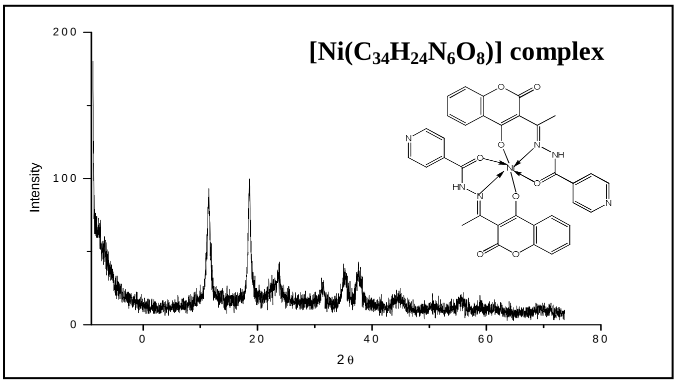


Fig. 7 X-ray powder diffraction of [Ni($C_{34}H_{24}N_6O_8$)] complex

4.5. Biological Study:

The biological and medicinal potency of coordination compounds have been established by their antitumor, antiviral, antimalarial activities. This characteristic property has been related to the ability of the metal ion form complexes with ligands containing nitrogen oxygen donor atoms[18-20].The increase antifungal activity of the metal chelates with increase in concentration is due to the effect of metal ion on the normal cell process. This activity of the metal chelates can be explained on the basis of overtone's concept and chelation theory[21].

In view of these factors the metal complexes of the ligand N-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl)ethyidene) isonicotinohydrazide (HCEIH) were tested for their antibacterial and antifungal activity verses four organism namely *Escherichia Coli*, *Saphylococcusaureus*, *Aspergillusniger* and *Aspergillusflavus* by the cup-plate method[22]. The standard drug streptomycin and Clotrimazole were used for the comparison with antibacterial and antifungal activities shown by these compounds. It is clear from Table 5 that it indicates that most of the complexes have higher values than that of the ligand.

The results of antibacterial activity testing of the ligand (HCEIH) and its metal complexes of Co(II), Cu(II), Ni(II), Zn(II), Mn(II) and Cd(II). Among these Cu(II), Ni(II) complexes shows weakly active with the zone of inhibition 12-14mm against the both organisms when compared to the standard drug streptomycin. The Mn(II), Co(II), Cd(II) shows moderately active as compared to its ligand with zone of inhibition 15-17mm and the complex Zn(II) shows highly active with the zone of inhibition of 18-20mm when compared to the standard drug streptomycin. The results of the antifungal activity testing revealed of the ligand (HCEIH) and its metal complexes Cu(II), Co(II), Ni(II), Zn(II), Mn(II) and Cd(II) . Among these complexes Co(II) complexes shows weakly active with zone of inhibition 12-14mm against the both organisms when compared to the standard drug clotrimazole. The Cu(II), Ni(II), Zn(II), Cd(II) shows moderately active as compared to its ligand with the zone of inhibition 15-17mm, the complex Mn(II) shows the highly active with the zone of inhibition of 18-20mm when compared to the standard drug clotrimazole

Table – 5: Antibacterial and antifungal activity

Sl.No.	**Compounds**	**Antibacterial activity Zone of inhibition (mm)**		**Antifungal activity Zone of inhibition (mm)**	
		E.Coil	***S.aureus***	***A.niger***	***A.flavus***
1.	$C_{17}H_{13}N_3O_4$	08	07	08	10
2.	$[Cu(C_{34}H_{24}N_6O_8)]$	14	12	15	16
3.	$[Co(C_{34}H_{24}N_6O_8)]$	15	16	13	12
4.	$[Ni(C_{34}H_{24}N_6O_8)]$	13	14	17	15
5.	$[Mn(C_{34}H_{24}N_6O_8)]$	14	15	20	19
6.	$[Zn(C_{17}H_{12}N_3O_4Cl)]$	20	19	16	15
7.	$[Cd(C_{17}H_{12}N_3O_4Cl)]$	16	17	17	16
8.	Streptomycin	21	22	--	--
9.	Clotrimazole	--	--	25	26

V. CONCLUSION

The elemental analysis, conductivity data, IR, ^{1}H NMR and ESR spectral observations reveals the mononuclear nature of all the complexes. In this work, we reported the synthesis, spectral characterization of ligand and its complexes. The non-electrolytic behavior of the complexes confirms the presence of chlorides within the coordination sphere.

The complexes Cu(II), Ni(II), Co(II) and Mn(II) complexes exhibited octahedral geometry as shown in Figure 8, whereas Zn(II), Cd(II) and Hg(II) complex exhibit tetrahedral geometry as shown in Figure 9. The data indicates that metal complexes are much more potent against microbial pathogens in comparison to free Schiff's base ligand

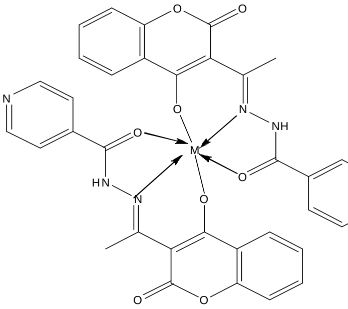


Fig. 8

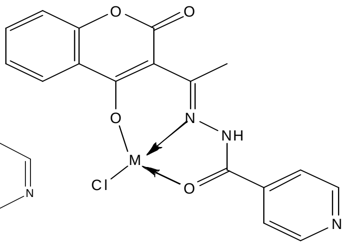


Fig. 9

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