Synthesis, Characterization, and Biological Studies on Riluzole Schiff base Metal Complexes

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ABSTRACT

Microwave assisted synthesis has received considerable attention as a powerful synthetic tool for metal complexes in many fields of inorganic chemistry, organic chemistry and material science. In this study, we focus on microwave-assisted synthesis of Schiff base ligand and their metal complexes. Schiff base ligand, was obtained from the condensation of Riluzole (6(trifluromethoxy) benzothiozole-2-amine) and 2-hydroxy acetophenone with high atom economy of 95% and metal complexes of the type $ML_{n=1,2}.(H_2O)_{n=0,1,2} Cl_{n=0,1}$, where M is the metal ion and L is the ligand Synthesized metal complexes were characterized by using elemental analysis, conductance, magnetic susceptibility measurements, mass, UV-Vis, IR, ^1HNMR and ESR. The Schiff base behaves as a bidentate ligand and it coordinates through the oxygen atom of the deprotonated phenolic group and the nitrogen of imine group. All these complexes were nonelectrolyte in nature. On the basis of the spectro-chemical data indicates that, the structure for all the coordination metal complexes of Mn(II), Co(II), Fe(III), Ni(II),Cr(III) and Cu(II) shows octahedral geometry, whereas Zn(II), Cd(II), and Hg(II) complexes gives tetrahedral geometry and ZrO(II) and VO(II) complexes indicate the square pyramidal geometry. All these complexes were screened for their antibacterial activity by agar cup-plate method against various organisms, and the results were compared.

Keywords: 2-hydroxy acetophenone; 6(trifluromethoxy) benzothiazole -2-amine; metal complexes; microwave-assisted synthesis.

INTRODUCTION

Schiff base ligand has been widely studied in the field of coordination chemistry mainly because of their facile syntheses, easy availability, electronic properties, and good solubility in common solvents. Transition metal complexes containing the Schiff base ligands have been of interest for many years because the transition metal complexes play a central role in the conduction of molecular materials, which display unusual conducting, magnetic, thermal properties and find applicability in material chemistry and biochemistry[1]. A large number of Schiff bases and their metal complexes have been found to possess important biological and catalytic activity. Because of their great flexibility and diverse structural aspects,

a wide range of Schiff bases have been synthesized and their complexation behavior was studied[2-4]. Heterocyclic compounds are very widely distributed in nature and are essential to many fields of material science and biological systems. Benzothiazole derivatives secured special consideration because of their interesting biological activities like antitumor, antimicrobial, antitubercular, antimalarial, anticonvulsant, anthelmintic, analgesic and antiinflammatory activity [5-8].

The applications of microwave irradiation are used for carrying out chemical transformation, which are pollution-free, eco-friendly, low cost, and offer high yields, together with simplicity in processing and handling [9-10].Many benzothiazole derivatives and their complexes with metal have biological and pharmaceutical activities. The most widely studied metal with this respect is copper (II), which proved beneficial in diseases such as tuberculosis, gastric ulcers and rheumatoid arthritis [11-12]. These results encouraged us to investigate coordination chemistry of Schiff base compounds derived from reaction between Riluzole and 2-hydroxy-acetophenone with transition metal ions. Synthesized complexes were characterized by using spectral techniques like, IR, [1] HNMR, Mass, ESR, SEM-EDX and electronic spectral studies.
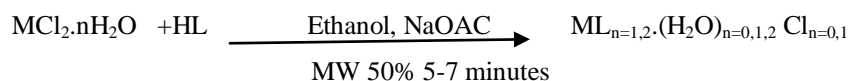
MATERIALS AND METHODS

All the chemicals were of analytical grade, used as supplied. Solvents were purified by distillation before use. Drug molecules were purchased from the pharma industry.

Synthesis of Schiff Base Ligand: Equimolar ratio of Riluzole and 2- hydroxy acetophenone was transferred into the round-bottom flask; 3 to 4 mL of ethanol is added to dissolve the substance. The reaction mixture was irradiated in microwave oven at 80% intensity. The progress of the reaction and purity of the product was monitored by TLC. The resulting product was recrystallized from ethanol stored in desiccator.

Scheme for Ligand preparation:

Schiff base = HL
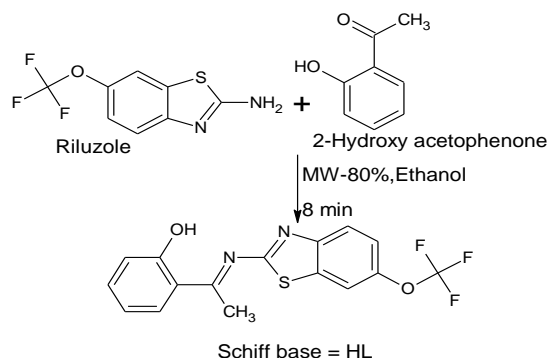
Synthesis of complexes: Metal complexes were synthesized by irradiating equimolar ratio of hydrated metal chlorides and ligand in minimum quantity of solvent, in the presence of sodium acetate. Solid separated was filtered and washed with distilled water and recrystallized from ethyl alcohol. All complexes were dried in air and kept in vacuum desiccator. Formation of the complexes may be represented as follows:

$$MCl_2 \cdot nH_2O + HL \xrightarrow[\text{MW 50\% 5-7 minutes}]{\text{Ethanol, NaOAC}} ML_{n=1,2} \cdot (H_2O)_{n=0,1,2} Cl_{n=0,1}$$

Where M= Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), VO(II) and ZrO(II)

Physical Measurements: Metal content of the complexes were estimated by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer, Perkin Elmer-Optima7000DV). SEM-EDX analysis was carried out on Carlzeiss EVO-18 model at TUV Rheinland India Pvt Ltd. CHNS analysis was carried out microanalyticaly on an Elementar Vario EL III model at the sophisticated test and instrumentation center (CUSAT), Cochi. Chloride was determined using argentometric method. Magnetic susceptibility measurements were made at room temperature on a Gouy balance using Hg[Co(NCS)4] as the calibrant, with diamagnetic corrections made using PASCAL's constants. Conductance measurements were made on an Elico conductivity bridge in DMSO using dip-type conductivity cell fitted with platinum electrode having cell constant 1.0 S cm^{-1}. The IR spectra of ligands and their complexes were recorded in KBr discs in the 4000 to 400 cm^{-1} Thermo Nicolet, Avatar 370 FT-IR spectrophotometer. NMR spectra were recorded in DMSO-d$_6$ on a Varian AS 400 MHz spectrophotometer using TMS as internal standard. The electronic spectra were recorded on an Elico-SL-164 double beam UV-visible spectrophotometer in the 200 to 1100 nm range in DMSO (10^{-3} M) solution. ESI mass spectra were recorded on a Waters Xevo TQD mass spectrophotometer with Acquity H-Class UPLC System. Powder x-ray diffraction has been carried out in the Bruker AXS D8 Advance using Cu, Wavelength 1.5406 A° as x-ray source.

Biological activity: The in vitro biological activity of the Schiff bases and their complexes were tested against bacteria's like *Escherichia coli, Salmonella, Klebshella, Streptococci*, and *Staphylococcus aurous* by disc diffusion method using nutrient agar as the medium and streptomycin as the control. All these complexes were dissolved in DMSO. The solutions of the concentration 100 ppm were prepared separately. In a typical procedure, a well was made on the agar medium inoculated with micro-organisms. The well was filled with the test solution using a micropipette and the plate was incubated aerobically for 24h at 35 °C the diameter of the zone of inhibition was measured [13-15].

RESULTS AND DISCUSSION

As a result of microwave-assisted synthesis, it was observed that the reaction was completed in a short time with higher yields compared with the conventional method. The confirmation of the results was also checked by repeating the synthesis process. Results obtained by microwave-assisted synthesis completed within 6 to 10 min, with high yield ranging from 84% to 93%. Metal complexes were colored, solid and stable towards air and moisture at room temperature and soluble in common organic solvents. Analytical data of the compounds and together with their proposed molecular formula are given in Table 1. All the metal complexes have 1:2 and 1:1 (metal: ligand) stoichiometry. The observed molar conductance of these complexes in DMSO at room temperature was too low to account for their electrolytic nature[16].

Magnetic properties: Magnetic susceptibility measurements were done at room temperature for Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and VO(II) complexes given in the table1 . The Cr(III) complex exhibited magnetic moment of 3.89 B.M, suggesting octahedral geometry for Cr(III) complexes.[17] Mn(II) and Fe(III) complexes showed magnetic moments of 5.51 B.M and 5.82 B.M, respectively, suggesting the octahedral geometry. [18-19] The Co(II) complex showed 4.96 B.M magnetic moment supporting the octahedral geometry[20]. The Ni(II) complex showed magnetic moment value of 2.93 B.M., slightly higher than the spin only (2.83 B.M.) value, which was because of spin orbit coupling and contribution from $^3A_{2g}$ and $^3T_{2g}$ states, indicating an octahedral environment around Ni(II).[21] The observed magnetic moment for the Cu(II) complex was 1.72 B.M., suggesting a distorted octahedral geometry around the central metal atom. It was reported that the distorted octahedral geometry of copper(II) complex devoid of spin interaction exhibited magnetic moment of 1.80 B.M. [22]. The magnetic moment obtained for the oxovanadium (II) complex was 1.69 B M this is in the vicinity of spin only value, supporting the square pyramidal configuration of oxovanadium (II) complex[23].

ESI-mass spectral studies: The ESI-mass spectral data suggest that all the complexes have monomeric nature. These complexes show molecular ion peaks in good agreement with the empirical formula suggested by elemental analyses.

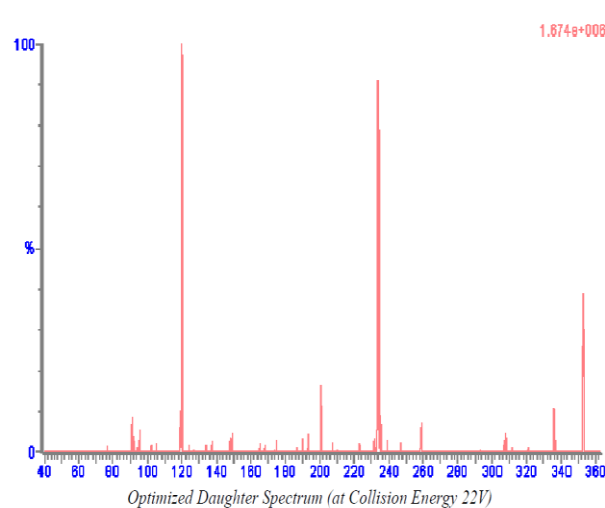**Table 1.** Elemental analysis, molar conductance and magnetic susceptibility data for ligand and their metal complexes.

| Molecular Formula | Color | Formula weight | MP (^{0}C) | Yield (%) | Elemental analysis found (calculated) in % | | | | | Cl | µeff (B. M) | Λ ($\Omega^{-1}cm^2 mol^{-1}$) |
					C	H	N	S	M			
HL	Pale Yellow	352.349	103-105	95	54.67 (54.49)	3.23 (3.12)	7.07 (7.95)	9.95 (9.08)		—	—	5.6
CrL$_3$	Dirty Green	790.69	90(D)	92	52.23 (52.08)	2.63 (2.71)	6.85 (7.59)	7.95 (8.68)	4.23 (4.70)	—	3.75	2.8
MnL$_2$(H$_2$O)$_2$	Blackish pink	793.64	>250(NM)	82	48.75 (48.38)	2.88 (3.02)	6.68 (7.06)	7.51 (8.06)	7.05 (6.92)	—	5.51	6.7
FeL$_2$(H$_2$O)$_2$	Brick Red	794.55	>250(NM)	85	48.93 (48.33)	2.69 (3.02)	6.43(7.05)	7.72 (8.05)	6.75 (7.03)	—	5.57	7.7
CoL$_2$(H$_2$O)$_2$	Green	797.63	170-172(D)	80	47.96 (48.14)	2.91 (3.01)	6.57 (7.02)	7.89 (8.02)	6.85 (7.39)	—	4.65	8.9
NiL$_2$(H$_2$O)$_2$	Light Green	797.40	(158-160(D)	87	48.61 (48.16)	2.78 (3.01)	6.63 (7.02)	7.62 (8.03)	7.03 (7.36)	—	3.32	6.5
CuL$_2$(H$_2$O)$_2$	Dirty Green	802.24	(120-122)(D)	91	48.08 (47.87)	2.27 (2.99)	6.79 (6.98)	7.27 (7.98)	7.87 (7.92)	—	1.72	9.1
ZnL(H$_2$O)Cl	Yellow	470.50	250(D)	83	41.13 (40.81)	2.13 (2.55)	5.85 (5.95)	6.46 (6.80)	12.95 (13.96)	7.01 (7.54)	----	12.7
CdL(H$_2$O)Cl	Pale Yellow	517.21	>250(NM)	87	36.91 (37.12)	2.03 (2.32)	5.92 (5.41)	6.46 (6.19)	22.45 (21.73)	6.07 (6.85)	----	13.5
HgL(H$_2$O)Cl	Yellow	605.39	118-120(M)	96	31.03 (31.71)	2.19 (1.98)	5.01 (4.63)	5.84 (5.29)	32.05 (33.13)	5.31 (5.86)	----	16.7
VOL$_2$	Green	769.64	98-100(D)	86	49.31 (49.89)	2.04 (2.60)	7.75 (7.28)	7.89 (8.32)	6.82 (6.62)	—	1.69	8.6
ZrOL$_2$	Bright Yellow	809.92	>250(NM)	94	47.89 (47.41)	2.19 (2.47)	6.59 (6.91)	7.07 (7.90)	11.01 (11.26)	—	----	7.3

Mass spectra of the HL ligand were performed in both the positive and negative ion mode. Mass spectra of the ligand at positive ion mode shows the parent mass 353.13 and daughter mass 233.97, 120.0 and 101.99.Mass spectra of the ligand in negative ion mode gives the parent mass at 350.94 with daughter

mass 232.88,256.99 and 85.03   which clearly indicates the molecular ion peak is in good agreement with the empirical formula.   [Cd(L)(H$_2$O)Cl] complex showed a characteristic molecular ion (M$^+$) peak at m/z = 517.84 This value is well agreement with the calculated molecular weight of the complex which is given in the table 1 . The mass spectrum (Figures 1,2) showed multiple peaks representing successive degradation of the complex molecule by the formation of different fragments. The mass spectra of the [Cr(L)$_3$] complex exhibited the molecular ion (M$^+$) peak at m/z = 1115(1106). The elemental analysis and the molecular ion peak indicate that the complex is monomeric in nature. The other important peaks of appreciable intensity have been observed at the m/z values, obs. (calcd.) – 1005(1006), 899(906), 432(430), suggesting the ion species after the successive fragmentation of different groups. The intensities of these peaks give the idea of stabilities of the fragments. The m/z value 101.63 corresponds to Cr metal with chelated Oxygen atom of the ligand moiety[24-25].

Optimized Daughter Spectrum (at Collision Energy 24V)
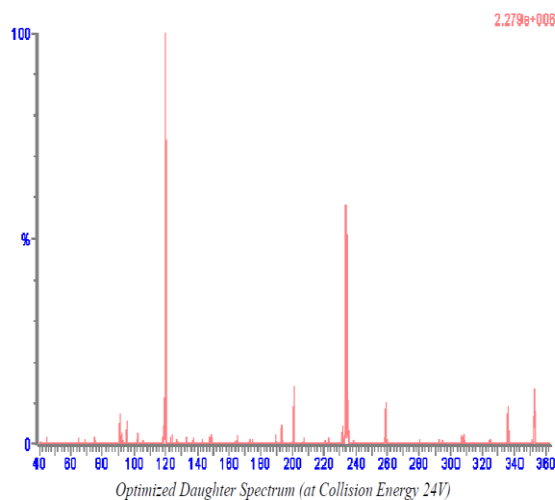
Transition 2: ES+, m/z 353.13 -> 233.97

Optimized Daughter Spectrum (at Collision Energy 22V)

Transition 3: ES+, m/z 353.13 -> 101.99

Figure 1: ESI mass spectra of Ligand   **Figure 2:** ESI mass spectra of Ligand

[1]**H-NMR spectra:** The proton NMR spectra of the Schiff base ligands were recorded in DMSO-d6 solution using TMS as the internal standard. The ^{1}H-NMR spectra of the ligand shows multiplet at δ 7.165–7.771 ppm because of aromatic and thiazole protons, whereas the H$_3$C–C=N protons resonates as singlet at δ 2.637 ppm. Cd (II), Zn (II), and Hg (II) complexes, H$_3$C–C=N proton signals shift down field supporting the coordination of the 'N' of the H$_3$C–C=N group with the metal ion [26-27].

Electronic spectral studies: The electronic spectra of the Cu(II), Co(II), Ni(II), Mn(II), Fe(III), Cr(III) and VO(II) complexes were measured in DMSO(10^{-3}M) solution. Cu(II) complexes exhibit a single broad band in the region 18281 to 11148cm^{-1}.The broadness of the band indicates the dynamic Jahn-Tellor distortion. All these data suggest distorted octahedral geometry of Cu(II) complex[28]. The electronic spectra of oxovanadium complexes exhibit three bands at 9871, 11834 and 23148 cm^{-1} assigned, respectively to transitions $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$. this data indicates that the complex is having C$_{4V}$ microsymetry (five coordinate square pyramidal) [29]. Ni(II) complex exhibits three bands at 15244 and 23584cm^{-1} these transitions are assigned to $^3A_2g(F) \rightarrow {}^3T_{1g}$ (F) (ν_2) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}$ (P) (ν_3), respectively. The lowest band ν_1 ($^3A_{2g}$ (F) $\rightarrow {}^3T_{2g}$(F) transition could not be observed because of limited range of the instrument used. However, it is calculated by using band-fitting procedure [30]. The ratio ν_2/ν_1 is in the range of 1.21 to 1.38, which is indicative of octahedral geometry for Ni (II) complex. Co (II) complex exhibits two bands at 17064 and 23640cm^{-1}; these are because of the $^4T_{1g}$ (F) $\rightarrow {}^4A_{2g}$ (F) (ν_2) and $^4T_{1g}$(F) $\rightarrow {}^4T_{1g}$ (P) (ν_3) transitions, respectively, in an octahedral geometry, ν_1 would be calculated using

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band-fitting procedure [30]. The electronic spectra of the manganese(II) complex shows high-intensity band maximum around 27855cm^{-1} region, and this has been assigned to the ligand metal charge transfer band the d-d band is observed in the region 19230cm^{-1}. The Cr(III) complex showed electronic spectral bands at 17,391 and 24,638cm^{-1}; these are tentatively assigned to $^4A_{2g}{\rightarrow}^4T_{2g}(F)$ (v_1) and $^4A_{2g}{\rightarrow}^4T_1(F)$ (v_2) transitions, respectively which is the characteristic of octahedral geometry. The electronic spectra of Fe(III) complex showed high intensity charge transfer band at 32362 cm^{-1} because of ligand metal charge transfer. Generally, the tentative interpretation of the structure of Fe (III) complex showed octahedral geometry[31] .The different parameters such as ligand field splitting energy (10 Dq), Racah inter-electronic repulsion parameter (B), nephelauxetic ratio (β), percent of covalent character (β%), and ligand field stabilization energy (LFSE) have been calculated. The values of these parameters are given in table 2. All the complexes exhibit the lower value of B, than that of the free ion, which indicates the orbital overlapping and delocalization of the d-orbital. The value of β lies in the range of 0.59 to 0.72 indicates the appreciable covalent character of the metal-ligand bonds [32].

Table 2   Electronic spectral bands and ligand field parameters of the Cu(II), Co(II), Cr(II), Ni(II) and Mn(II) in DMSO(10-3) solution.

Metal complex	Transitions in cm-1			10Dq (cm-1)	B(cm-1)	β	β%	v2/v1	L F S E kJ/mol
	v1	v2	v3						
VOL2	9871	11834	23148						
CrL3	17391	24637	35415	17391	735	0.713592	28.64	1.42	249.33
MnL2(H2O)2				27855	M-L Charge transfer				
FeL2(H2O)2				32362	M-L Charge transfer				
CoL2(H2O)2	7941	18050	21322	10101	971	0.867	13.3	2.27	96.545
NiL2(H2O)2	9960	15244	23585	9960	597	0.552778	44.72	1.53	142.79
CuL2(H2O)2		11764	18282	---					

IR spectra: The main stretching frequencies of the IR spectra of the ligand and their metal complexes are presented in table 3. The IR spectrum of the free ligand is compared with the complexes. The IR spectra of the ligand exhibits most characteristic peak at 1644 cm^{-1}ν(C = N, azomethine) [33], 1544 cm^{-1} ν(C = N, thiazole), 1211 cm^{-1} ν(C–O) and 747 cm^{-1} ν(C–S–C). All the metal complexes showed abroad band at 3390 to 3450 cm^{-1}, which may be due to (O-H) stretching frequency. The characteristic peak of azomethine group of Schiff base ligand observed at 1644 cm^{-1} is shifted to lower frequency side after complexation at 1605 to 1622 cm^{-1}, indicates that the coordination takes place through   nitrogen atom of the azomethine group. [34] The phenolic C–O stretching vibration that appeared at 1244 cm^{-1} in Schiff base shift towards higher frequencies (27 to 35 cm^{-1}) in the complexes.

This shift confirms the participation of oxygen in the C–O–M bond. In the IR spectra of the complexes, the stretching vibration of the free ligand ν(O–H) 3298 cm^{-1} was not observed, suggest the M-O bond is formed via deprotonation [35]. In the low frequency region, the band of weak intensity observed for the complexes in the region 524 to 560 cm^{-1} was attributed to (M–O), in the region 460 to 494 cm^{-1} assigned to (M–N) bond [36-37]. The ν(C = N) at 1544 cm^{-1} and ν(C–S–C) at 747 cm^{-1} of the thiazole ring remained unchanged, reveals the thiazole group does not take part in the co-ordination of metal ion[38].

Table 3 IR stretching frequency for Schiff base ligand and its metal complexes

Compound	ν (O-H)	ν (C=N)	ν (C=N)ring	H2O	ν (C-O)	ν (C-S-C)	ν (M-O)	ν (M-N)
HL	3278	1606	1544	----	1196	744	-----	------
[Cr(L)3	------	1583	1544	814	1222	745	556	481
[Fe(L)$_2$(H$_2$O)$_2$]	------	1578	1541	812	1214	735	524	483
[Co(L)$_2$(H$_2$O)$_2$]	------	1585	1536	817	1222	747	528	478
[Ni(L)$_2$(H$_2$O)$_2$]	------	1588	1536	814	1221	757	557	481
[Mn(L)$_2$(H$_2$O)$_2$]	------	1588	1542	817	1215	740	557	480
[Cu(L)$_2$(H$_2$O)$_2$]	------	1588	1535	815	1226	740	524	460
[Zn(L)(H$_2$O)Cl]	------	1579	1540	815	1215	738	557	478
[Cd(L)(H$_2$O)Cl]	------	1579	1540	813	1125	747	524	485
[Hg(L)(H$_2$O)Cl]	------	1579	1529	815	1215	755	524	483
[ZrO(L')$_2$]	------	1585	1540	815	1215	738	559	483
[VO(L')$_2$]	------	1579	1541	815	1213	739	555	482

ESR Spectra: The X-band ESR spectra of the VO (II), Cu(II) (Figures 3,4) and Cr(II) complexes were recorded in the powder form at room temperature. The ESR spectra of the Cu(II) complex shows four hyperfine line characteristics of monomeric Cu(II) complexes corresponding to -3/2,-1/2,1/2 and 3/2 transitions, which arises from the coupling of the odd electron with Cu nuclei ([65]Cu). As the $g_\parallel$ and $g\perp$ values are closer to 2, $g_\parallel > g\perp$ suggests that a tetragonal distortion around the Cu(II) ion. The trend $g_\parallel > g\perp > g_e(2.0023)$ shows that the unpaired electron is localized in $d_{x^2-y^2}$ orbital in the ground state of Cu(II), spectra are characteristic of axial symmetry. The $g_\parallel > 2.3$ is a characteristic of an ionic environment and $g_\parallel < 2.3$ indicates a covalent environment in the metal ligand bonding. The exchange coupling interaction between two Cu (II) ions is explained by the Hathaway expression, that is,

Table 4. ESR-spectral data of Cu(II) complex and bonding coefficient parameters.

Complexes	$g\|\|$	$g\perp$	gav	A$\|\|$ X 10^{-4}cm^{-1}	A$\perp$ X 10^{-4}cm^{-1}	Aav	G	K$\|\|$	K$\perp$	α2	β2	γ2	f	K
CuL$_2$(H$_2$O)$_2$	2.1539	2.0755	2.1016	179.56	16.89	71.11	2.07	0.573	0.632	0.721	0.795	0.88	120	0.37

G = ($g_\parallel$−2.0023) / ($g\perp$−2.0023). According to Hathaway, if the value G >4 the exchange interaction is negligible, whereas when the value of G < 4.0 a considerable exchange coupling is present in the solid complex. The G values for these Cu(II) complex <4, showed considerable exchange interaction in the complex. The ESR parameters $g_\parallel$, $g\perp$, $A_\parallel$, $A\perp$, and d-d transition energies were used to estimate the bonding parameters of α^2, β^2, and γ^2, which is the measure of covalence for the metal complex given in the table 4 [39]. The value of α2 was estimated from the following expression:

$$\alpha^2 = -A_\parallel/0.036 + (g_\parallel -2.00227) + 3/7 (g\perp -2.00227)+0.04$$

The orbital reduction factors $K_\parallel^2 = \alpha^2 \beta^2$ and $K\perp^2 = \beta^2 \gamma^2$ were calculated using the following expressions:

$$K_\parallel^2 = (g_\parallel -2.00227) E_{d-d}/8\lambda_0$$

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$$K\perp^2 = (g\perp - 2.00227) E_{d-d}/2\lambda_0$$

Where λ_0 is the spin orbit coupling constant value -828 cm^{-1} for Cu (II) complex.

According to Hathway, for pure σ bond $K_{||} \approx K\perp \approx 0.77$, and for in plane π bonding $K_{||} < K\perp$, whereas for out of plane π bonding, $K\perp < K_{||}$. In all the complexes it is observed that $K_{||} < K\perp$, which indicates the significant in-plane π bonding. The values of the bonding parameters α^2, β^2, and $\gamma^2 < 1.0$ (value of 1.0 for 100% ionic character) indicate the significant in-plane π bonding.

The Fermi contact hyperfine interaction term K, which is a dimensionless quantity and is generally found to have a value of 0.36, which is a measure of contribution of 's' electrons to the hyperfine interaction which is calculated from the following expression:

$$K = A_{||} / P \beta^2 + (g_{||} - 2.00227) / \beta^2$$

Where P is the free ion dipolar term and its value is 0.036. The empirical factor $f = g_{||} / A_{||}$ (cm^{-1}) is an index of tetragonal distortion. The value may vary from 105 to 135 for small to extreme distortion and that depends on the nature of the coordinated atom. In this complex, 'f' falls in the range of 105 to 135, corresponding to a copper (II) center with medium distortion [40-41].
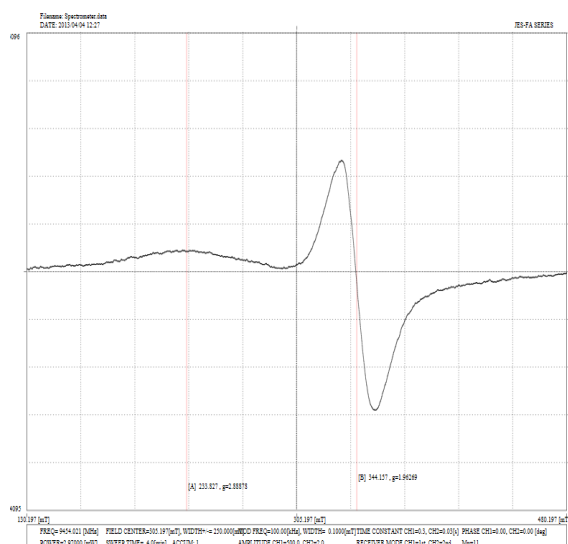

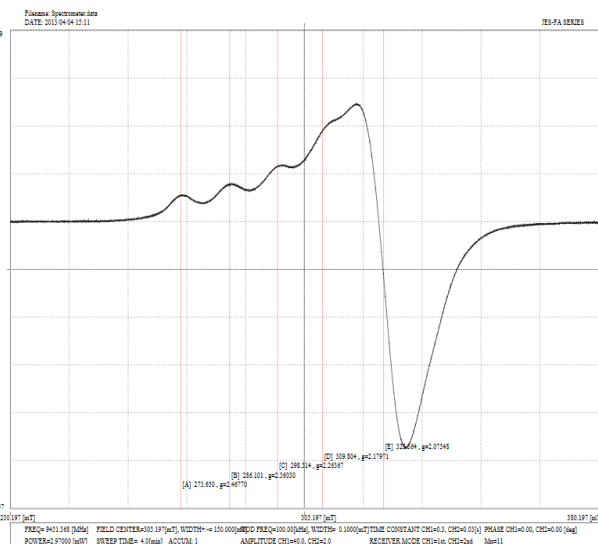**Figure 3**: ESR spectra of VO(II) complex   **Figure 4**: ESR spectra of Cu(II) complex

Thermal Analysis: The thermal behavior of metal complexes shows that the hydrated complexes lose water molecules of hydration first, followed by the decomposition of ligand molecules in the subsequent steps. All the steps are summarized in Table 5.

The thermal degradation behavior of the Co (II) complex has been studied by thermo gravimetric analysis. The TGA curve of the complex shows weight loss up to 120 °C, reveals the presence of lattice water molecule, which is corresponding to four water molecules (remaining wt.%, obs./calcd., 91.99/91.74). After 120 °C, a weight loss has been observed in general up to 205 °C corresponding to two coordinated water molecules and part of the ligand (remaining wt.%, obs./calcd., 36.68/37.57). The decomposition of the remaining ligand moiety occurs between 205 and 320 °C; above 320 °C a horizontal curve has been observed suggesting the ultimate pyrolysis product as the metal oxide (remaining wt. %, obs. /calcd, 8.36/8.62). The DTG curve of the complex shows a peak at 160.16 °C [42]. The thermal analysis evaluating the thermal stability of the metal complexes, this study also helped to characterize the metal complexes [43].

Table 5. Thermal analysis data for Co(II) complex

Complex	Temp Range(^{0}C)	Mass loss % found (calc)	Total mass Loss	Assignment	Metallic Residue
[CoL2(H2O)2].4H2O	40-120	8.01(8.26)	8.01	4 H2O	CoO 8.82%
	120-205	55.31(54.17)	63.32	2H2O& part of Ligand	
	205-320	28.32(28.95)	91.64	Remaining part of Ligand	

Kinetic Study: The kinetic studies of the thermal decomposition of the metal complex were carried out. All stages were taken for the kinetic studies of decomposition of the complex. The kinetic parameters' are summarized in the table 6. On the basis of thermal decomposition, parameters such as activation energy (E*), pre-exponential factor (Z), entropy of activation (ΔS*), enthalpy of activation (ΔH*) and free energy of activation (ΔG*) were calculated by using the Piloyan and Novikova (1966) Coats and Red fern (1964) equation:

Piloyan – Novikova: $\ln[\alpha/T^2] = \ln(ZR/\beta E^*) - E^*/RT$

Coats – Red fern: $\ln[g(\alpha)/T^2] = \ln(ZR/\beta E^*) - E^*/RT$

In the above equation, α is the fraction of the reacted material, T is the absolute temperature, $g(\alpha)$ is the integral mechanism function, E* is the activation energy in kJ/mol, Z is the pre-exponential factor, β is the heating rate and R is the gas constant. A straight line plot of the left hand side of the above equations against 1/T gives the value of E* and Z from the slope and the intercept, respectively. The entropy of activation (ΔS*), enthalpy of activation (ΔH*) and free energy of activation (ΔG*) were calculated using the following equation:

ΔS*= 2.303(log Zh/Kt) R

ΔH*= E* - RT

ΔG*= ΔH* -T ΔS*

Where k and h are the Boltzmann and Planck constants, respectively. The high values of the activation energies reflect the thermal stability of the complexes. The complexes have negative entropy, which indicates that the decomposition reactions proceed with a lower rate than the normal ones. The negative value of entropy also indicates that the activated complexes have a more ordered and more rigid structure than the reactants or intermediates. The negative values of the entropies of activation are compensated by the values of enthalpies of activation, leading to the same values for the free energy of activation [44-45].

Table 6. Kinetic and thermodynamic parameters of Ni(II) complex

Complex	Method	Dec Stage/ Temperature	E (kJ/ mol)	Z S^{-1}	ΔS* (J K^{-1}mol^{-1})	ΔH* (kJ mol^{-1})	ΔG* (kJ mol^{-1})
Ni L$_2$(H$_2$O)$_2$	P-N	I / 80	49.49	0.77	-248.52	46.55	87.78
	C-R		14.69	3.06	-237.07	11.76	83.70
	P-N	II / 162.5	70.24	7.77	-231.07	66.62	100.70
	C-R		33.95	10.36	-226.92	30.33	98.86
	P-N	III / 262.5	49.52	3.93	-238.45	45.07	127.73
	C-R		31.41	8.51	-228.57	26.96	122.42

X-RAY diffraction: X-ray powder diffractograms of the complexes (Figures 5,6) were recorded using CuKα as the source in the range of 5° to 70° (2θ). The diffractogram of Ni (II) complex has recorded 17 reflections with maxima at 2θ = 21.202 and with interplanar distance d = 4.18716. We observe more peaks in the X-ray diffractogram indicates more crystalline in nature.
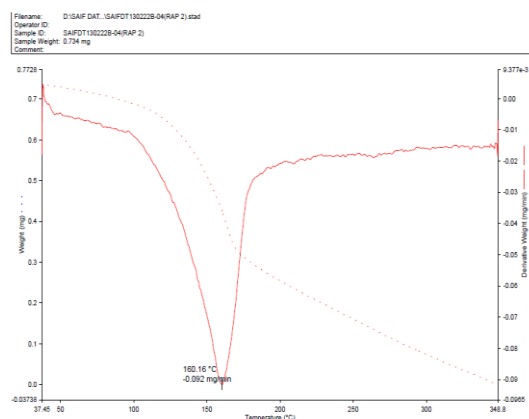
RA-8

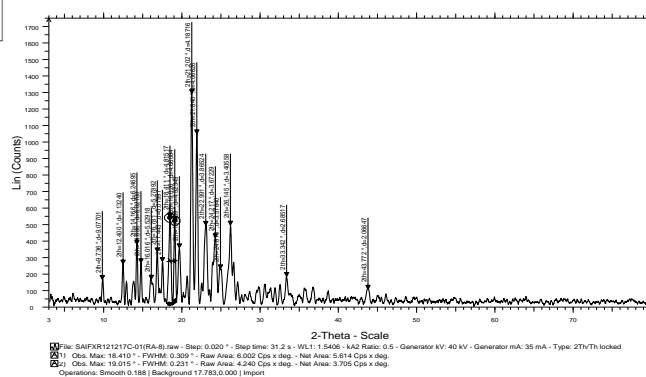**Figure 5:** TGA/DTA of Co(II) complex   **Figure 6:** PXRD of Ni(II) complex

SEM-EDX (Scanning Electron Microscope – Energy Dispersive X-ray Spectroscopy) analysis: SEM-EDX analysis is performed on Ni(II), Cr(III), Cd(II) and Zn(II) complexes non destructively. The electron beam stimulates the atoms in the sample with uniform energy and they instantaneously sent out x-rays of specific energies for each element, the so-called characteristic x-rays. This characteristic radiation gives information about the elemental composition of the sample. SEM- EDX analysis of Ni(II), Cr(III), Cd(II) and Zn(II) complexes are shown in figures 7-9. It is seen from the figures that the Ni(II) and Zn(II) complexes show the agglomeration of needle-like structure.

Cr(III) complex shows flake-like structure, whereas Cd(II) complex shows amorphous in nature.
EDX spectrum of the Cr (II) and Ni(II) complexes reveals the absence of the chloride, whereas in case of Cd(II) and Zn(II) complexes shows the presence of chloride.
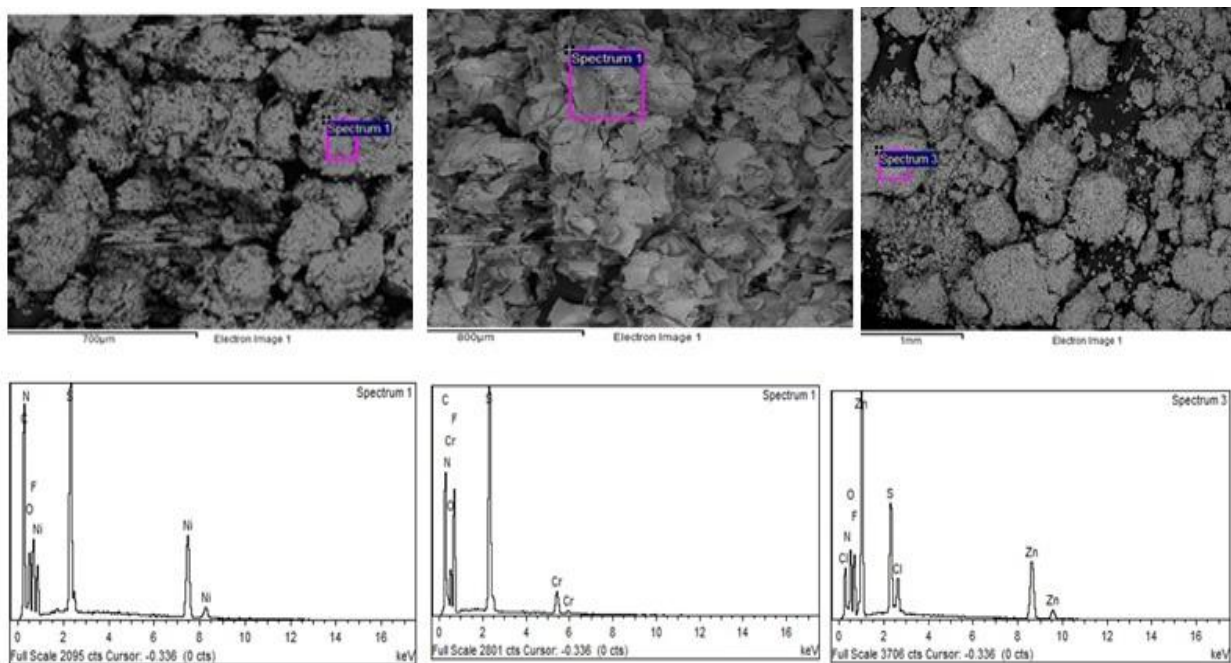

Figure 7: SEM-EDX of Ni(II) complex   **Figure 8:** SEM-EDX of Cr(III) complex   **Figure 9:** SEM-EDX of Zn(II) complex

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APPLICATIONS

Antimicrobial Activities: The in vitro antimicrobial activity of the synthesized Schiff base ligands and their corresponding metal complexes on the selected bacteria *E. coli, Salmonella, Klebshella, Streptococci and S. aurous* were carried out. The results of the antibacterial studies of ligands and the complexes are presented in table 7. Results confirm the low to moderate activity against bacterial species. Ligands exhibit slightly higher activity against gram-negative bacteria than the gram-positive bacteria. However, compared with the antibacterial activity of the standard antibiotic streptomycin, the activities exhibited by the ligand and metal complexes were less.

**Table 7** Antimicrobial activity results of ligands and their metal complexes.

| Compound | Zone of inhibition (mm) | | | | |
| | Gram positive bacteria | | | Gram negative bacteria | |
	E-coli	Salmonella	Klebshilla	S.aurioes	Streptococci
HL	7	15	11	6	10
$CrL_2(H2O)_2$	5	14	13	9	13
$MnL_2(H2O)_2$	8	6	16	7	7
$FeL_2(H2O)_2$	6	7	7	6	7
$CoL_2(H2O)_2$	7	12	13	7	9
$NiL_2(H2O)_2$	6	14	14	7	8
$CuL_2(H2O)_2$	8	16	9	9	9
$ZnL(H2O)Cl$	8	17	10	7	7
$CdL(H2O)Cl$	7	13	11	8	15
$HgL(H2O)Cl$	17	17	9	20	17
VOL_2	7	8	13	9	14
$ZrOL_2$	5	17	12	8	11
Streptomycin	22	20	11	21	20
Pencilin	----	----	----	24	16
Control (DMSO)	00	00	00	00	00

CONCLUSIONS

The Schiff base and their metal complexes have been synthesized using microwave radiation and characterized by elemental analysis, conductance, magnetic susceptibility measurements, mass, UV-Vis, IR, H1NMR and ESR data which concludes that the Mn(II), Co(II), Fe(III), Ni(II),Cr(III) and Cu(II) shows octahedral geometry, whereas Zn(II), Cd(II), and Hg(II) complexes gives tetrahedral geometry and ZrO(II) and VO(II) complexes indicate the square pyramidal geometry. The stoichiometry of these complexes are of the type $ML_{n=1,2}(H_2O)_{n=0,1,2} Cl_{n=0,1}$. The prepared complexes are colored, amorphous in nature and stable in air. Some of these complexes have exhibited good antibacterial activities.
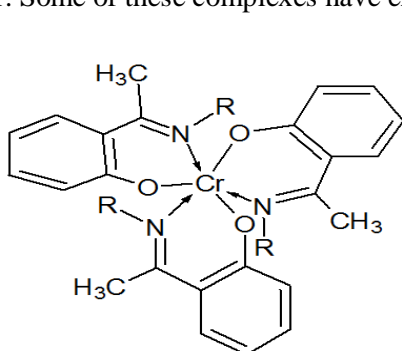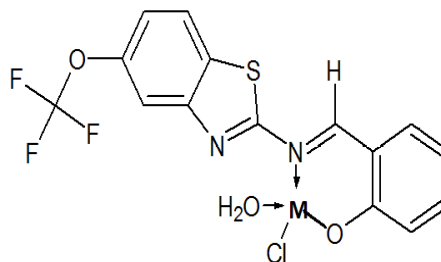

R=$C_8H_3SNOF_3$ M= Co(II), Mn(II) & Ni(II)   M= Fe (III)

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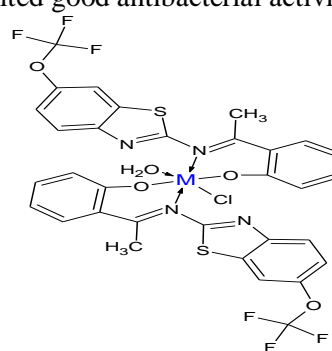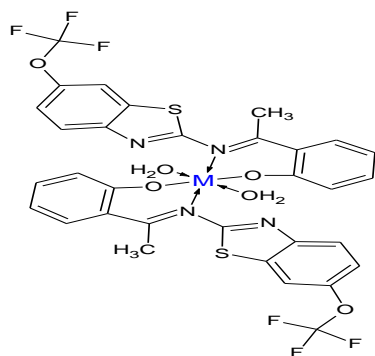
M= Cu(II), Co(II), Ni(II) and Mn (II)   M= Zn (II), Cd (II) & Hg(II)

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