Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2013, 2 (3): 405-414

(International Peer Reviewed Journal)

Synthesis, Characterization and Antimicrobial studies of N^1-(1-(2-Hydroxy-5-Methylphenyl) Ethylidene)-2-Oxo-2H-Chromene-3-Carbohydrazide and its Metal Complexes

K. Siddappa[*] and Mallikarjun Kote

[*]Department of Studies and Research in Chemistry, Gulbarga University, Gulbarga-585106, Karnataka-**INDIA**

Email: siddappa_65@rediffmail.com

Received on 7th January and finalized on 10th January 2013.

ABSTRACT

A new complexes of the type ML and M′L [where M=Cu(II), Co(II), and Ni(II), Mn(II) and Fe(III) M′=Zn(II), Cd(II) and Hg(II)]. L=N'-(1-(2-hydroxy-5-methylphenyl)ethylidene)-2-oxo-2H-chromene-3-carbohydrazide (HL) Schiff base have been synthesized and characterized by elemental analysis, magnetic susceptibility, molar conductance, IR, ^{1}H NMR, UV-Visible and ESR data. The studies indicate the HL acts as doubly Monodentate Bridge for metal ions and form mononuclear complexes. The complexes Ni(II), Co(II), Cu(II), Mn(II) and Fe(III) complexes are found to be octahedral, where as Zn(II), Cd(II) and Hg(II) complexes are four coordinated with tetrahedral geometry. The synthesized ligand and its metal complexes were screened for their antimicrobial activity.

Keywords: Coumarin, metal complexes, antimicrobial activity, spectral data.

INTRODUCTION

Coumarins are important natural products displaying a broad range of biological activities [1]. Owing to their diverse bioactivities viz. anticoagulant [2, 3] antibacterial, antifungal [4], antibiotic [5], spasmolytic [6], anthelmintic [7], diuretic [8], anti-inflammatory [9], antitubercular agents [10], anti-histamic agents [11], antidepressant [12] and anti- malarial [13]. Hence it was thought to undertake such study. Chelating ability of coumarin derivatives has been studied to suggest their use as a chelating agent [14, 15]. The literature survey reveals that the reaction of 2-oxo-2H-Chromene-3-Carbohydrazide and 1-(2-hydroxy-5-methylphenyl)ethanone Schiff base have not been reported so far. On the basis of this, we have synthesized ligand (HL) and its metal complexes also investigated their coordination behavior.

The present paper deals with the synthesis, spectral, magneto chemical and biological studies of metal complexes with the following ligand (HL).

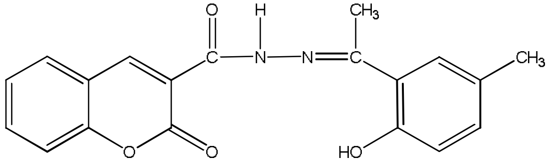

Figure1. N'-(1-(2-hydroxy-5-methylphenyl) ethylidene)-2-oxo-2H-chromene-3-carbohydrazide

MATERIALS AND METHODS

All the chemicals used were of analytical grade and were used without further purification.

Preparation of ligand (HL): The Schiff base ligand was prepared by condensation of 2-oxo-2H-Chromene-3-Carbohydrazide (0.1 M) and 1-(2-hydroxy-5-methylphenyl) ethanone (0.1 M) in ethanol was refluxed on water bath for 5-6 hours in presence of few drops of acetic acid. The reaction mixture was cooled to room temperature the separated Schiff base was filtered, washed with hot alcohol and recrystallized from alcohol to get a pure sample. The purity of the Schiff base HL was checked by TLC. Yield: 80%, MP: 207^{o}C, Mol.Wt: 336.34.

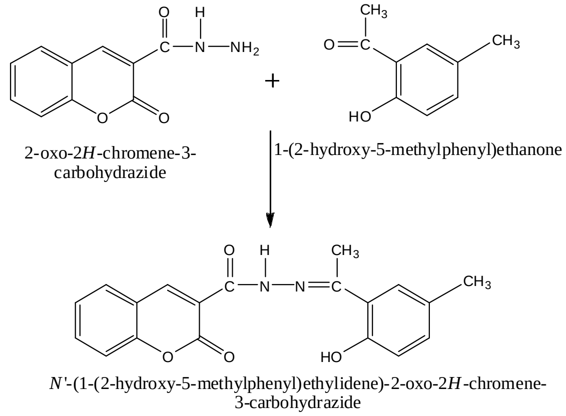

Figure-2

Preparation of metal complexes: A solution of 0.01 mole of metal chloride in ethanol was mixed with ethanolic solution of 0.01 mole of HL ligand and refluxed for 3-4 hours on water bath to get clear solution. 0.5 gm of excess sodium acetate was added to the reaction mixture to adjust the pH 7-8 of the solution. The reaction mixture was further, refluxed for 2 hours more. The resulting mixture was decomposed by pouring into a 100 mL of distilled water with constant stirring. The suspended solid complex was allowed to settle and collected by filtration, washed with sufficient quantity of distilled water and then with little hot ethanol to apparent dryness and dried in a vacuum over anhydrous calcium chloride in a desiccator (Yield, 65-75 %).

Analysis

The complexes were analyzed for their metal and chloride contents were determined by standard methods [16].

Physical measurements : Infrared spectra of the ligand and its metal complexes in KBr pellets were recorded in the spectral range 4000-350 cm^{-1} range with Perkin Elmer Spectrum one FT-IR Spectrometer. UV-Visible spectra were recorded on a Elico.SL-164 DOUBLE BEAM UV-Visible Spectrophotometer in the range of 200-1200 nm. Magnetic susceptibilities were measured on a Guoy Balance at a room temperature using Hg $Co(NCS)_4$ as calibrant. The molar conductance of the complexes were measured on ELICO CM-82 conductivity bridge in DMF solution at conc. ~10^{-3} M. ^{1}H NMR spectra were recorded on AMX-400 NMR spectrometer, using TMS as internal standard and DMSO as a solvent. The elemental analysis (CHN), ESR Spectra recorded on STIC Cochin.

RESULTS AND DISCUSSION

All the complexes were sparingly soluble in common organic solvents but soluble in DMF, DMSO and acetonitrile. The analytical data indicates that the complexes are agree well with 1:1 metal to ligand stoichiometry for Fe(III), Zn(II), Cd(II) and Hg(II) and 1:2 for Cu(II), Co(II), Ni(II) and Mn(II) complexes shown in Table 1 . The observed molar conductance (Table 1) values measured in DMF solution fall in the range (12-20 Ohm^{-1} cm^2 mol^{-1}). These observed values of the molar conductance are well within the expected range for non-electrolytic [16,17].

Table 1 Analytical, magnetic susceptibility, molar conductance of the ligand [HL] and its metal complexes

Ligand / Complex	Mol. Wt.	M.P. (^{0}C)	Yield (%)	Found / (Calculated) %					μ_{eff} B.M.	Molar Conductance ^m Ohm^{-1} cm^2 mol^{-1}
				M	C	H	N	Cl		
$C_{19}H_{16}N_2O_4$	336.34	207	80	-	67.85 (67.80)	4.79 (4.70)	8.33 (8.29)	-	-	-
$[Cu(C_{39}H_{34}N_4O_8)]$	750.26	285	70	8.47 (8.95)	62.43 (62.46)	4.57 (4.61)	7.47 (7.50)	-	1.97	17
$[Co(C_{39}H_{34}N_4O_8)]$	745.64	295	65	7.90 (7.89)	62.82 (62.72)	4.60 (4.55)	7.51 (7.53)	-	4.88	20
$[Ni(C_{39}H_{34}N_4O_8)]$	745.40	285	65	7.87 (7.78)	62.84 (62.73)	4.60 (4.56)	7.52 (7.56)	-	2.97	20
$[Mn(C_{39}H_{34}N_4O_8)]$	741.65	300	70	7.41 (7.51)	63.16 (63.20)	4.62 (4.59)	7.55 (7.60)	-	5.65	14
$[Fe(C_{19}H_{17}N_2O_5Cl_2).H_2O]$	480.10	290	65	11.63 (11.60)	47.53 (47.50)	3.57 (3.55)	5.83 (5.75)	-	5.79	18
$[Zn(C_{19}H_{15}N_2O_4)Cl]$	436.20	300	60	15.00 (15.05)	52.32 (52.30)	3.47 (3.44)	6.42 (6.39)	8.40 (8.44)	Diamag	13
$[Cd(C_{19}H_{15}N_2O_4)Cl]$	483.20	285	65	23.26 (23.20)	47.23 (47.19)	3.13 (3.10)	5.80 (5.83)	7.56 (7.61)	Diamag	16
$[Hg(C_{19}H_{15}N_2O_4)Cl]$	571.38	300	75	35.11 (35.09)	39.94 (39.90)	2.65 (2.59)	4.90 (4.88)	6.36 (6.38)	Diamag	12

Magnetic Susceptibility: The magnetic susceptibility measurements of the complexes were performed at room temperature (table 1). The magnetic moment value for Cu(II) complexes of the ligand HL is 1.98 B.M. The copper atom which is less than the normal value [18] (1.84-2.20 B.M.). The lowered magnetic moment value observed for Cu(II) complex under present study is due to distorted octahedral geometry [19,20]. On the other hand Ni(II) and Co(II) complex have shown magnetic moment value 2.98 and 4.86 B.M. respectively. Which indicates octahedral geometry [21] for their Ni(II) and Co(II) complexes. The complexes of Mn(II) and Fe(III) exhibited the magnetic moments values 5.67 B.M. and 5.77 B.M. respectively[22]. These values indicates that the complexes are high-spin type paramagnetic, it lies within the octahedral range which very close to spin value 5.90 B.M. as the ground term is $^6A_{Ig}$ and thus supports the octahedral geometry [23].

Electronic spectra: The electronic spectral data of Cu(II), Co(II) Ni(II), Mn(II) and Fe(III) complexes were recorded in DMF as shown in Table 2**.** They have been studied with the view to obtain more information on stereochemistry of the complexes and to procure more support for the conclusion, deduced with the help of magnetic data. The light green colored Cu(II) complex exhibits a broad asymmetric band in the region 16530-12420 cm^{-1} with maxima at 14480 cm^{-1} in an distorted octahedral geometry [24]. The broadness of the band may be due to dynamic John-Teller distortion and is assigned to $^2T_{2g} \rightarrow {}^2E_g$ transitions.

The Co(II) complex (light purple) of the electronic absorption bands appears at 10150 and 20620 cm^{-1}, due to $^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (ν_1) and $^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$ (P) (ν_3) transition, respectively, in an octahedral environment [25,26]. The bands due to the $^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (F) (ν_2) transition could not observed because of its very low intensity. However the position of the ν_2 band has been computed (16261 cm^{-1}) by the equation. $\nu_2 = \nu_1 +$ 10Dq. The intense band around 30000 cm^{-1} may be a charge transfer band. The ligand field parameter such as Dq, B$'$, β and β% have been calculated by using band-fitting equation given by Underhill and Billing [27]. The crystal field splitting energy (Dq) value at 869 cm^{-1}. These values are well within the range reported are most of the octahedral Co(II) complexes. The Co(II) complex under present investigation process interelectronic repulsion parameter (B$'$) 947 cm^{-1}. The Racah parameter (B) is less than free ion value (971) suggesting a considerable orbital overlap and delocalization of electrons on the metal ion. The nephelauxetic ratio (β) for the present Co(II) complex (0.975). This is less than one, suggesting partial covalency in the metal ligand bond. The values Dq, β%, LFSE and ν_2 / ν_1 (Table 2) suggest the octahedral geometry for Co(II) complex [28]. The electronic spectrum of Ni(II) complex shows two bands at 15305 and 26117 cm^{-1} assignable to $^3A_{2g} \rightarrow {}^3A_{1g}$ (F) (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}$(P) ($\nu_3$) transitions respectively, in an octahedral environment [29]. The lowest band ν_2 (10 Dq) was not observed due to limited range of the instrument used. However, it is calculated by using equation suggested by Billing and Underhill. Racah parameter B^1 is less than the free ion value of 1040 cm^{-1} indicating the covalent character of the complex. The ratio ν_2/ν_1 and β% are further support the octahedral geometry around the Ni(II) ion [30]. The Electronic spectra of the Mn(II) complex display absorption bands at 12805-19295 cm^{-1} due to the transition $^6A_{1g} \rightarrow {}^4A_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$(G) and $^6A_{1g} \rightarrow {}^4E_g$ (G) respectively. The ligand field parameters such as Dq, B$'$, β and β % have been calculated (Table 2). These values suggest the high spin octahedral geometry around the metal ion [31]. The Electronic spectra of the Fe(III) complex observed band at (ν_1) 12908, (ν_2) 15980 and (ν_3) 19626 cm^{-1} due to the transitions $^6A_{1g} \rightarrow {}^1T_{1g}$, $^6A_{1g} \rightarrow {}^1T_{2g}$(G) and $^6A_{1g} \rightarrow {}^1T_{2g}$ (D) respectively. The ligand field parameters such as Dq, B$'$, β and β % have been calculated (Table 2). These values suggest the high-spin octahedral geometry around the metal ion [32].

Table 2 Electronic spectral data, ligand field parameters of Cu(II), Co(II) Ni(II), Mn(II) and Fe(III) coumarin complexes

Complexes	ν_1	ν_2 (cm^{-1})	ν_3	Dq (cm^{-1})	B^1	β	β%	ν_2/ν_1	ν_3/ν_2	LFSE k cal mol^{-1}
[Cu($C_{39}H_{34}N_4O_8$)]		12422-16528		1447	-	-	-	-	-	24.80
[Co($C_{39}H_{34}N_4O_8$)]	10152	16260	20618	869	945	0.973	2.67	1.601	1.268	14.89
[Ni($C_{39}H_{34}N_4O_8$)]	11049	15302	26115	933	895	0.860	13.94	1.385	1.706	31.98
[Mn($C_{39}H_{34}N_4O_8$)]	12795	16025	19305	855	861	0.816	18.03	1.252	1.2046	14.67
[Fe($C_{19}H_{17}N_2O_5Cl_2$).H_2O]	12906	15978	19624	853	885	0.838	16.11	1.238	1.228	14.62

Infrared Spectra: The significant IR bands for the ligand N'-(1-(2-hydroxy-5-methylphenyl)ethylidene)-2-oxo-2H-chromene-3-carbohydrazide (HL) as well as for its metal complexes and their tentative assignments are compiled and represented in table 3. The broad band observed at 3470 cm^{-1} in the IR spectra of the ligand (HL) assigned to ν(OH), which were found to have disappeared in all their respective complexes, there by indicating the involvement of phenolic oxygen is bonding with metal ions through deprotonation [33]. The band ν(NH) observed at 3181 cm^{-1}in ligand and complexes ν(NH) observed at 3181-3189 cm^{-1} respectively. A strong sharp band observed at 1660 cm^{-1} is assigned to coumarin ring ν(C=O), which was shifted to 10-32 cm^{-1} in all complexes [34], indicates the involvement of coumarin ring carboxyl in complexation with metal ion [35], the band at 1604 cm^{-1} is assigned to the azomethine ν(C=N) group [36], lowering of ν(C=N) 9-20 cm^{-1} in the complexes as compared to its ligand, is due to reduction of double bond character carbon-nitrogen bond of the azomethine group [37].

The band observed at 1238 cm^{-1}, of the ligand is attributed to phenolic ν(C-O) in view of previous observations. This band is shifted to higher frequency and is found in the region 1238-1269 cm^{-1} (15-30 cm-^{1}) for the complexes. Thus, this further confirms the involvement of ν(C-O-C) in the complex formation. The low frequency skeletal vibrations due to ν(M–O) and ν(M–N) stretching provide direct evidence for complexation. In the present investigation the bands in the 525-521 cm^{-1} region for ν(M-O) and 482-461 cm^{-1} region for ν(M–N) vibration respectively [38]. The bands due to ν(M–Cl) were observed in the 325-320 cm^{-1} region and are characteristic of chlorine atom in Zn(II), Cd(II) and Hg(II) complexes is further confirmed by quantitative chloride estimation.

Table 3 Important spectral IR bands of the ligand [HL] and its metal complexes (cm^{-1})

Ligand / Complex	ν_{OH}	ν_{H2O}	ν_{NH}	$\nu_{L-C=O}$	$\nu_{C=O}$	$\nu_{C=N}$	ν_{C-O-C}	**Phenolic** ν_{C-O}	ν_{M-0}	ν_{M-N}	ν_{M-Cl}
$C_{19}H_{16}N_2O_4$	3471	-	3184	1659	1603	1501	1299	1239	-	-	-
$[Cu(C_{39}H_{34}N_4O_8)]$	-	-	3189	1656	1594	1491	1302	1246	524	480	-
$[Co(C_{39}H_{34}N_4O_8)]$	-	-	3187	1630	1593	1491	1301	1247	522	460	-
$[Ni(C_{39}H_{34}N_4O_8)]$	-	-	3181	1610	1589	1493	1300	1245	521	458	-
$[Mn(C_{39}H_{34}N_4O_8)]$	-	-	3185	1613	1572	1491	1300	1246	522	463	-
$[Fe(C_{19}H_{17}N_2O_5Cl_2).H_2O$	-	3381	3186	1618	1573	1485	1303	1269	523	464	320
$[Zn(C_{19}H_{15}N_2O_4)Cl]$	-	-	3185	1611	1571	1492	1300	1247	521	461	320
$[Cd(C_{19}H_{15}N_2O_4)Cl]$	-	-	3184	1612	1572	1493	1300	1247	522	462	321
$[Hg(C_{19}H_{15}N_2O_4)Cl]$	-	-	3186	1614	1573	1491	1301	1243	520	461	323

^{1}H NMR spectra : Spectrum of ^{1}H NMR in DMSO-d_6 solvent used. In ligand N'-(1-(2-hydroxy-5-methylphenyl)ethylidene)-2-oxo-2H-chromene-3-carbohydrazide (HL) showed sharp peak at δ 13.7 (S, 1H) due to OH at 2-position of phenyl ring of 1-(2-hydroxy-5-methylphenyl)ethanone moiety has resonated, but in the case of Zn(II) complex which has been disappeared indicating the involvement of phenolic oxygen in the coordination via. Deprotonation [39]. The peak appears at δ 2.3 (S, 3H, CH_3) due to the azomethine group in ligand but in case of Zn(II) complex the peak observed at δ 2.2 (S, 3H,–CH_3). The nine aromatic protons due to coumarin and phenyl rings have resonated in region δ 10.8(m, 9H, Ar-H) as a multiplet, in Zn (II) complex the eight aromatic protons have been observed in the region δ 10.7(m, 8H, Ar-H) as multiplet. The Zn(II) complex suggests coordination of the phenolic OH with metal ion [40].

ESR Spectra; ESR spectrum of Cu(II) complexes of ligand 1-(2-hydroxy-5-methylphenyl)ethanone (HL) scanned at room temperature (table 4) using DPPH as a standard. Showed a broadened feature without hyperfine splitting due to the dipolar interaction from the ESR spectrum of a set of magnetic parameter $g_{||}$

2.3954 and $g_{\perp}$ 2.1732.The observed ESR spectrum is characteristic of distorted octahedral geometry g value averaged to overall directions and G which is measure of extent of exchange interaction between metal ion have been calculated. In present case the value of G was found to be 4.217 according to Hathway [41]. If G value is greater than 4, the spin exchange interaction is negligible where as G values less than 4 indicate considerable interaction between metal ions in solid complex clearly indicate that Cu(II) ion in the complex is mono-nuclear nature of the complex.

Table 4 ESR data of the Cu(II) complex of the ligand [HL]

Complexes	$g_{\perp}$	$G_{\parallel}$	g_{av}	g_{iso}	**G**
$[Cu(C_{39}H_{34}N_4O_8)]$	2.173	2.395	2.249	2.323	4.218

X-ray diffraction studies: The Cu(II) complex has characterized by powder XRD studies with a view to find the type of the crystal system. $[Cu\ (C_{39}H_{34}N_4O_8)]$ complex is chosen for powder XRD study. The XRD data is given in the table 5. The diffractogram of Cu(II) complexes consists of nine reflections with maxima at 2θ = 11.06742 corresponding to the value of d = 4.8823 A^{o}. The interplanar spacing (d) has been calculated from the positions of intense peaks using Bragg's relation $n\ \lambda = 2d\sin\theta$, where λ is wavelength of X-ray used CuKα = 1.54056 A^{o}. The observed and calculated values of d and θ are quit consistent (table 5). The unit cell calculations have been carried out for the cubic system. The cell parameters have been calculated by using the equation for cubic system, $\sin^2\theta = \lambda^2 / 4a^2\ (h^2 + k^2 + l^2)$.Where $\lambda^2 / 4a^2$ is a common factor. The present case Cu(II) complex has $\lambda^2 / 4a^2 = 0.0048$.The $h^2 + k^2 + l^2$ values of primitive type cubic cell with lattice parameter equal to a = b = c = 11.09A^{0}. Thus it may concluded that the crystal system of the Cu(II) is cubic.

Table 5. Powder X-ray diffraction data of Cu(II) complex of the ligand HL

2θ	θ	$\sin\theta$	$Sin^2\theta$	$h^2 + k^2 + l^2$ (a)	$h^2 + k^2 + l^2$ (b)	h k l	d-spacing Cal.	d-spacing Abs.	Relative intensity (%)	a (A^0)
8.01349	4.006745	0.069874	0.004882	1	1	1 0 0	11.02447	11.02386	82.81	11.0909
11.06744	5.53374	0.096431	0.009299	1.90461	2	1 1 0	7.9893	7.98784	97.56	11.0240
13.15907	6.579535	0.114582	0.013129	2.68909	3	1 1 1	6.72254	6.72250	20.46	11.0240
15.87873	7.939363	0.138125	0.019078	3.90764	4	2 0 0	5.57688	5.57668	60.39	11.0241
18.14028	9.07014	0.157643	0.024851	5.090046	5	2 1 0	4.94517	4.88622	49.37	11.0243
20.18788	10.09394	0.175262	0.030716	6.291416	6	2 1 1	4.39469	4.39500	40.95	11.0240
22.95993	11.479965	0.199025	0.039611	8.113091	8	2 2 0	3.87026	3.87026	100.00	11.0240
29.50839	14.754195	0.254672	0.064858	13.28418	13	3 2 0	3.02462	3.02459	15.07	11.0240
75.08243	37.541215	0.609331	0.371285	76.04625	76	6 6 2	1.26412	1.26414	5.19	11.0240

Antimicrobial Activity: The in *vitro* antibacterial screening of the ligand HL and its complexes was undertaken against the bacteria *E. coli* and *S. aureus* by cup-plate method [42] using nutrient agar as medium. In a typical procedure, molten nutrient agar kept at 45 ^{0}C was then poured into Petri dishes and allowed to solidify. Then holes of 5mm diameter were punched carefully using a sterile cork borer and these were completely filled with test solutions (1mg/ml in DMF). The plates were incubated for 24 hours at 37^0C. The diameter of the zones of inhibition for all the test compounds was measured and the results were compared with the standard drug streptomycin of the same concentration as that of the test compound under identical conditions [43]. The antifungal activity of the test compounds was evaluated against the *A.niger* and *A. flavous* by cup-plate method cultured on potato-dextrose agar medium adapting similar procedure described above. The plates were incubated at 37 ^{0}C for 48 hours. The diameters of the zone of inhibition for all the test compounds were measured and the results were compared with the standard drug streptomycin and chlotrimazole of the same concentration as that of the test compound under identical conditions [44]. Since all the test compounds and standard drugs were prepared in freshly distilled DMF, its zone of inhibition was found to be very negligible and taken as zero mm. The antibacterial activity results revealed that the ligand (HL) and its complexes shown weak to good activity (table 6). The ligand and its Cu(II) Co(II), and Hg(II) complexes shows weakly active with the zone of inhibition 12-14 mm against the both organisms when compared to the standard drug streptomycin. The Ni(II), Mn(II) and Fe(III) complexes shows active and moderate activity as compared to its ligand with zone of inhibition 15-17 mm and Zn(II) and Cd(II) complexes have exhibited good activity with the zone of inhibition 18-20 mm when compared to the standard drug streptomycin.

Table 6 Antimicrobial, Antifungal activity results of the ligand [HL]and its metal complexes

Compound	**Antibacterial Activity of zone of inhibition (in mm)**		**Antifungal Activity of zone of inhibition (in mm)**	
	E. coli	***S. aureus***	***A. niger***	***A. falvous***
$C_{19}H_{16}N_2O_4$	10	-	08	09
$[Cu(C_{39}H_{34}N_4O_8)]$	13	13	14	13
$[Co(C_{39}H_{34}N_4O_8)]$	14	12	12	14
$[Ni(C_{39}H_{34}N_4O_8)]$	16	15	16	17
$[Mn(C_{39}H_{34}N_4O_8)]$	15	16	19	20
$[Fe(C_{19}H_{17}N_2O_5Cl_2).H_2O]$	15	17	12	14
$[Zn(C_{19}H_{15}N_2O_4)Cl]$	20	20	15	16
$[Cd(C_{19}H_{15}N_2O_4)Cl]$	18	20	15	16
$[Hg(C_{19}H_{15}N_2O_4)Cl]$	13	11	18	19
Streptomycin	25	24	-	-
Chlotrimazole	-	-	24	26
DMF (Control)	0	0	0	0
Bore size	08	08	08	08

The antifungal activity, results revealed that the ligand and its Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Mn(II) and Fe(III) complexes have exhibited weak to good activity. The ligand (HL) and its Cu(II), Co(II) and Fe(III) complexes shows weak activity with the zone of inhibition 12-14 mm when compared to the standard drug chlotrimazole. The Ni(II), Cd(II) and Zn(II) complexes shows moderate activity as compared to its ligand (HL) with the zone of inhibition 15-17 mm respectively. The Mn(II) and Hg(II) complexes have exhibited good activity with the zone of inhibition 18-20 mm when compared to the standard drug chlotrimazole.

APPLICATIONS

The antibacterial activity of prepared ligand and their metal complexes of Cu(II), Co(II), Ni(II), Mn(II), Fe(III), Zn(II), Cd(II) and Hg(II) have been evaluated using cup-plate method. These complexes are found to be more active than the ligand and among the metal complexes. The Zn(II) and Mn(II) complexes exhibited better activity and comparable with the activity of the standard drugs using streptomycin and chlotrimazole.

CONCLUSIONS

The elemental analysis, magnetic susceptibility, electronic spectra, IR, ^{1}H NMR and ESR spectra observations projects the following structures for these complexes where in Cu(II), Co(II) Ni(II) Mn(II) and Fe(III) exhibit coordination number of six, Zn(II), Cd(II) and Hg(II) are four coordinated tetrahedral geometry.

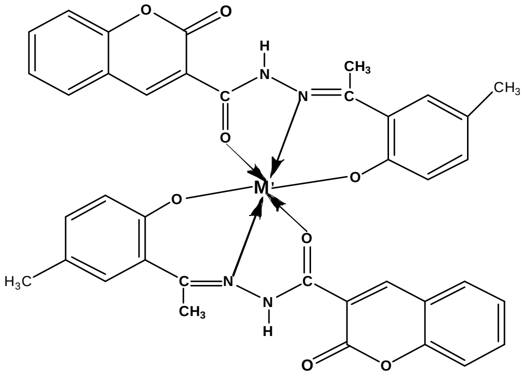

Figure 3. Structure of complexes
Where M = Cu(II), Co(II), Ni(II) and Mn(II).

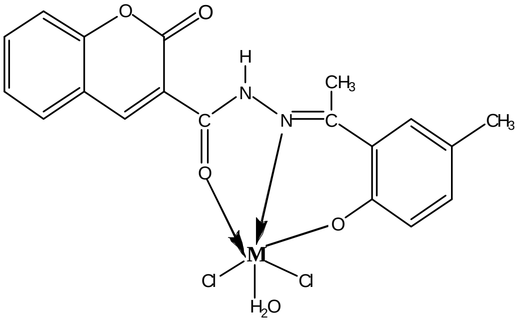

Figure 4. Structure of Complexes
Where M′ = Fe(III)

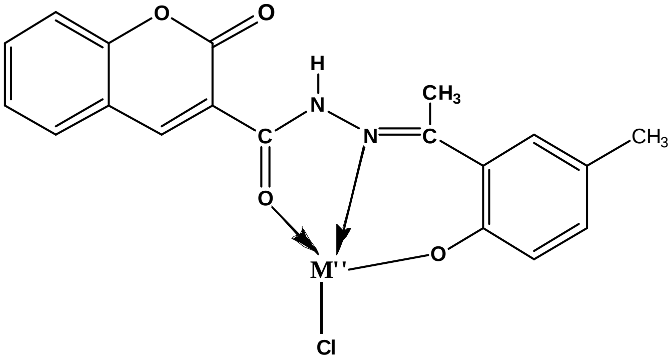

Figure 5. Structure of Complexes, Where M″ = Zn(II), Cd(II) and Hg(II).

ACKNOWLEDGEMENTS

The authors are thankful to the Chairman, Department of Chemistry, Gulbarga University, Gulbarga for providing the facilities. They also thank to Chairmen of to Department of Microbiology and Botany, Gulbarga University, Gulbarga for carrying microbial activities. They also thank IISc Bangalore, STIC Cochin, and IIT Bombay for providing ^{1}HNMR, ESR and Elemental analysis.

REFERENCES

[1] Dinesh kumar *et. al., J. Chem. Sci.*, **2009**, 121(1), 59.
[2] M.S.Y. Khan and P.Sharma *Indian J. Chem.*, **1993**, 32B, 374
[3] S.K. Hafijur Rahaman, Rajarshi Ghosh, Lu.Tian-Huey and Barindra Kumar Ghosh, *Ind. J. Chem.*, **2005,** 11A, 2427.
[4] Nirdosh Patil and B.R. Patil, *Oriental J. of Chemistr,*. **2002**, 18(3), 547.
[5] Mishra, Sharma Sunil Kumar, Taneja Ajay and D.S. Seth, *Proc Nat Acad. Sci. India Sect. A*, **1998**, 68(2), 129.
[6] S.Nakajima, S.Sugiyamer and M.Suto, *Org. Prep. Proceed. Int.*, **1979,** 11, 77.
[7] Y .L. Zhang, B.Chen, K. Zheng, M. L. Zhang and X .Lei, Yaoxue XueBao, **1982**, 17, 17: *Chem. Abstr.*, **1982, 96,** 135383.
[8] L. Bonsignore, , D. Secci & L. Calignano, *European J. Med. Chem.*, **1993**, 28, 517.
[9] M. V. Kulkarni, B. G. Pujar and V. D. Patil, *Arch Phram.*, **1981**, 316(1), 15.
[10] L. Jurd, A.D. King Jr. and K. Mihara, *Experientia,* **1970,** 26**,** 1981.
[11] De. Geey and Vam C.F. Sumare *Arch Int. Physiological Biochem.*, **1966,**74,512.
[12] Hino K, Nagai Y and Uno H, *Chem. Pharm. Bull.*, **1987**, 35, 2819.
[13] G. S. Bajwa, K. E. Hartman and M. M. Joullie, *J. Med. Chem.*, **1973,** 16, 134.
[14] P. Sanket, Chaudhari, and R. P. Nandini, *Ind. J. Het. Chem.* **2007**, 17, 149.
[15] J. B. Hudson, Eds., "*In Antiviral Compounds from plants*", CRC Press, Boca Raton, Florida **1990**.
[16] A. I. Vogel, A Text book of Quantitative inorganic Analysis: 3rd Edn. ELBS and Langman's Green and Co.Ltd., London, **1962**.
[17] W. J. Geary, Coord. *Chem. Rev.*, **1972**, 1, 81.
[18] M. A. Hassan, *J. Islamic Acad. Sci*, **1991** 4(4), 272.
[19] M. B. Halli and Z. S. Qureshi, *Indian. J. Chem.*, **2004**, 43A, 2347.
[20] S. J. Swamy, E. R Reddy, D Nagaraju and S Jyothi, Molecules, **2006,** 11, 1000.
[21] M. M. Bekhet and K. M. Ibrahim, Synth. *React. Inorg. Met. Org. Chem.*, **1986**, 16, 1135.
[22] T. Singh and R. N. Singh, Synth. *React. Inorg. Met. Org. Chem.*, **1989**, 19(3), 251.
[23] G. G. Mohamed *et. al.*, *Turk J. Chem.*, 200,660, 366.
[24] J. K. Verma and G. S. P. Verma, *Indian J. Chem.*, **1982**, 21A, 825.
[25] B. P. Lever A, *Inorganic Electronic Spectroscopy; Elsevier*, New York, **1984**.
[26] Sulekh Chandra and K. Gupta, *Indian J. Chem.*, **2001**, 40A, 775.
[27] A. E. Underhill and D. Billing, *Nature*, **1996**, 210, 834.
[28] D. P. Singh, S.Singh and V. B. Rana, *J. Ind. Chem. Soc.*, **2002**, 79, 889.
[29] B. N. Figgs, Introduction to ligand Fields; Interscience, John-Wiley and Sons, New York, **1967**.
[30] G. Chitra, *J. Ind. Coun. Chem.*, **2007**, 24(1), 16.
[31] G. G. Mohamed, *Spectrochim. Acta.*, **2001, 57A,** 1643.
[32] R. K.Dubey, U.K. Dubey and C. M. Mishra, *Ind. J. Chem.*, **2006,** 45(A), 2632.
[33] K. Siddappa and S. D. Angadi, *Proc. Nat .Acad. Sci. India,* **2003**, 3A, 75.
[34] K. M. Chetan, S. P. Ashwin and T. T. Bharat, *E-J. Chem.*, **2005**, 2(6), 21.
[35] K. B. Gudasi, R. V. Shenoy, R. S. Vadavi, M. S. Patil, and S. A. Patil, *Indian J.Chem.*, **2005**, 44A, 2247.
[36] Sulekha and Lokesh Kumar Gupta, *Spectrochimica Acta.*, **2005**, 61A, 269.
[37] K. Siddappa, Tukaram Reddy, M. Mallikarjun and C. V. Reddy, *E-J. Chem.* **2008**, 5(1), 155.
[38] B. B. Mahapatra and S. K. Saraf, *J. Indian Chem. Soc.*, **2003**, 80,696.
[39] J. R. Dyer, Application of Absorption Spectroscopy of Organic compounds; Printice Hall of Indian Pvt.Ltd., **1986**.
[40] N. K. Singh and S. B. Singh, *Indian J. Chem.*, **2001**, 40A, 1047.
[41] B. J. Hathway and D. E. Billing, *coord . Chem. Rev.* **1970**.
[42] A. L. Barry, The Antimicrobic Susceptibility test principle and practices; **1976**, 180.

[43] F. Simoncini, R. Rangone and C. Calanni, Farnance Edn. Part, **1968**, 23, 559; *Chem. Abstr.*, **1968, 69,** 109851d.
[44] H. W. Seely and P. J. Van Demark, Microbes in Action, Laboratory of Mcrobiology, 3rd Edn, W H Freeman and Co. U.S.A, **1981**, 385.