



MICROWAVE SYNTHESIS, SPECTROSCOPIC, THERMAL AND BIOLOGICAL STUDIES OF SOME TRANSITION METAL COMPLEXES CONTAINING HETEROCYCLIC LIGAND

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ABSTRACT

The microwave (MW) assisted synthesis of coordination metal complexes is most important technique, because of reducing chemical waste and reaction times in various chemical transformations. In the present study, some new Schiff base metal complexes of ZrO(II), VO(II), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) derived from o-vanillin with 6-(trifluoro methoxy) benzothiazole-2-amine have been synthesised by using microwave radiation. Obtained coordination metal complexes were characterized with the help of several physical methods such as elemental analysis, FT-IR, molar conductance, electronic spectra, ¹H-NMR, ESR, magnetic susceptibility, thermal, electrical conductivity and XRD analysis. All these data reveals the coordination number were 4, 5 and 6. Elemental analysis indicates that the complexes are of the type 1:1, 1:2 and 1:3 (M: L). The ¹H-NMR spectral data attribute that the phenolic protons have been displaced during the complexation. The thermo gravimetric analysis shows that the presence of water molecule in the coordination metal complexes, which confirmed the loss of water molecule in the first step; followed by decomposition of ligand in the subsequent step. The ligand and coordination metal complexes were also tested against the Gram-positive bacteria; *E-coli*, *Salmonella* and *Klebshilla*, Gram-negative bacteria; *S.aurioes* and *Streptococci*.

Key words: Microwave method, Heterocyclic ligand, Thermal study.

INTRODUCTION

Schiff bases are derived from an amine and aldehyde form important class of ligands that coordinate to metal ions through azomethine nitrogen and have been studied

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extensively¹⁻⁴. These complexes play an important role in the development of coordination chemistry⁵⁻⁸. Thiazole derivatives have found a number uses in medicinal and pharmaceutical fields^{9,10}. Some of them have been used as antitumoragents^{11,12}, anti-candida agents^{13,14}. Some of them have been used in Parkinson's disease^{15,16}. They have also shown to possess antihistaminic and anti-inflammatory^{17,18} activities. Benzothiazole and its derivatives have also shown significant effect against cancer¹⁹ and antibacterial agent²⁰. Schiff bases have found applications in analytical chemistry, where some of compounds were used as ligand to prepare complexes and catalysts as a corrosion inhibitor in chemical industry²¹. Microwave irradiation has gained popularity as it accelerates the reaction rate in a solvent-free condition without use of supporting reagent, and hence, are eco-friendly. Chemical transformations that took hours or even days to complete the reaction, but it can be completed in minutes. Microwave irradiation offers numerous benefits including enhancement in yields, shorter reaction times, eco-friendly and simple reaction condition²²⁻²⁶. Thus the aim of this work was to synthesize and characterise some new transition metal complexes of Schiff bases ligand derived from substituted benzothiazoles with aldehydes using microwave assisted synthesis and also to screen their antibacterial activity.

EXPERIMENTAL

All the reagents used were of Analytical Grade. Metal chlorides were used as such and were procured from Sigma Aldrich. Drug molecules were purchased from Pharma industry. All solvents were distilled before use.

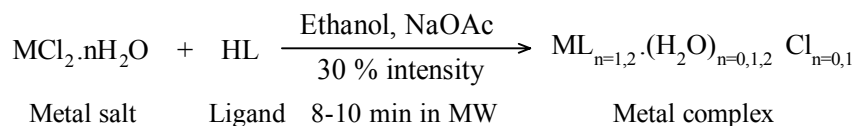
Synthesis of Schiff base ligand

Riluzole, 6-(trifluoromethoxy)benzothiazole (0.01 M, 0.235 g) and 0.152 g (0.01 M) of o-vanilline was taken in a clean and dried round bottom flask, dissolved in 0.5 mL of ethanol. This reaction mixture was kept in microwave at 10% intensity (110 watt) for 1 min with an interval of 30 sec. The reaction was monitored by TLC. The reaction mixture was cooled at 25°C after completion of the reaction. The Schiff base separated was dissolved in ethanol (~1.5-2 mL). Then it was kept in ice bath for the crystallization. The yellow crystals were separated out and kept over the anhydrous calcium chloride in desiccator.

Synthesis of metal complexes

Metal complexes were synthesized by irradiating equimolar ratio of hydrated metal chlorides and ligand in ethanol (1-2 mL) as a solvent and a pinch of sodium acetate was added to initiate the precipitation. Solid was separated out, filtered, washed with distilled water, and recrystallized from ethyl alcohol. All complexes were dried in air and kept over

anhydrous calcium chloride in the desiccator. Formation of the complexes may be represented as follows:



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

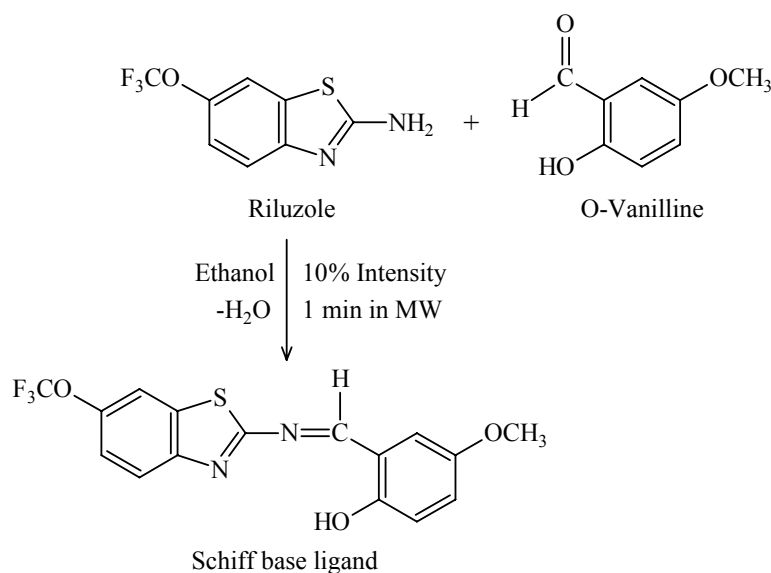


Fig. 1: Scheme for synthesis of Schiff base ligand (HL) C₁₆H₁₁O₃N₂F₃S [RO]: Mol. wt. 368.247, m.p. 108-110°C, yield 89.58%

Physical measurements

Metal content of the complexes were estimated by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer, Perkin Elmer-Optima 7000 DV). SEM-EDX analysis was carried out on Carlzeiss EVO-18 model at TUV Rheinland India Pvt. Ltd. CHN and S analysis was carried out microanalytically 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} . IR spectra of ligands and their complexes were recorded in KBr discs in the 4000 to 400 cm^{-1} on Thermo Nicolet, Avatar 370 FT-IR spectrophotometer. NMR spectra were recorded in DMSO-d₆ 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. Powder X-ray diffraction has been carried out in the Bruker AXS D8 Advance using Cu, Wavelength 1.5406 \AA as X-ray source.

Biological activities

The *in vitro* biological activity of the Schiff bases and their complexes were tested against bacterias 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 24 hr at 35°C . The diameter of the zone of inhibition was measured²⁷⁻²⁹.

RESULTS AND DISCUSSION

Melting point and elemental analysis of the ligand and their metal complexes are tabulated in Table 1. The calculated values were in good agreement with the experimental values. In the microwave assisted synthesis, it was observed that the reaction was completed within short time with higher yields as compared to the conventional method. The spectral and analytical data show that all the metal complexes have 1:2 (metal: ligand) stoichiometry, whereas in case of Zn(II), Cd(II), Hg(II) complexes, it shows 1:1 (metal: ligand) stoichiometry. The molar conductance values of complexes in DMF are in the range of 4.69 - $16.5 \text{ ohm}^{-1} \text{ mole}^{-1} \text{ cm}^2$. The values are too low to account for any electrolytic behaviour.

Electronic spectral studies and magnetic properties

The magnetic moment for all these metal complexes are listed in Table 1. The magnetic moment of Fe-complex is 5.82 BM with 5 unpaired electrons. The magnetic susceptibility values of Fe(II) complex is agreeable with the reported and represents the coordination number six having octahedral geometry. Co(II) complexes was found to have the magnetic moments 5.1 BM indicating that the Co(II) complex is typically high spin complex with octahedral geometry^{30,31}, whereas Ni(II) complex have a magnetic moment value of 3.09 BM , closely related to the value expected for octahedral complexes. The

distorted octahedral geometry around Cu(II) was confirmed by magnetic moment value of 1.85 BM³².

The electronic spectra of the Co(II), Ni(II), Mn(II), Cr(III), Cu(II) and VO(II) complexes were recorded in DMSO (10⁻³M) at room temperature. The electronic spectra of Co(II) complex showed two bands at 17,873 cm⁻¹ and 23,737 cm⁻¹, which are assignable to ⁴T_{1g} (F) → ⁴A_{2g} (F) (ν₂) and ⁴T_{1g} (F) → ⁴T_{1g} (P) (ν₃) transitions, respectively, which are characteristic of octahedral stereochemistry³³. The values of various ligand field parameters 10Dq, B, β, β% and LFSE were calculated and are given in Table 2.

The iron (III) complexes have a tendency to possess high intensity charge transfer bands, which makes the identification of d – d bands rather difficult. Iron (III) complex exhibit a very high intensity band around 23696.68 cm⁻¹ due to ligand metal charge transfer, which obscures the other d – d transition in visible region.

The electronic spectra of the copper (II) complex shows a broad band at 12820.51 cm⁻¹ assigned to 2B_{1g} → 2B_{2g}, 2B_{1g} → 2E_{2g} transition. These are in conformity with expected tetragonally distorted octahedral geometry³⁴. The broadness of the band may be due to dynamic and Jahn–Teller distortion. Present study of electronic spectra suggests that our copper (II) complex has distorted octahedral geometry.

The Cr(III) complex show electronic spectral bands at 17380 cm⁻¹, 24430 cm⁻¹ and 35872 cm⁻¹ these are tentatively assigned to ⁴A_{2g} → ⁴T_{2g}(F) (ν₁), ⁴A_{2g} → ⁴T₁(F) (ν₂) and ⁴A_{2g} → ⁴T_{1g}(P) (ν₃) transitions, respectively. The magnetic moment value is 3.89 B.M. Thus the octahedral structure has been suggested for this complex. The electronic spectra of manganese (II) complex shown high intensity band maximum around 28318.99 cm⁻¹ region and this has been assigned to the ligand metal charge transfer band. The remaining d – d bands are observed in the region 23738.87 and 17041.58.14 cm⁻¹⁴⁰. The six coordinate Ni(II) complex exhibit bands at 14,633.79 cm⁻¹ and 23,681.33 cm⁻¹, assignable to ³A_{2g} → ³T_{1g} (F) (θ₂) and ³A_{2g} → ³T_{1g} (P) (θ₃) transition, respectively, in an octahedral environment. The lowest band θ₁ (10 Dq) could not be observed due to limited range of the instrument used. However, it is calculated by using an equation suggested by Underhill and Billing³⁵. In general, oxovanadium (II) complexes exhibit three low intensity d – d transitions in the 7500-30000 cm⁻¹³⁶. According to Balhausen and Gray³⁷, oxovanadium complex having C_{4v} micro symmetry (five coordinate square pyramidal) have the following types of energy level schemes. d_{xy} < d_{xz}, d_{yz} < d_{x²-y²} < d_{z²}. In the present study oxovanadium (II) complex display bands at 9302.32, 11568.32 and 25643 assigned, respectively, to the transition 2B₂ → 2E, 2B₂ → 2B₁ and 2B₂ → 2A₁.

Table 1: Analytical data of ligand and its metal complexes

Ligand/ complexes	Analysis (%), Found (calculated)				Colour	Formula weight	Yield (%)	Melting point (°C)	Molar conductance $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-2}$	μ eff. B. M.
	C	H	N	S						
$\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}_2\text{F}_3\text{S}$ /Ligand	52.29 (52.18)	3.12 (3.02)	7.45 (7.60)	8.85 (8.70)	- Pale yellow	368.247	94.5	108-109	04.62	-
$\text{Cr}(\text{C}_{16}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_3\text{S})_3$	46.76 (46.84)	1.98 (2.09)	7.36 (7.28)	8.42 (8.33)	4.70 (4.50)	1153.74	82.5	115-117 (D)	04.84	3.89
$\text{Fe}(\text{C}_{16}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_3\text{S})_2$ (H_2O) ₂	46.63 (46.51)	2.39 (2.44)	6.83 (6.78)	7.52 (7.76)	6.25 (6.76)	826.334	91.2	>98 (D)	08.76	5.82
$\text{Co}(\text{C}_{16}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_3\text{S})_2$ (H_2O) ₂	46.16 (46.34)	2.51 (2.43)	6.57 (6.76)	7.89 (7.73)	6.95 (7.10)	829.424	92.6	>130 (D)	07.88	5.10
$\text{Cu}(\text{C}_{16}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_3\text{S})_2$ (H_2O) ₂	45.78 (46.08)	2.27 (2.42)	6.89 (6.72)	7.47 (7.69)	6.97 (7.62)	834.044	91.0	125 (D)	05.38	1.85
$\text{Mn}(\text{C}_{16}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_3\text{S})_2$ (H_2O) ₂	46.75 (46.56)	2.58 (2.44)	6.68 (6.79)	7.61 (7.77)	6.75 (6.65)	825.434	80.6	100-102 (M)	05.78	5.25
$\text{Ni}(\text{C}_{16}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_3\text{S})_2$ (H_2O) ₂	46.61 (46.35)	2.28 (2.43)	6.93 (6.76)	7.62 (7.73)	7.03 (7.36)	829.184	89.1	100-102 (M)	16.52	3.09
$\text{Zn}(\text{C}_{16}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_3\text{S})_2$	47.91 (48.05)	2.83 (2.77)	6.85 (7.01)	8.16 (8.01)	8.25 (8.17)	799.73	95.1	128-130 (D)	02.49	Dia
$\text{Cd}(\text{C}_{16}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_3\text{S})_2$	45.41 (45.38)	2.83 (2.62)	6.72 (6.62)	7.36 (7.57)	13.45 (13.27)	846.73	91.7	220 (D)	03.51	Dia

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Ligand/ complexes	Analysis (%), Found (calculated)						Colour	Formula weight	Yield (%)	Melting point (°C)	Molar conductance $\Omega^{-1} \text{cm}^2 \text{mol}^{-2}$	μ eff. B. M.
	C			H								
	N	S	M	N	S	M						
Hg(C ₁₆ H ₁₀ F ₃ N ₂ O ₃ S) ₂	41.03 (41.11)	2.19 (2.37)	6.01 (5.99)	6.74 (6.86)	21.57 (21.45)		Orange yellow	934.91	84.5	205 (D)	06.71	Dia
ZrO(C ₁₆ H ₁₀ F ₃ N ₂ O ₃ S) ₂	46.14 (46.54)	2.67 (2.44)	6.91 (6.79)	7.90 (7.76)	11.41 (11.04)		Yellow	825.714	94.4	>250 (NIM)	08.66	Dia
VO(C ₁₆ H ₁₀ F ₃ N ₂ O ₃ S) ₂	50.32 (48.93)	2.60 (2.57)	7.28 (7.13)	8.32 (8.16)	6.49 (6.16)		Black brown	785.434	86.2	108-110 (D)	08.75	1.76

Table 2: Electronic spectral data and ligand field parameters of the Co(II), Ni(II) and Cu(II) complexes in DMF (10⁻³M) solution

Metal complexes	Transitions in cm ⁻¹			10 Dq (cm ⁻¹)	B (cm ⁻¹)	B (cm ⁻¹)	$\beta\%$	v_2/v_1	L F S E kJ/mol
	v_1	v_2	v_3						
VO _{L2}	9302.3	11568.3	25643	---	---	---	---	---	---
Cr _{L3}	17380	24430	21422	17380	708	0.687379	31.26214	1.405639	249.175
Mn _{L2} (H ₂ O) ₂	28318.99 M-L Charge transfer								
Co _{L2} (H ₂ O) ₂	8430.2	17837.1	23737.7	8430.2	1114	0.99464	0.5357	1.89276	80.57
Ni _{L2} (H ₂ O) ₂	9173	14633	23681	9173	720	0.666667	33.3333	1.595225	133.51
Cu _{L2} (H ₂ O) ₂	---	12820.5	16760.2	---	---	---	---	---	---

¹H NMR spectra

¹H NMR spectra of ligand and metal complexes were recorded in DMSO-d₆. The chemical shifts of the different types of protons observed in the ¹H NMR spectra of the Schiff base ligand were compared with its Hg(II), ZrO(II) and diamagnetic Zn(II) complex. The ¹H NMR spectra of ligand (HL) shows proton signal at 3.333, 3.841, 7.164-7.192 ppm (m) and 7.642 ppm (s) due to solvent, -OCH₃, aromatic protons, and azomethine (-N=CH-) protons, respectively³⁸. It is noticed that while the ¹H NMR peak of (-N=CH-) in Zn(II), Cd(II), Hg(II) and ZrO(II) is shifted downfield (7.65, 7.781, 7.781, 7.769 ppm) due to complexation, the signal due to -OCH₃ does not show significant shift in chelation mode.

IR spectra

The IR-spectra of complexes clearly indicates the bonding association of ligand with metal ion. The spectrum of free ligand showed a band in the region 1654 cm⁻¹, which is a characteristic peak of the $\nu(\text{C}=\text{N})$ (azomethine) stretching mode showing the formation of the Schiff base ligand. This band was shifted towards lower frequencies side in the IR spectra of its metal complexes (1643-1621 cm⁻¹) compared with free ligand $\nu(\text{C}=\text{N})$ in the ligand representing the involvement of azomethine nitrogen atom in the complexes with metal ion³⁹. The coordination of nitrogen to the metal ion could be expected to reduce the electron density of the azomethine group and thus, caused a shift in the $\nu(\text{C}=\text{N})$ group. A band at 1645 cm⁻¹ due to C=N cyclic of thiazole ring does not shift in the spectra of complexes. This rules out the participation of $\nu(\text{C}=\text{N})$ cyclic group in coordination. The phenolic C-O stretching vibration that appeared at 1249 cm⁻¹ in ligand shift towards higher frequencies (5-15 cm⁻¹) in the complexes. This shift confirms the participation of oxygen in the C-O-M bond. The bands $\nu(\text{C-S-C})$ in region 735-740 cm⁻¹, which remains in the same region in free ligands and after complexation that mean's the sulphur atom in thiazole group doesn't involve in the bonding⁴⁰. This is further substantiated by the presence of new band at 420-435 cm⁻¹, assignable to $\nu(\text{M-N})$. The appearance of new non-ligand band at 555-580 cm⁻¹ in all complexes is due to $\nu(\text{M-O})$.

Table 3: IR stretching frequencies of ligand and its metal complexes

Compound	ν (O-H)	ν (C=N)	ν (C=N) ring	ν (C-O)	ν (C-S-C)	ν (M-O)	ν (M-N)
HL'	3371	1644	1540	1175	737	---	---
[Cr(L') ₃]	---	1625	1543	1214	739	567	430
[Fe(L') ₂ (H ₂ O) ₂]	---	1641	1544	1212	737	557	429

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Compound	ν (O-H)	ν (C=N)	ν (C=N) ring	ν (C-O)	ν (C-S-C)	ν (M-O)	ν (M-N)
[Co(L') ₂ (H ₂ O) ₂]	---	1630	1542	1217	728	582	443
[Ni(L') ₂ (H ₂ O) ₂]	---	1635	1545	1213	737	556	430
[Mn(L') ₂ (H ₂ O) ₂]	---	1630	1544	1214	740	556	429
[Cu(L') ₂ (H ₂ O) ₂]	---	1621	1532	1217	735	555	434
[Zn(L')(H ₂ O)Cl]	---	1626	1540	1218	734	562	431
[Cd(L')(H ₂ O)Cl]	---	1623	1532	1215	739	556	423
[Hg(L')(H ₂ O)Cl]	---	1628	1542	1215	739	549	427
[ZrO(L') ₂]	---	1640	1544	1214	739	559	430
[VO(L') ₂]	---	1642	1541	1213	735	555	432

ESR spectra

The ESR spectra of complexes provides valuable information about the coordination environment around Cu(II) ion. The X-band ESR spectra of the Cu(II) and VO(II) complexes were recorded in the powder form at room temperature. EPR studies of Cu(II) complexes of some salicylaldehyde thiosemicarbazones were reported earlier^{41,42}.

The ESR spectra of the Cu(II) complex shows the g_{\parallel} and g_{\perp} values are closer to 2. $g_{\parallel} > g_{\perp}$ suggests 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 spectra of complex is axial without any super or hyperfine line. The third hyperfine line is expected to overlap with high field component (g_{\perp}) in the complex. The g_{\parallel} value in the complex is less than 2.3, which is an indication of significant covalent bonding in the complex. The geometric parameter G , which is a measure of the exchange interaction between the copper centres in the polycrystalline compound, is calculated using the equation; $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$ for axial spectra. If $G < 4.0$, considerable exchange interaction is indicated in the solid complex^{43,44}. G value for the Cu(II) complex is 2.15, which is consistent with the $d_{x^2-dy^2}$ ground state. The ESR parameters g_{\parallel} , g_{\perp} , A_{\parallel} , A_{\perp} were calculated and d-d transition energies were used to estimate the bonding parameters. The molecular orbital coefficient parameters, α^2 , a measure of the covalency of the in-plane σ bonding between the 3d and ligand orbitals, β^2 , the covalency in plane π bonding, γ^2 , out-of-plane π bonding were calculated. α^2 was calculated employing following equation:

$$\alpha^2 = -A_{\parallel}/0.036 + (g_{\parallel}-2.00227) + 3/7 (g_{\infty}-2.00227) + 0.04 \quad \dots(1)$$

The orbital reduction factors $K_{\parallel}^2 = \alpha^2 \beta^2$ and $K_{\infty}^2 = \beta^2 \gamma^2$ where calculated using the following expressions⁴⁵⁻⁴⁹.

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

$$K_{\infty}^2 = (g_{\infty}-2.00227) E_{d-d}/2\lambda_0 \quad \dots(3)$$

Where λ_0 represents the one electron spin-orbit coupling constant, which equals 828 cm^{-1} for Cu(II).

Table 4: EPR spectral assignments for Cu(II) complex at 298 K

Complex	g_{\parallel}	g_{\perp}	g_{av}	A_{\parallel}	A_{\perp}	A_{av}
[CuL ₂ (H ₂ O) ₂]	2.20875	2.0979	2.13485	$164.093 \times 10^{-4} \text{ cm}^{-1}$	$11.663 \times 10^{-4} \text{ cm}^{-1}$	$62.473 \times 10^{-4} \text{ cm}^{-1}$

Table 5: EPR bonding parameters for Cu(II) complex

Complex	G value	α^2	β^2	γ^2	K_{\parallel}	K_{\perp}	F	K
[CuL ₂ (H ₂ O) ₂]	2.15961	0.742574	0.89365	1.095	0.6636	0.81349	134.603	0.4073

The values of the bonding parameters α^2 , β^2 and $\gamma^2 < 1$ (for 100% ionic character, value is 1.0) indicated significant in-plane π bonding and in-plane σ bonding. According to Hathway for pure σ bonding $K_{\parallel} \approx K_{\infty} \approx 0.77$, and for in plane π bonding $K_{\parallel} < K_{\infty}$; while for out of plane π bonding $K_{\infty} < K_{\parallel}$. In the complex, it is observed that $K_{\parallel} < K_{\infty}$, which again supports 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 the contribution of 's' electrons to the hyperfine interaction can be calculated from the expression below⁵⁰.

$$K = A_{\parallel}/P \beta^2 + (g_{\parallel}-2.00227)/\beta^2 \quad \dots(4)$$

Where, P is a free ion dipolar term, which is equal to 0.036. The K value obtained for the copper complex is in good agreement with those estimated values by Assour⁵¹ and Abragam and Pryce⁵². The empirical factor $f = g_{\parallel}/A_{\parallel} (\text{cm}^{-1})$ is an index of tetragonal distortion. The value may vary from 105-135 for small to extreme distortion and that

depends on the nature of the coordinated atom. For the copper complex the value is 134.60, which indicates medium to high distortion around Cu(II) centre.

Thermal analysis

The thermal behaviour of the metal complexes shows that the hydrated complex lose molecules of hydration first; followed by the decomposition of ligand molecules in the subsequent step. The thermal degradation behaviour of the Hg(II) complex of the HL ligand has been studied by thermogravimetric analysis. The complex decomposes in three steps within the range 37-427°C. In the TG curve of the complex, elimination of lattice water molecules has been observed at temperature 110°C, corresponding to one water molecule (remaining Wt%, obs./cald., 98.24/98.12). After 110°C, in the second step, a weight loss has been observed in general up to 222°C corresponding to loss of (non-coordinated) partially decomposed ligand part of the complex (remaining wt %, obs./cald., 45.46/45.82). Above 222°C in the third step, a weight loss has been observed up to 250°C. This indicates elimination of coordinated part of the complex. Above 250°C, a horizontal line is observed in the TGA curve, which corresponds to metal oxide as an ultimate pyrolysis product (remaining wt%, obs./cald., 20.5/21.06). The DTG curve of the complex shows peak at 218.07 and 233.58°C⁵³. Thermal analysis data for Hg(II) complex is summarised in Table 6. Apart from evaluating the thermal stability of the metal complexes, this study also helps us to characterize the metal complexes.

Table 6: Thermal analysis data for Hg(II) complex

Complex	Temperature range (°C)	Mass loss% found (Cald.)	Total mass loss	Assignment	Metallic residue
[Hg(L) ₂]	37-110	1.76 (1.88)	9.129	1H ₂ O	HgO
	110-222	52.78 (52.30)	54.54	part of ligand	20.44%
	222-250	24.96 (24.76)	79.50	Remaining part of ligand	

Kinetic study

The kinetic study of thermal decomposition of one of the complex was carried out. All stages were selected for the study of kinetics of decomposition of complex. The kinetic data is summarized in Table 7. On the basis of thermal decomposition, the kinetic study 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 Piloyan and Novikova⁵⁴ Coats and Redfern equation⁵⁵:

$$\text{Piloyan – Novikova: } \ln [\alpha/T^2] = \ln (ZR / \beta E^*) - E^*/RT \quad \dots(5)$$

$$\text{Coats – Red fern: } \ln [g(\alpha)/T^2] = \ln (ZR / \beta E^*) - E^*/RT \quad \dots(6)$$

Where α , is the fraction of the reacted material, T is the absolute temperature, g (α) is the integral mechanism function, E* is the activation energy in KJ/mole, 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:

$$\Delta S^* = 2.303 (\log Zh/kT) R \quad \dots(7)$$

$$\Delta H^* = E^* - RT \quad \dots(8)$$

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad \dots(8)$$

Where k and h are the Boltzmann and Planck constant, respectively.

Table 7: Kinetic and thermodynamic parameters of complexes

Complexes	Method	Temp. (⁰ C)/Dec., Stage,	E* (KJ/mol)	Z (S ⁻¹)	ΔS^* (J.K ⁻¹ mol ⁻¹)	ΔH^* (kJ.mol ⁻¹)	ΔG^* (kJ.mol ⁻¹)
[HgL.H ₂ O.Cl]	P-N	73.5/1 st	17.48	0.0108	-283.810	14.604	98.358
	C-R		15.43	3.306	-236.268	12.550	81.879
	P-N	166/2 nd	24.55	0.616	-252.208	22.902	110.740
	C-R		13.12	2.390	-240.934	09.470	105.779
	P-N	236/3 rd	127.97	20.858	-224.150	74.837	114.167
	C-R		79.07	120.51	-209.564	142.017	106.809

The high value of activation energies reflects the thermal stability of the complex. The complexes have negative entropy, which indicates two things, (i) The decomposition reactions proceed with a lower rate than the normal ones and (ii) the activated complex have a more ordered and more rigid structure than the reactants or intermediates. The value of free energy of activation is almost same for both the methods^{56,57}.

X-ray diffraction study

X-ray powder diffractogram of the complexes were recorded using $\text{CuK}\alpha$ as a source in the range $5^\circ \sim 70^\circ$ (2θ). The diffractogram obtained for Hg(II) complex has recorded 12 reflections with maxima at $2\theta = 23.717$ with interplanar distance $d = 3.7484$. The XRD patterns indicate crystalline nature of the coordination metal complex.

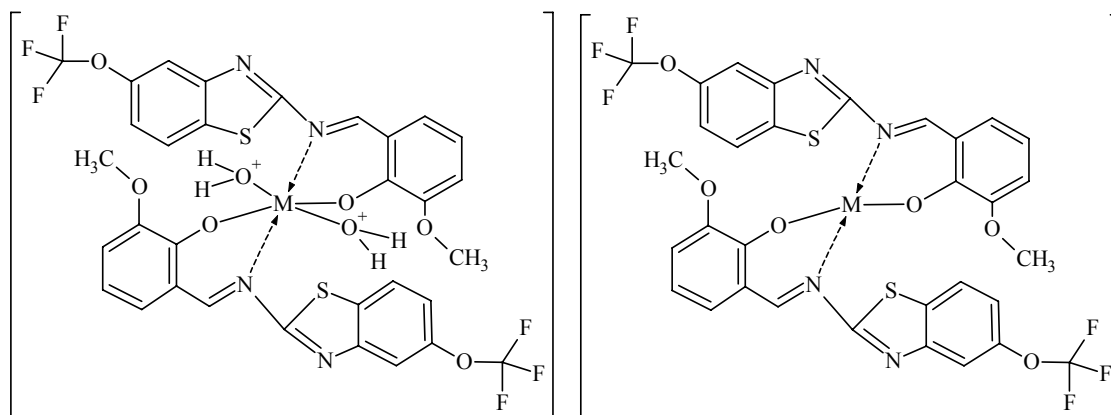
Antimicrobial activities

The *in vitro* antimicrobial activity of the synthesized Schiff base ligands and their corresponding metal complexes on the selected bacteria *E. coli*, *Salmonella*, *Klebshilla*, *Streptococci* and *S. aureus* was carried out. The results of the antibacterial studies of ligands and the complexes are given in the Table 8.

Table 8: Antimicrobial activity results of ligands and their metal complexes

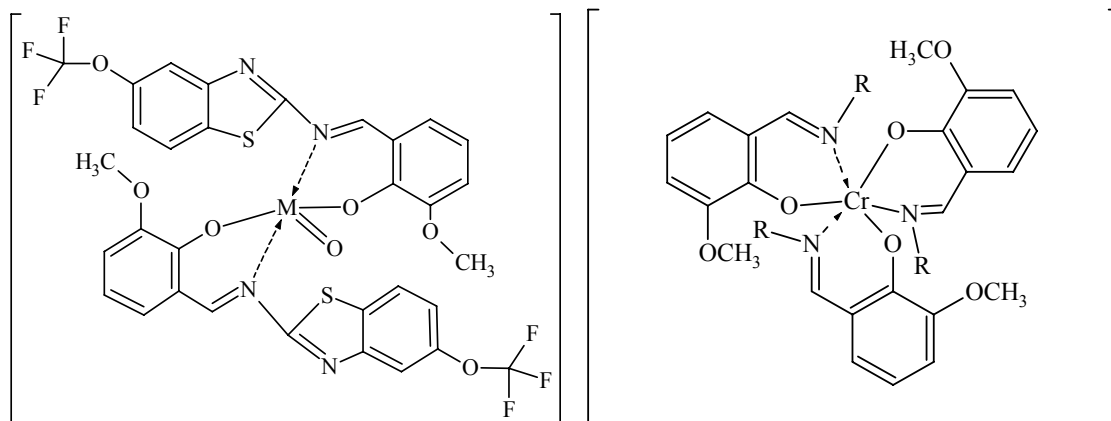
Compound	Zone of inhibition (mm)				
	Gram positive bacteria			Gram negative bacteria	
	<i>E-coli</i>	<i>Salmonella</i>	<i>Klebshilla</i>	<i>S.aurioes</i>	<i>Streptococci</i>
HL	5	15	12	6	12
CrL ₃	5	11	13	9	14
MnL ₂ (H ₂ O) ₂	8	8	16	5	7
NiL ₂ (H ₂ O)	6	7	7	4	6
FeL ₂ (H ₂ O) ₂	7	10	13	8	8
CoL ₂ (H ₂ O) ₂	6	16	11	6	8
CuL ₂ (H ₂ O) ₂	5	15	6	8	11
ZnL (H ₂ O)Cl	6	14	8	7	6
CdL (H ₂ O)Cl	7	10	12	8	14
HgL (H ₂ O)Cl	14	17	7	11	14
VOL ₂ (H ₂ O)	7	8	12	7	12
ZrOL ₂ (H ₂ O)	6	4	12	8	9
Streptomycin	22	20	11	21	20
Penciline	----	----	----	24	16
Control (DMSO)	00	00	00	00	00

Results indicate the low to moderate activity against bacterial species. Ligands exhibit slightly higher activity against gram negative bacteria than the gram positive bacteria. However, compared to the antibacterial activity of the standard antibiotic streptomycin, the activities exhibited by the ligand and metal complexes were less.



Where M = Cu, Co, Ni, Mn and Fe

Where M = Zn, Cd and Hg



Where R = C₈H₃SNOF₃

Where M = ZrO and VO

CONCLUSION

In the present work, Schiff base and their metal complexes have been synthesised using microwave assisted synthesis. Based on stoichiometries and spectrochemical studies the Schiff base ligand derived from 6-(trifluoromethoxy) benzothiazole-2-amine and salicylaldehyde act as bidentate ligand coordinating through N of azomethine group and O

of phenolic group. Based on various spectral data, octahedral geometry around Cu(II), Co(II), Mn(II), Ni(II), Cr(III), Fe(II) complexes, tetrahedral geometry around Zn(II), Cd(II) and Hg(II) complexes with M:L ratio 1:2, and square pyramidal geometry around ZrO(II) and VO(II) complexes have been suggested. The microwave assisted syntheses have been found to be much easier, convenient, quicker and eco-friendly. On the basis of above characterization, the structures for the metal complexes have been proposed.

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