INTERNATIONAL JOURNAL OF PHARMACEUTICAL, CHEMICAL AND BIOLOGICAL SCIENCES

Available online at www.ijpcbs.com

Research Article

SYNTHESIS, SPECTRAL CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF METAL (II) COMPLEXES OF SCHIFF BASE DERIVED FROM 4-AMINIOANTIPYRINE AND 2-(4-CHLOROPHENYL)CHROMAN-4-ONE

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ABSTRACT

A series of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with a Schiff base derived from 2-(4-chlorophenyl)chroman-4-one and 4-aminoantipyrine have been synthesized and characterized. The nature of bonding and the geometry of the complexes have been deduced from elemental analysis, spectral (IR, UV-Vis, ^{1}H NMR, ESR and EI-mass), magnetic moment measurements and conductivity measurements. The electronic absorption spectra and magnetic susceptibility measurements of the complexes indicates octahedral geometry for all the complexes. The EPR spectra of copper complex in DMSO at 300 K and 77 K were recorded. The antimicrobial activities of the compounds have been studied against microorganisms such as *Escherichia coli*, *Chromobacterium*, *Staphylococcus aureus*, *Bacillus subtilis*, *Candida albicans and Aspergillus niger* by well-diffusion technique using DMSO as the solvent and the results revealed that the complexes are more potent bactericides and fungicides than the ligand. The redox behaviour of the copper(II) complex studied using cyclic voltammetry are reported

Keywords: 4-aminoantipyrine, 2-(4-chlorophenyl)chroman-4-one, antimicrobial studies.

1. INTRODUCTION

Antipyrine and its derivatives are the extremely important active molecules and intermediates for synthesis of pharmaceuticals and natural products due to a wide range of activities and applications. Antipyrine and its derivatives posses anti-inflammatory and anti-bacterial properties . 4-aminoantipyrine also has insulin mimic property.[1-4]Since the antipyrine (AP) was first synthesized by Knorr in 1883, there has been a continued interest in the studies of antipyrine derivatives (APDs). Schiff bases of 4-aminoantipyrine and its complexes continue to be a subject of current interest, not only because of their various applications in the areas of catalysis and fluorescence,[5,6] but also due to their interesting pharmacology and clinical applications, such as the intravenous detection to liver disease in clinical treatment and the new chemotherapeutic agents[7]. Even though 4-aminoantipyrine itself exhibits some anti-microbial activity it has been markedly increased due to condensation with aldehyde, ketone etc. Antipyrine is also used in medicine as febrifuge[8]. In-situ synthesis of metal complexes is a well established procedure where isolation of ligands is difficult owing to their instability[9]. In most of this synthesis the reactants are open chain compounds. o-hydroxy-p-chlorophenyl styrylketone undergoes cleavage at the double bond in the presence of amines to give o-hydroxy acetophenone imine[10]. Also, the heterocyclic ring cleavage is found to occur with 7, 8-benzoflavanone in the presence of a base to give o-hydroxy-p-chlorophenyl styryl ketone[11]. This observation prompted us to use ring opening reaction as a route for the in-situ preparation of metal(II) complexes[12-14]. In this paper we report the in- situ direct synthesis of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Schiff base complexes from 7,8-benzoflavanone and their characterization. Due to the great flexibility and diverse structural aspects, a wide range of Schiff bases have been synthesized and their complexation behavior was studied.

2. EXPERIMENTAL

The chemicals and solvents were purchased from Aldrich Chemical & Co. and the solvents were purified by standard methods. Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. Molar conductance of the complexes was measured at room temperature using a Systronic Conductivity Bridge 304. Magnetic susceptibility of the complexes was performed on a Sherwood MSB mark1 Gouy balance. Infrared spectral studies were carried out on a Shimadzu FT IR 8000 spectrophotometer using KBr discs. UV-Vis spectra were obtained using a THERMO SPECTRONIC 6 HEXIOS α and fluorescence spectra were determined with an ELICO SL174 Spectrofluorometer. NMR spectra were recorded on Bruker DRX-300, 300MHz NMR Spectrometer using TMS as reference. ESR spectra of the Cu(II) complex was recorded in Varian E-112 machine at 300 and 77 K using TCNE (Tetracyanoethylene) as the g-marker. Cyclic voltammetric measurements for Cu(II) complex was carried out on a Electrochemical analyzer CH Instruments (USA) using a three electrode cell containing an Ag/AgCl reference electrode, Pt wire auxiliary electrode and glassy carbon working electrode with tetrabutylammonium perchlorate as supporting electrolyte. Electrospray ionization mass spectrometry(ESI-MS) analysis was performed in the positive ion mode on liquid chromatography-ion trap mass spectrometer (LC Q Fleet, Thermo Fisher Instruments Limited, US).

2.1. Preparation of ligand

To (1.37g, 0.005 mol) of (2-(4-chlorophenyl)chroman-4-one) dissolved in 30 mL of ethanol, was added (1.0 g, 0.005 mol) of 4-aminoantipyrine in 15mL of ethanol and the mixture was refluxed for 3 h. After the reaction was over, the reaction mixture was concentrated under reduced pressure and the solid was separated which is [4-((E)-((E)-3-(4-chlorophenyl)-1-(2-hydroxyphenyl)allylidene)amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one] and kept in refrigreator. After refrigeration, it was recrystallized from ethanol. (Yield: 77%, m.p. = 112°C).

2.2. Preparation of metal(II) complexes

All the complexes were prepared from hydrated metal salts. To a solution of Schiff base ligand [CHAADP] (0.5 g, 2 mmol) in 20mL ethanol was added 1 mmol of $MCl_2.xH_2O$ (M=Cu(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)) The solution was stirred for 2 h and the resulting solution was refrigerated for 1 day. The complexes were precipitated by adding petroleum ether (60–80°C). The colored complexes were filtered and washed with hot water and dried under vacuum.

2.3. Antimicrobial activity

Antimicrobial activity of the compounds were tested *invitro* by the well diffusion method[15] against the bacteria*, Escherichia coli, Chromobacterium, Staphylococcus aureus and Bacillus subtilis* using agar nutrient as the medium and antifungal activities against the fungus *Candida albicans and Aspergillus niger.* Amikacin and Ketoconozole were used as references for antibacterial and antifungal studies. The stock solution (10^{-2}mol/L) was prepared in DMSO. The well was made on the agar medium inoculated with microorganisms and filled with the test solution. The plate was incubated for 24 h for bacteria and 48 h for fungi at 35°C.

3. RESULTS AND DISCUSSION

The analytical data of the complexes are summarized in Table 1. The ligand on interaction with MCl_2 [M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)] yields complexes corresponding to the 1:2 metal - ligand ratio. The analytical data show a good agreement between experimental and theoretical value confirming the composition to be ML_2. All the complexes are air stable, non-hygroscopic with high melting point, insoluble in water. The molar conductance of all complexes are recorded in DMSO. The observed molar conductance values of these metal complexes are in the range of 8.14 – 11.08 ($Scm^2\ mol^{-1}$) and are consistent with the non-electrolytic nature of these complexes.

3.1. IR spectra

IR stretching frequencies of the ligands and its metal(II) complexes are shown in Table 2. The IR spectrum of ligand shows bands at 1700, 1643, 1404 cm^{-1} due to ν(C=O), ν(C=N) and ν(C-O) respectively. The ν(C=O) vibration in the complexes are shifted to lower frequencies (13 – 39 cm^{-1}) which indicates that oxygen of antipyrine is coordinated with metal. The band at 1643 cm^{-1} which can be assigned to ν(C=N) of 4-aminoantipyrine ligand and it is also shifted to lower wave number 1631 cm^{-1} after complexation indicating coordination of 4-aminoantipyrine nitrogen to metal .The band at 1550-1565cm^{-1} in the spectrum of complexes assigned to aromatic ν(C=C) stretching vibration. The broad band of medium intensity occurring at 3425cm^{-1} is due to ν(OH) stretching vibration of ligand which is disappeared in the complexes shows the complex formation. Proof of nitrogen and oxygen coordination is further demonstrated by new bands at 547 – 563 cm^{-1} and 437 – 480 cm^{-1} assigned as ν(M-O) and ν(M-N).

3.2. Mass spectra

The ESI-MS spectrum of ligand, Zn(II) and Cd(II) complexes are given in Figure 1,2 and 3 respectively. The Schiff base shows the molecular ion peak at m/z=444 which is equivalent to $[M+H]^+$ ion, whereas the molecular ion peak at m/z=950 and 997 which is equivalent to $[M+H]^+$ ion, $[M+H]^+$ ion for Zn(II) and Cd(II) complexes respectively confirms the stoichiometry of metal chelates as $[ML_2]$ type.

3.3. ¹H NMR spectra

The ^1H NMR spectra of the Schiff base ligand and its diamagnetic Zn(II) complex were recorded in DMSO-d_6 which is given in Figure 4and 5, and compared. The spectrum of the free ligand showed a singlet at 2.5ppm due to methyl group attached to carbon in 4-aminoantipyrine. Proton in CH_3 group attached to nitrogen in 4-amino antipyrine showed a singlet at 3.3ppm. Phenyl ring protons gave a multiplet between 7.2 – 7.8 ppm. The Ph-CH=CH- protons shows a doublet at 6.8ppm. All the other signals appeared almost at the same point with decrease in intensity except phenolic OH signal at 12.5ppm in ligand which is disappeared in the spectrum of Zn(II) complex indicates the deprotonation upon complex-formation.

3.4. Electronic spectra and magnetic moment

Electronic absorption spectral data of the ligand and its complexes are given in Table 3. The free ligand exhibits strong band around 30,960 and 40,980 cm^{-1} which are reasonably accounted for $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The electronic spectrum of the Co(II) complex gave three bands observed at 24,984, 15,752 and 11115 cm^{-1} are assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ [ν_1], $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ [ν_2], and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$ [ν_3] transitions respectively suggesting that there is an octahedral geometry around Co(II) ion, which is also supported by its magnetic moment value 4.92 B.M. Ni(II) complex exhibits three d-d bands at 22195, 20156 and 10345 cm^{-1} due to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ [ν_1], $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ [ν_2], $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ [ν_3] transitions arises from an octahedral geometry and the same is confirmed by its magnetic moment value 2.99 B.M.

Various ligand field parameters, such as the field splitting energy (10Dq), Rachah inter electronic repulsion parameter (B), covalent factor (β) and ligand field stabilization energy (LFSE) have been calculated for the Ni(II) complex. The transition $^3A_{2g} \rightarrow {}^3T_{2g}$ corresponds to 10 Dq and since all the three transitions are observed, the calculation of B' is tried. Since $15B' = \upsilon_2 + \upsilon_3 - 3\,\upsilon_1$. The B' value of the Ni complex is calculated and found to be 883 cm^{-1}. Taking the B value of Ni(II) ions as 1041 cm^{-1}, the interelectronic repulsion parameter $\beta = B'/B$ is found to be 0.85. The B' value is lower than the free ion value, which is an indication of orbital overlapping and delocalisation of d-orbitals. The β value is less than 1 suggesting a considerable amount of covalent character in M-L bonds. The 15% covalency calculated using the formula $(B-B')/B^*100$ reflect the extent of covalency in M-L bonding. An approximate value of spin orbit coupling constant λ has been obtained for Ni complex from $\lambda = 2.7 \times B^2 / 10\,Dq$ using the value of B. The calculated μ_{eff} value is in good agreement with the octahedral stereochemistry, which is calculated by substituting the experimental 10 Dq and λ values in the relationship $\mu_{eff} = \mu_{s.o}\,(1 - 4\,\lambda / 10\,Dq)$. μ_{eff} value is found to be 2.99 BM.

The Cu(II) complex shows three bands, which are assigned as an intraligand charge-transfer band (27,069 cm^{-1}), ligand - metal charge transfer band (22,752 cm^{-1}) and a d-d band (15,918 cm^{-1}). The d-d band may due to $^2E_g \rightarrow {}^2T_{2g}$ transition which suggests distorted octahedral geometry around the metal(Cu) ion and the magnetic moment value 1.84 B.M which also supports the distorted octahedral geometry of copper complex. The complexes of Zn(II) and Cd(II) are diamagnetic. In analogy with those described for these complexes containing N-O donor Schiff bases and according to the empirical formulae of these complexes, except copper complex we proposed an octahedral geometry for other complexes.

3.5. ESR spectra

A powder ESR spectrum of Cu(II) complex was recorded at room temperature given in Figure 6 and the spin Hamiltonian parameters are listed in Table 4. The observed spectral parameters for this compound are $g_{\|} = 2.51$ and $g_{\perp} = 2.07$ and $g_{iso} = 2.27$. It is evident that the unpaired electron lies predominantly in the d_{x2-y2} orbital as $g_{\|} > g_{\perp}$. The complex also shows of anisotropic ESR spectrum with $g_{\|} > g_{\perp}$ characteristic of axially elongated octahedral geometry[16]. The octahedral geometry can also be supported by the fact that the unpaired electron lies predominantly in the d_{x2-y2} orbital, as evident from the value of the exchange interaction term G estimated from the expression, $G = g_{\|}-2.0023/g_{\perp}-2.0023$.

The observed value for the exchange interaction parameter for the Cu(II) complex (G = 6.9) suggest that the local tetragonal axes are aligned parallel or slightly misaligned. The α^2 values for the present complex fall in the range 0.97 indicating the presence of appreciable in-plane covalency. Significant information about the nature of bonding can also be derived from the magnitude of the orbital reduction factors $K_{\|}$ and $K_{\perp}$. For this complex, $K_{\|} = K_{\perp}$ indicating σ -bonding which is also reflected in β^2 values[17,18].

3.6. Electrochemical Behavior

The cyclic voltammetry data of the Cu(II) complex with three different scan rates are listed in Table 5. The cyclic voltammogram of the Cu(II) complex in DMSO shows a well defined redox process corresponding to the formation of Cu(II) / Cu(0) couple at $E_{pa} = -0.0128V$ and $E_{pc} = 0.6127V$[19,20]. The reversibility of the copper(II) / copper(0) couple was checked by varying the scan rates with peak potentials. From the table it is observed that E_{pc} and E_{pa} value changes with the scan rate and ΔE_p values increase with increasing scan rate and is found to be more than 400 mV. The difference in the value of $E_{pc} - E_{pa}$ is ΔE_p which is larger than the value required for a reversible process (59 mV) indicating that reduction of Cu(II) at silver electrode is not only diffusion controlled but also by electron transfer kinetics. These observations indicate that the electron transfer process is irreversible.

3.7. Antimicrobial activity

The biological activities of new Schiff base ligand and Cu(II), Co(II), Ni(II), Zn(II) and Cd(II) complexes have been studied for their antibacterial and antifungal activities by well-diffusion method using DMSO as the solvent against microorganisms such as *Escherchia coli, Chromo bacterium, Staphylococcus aureus, Bacillus subtilis* bacterial and *Candida albicans, Aspergillus niger* fungi species. The results are recorded in the form of inhibition zones(mm) and summarized in Table 6. The zone of inhibition values was determined at the end of an incubation period of 48h at 37°C. Standard antibacterial drug, Amikacin and standard antifungal drug, Ketokonazole was used for comparison.

In the case of antibacterial studies, it was observed that, Cd(II) complex shown enhanced activity against *Escherchia coli* and *Chromo bacterium.* Ni(II) complex shows very high activity against *Staphylococcus aureus* and *Bacillus subtilis* and Cu(II) complex shows moderate activity against *Escherchia coli* and *Chromo bacterium.* Then the Cu(II), Ni(II) and Cd(II) complexes shown enhanced activity against all fungus. The order of activity against all bacteria is Cd(II)>Ni(II)>Cu(II)>Co(II) complexes. The order of activity against fungus is Cu(II)>Cd(II)>Ni(II) complexes.

Moreover, coordination reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with the donor groups within the chelate ring system formed during coordination. This process, in turn, increase the lipophilic nature of the central metal atom, which favors its permeation more efficiently through the lipid layer of the micro-organism thus destroying them more rapidly.

Scheme 1: Synthesis of the ligand and complexes

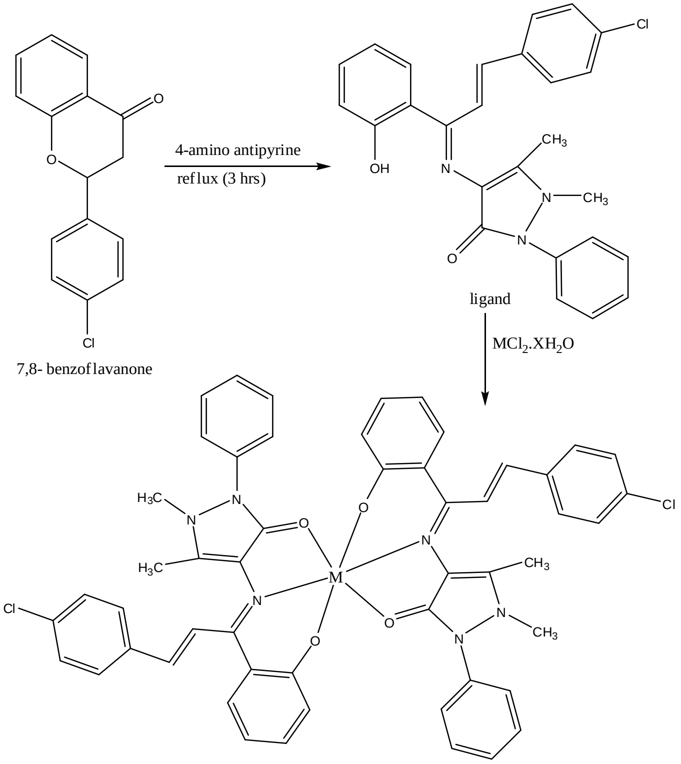

Table 1: Physical characterization, analytical and molar conductance data of the ligand and its metal(II) complexes

Compound	Analysis found (Calcd) (%)							
	Formula weight	M	C	H	N	Yield %	m. p / °C	Λ_M/S cm^2 mol^{-1}
[CHAADP]	443.42	-	69.84 (70.34)	4.93 (5.01)	9.32 (9.47)	91	127	11.08
CuL_2	947.54	6.46 (6.69)	65.47 (65.79)	4.38 (4.46)	8.79 (8.82)	78	254	10.50
CoL_2	942.90	6.11 (6.24)	66.02 (66.11)	4.53 (4.48)	8.98 (8.90)	75	219	08.14
NiL_2	942.63	6.12 (6.21)	66.04 (66.12)	4.40 (4.48)	8.87 (8.92)	82	269	11.01
ZnL_2	949.39	6.45 (6.88)	65.37 (65.66)	4.39 (4.45)	8.78 (8.83)	79	293	7.01
CdL_2	996.42	11.04 (11.26)	62.38 (62.57)	4.19 (4.24)	8.31 (8.42)	78	240	9.08.

Table 2: IR spectral data of the ligand and its complexes (cm^{-1})

Compound	Frequency (cm^{-1})						
	$\nu_{(OH)}$	$\nu_{(C=N)}$	$\nu_{(C=O)}$	$\nu_{C\text{-}O\ (phenolic)}$	$\nu_{(Ph\text{-}C=C)}$	$\nu_{(M\text{-}O)}$	$\nu_{(M\text{-}N)}$
[CHAADP]	3425	1635	1700	1404	1564	-	-
CuL_2	-	1631	1687	1369	1552	547	447
CoL_2	-	1630	1677	1365	1577	563	480
NiL_2	-	1635	1666	1367	1562	561	437
ZnL_2	-	1596	1639	1367	1564	561	441
CdL_2	-	1577	1639	1359	1564	563	439

Table 3: Electronic spectral data of the ligand and metal(II) complexes $\lambda_{max}(cm^{-1})$

Compound	Frequency	Transition	Geometry	μ_{eff} (BM)
[CHAADP]	30960	$n \rightarrow \pi^*$	-	-
	40980	$\pi \rightarrow \pi^*$		
[$CoL_2.2H_2O$]	11115	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$	Octahedral	4.92
	15752	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$		
	24984	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$		
[$NiL_2.2H_2O$]	10345	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	Octahedral	2.99
	20156	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$		
	22195	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$		
[CuL_2]	15918	$^2E_g \rightarrow {}^2T_{2g}$	Octahedral	1.84
	22752	LMCT		
	27069	LMCT		

Table 4: ESR spectral parameters of Cu(II) complex

compound	$g_{\parallel}$	$g_{\perp}$	g_{iso}	α^2	β^2	$A_{\parallel}$ x $10^{-4}cm^{1}$	$A_{\perp}$ x $10^{-4}cm^{1}$	A_{iso} x $10^{-4}cm^{1}$	$g_{\parallel}/A_{\parallel}$ cm	μ (BM)
CuL_2	2.51	2.07	2.77	0.97	0.50	140	56.84	84.56	179	1.97

Table 5: Redox potential of Cu(II) complex

Compound	Scan rate (mV)	E_{pc} (V)	E_{pa} (V)	ΔE_p (V)
CuL_2 Complex	100	0.612	-0.0128	599
	150	0.640	-0.0239	616
	200	0.695	-0.0215	674

Table 6: Antimicrobial activity of the ligand and its metal(II) complexes

Compound	Concentration (μgmL^{-1})	Zone of inhibition (in mm)[a]					
		E. coli	*Chromo Bacterium*	*S. aureus*	*B. subtilis*	*C.albicans*	*A. niger*
[CHAADP]	05	16	8	6	7	R	R
	10	10	10	10	R	R	12
	15	15	15	22	9	R	14
CuL_2	05	8	15	R	12	19	15
	10	12	20	R	13	23	21
	15	18	22	R	15	20	25
CoL_2	05	R	18	R	9	15	10
	10	R	16	R	12	18	12
	15	R	12	21	17	19	18
NiL_2	05	14	7	25	10	21	12
	10	12	13	18	15	19	10
	15	14	R	19	23	13	19
CdL_2	05	17	10	R	R	22	14
	10	15	12	16	18	9	17
	15	23	25	R	12	18	16
Standard	5	5	10	7	8	7	7
	10	5	10	7	8	7	7
	15	5	10	7	8	7	7

Standard (Amikacin and Ketoconozole), [a]Each value observed is within the error limits of ±2, .R = Resistant

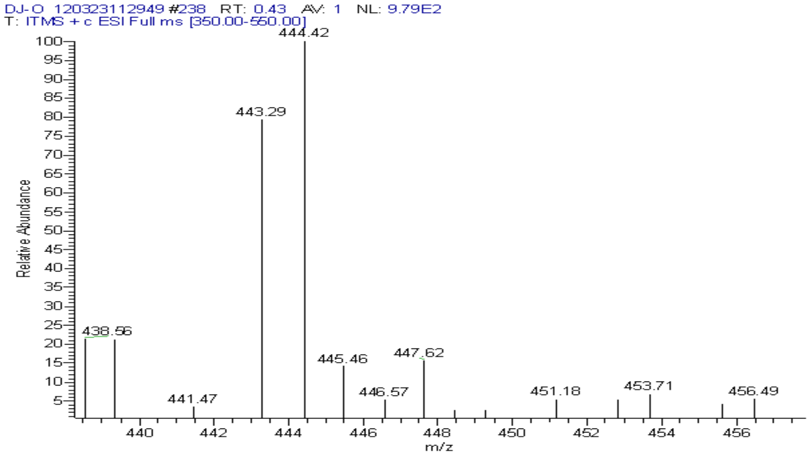

Fig. 1: ESI-Mass spectrum of Ligand

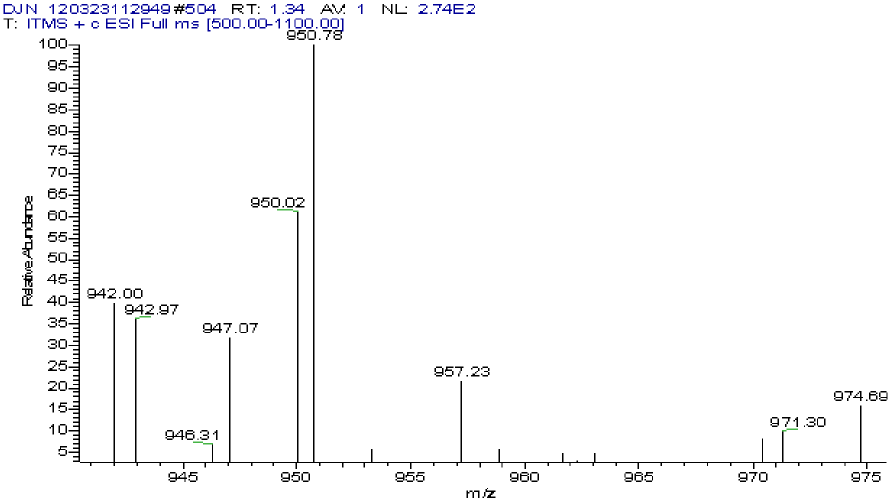

Fig. 2: ESI-Mass spectrum of Zn(II) complex

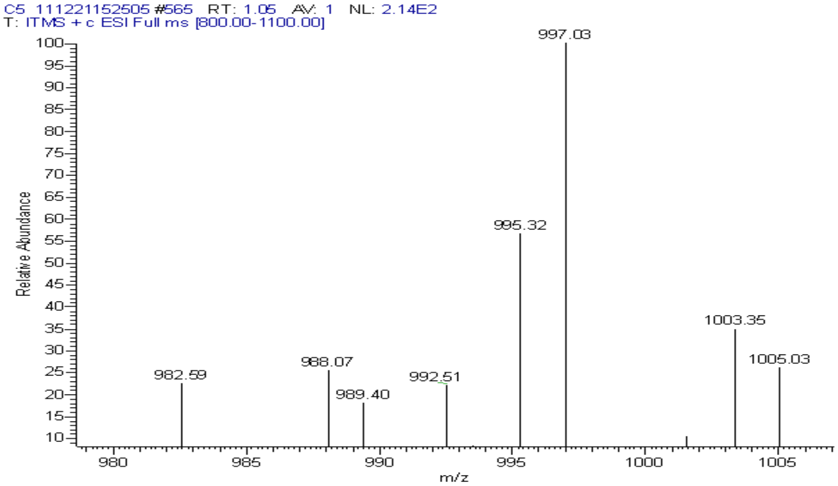

Fig. 3: ESI-Mass spectrum of Cd(II) complex

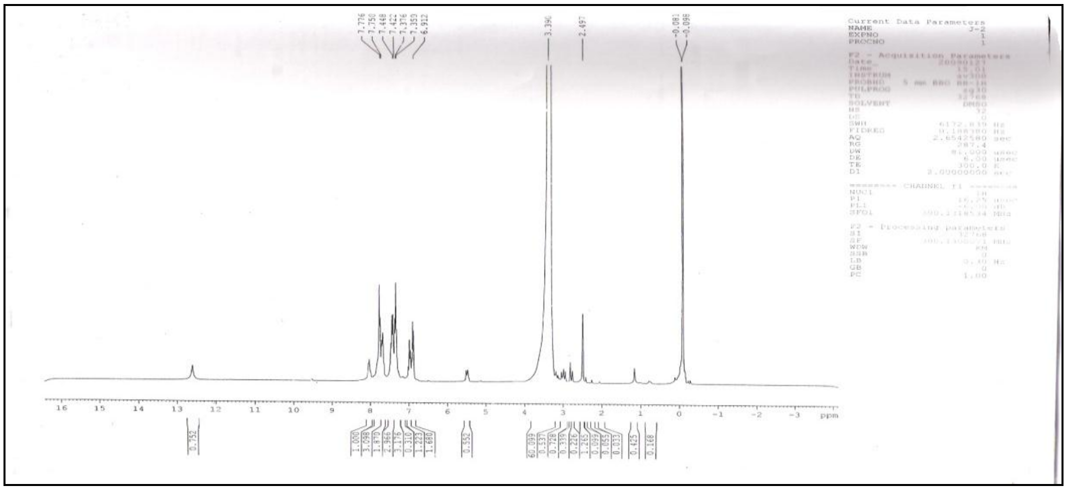

Fig. 4:1H NMR spectrum of Ligand

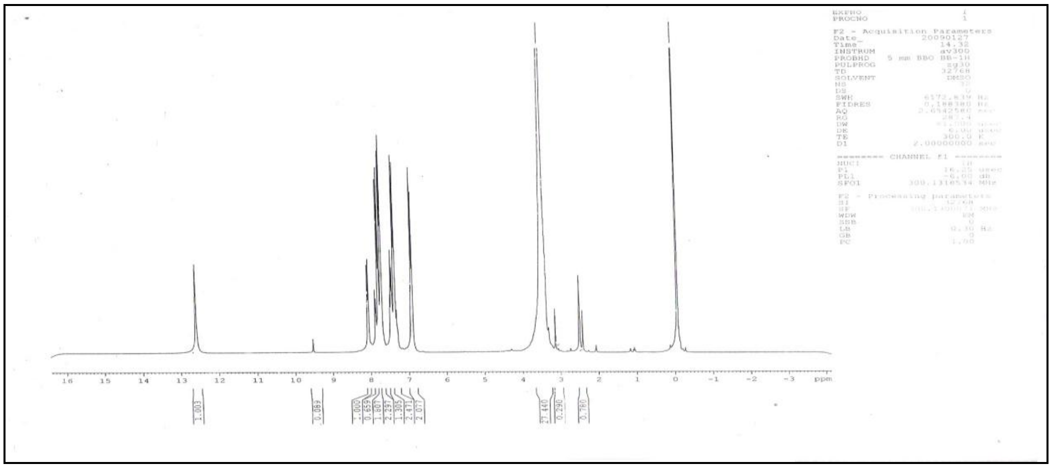

Fig. 5: 1H NMR spectrum of Zn(II) complex

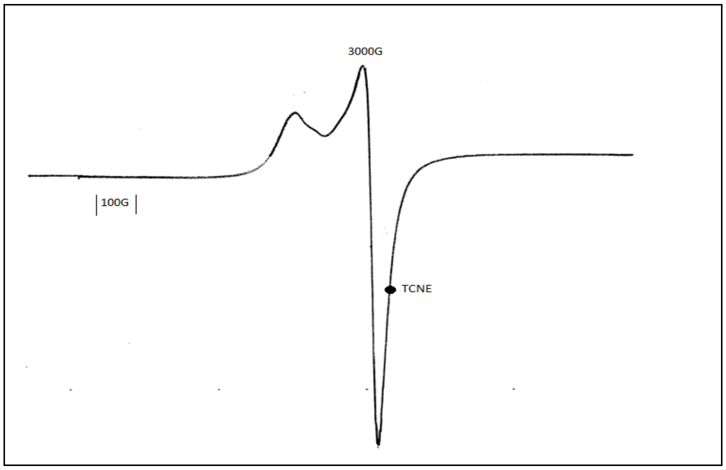

Fig. 6: ESR spectrum of Cu(II) complex

4. CONCLUSION

In this paper, coordination chemistry of a schiff base ligand obtained from 2-(4-chlorophenyl)chroman-4-one and 4-amino antipyrine is described. Cu(II), Co(II), Ni(II), Zn(II) and Cd(II) complexes of above Schiff base ligand have been synthesized. The structure of the ligand and complexes were confirmed by IR, UV-Visible, NMR spectroscopy, elemental analysis, molar conductance and EPR spectroscopic analysis. Based on these data, octahedral geometry has been assigned to the all complexes. These analytical and spectral data suggests that the ligand coordinates through its azomethine nitrogen, the carbonyl group of the five member ring and phenolic –OH via deprotonation. The Schiff base ligand behaves as tridentate ligand. The molar conductance measurement suggests that the complexes are non-electrolytic in nature. From the analytical data the metal forms 1:2 complexes with the Schiff base ligand. The antimicrobial study shows that, the complexes are more active than the ligand. The Ni(II), Cd(II) complexes are found to be possess more antibacterial activity and Cu(II) complex found to be possess more antifungal activity compared to other complexes.

5. ACKNOWLEDGEMENTS

Authors thank the Management of Thiagarajar College, Madurai and the Defence Research and Development Organization (DRDO) New Delhi for financial support and CDRI (SAIF) Lucknow for providing analytical facilities.

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