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Research Article

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Preparation and characterization of Ni(II), Co(II), Cu(II), Cd(II), Zn(II) and Hg(II) complexes with schiff base derived from benzofuran-2- carbohydrazide and p-chloroacetophenone

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ABSTRACT

The complexes of Ni(II), Co(II), Cu(II), Cd(II), Zn(II) and Hg(II) ions with Schiff base derived from reaction between benzofuran-2-carbohydrazide and p-chloroacetophenone have been synthesized. All the complexes have been characterized on the basis of elemental analysis, magnetic moments and spectral studies. All the complexes are light in colour and stable to atmosphere. The elemental analysis shows that $MLCl_2$ stoichiometry for all the complexes. The IR spectral data indicates the coordination through carbonyl oxygen and azomethine nitrogen groups. The molar conductance values of all the complexes fall in the range 11.5-18.05 $ohm^{-1}cm^2mol^{-1}$, indicating non-electrolytic behaviour of all the complexes. The electronic spectral data suggest that polymeric octahedral structures for Cu(II), Ni(II) and Co(II) complexes. The magnetic moment values for these complexes are 4.95, 2.85 and 1.92 respectively suggesting octahedral geometry. The Cd(II), Zn(II) and Hg(II) complexes are monomeric tetrahedral in nature.

Keywords: Schiff's base, Metal complexes, Spectral studies, Antimicrobial activity.

INTRODUCTION

Schiff base and their metal complexes have aroused considerable research interest for several decades [1, 2]. Schiff base ligand have been widely studied in the field of coordination chemistry mainly due to their facile synthesis, easily availability, electronic properties and good solubility in common solvents [3, 4]

The several compound having benzofuran moiety are more abundantly occurring in nature, in particularly plant kingdom after such products with benzofuran nucleus are possessing useful pharmacological properties and biological properties [5, 6] and also act as good chelating agents[7]. The benzofuran derivatives like 2 nitrobenzofuran are used as microbicidal and nematicidal, 2-acetylbenzofuran etc, are used as anti-inflammatory, diuretic agents [8] and particularly the aminodarone hydrochloride found to be highly effective antiarrhythemic drug [9,10]. The Schiff bases and metal complexes are frequently used as anticancer [11], antitubercular and fungicidal agents[12] and act as an intermediate[13] in many biological processes. It is believed that azomethine linkage might be responsible for their activity [14]. The enhanced biological activities of the Schiff's bases have been seen when complexed with metal ions [15]. In the present investigation, we report the synthesis of Schiff base derived from reaction between benzofuran-2-carbohydrazide and p-chloroacetophenone and synthesis of metal complexes with Ni (II), Co (II), Cu (II), Zn (II), Cd (II) and Hg (II) metal ions. All the complexes were characterized on the basis of elemental analysis, molar conductance, IR, ^{1}H NMR, ESR, electronic spectral studies and magnetic susceptibility measurement. Schiff's base and its metal complexes are screened for their biological activity studies.

EXPERIMENTAL SECTION

All the chemicals used were of analytical grade. The compound benzofuran-2-carboyhydrazide was prepared by the literature method [16]. The metal and chloride contents are determined as per Vogel's procedure [17].

Physical Measurements

The CHN analysis was carried out microanalytically on a perkin-Elmer 240C model at the central drug research institute (CDRI), Lucknow. The IR spectra of the Schiff base and its metal complexes were recorded in KBr pellets in the region of 4000-350 cm^{-1} on a perkin-Elmer FT-IR Spectrophotometer. Conductance measurements were made on Elico CM- 180 Conductivity bridge in DMF (10^{-3}M) solution using a dip-type conductivity cell fitted with a platinum electrode having cell constant 0.1 $ohm^{-1}cm^{2}mole^{-1}$. The magnetic susceptibility measurement was made on Gouybalance using Hg $[Co(NCS)_4]$ as the calibrant at room temperature. The ESR spectra of Cu (II) complex in polycrystalline state was recorded on Varian E-4X band spectrophotometer using (TCNE) as a 'g' marker (g = 2.00277) at room temperature. The ^{1}H NMR spectra were recorded in DMSO-d_6 on Bruker 400 MHz spectrophotometer, using TMS as internal standard. The electronic spectra were recorded on Elico SL - 159 double beam UV-Vis spectrophotometer in the range of 200-1100 nm in DMF (10^{-3}M) solution. The FAB Mass spectra were recorded on a Jeol SX 102/Da- 600 Mass spectrophotometer at the central drug research institute (CDRI), Lucknow.

Synthesis of Schiff base

A solution of benzofuran-2-carbohydrazide (1.76g, 0.01mol) was added to p-chloroacetophenone (1.29ml, 0.01mol) in methanol (25 mL). The reaction mixture was refluxed on a water bath for about 4-5 hrs. The Schiff base was separated on removal of 50% of the solvent and cooling to room temperature. The product was filtered out and washed with ethanol and recrystallised from ethanol. The Schiff base was dried in vacuum over the anhydrous $CaCl_2$. The purity of the Schiff base was checked by TLC.

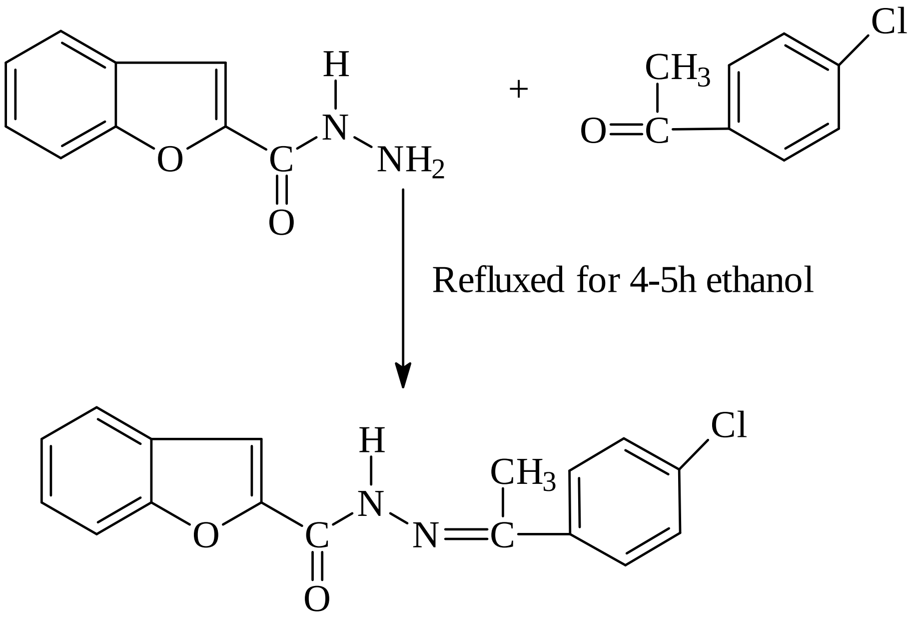


Fig. 1: Synthesis of Schiff base (BCClACP)

$C_{17}H_{13}N_2O_2Cl$[BCClACP]: Mol. Wt = 313, m. p = 144^{0}C, Yield = 76%

Synthesis of Metal (II) complexes

Metal complexes were prepared by adding (0.1 mol, 20 mL) of aqueous solution of metal (II) chlorides to the Schiff base in ethanol (0.1 mol, 50mL). The reaction mixture was refluxed on a water bath for about 2 hours, during which complexes started separating out. The solution was concentrated and cooled to room temperature. The precipitated light colored complexes were filtered out, washed with water and ethanol to remove the unreacted salts and ligand. All the complexes were dried in open air and kept in vacuum desiccator.

Antibacterial and antifungal assays

The ligand and complexes were screened for their antibacterial and antifungal activity by agar cup plate zone of inhibition technique [18, 19] against two bacteria *E. coli*, and *S. aureus* and two fungal species *A. niger* and C. *albicans*.

Antibacterial screening using agar-cup plate method

Peptone 10g, NaCl 10g, Yeast extract 5g, Agar 20g in 1000mL of distilled water were used as the medium.

Initially, the stock cultures of bacteria were revived by inoculating in broth media and grown at 37°C for 18 hrs. The agar plates of the above media were prepared and wells were made in the plate. Each plate was inoculated with 18 hrs old culture (100 µ1, 10^{-4} cfu) and spread evenly on the plates. After 20 min, the wells were filled with the compound (20mg/ml stock solution). All the plates were incubated at 37°C for 24 hrs and the diameter of inhibition zone were recorded. Gentamycine was used as standard.

Antifungal screening using cup-plate method

Methodology: Potato Dextrose Agar (PDA) 250g of peeled potato were boiled for 20 min and squeezed and filtered. To this filtrate, 20g of dextrose was added and the volume was made up to 1000mL by distilled water.

Initially the stock cultures were revived by inoculating in broth media and grown at 27°C for 48hrs. The agar plates of the above media were prepared and wells were made in the plate, each plate was inoculated with 48 hrs, old culture (100µL, 10^{-4} cfu) and spread evenly on the plate. After 20 min, the wells were filled with a compound (20mg/ml stock solution). All the plates were incubated at 27°C for 48 hrs and the diameter of inhibition zone were noted. Amphotericin was used as standard.

RESULTS AND DISCUSSION

Analytical data for the complexes indicates 1:1 stoichiometry for all the complexes (Table-1). All the complexes possess high melting point and are stable in air and are partially or insoluble in common organic solvents and soluble in DMF, DMSO and pyridine. The molar conductance of the complexes falls in the range of 11.5 – 18.05 $ohm^{-1}cm^2mole^{-1}$ in DMF (10^{-3}M) solution. These values suggest non - electrolytic behavior of the complexes [20].

Table -1 Analytical, molar conductance and magnetic susceptibility data for Schiff base and their Metal (II) complexes

Compound	Yield (%)	Mol wt	M P (^{0}C)	Elemental analysis(%)found /(calculated)					$\wedge^*_M$	µeff. (BM)
				C	H	N	M	Cl		
BCClACP [$C_{17}H_{13}N_2O_2Cl$]	76	313	144	65.25 (65.38)	4.08 (4.16)	8.78 (8.97)	--	11.26 (11.37)	--	--
[$Cu(C_{17}H_{13}N_2O_2Cl)Cl_2]_n$	66	447.54	>300	45.14 (45.58)	2.35 (2.90)	6.02 (6.25)	14.03 (14.19)	7.78 (7.93)	15.65	1.92
[$Co(C_{17}H_{13}N_2O_2Cl)Cl_2]_n$	65	442.93	295d	45.89 (46.05)	2.78 (2.93)	6.13 (6.32)	13.12 (13.30)	7.88 (8.01)	11.45	4.95
[$Ni(C_{17}H_{13}N_2O_2Cl)Cl_2]_n$	68	442.70	290d	45.91 (46.08)	2.82 (2.94)	6.11 (6.33)	13.02 (13.26)	7.89 (8.02)	13.5	2.85
[$Zn(C_{17}H_{13}N_2O_2Cl)Cl_2$]	68	449.38	272d	45.11 (45.39)	2.72 (2.89)	6.04 (6.23)	14.33 (14.54)	7.78 (7.90)	11.95	--
[$Cd(C_{17}H_{13}N_2O_2Cl)Cl_2$]	64	496.40	>295	40.98 (41.10)	2.48 (2.61)	5.44 (5.64)	22,42 (22.63)	7.04 (7.15)	14.5	--
[$Hg(C_{17}H_{13}N_2O_2Cl)Cl_2$]	65	584.60	>290	34.66 (34.89)	2.11 (2.22)	4.66 (4.78)	34.18 (34.31)	5.98 (6.07)	18.05	--

** Molar conductance values in* $ohm^{-1}cm^2mol^{-1}$

Magnetic properties

The observed magnetic moment for Co (II) complex (4.95 BM) has been used as criteria to determine the type of geometry around the Co (II). The values suggest an octahedral geometry for this complex [21]. The magnetic moment values for Ni (II) complex (2.85 BM) slightly higher than the spin only value (1.83 BM) indicating an octahedral environment around Ni (II) complex [22]. The observed magnetic moment for the Cu (II) complex is (1.92 BM) suggesting a distorted octahedral geometry around the Cu (II) complex.

Electronic spectral studies

The electronic spectra of the Co(II), Ni(II) and Cu(II) complexes were taken in DMF solution (10^{-3}M) at room temperature and spectral data are given in Table -2. The electronic spectra of the Co(II) complex showed bands at 16133 and 20623 cm^{-1}. These two bands are assigned to $^4T_{1g}$ (F) → $^4A_{2g}$ (F) (ν_2) and $^4T_{1g}$ (F) → $^4T_{2g}$ (F) (ν_3)

transitions, respectively, in an octahedral environment [23]. The band ν_1 has been calculated using band-fitting procedure [24].The octahedral geometry is further supported by the values of ligand filed parameters like Dq, B′, β, β% and LFSE. All these values are given in Table-2. The reduction in Rachah parameter values from free ion value (971) suggests measure of covalent character of the M-L bond. The six coordinated Ni(II) complex exhibit two bands at 15231and 25520 cm^{-1}, are assignable to $^3A_{2g}$ (F) → $^3T_{1g}$ (F) (ν_2) and $^3A_{2g}$ (F)→ $^3T_{1g}$ (P) (ν_3) transitions, respectively, in an octahedral environment. The lowest band ν_1 (10Dq) could not be observed due to limited range of the instrument used. However, it was calculated by using an equation suggested by Underhill and Billing [25]. The β value for Ni(II) complex is less than the Co(II) complex indicating more covalency of M-L bond. The Cu(II) complex show broad asymmetric band in the region 13840-16820 cm^{-1}. The broadness of the band may be due to dynamic Jahn-Teller distortion [26].These observations suggest the distorted octahedral structure around Cu(II) ion.

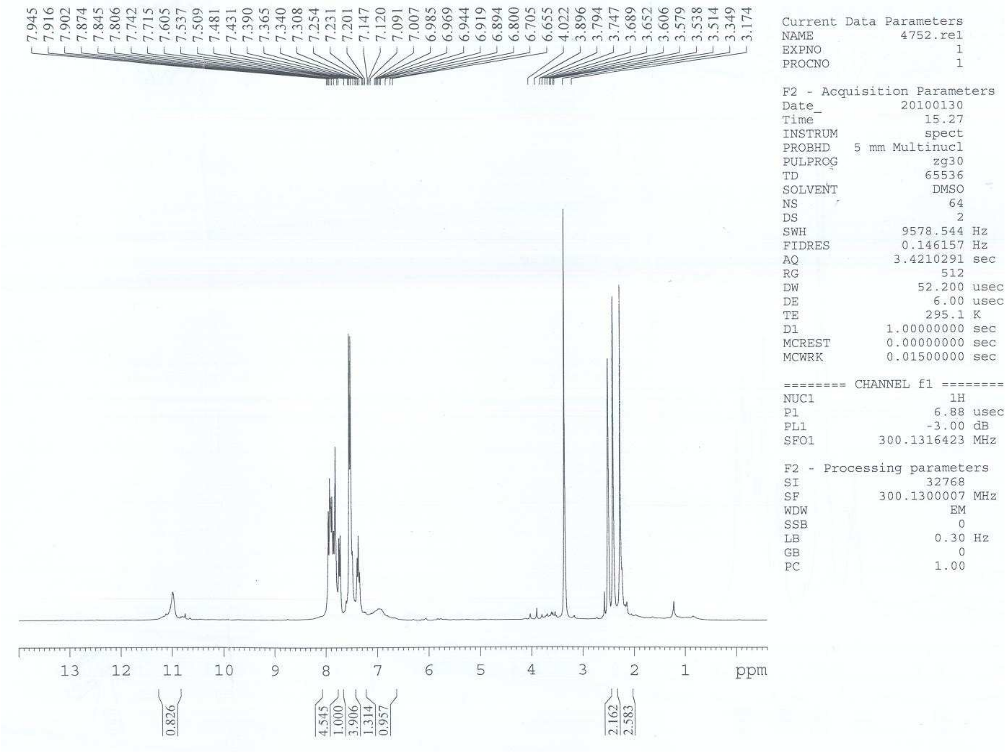
Table -2 Electronic spectral data and ligand field parameters of the Co(II), Ni(II) and Cu(II) complexes

Complexes	Transitions in cm^{-1}			Dq cm^{-1}	B′cm^{-1}	β	β%	ν_2/ν_1	LFSE kcal/mole
	ν_1^*	ν_2	ν_3						
$[Co(C_{17}H_{13}N_2O_2Cl)Cl_2]_n$	7503	16133	20623	863	950	0.978	2.163	2.150	14.794
$[Ni(C_{17}H_{13}N_2O_2Cl)Cl_2]_n$	9360	15231	25520	936	844	0.811	18.850	1.621	32.091
$[Cu(C_{17}H_{13}N_2O_2Cl)Cl_2]_n$	13840-16820			1533	--	--	--	--	26.280

** Calculated values*

^{1}H- NMR spectral studies

The ^{1}H- NMR spectra of Schiff base and its Zn (II) and Cd (II) complexes are taken in DMSO-d_6. The signal at δ 10.94 (s, 1H) is assigned to amide proton (-CONH). The signal due to (-CONH) shifted downfield in the spectra of the Zn (II) (Fig-2) and Cd (II) complexes in the region of δ (11.12, 11.10 s, 1H), indicating the coordination of the oxygen of –CONH- with metal ions. The aromatic protons at δ (8.10 - 7.36) (m, ArH) shift down field in the complexes. The signal at δ 3.67 (s, 3H) is assigned to methyl group of p-chloroacetophenone. Thus the ^{1}H-NMR spectral observations supported the assigned geometry.



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FIDRES            0.146157 Hz
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RG                     512
DW                  52.200 usec
DE                    6.00 usec
TE                   295.1 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    6.88 usec
PL1                  -3.00 dB
SFO1           300.1316423 MHz

F2 - Processing parameters
SI                   32768
SF             300.1300007 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
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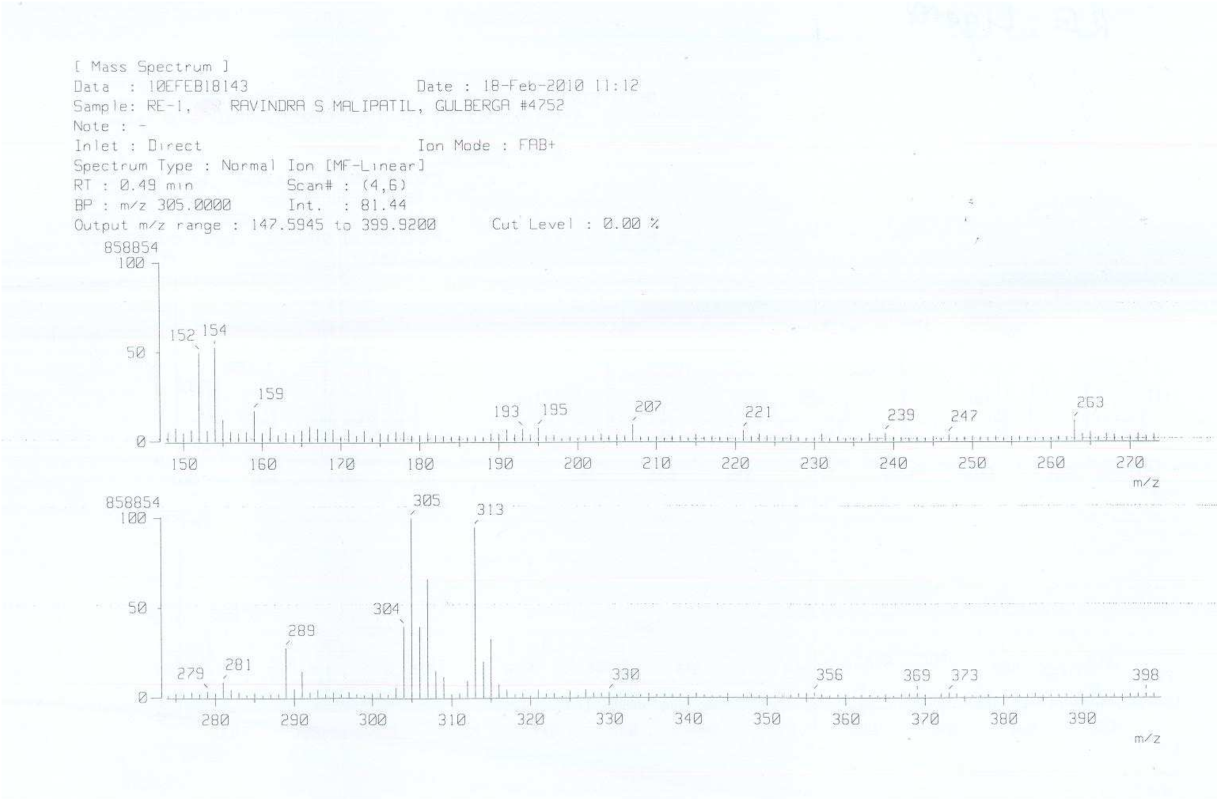
Fig-2 ^{1}H-NMR-spectra of the Zn(II) complex

Mass spectra studies

The FAB-mass spectra of the Schiff base shows molecular ion peak at m/z 313, indicating the molecular weight of the ligand. (Fig-3)



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Note : -
Inlet : Direct                           Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.49 min            Scan# : (4,6)
BP : m/z 305.0000        Int.   : 81.44
Output m/z range : 147.5945 to 399.9200      Cut Level : 0.00 %
```

Fig-3 FAB-Mass spectra of the Schiff base

IR spectral studies

The main stretching frequencies of the ligand and its metal complexes are presented in Table-3. The IR spectra of the ligand gives a broad band at 3219 cm^{-1} assignable to ν(NH) of the CONH group. The shifting of these band to higher wave number side in the complexes by 3-74 cm^{-1} indicates non-involvement of 'N' of the amide group in the coordination.

The strong band observed at 1657 cm^{-1} in free ligand is assigned to ν(C=O) stretch of CONH group. This band shift to lower wave number side in all of the complexes by about 8-71 cm^{-1}, indicating participation of the carboxyl oxygen atom in coordination. Medium to strong intensity band at 1602 cm^{-1} in the free ligand is assigned to ν(C=N) stretch of the azomethine group. This ν(C=N) stretch shift to lower wave number side in all the complexes by about 8-48 cm^{-1} indicating involvement of the azomethine nitrogen in bonding with all the metal ions [27].

Metal ligand vibrations are generally observed in the far-IR region and usually give valuable information regarding the bonding of ligand to the metal-ions. The weak intensity non-ligand bands observed in the complexes in the region 560-535 cm^{-1} and 446-436 cm^{-1} are assigned to ν(M-O) and ν(M-N) stretching vibration respectively in all the complexes[28].

Table-3 Important IR spectral bands (cm^{-1}) for ligand and its metal complexes)

Complexes	ν(NH)	ν(C=O)	ν(C=N)	ν(M-O)	ν(M-N)
BCClACP [$C_{17}H_{13}N_2O_2Cl$]	3219	1657	1602	--	--
[$Cu(C_{17}H_{13}N_2O_2Cl)Cl_2]_n$	3290	1620	1594	535	438
[$Co(C_{17}H_{13}N_2O_2Cl)Cl_2]_n$	3293	1590	1561	560	442
[$Ni(C_{17}H_{13}N_2O_2Cl)Cl_2]_n$	3283	1645	1564	543	441
[$Zn(C_{17}H_{13}N_2O_2Cl)Cl_2$]	3278	1643	1569	553	438
[$Cd(C_{17}H_{13}N_2O_2Cl)Cl_2$]	3222	1649	1562	559	436
[$Hg(C_{17}H_{13}N_2O_2Cl)Cl_2$]	3210	1586	1554	558	446

ESR Spectra of Cu(II) Complex

The ESR spectra of the Cu(II) complex in a polycrystalline state was recorded at room temperature. The spectra having asymmetric bands with two g values, g_{11} and $g_{\perp}$. The g_{11} and $g_{\perp}$ values were found to be 2.121 and 2.035 respectively. The trend $g_{11} > g_{\perp} > (2.00277)$ observed for this complex indicating that the unpaired electron lie predominately in the dx^2-y^2 orbital with possibly mixing of dz^2 because of the low symmetry [29]. The axial symmetry parameter 'G' is defined as G= (g_{11} -2.00277)/($g_{\perp}$- 2.00277) as shown to be a measure of the exchange interaction between copper center in polycrystalline solid state[30].

Biological Activity

Antibacterial and antifungal activity

The Antimicrobial activity of the synthesized Schiff base and its metal complexes on selected bacteria *E. Coli* and *S. aureus* and two fungi *A. niger* and *C. albicans* was carried out. On comparing the biological activity with Schiff base ligand, Cu(II) and Co(II) complexes show moderate activity, while Hg(II) complex show high activity against bacteria *E. coli*. The Ni(II), Cu(II) and Cd(II) complexes show moderate activity while Hg(II) show very high activity against bacteria *S. aureus*. In the case of fungicidal activity all complexes show high activity compared to ligand except Zn(II) complex against fungi *C. albicans* where as against fungi *A. niger*, all complexes show moderate activity. However, the activities are less than the standards used. The activity of the complexes may be due to the presence of metal ions in the complexes (table -4).

Table -4 Antibacterial and antifungal activity results of ligand and its metal complexes (20mg/ml concentration)

Ligand/salts complexes	Zone of inhibition in mm			
	Antibacterial activity		Antifungal activity	
	E. coli	*S. aureus*	*A. niger*	*C.albicans*
BCClACP [$C_{17}H_{13}N_2O_2Cl$]	9	16	10	8
[$Cu(C_{17}H_{13}N_2O_2Cl)Cl_2]_n$	12	17	8	13
[$Co(C_{17}H_{13}N_2O_2Cl)Cl_2]_n$	11	12	9	16
[$Ni(C_{17}H_{13}N_2O_2Cl)Cl_2]_n$	7	15	8	19
[$Zn(C_{17}H_{13}N_2O_2Cl)Cl_2$]	9	16	7	7
[$Cd(C_{17}H_{13}N_2O_2Cl)Cl_2$]	9	17	7	9
[$Hg(C_{17}H_{13}N_2O_2Cl)Cl_2$]	19	29	13	17
Gentamycine	26	25	--	--
Amphotericin	--	--	20	22

CONCLUSION

Based on the analytical data and spectral studies we assigned the possible structures for all the complexes. Co(II),Cu(II) and Ni(II) complexes are chloride bridged polymeric in nature while Zn(II), Cd(II) and Hg(II) complexes are monomeric tetrahedral in nature. The Schiff base and its complexes have been screened for their antimicrobial activities. The results show that some of the complexes exhibit good activity as compared to the ligand.

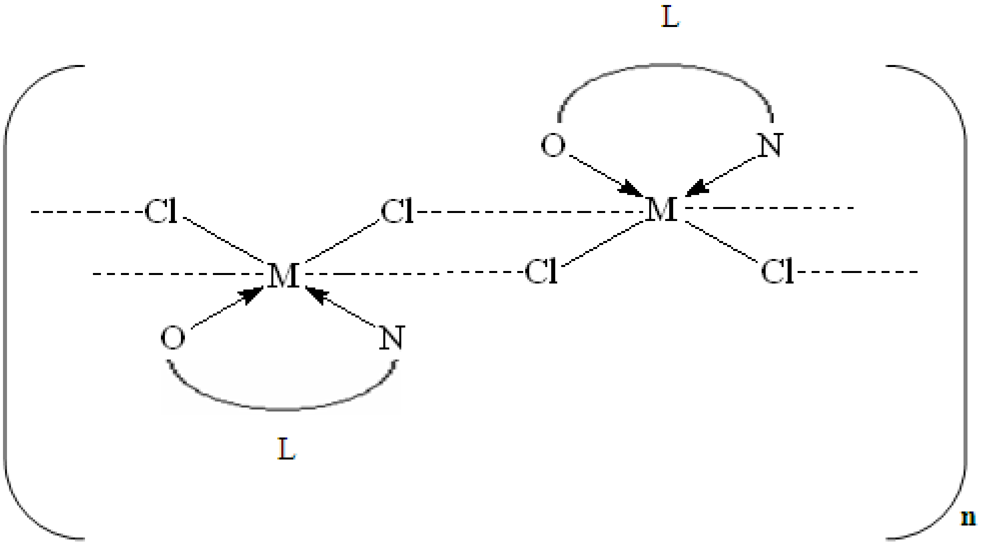

Fig-4: Structure of Co(II), Cu(II) and Ni(II) complexes

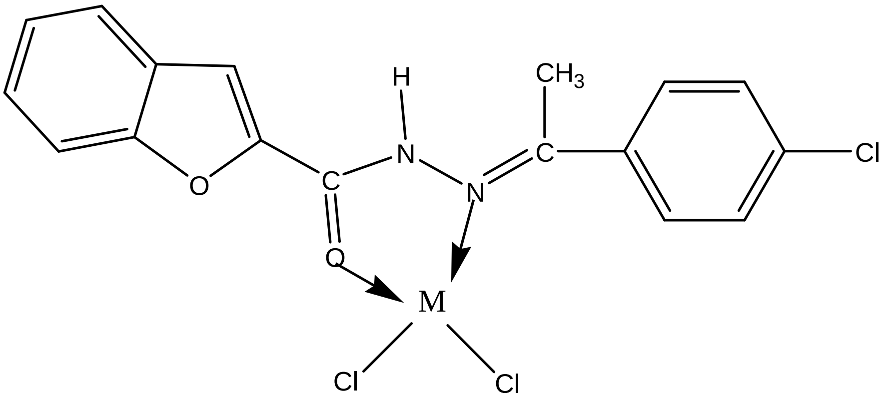

Fig. 5: Structure of Zn(II), Cd(II) and Hg(II) complexes

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