

Synthesis, spectral and thermal studies of Co(II), Ni(II), Cu(II) and Zr(IV) complexes of salicylaldehyde salicyloyl hydrazone and their antimicrobial activity

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Abstract: A series of metal complexes of Co(II), Ni(II), Cu(II) and Zr(IV) with a Schiff base derived from salicylaldehyde and salicyloyl hydrazide were synthesized and characterized by several techniques, including elemental analyses, molar conductance, magnetic moments, electronic, ¹H NMR, mass, IR, ESR spectra, and thermal studies (TGA & DTA). All the complexes are coloured solids, air stable, non-hygroscopic and soluble in DMF and DMSO only and are non-electrolytes. The magnetic moment values and electronic spectral data indicate a square planar geometry for Co(II), Ni(II) and Cu(II) and octahedral geometry for Zr(IV) complexes. IR spectral data suggest that the ligand behaves as dibasic tridentate with ONO (enol form) donor sequence towards Co(II), Ni(II), Cu(II) and Zr(IV) complexes. The thermal data has been investigated to observed degradation pattern and kinetic parameters Entropy Change (ΔS), Free Energy Change (ΔF) and apparent entropy change (S^*) were calculated using Freemann-Carroll and Sharp-Wentworth method. ESR spectra of copper complex are recorded and discussed. The antimicrobial activity of the ligand and its metal complexes by well diffusion method against *Staphylococcus aureus*, *Streptococcus pneumoniae*, *Escherichia coli* and *Klebsiella pneumoniae* are also reported. The complex exhibit increased activity than the ligand.

Index Terms: Salicyloyl hydrazone, complexes, TGA, electronic spectral data, antimicrobial.

I. INTRODUCTION

Since over 200 years salicylates have been used in medicine as analgesic, antipyretic and antiphlogistic drugs. Derivatives like acetylsalicylic acid (aspirin), sodium salicylate, salicylamide, methyl salicylate are used as analgesic, antipyretic and antiaggregation agents [1]. Hydrazones of salicylate possessing an azomethine -NHN=CH- proton constitute an important class of compounds for new drug development. Hydrazone ligands and their complexes have wide applications as anti-tumour, anti-cancer, anti-neoplastic and anti-proliferative agents [2-5]. The interest in the design, synthesis and characterization of hydrazones and their metal complexes has come from their flexidentate nature as well as ability to form a wide range of coordination compounds and their wide applications in various fields.

In view of this, we report the synthesis, characterization and antimicrobial studies of Co(II), Ni(II), Cu(II) and Zr(IV) complexes of Schiff base ligand derived from salicylaldehyde and salicyloyl hydrazide.

II. EXPERIMENTAL –

2.1 Reagents and materials-

All the chemicals used were of the analytical reagent grade and solvents were dried and distilled before use according to standard procedure. Metal salts were purchased from Merck, Sigma-Aldrich, S.D. Fine and were used as received. The precursor salicyloyl hydrazide ($C_6H_4(OH)CONHNH_2$) was prepared by the reported procedure [6] by refluxing methyl salicylate with hydrazine hydrate in 1:1 molar ratio containing 10 mL ethanol for 2 hours. The pure product was characterized by its melting point. M.P. 150°C

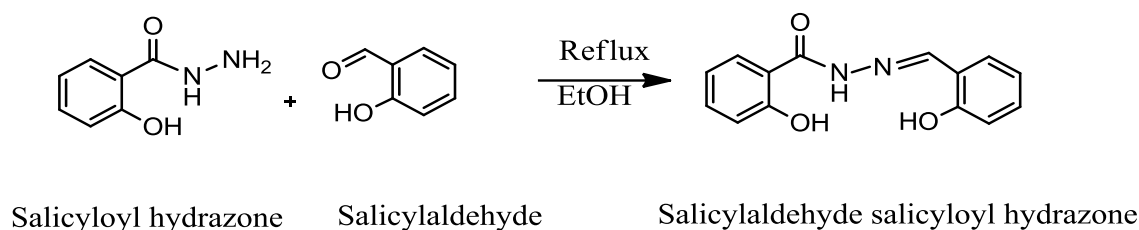
2.2 Physical measurements-

C, H and N content of the ligand were determined by Perkin Elmer CHN 2400 elemental analyzer. The infrared spectra of the ligand and its complexes were recorded in the range 4000 cm^{-1} to 400 cm^{-1} with a Bruker IF566V KBr and polyethylene medium for manganese complex. ¹H-NMR spectra of the ligand were recorded in DMSO- d_6 solution on a Bruker 400 FT-NMR spectrophotometer. Thermal analysis of complexes was carried out by heating in air at a rate of 10°C per minute on a Perkin Elmer thermobalance. The magnetic susceptibility values were recorded at room temperature by Gouy method using $Hg[Co(NCS)_4]$ as a calibrant type magnetic balance. The molar conductance of the complexes was determined in dimethylsulphoxide using solution of about $10^{-3}M$ concentration. The electronic spectra of the ligand and complexes were recorded on a shimadzu UV/Vis spectrophotometer in the region 200-1100 nm. ESR spectra of copper complex at room temperature and liquid nitrogen temperature were carried by using JES-FA 200 ESR spectrometer.

2.3 Synthesis of salicyloyl hydrazone ligand (LH₃) -

A hot ethanolic solution of salicyloyl hydrazide (1.52 g, 0.01 mol) was added to an ethanolic solution of salicylaldehyde (1.22 ml, 0.01 mol). The reaction mixture was refluxed in a water-bath for 4-6 h. The yellow coloured product was filtered off and recrystallized from hot ethanolic solution. Yield 80%, M. P. 210°C. It was characterized by elemental analysis, IR, UV, ¹H-NMR and mass spectra.

¹H-NMR- δ 12.39 (2H, S, Phenolic OH), δ 11.44 (1H, S, imino NH), δ 6.95- δ 7.95 (8H, M, Aromatic proton), δ 8.94 (1H, S, azomethine, HC=N)[7]. The schematic representation of synthesis of LH₃ is shown in reaction scheme 1.

Scheme1. Synthesis of LH₃ ligand

2.4 Synthesis of Co(II), Ni(II) and Cu(II) complexes-

Equimolar quantities (0.02M) of the metal salt and the ligand were dissolved separately in ethanol and refluxed for about 6-8 hrs. in water bath. The solid products obtained on cooling were filtered off, washed several time by diethyl ether and dried at room temperature over CaCl₂.

2.5 Synthesis of Zr(IV) complex-

Zirconyloxchloride octahydrate (0.64g, 0.002 mol) was dissolved in methanol (15ml) and to this a methanolic solution of anhydrous sodium acetate (0.32g, 0.004 mol in 15ml) was added and stirred for 5 min. The separated sodium chloride was filtered off. The respective ligand (0.002 mol) was dissolved separately in hot DMF-methanol (1:4 v/v). To these solutions, the solution containing oxozirconium(IV) diacetate was added and the reaction mixture was refluxed for 4-6 hours. The product obtained was filtered, washed several times with hot water followed by methanol and dried over fused calcium chloride.

III. RESULTS AND DISCUSSION –

All the complexes are coloured, non-hygroscopic solid and stable in air. They are insoluble in water and common organic solvents but soluble in coordinating solvents like DMF and DMSO. The analytical data (Table1) of the complexes indicates 1:1 (metal: ligand) stoichiometry except Zr(IV) complex having 1:2 stoichiometry. The molar conductance values of 10⁻³M solutions of complexes lie in the range 7.52-12.1 ohm⁻¹cm²mol⁻¹ indicating the non-electrolytic nature of all the complexes.

Table 1. Elemental analysis, colour and formula weight of the compound.

Compound	Formula wt.	Colour	Found (Calc.) %			
			C	H	N	M
C ₁₄ H ₁₂ N ₂ O ₃	256.26	Yellow	65.02 (65.12)	4.68 (4.72)	10.72 (10.93)	-
[Co(LH)] ₂	682.45	Brown	18.82 (18.49)	53.69 (53.36)	3.22 (3.51)	8.94 (8.90)
[Ni(LH)] ₂	681.97	Brown	18.76 (18.72)	53.73 (53.70)	3.22 (3.27)	8.95 (8.99)
[Cu(LH)] ₂	672.45	Green	20.00 (20.10)	52.91 (52.98)	3.17 (3.25)	8.82 (8.78)
[Zr(LH) ₂]	691.98	Yellow	15.21 (15.27)	56.08 (56.17)	3.36 (3.45)	9.34 (9.47)

3. Infrared spectra

The broad and strong band at 3270 cm⁻¹ in the spectrum of free ligand is ascribed to $\nu(\text{OH})$ vibration [8]. The other bands at 3048, 1645, 1620 and 1307 cm⁻¹ are assignable to $\nu(\text{NH})$, $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})$ (phenolic) respectively. The band due to intramolecular hydrogen bonded O-H disappeared in all the complexes [9] and shift of $\nu(\text{C}-\text{O})$ (phenolic) band to a higher frequency by 25-40 cm⁻¹, simultaneously indicated the coordination of ligand to metal ion by the oxygen of the hydroxyl group [10]. The upward shift displacement of the $\nu(\text{C}-\text{O})$ (phenolic) bands in Co(II), Ni(II) and Cu(II) indicates the involvement of phenoxide bridging [11]. The appearance of a new band at 564-588 cm⁻¹ also suggests metal-oxygen (phenolic) coordination [12]. The bands due to azomethine group shift to lower wave number by 20-22 cm⁻¹ in the spectra of all the complexes indicating the coordination of azomethine nitrogen [13]. It is further supported by an upward shift in $\nu(\text{N}-\text{N})$ stretch of the free ligand by 18-29 cm⁻¹ in the spectra of complexes [14] and occurrence of a non-ligand band in the region 447-478 cm⁻¹ due to $\nu(\text{M}-\text{N})$ frequency [15]. However the $\nu(\text{N}-\text{H})$ and $\nu(\text{C}=\text{O})$ bands disappeared in the Co(II), Ni(II), Cu(II) and Zr(IV) complexes indicating the destruction of carbonyl moiety as a result of the enolization and subsequent coordination of the enolic oxygen after dissociation of proton [16]. It is further supported due to the presence of $\nu(\text{C}-\text{O})$ (enolic) and $\nu(\text{C}=\text{N}-\text{N}=\text{C})$ (azine) group frequencies in their spectra [17]. The broad band in Co(II), Ni(II), Cu(II), and Zr(IV) at 2850-2950 cm⁻¹ corresponds to $\nu(\text{OH})$ vibration of the uncoordinated phenolic group. On the basis of above data it may be concluded that the ligand behave as a dibasic tridentate ONO donor towards Co(II), Ni(II), Cu(II) and Zr(IV) complexes. The data of the IR spectra of Schiff base ligand and their metal complexes are listed in Table 2.

Table 2. IR frequencies of ligand and its metal complexes (cm⁻¹).

Compound	$\nu(\text{OH})$ (Hydrogen bonded)	$\nu(\text{C}-\text{O})$ phenolic	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$ enolic	M-O	M-N	H ₂ O
LH ₃	3270	1307	1620	979	3048	1645	-	-	-	-
[Co(LH)] ₂	-	1329	1598	1002	-	-	1243	588	447	-
[Ni(LH)] ₂	-	1337	1599	1008	-	-	1250	585	454	-
[Cu(LH)] ₂	-	1322	1600	999	-	-	1249	564	478	-
[Zr(LH) ₂]	-	1347	1598	997	-	-	1253	576	448	-

3.2 Mass Spectra

The mass spectra of ligand displayed an intense molecular ion peak at m/z 253.1 due to $[M]^+$ while the other peaks are appeared at m/z 241.1, 218.2 and 153.1. The mass spectra suggested that all the complexes have a dimeric nature except Zr(IV). These complexes show molecular ion peaks in good agreement with the empirical formula suggested by elemental analyses. The mass spectra of Co(II), Ni(II), Cu(II) and Zr(IV) complexes with molecular formula, $[\text{Co}(\text{LH})_2]$ (F.W., 626.35), $[\text{Ni}(\text{LH})_2]$ (F.W., 625.87), $[\text{Cu}(\text{LH})_2]$ (F.W., 635.57), $[\text{Zr}(\text{LH})_2]$ (F.W., 599.71) as representative showed the highest mass peak with m/z at 626.80, 625.03, 639.07 and 599.08 respectively which agree well with the formula weights of the complexes.

3.3 Electronic spectra and magnetic moment

The magnetic moments, absorption region, assignment and proposed geometry of the complexes are given in Table 3. The Co(II) complex shows two bands at 27933 and 19417 cm^{-1} , which may be assigned to INCT and $^1A_{1g} \rightarrow ^1B_{1g}$ showing square planar geometry for the complex [18]. The magnetic moment value is found to be 2.10 B.M. The value is lower than the expected spin only value, indicating some amount of antiferromagnetic interaction [19] in the complexes. The electronic spectra of diamagnetic Ni(II) complex display three prominent bands at 18904, 13514 and 12626 cm^{-1} are assigned to $^1A_{1g} \rightarrow ^1A_{2g}$, $^1A_{1g} \rightarrow ^1B_{2g}$ and $^1A_{1g} \rightarrow ^1E_g$ in a square planar configuration [19]. The electronic spectrum of the green Cu(II) complex exhibit three bands at 28818, 18692 and 15504 cm^{-1} corresponding to INCT, $^2B_{1g} \rightarrow ^2A_{1g}$ and $^2B_{1g} \rightarrow ^2E_g$ transitions in a square planar geometry [20]. The magnetic moment value 1.35 B.M. recorded for the Cu(II) complex lies within the permissible range recorded for one unpaired electron. The electronic spectra of Zr(IV) complex show a single broad band at 23542 nm, which may be assigned due to LMCT [14].

Table 3. Electronic spectral data of the complexes.

Complex	Absorption region (nm)	Band assignment	μ_{eff} B. M.	Δ_M $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Geometry
[Co(LH) ₂]	358	INCT	2.10	7.52	Square planar
	515	$^1A_{1g} \rightarrow ^1B_{1g}$			
[Ni(LH) ₂]	529	$^1A_{1g} \rightarrow ^1A_{2g}$	Dia.	12.1	Square planar
	740	$^1A_{1g} \rightarrow ^1B_{2g}$			
	792	$^1A_{1g} \rightarrow ^1E_g$			
[Cu(LH) ₂]	347	INCT	1.35	9.68	Square planar
	535	$^2B_{1g} \rightarrow ^2A_{1g}$			
	645	$^2B_{1g} \rightarrow ^2E_g$			

3.4 Thermal analyses

The perusal thermograms of ligand and its metal complexes (Fig. 1-5) shows that Co(II), Ni(II), Cu(II) and Zr(IV) complexes are decompose in two stages. The TG curve of the Co(II), Ni(II), Cu(II) and Zr(IV) complexes do not show any weight loss upto 240°C indicating the absence of lattice and coordinated molecules in these complexes. In all the complexes rapid weight-loss has been observed above 250°C, indicative of decomposition of the free part of the coordinated ligand, a gradual weight-loss above ~450°C corresponding to the actual coordination part of the ligand. DTA thermograms shows peaks at 315°C, 450°C (exothermic) and 575°C (endothermic) for Co(II), at 410°C and 490°C (exothermic) for Ni(II), at 325°C and 460°C (exothermic) for Cu(II), and at 275°C (endothermic), 390°C, 405°C and 550°C (exothermic) for Zr(IV) complex. Finally, the horizontal level beyond 600°C suggests the formation of final decomposition product corresponding metal oxides. The half decomposition temperature and the basic parameters calculated for the compounds are given in Table 4. The relative thermal stability on the basis of half decomposition temperature is found to be Co(II) > Ni(II) > Cu(II) > Zr(IV) > LH₃.

Table 4. Thermoanalytical results of the compounds.

Complex	Half decom. Temp. (°C)	Step	Decom. Temp. (°C)	Ea (kJ)		(n)	-ΔS (J/mol/K)	ΔF (kJ/mol)	S* (kJ)	DTA Peak Temp. (°C)
				FC*	SW**					
LH ₃	320°C	I	100°C-400°C	21.94	21.71	0.95	-294.35	114.07	-28.01	100°C, 340°C, 400°C
[Co(LH) ₂]	480°C	I	250°C-400°C	10.01	15.36	0.96	-310.85	107.3	-28.19	315°C
		II	401°C-600°C	10.77	15.89		-332.04	114.69	-28.26	450°C, 575°C
[Ni(LH) ₂]	460°C	I	250°C-410°C	29.77	18.76	0.95	-265.80	112.96	-29.38	410°C
		II	411°C-550°C	18.02	16.24		-319.97	118.17	-28.87	490°C
[Cu(LH) ₂]	410°C	I	250°C-410°C	8.22	12.67	0.96	-316.93	107.41	-30.68	325°C
		II	411°C-550°C	39.78	42.74		-313.08	137.88	-32.25	460°C

[Zr(LH) ₂]	350°C	I	250°C-400°C	10.73	22.89	0.90	-298.04	104.01	-31.54	275°C, 390°C
		II	401°C-650°C	11.97	19.47		-340.51	118.54	-31.65	405°C, 550°C

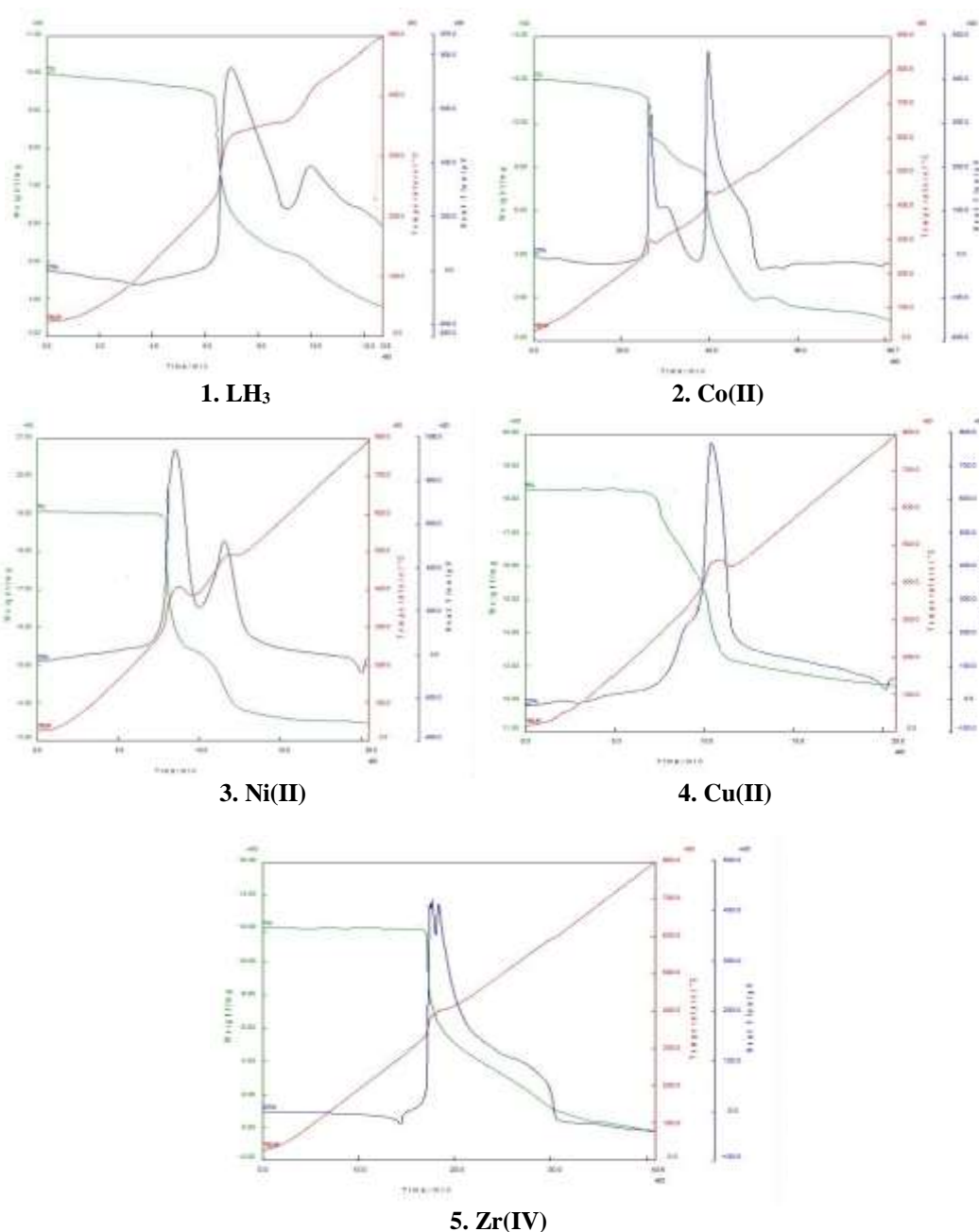


Figure 1-5. Thermograms (TGA/DTA) of salicylaldehyde salicyloyl hydrazone and its complexes.

3.5 ESR spectra

The ESR spectrum of Cu(II) complex in DMF at liquid nitrogen temperature were studied, which provided useful information of metal ion environment in complexes. The axial geometry pattern for Cu(II) ion has been observed, which is confirmed by the g_{\parallel} and g_{\perp} values, which are more than 2.00, which suggest that the unpaired electron lies in the $d_{x^2-y^2}$ orbital corresponds to square planer geometry. It is further confirmed by the value of G, which is calculated with the help of g_{\parallel} and g_{\perp} . The value of G is less than 4.0, suggesting the considerable exchange interaction in the Cu complexes. The partial covalent character of metal-ligand has been proposed with the help of g_{\parallel} value that is less than 2.3.

The ESR spectral parameters and typical ESR spectra of the Cu(II) complex at liquid nitrogen temperature are listed in Table 5. and shown in fig. 6.

Table 5. ESR spectral data of the Cu(II) complex.

Complexes	Spectral Parameters						
	g_{\parallel}	g_{\perp}	$/g/$	A_{\parallel}	A_{\perp}	$/A/$	G
Cu(II)	2.1354	2.0343	2.06803	185.18	87.14	119.82	3.9430

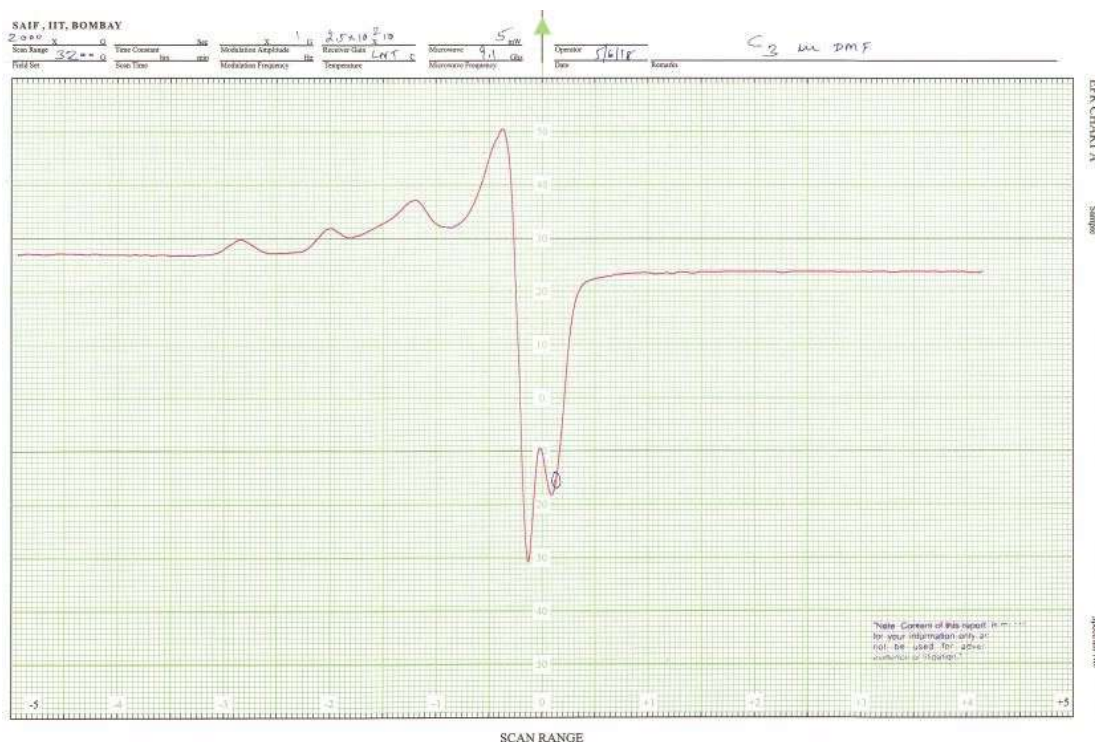


Figure 6. ESR spectrum of Cu(II) salicylaldehyde salicyloyl hydrazone complex at LNT.

On the basis of the above characterization, the proposed structures of complexes are shown in Fig. 7.

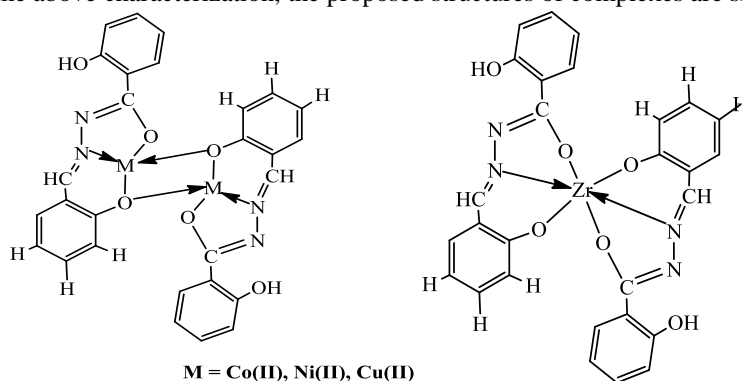


Figure 7. Suggested structures of the salicyloyl hydrazone complexes.

IV. ANTIMICROBIAL ACTIVITY

The in vitro antibacterial activity of the synthesized ligand, its complexes and standard antibacterial agent on selected bacteria *Staphylococcus aureus*, *Streptococcus pneumoniae*, *Escherichia coli* and *Klebsiella pneumoniae* were carried out. The activity of the ligand and complexes are compared with the activity of common standard antibiotic and % activity index for ligand and complexes are also calculated. The DMSO control showed no activity against any bacterial strain. The ligand displays lower activity against *S. pneumoniae* and *K. Pneumoniae* and no activity towards *S. aureus* and *E. coli*. All the complexes individually show varying degrees of inhibitory effect on the growth of tested bacterial species. On the basis of maximum inhibitory activities shown against strains, Cu(II) complex are found to be most effective against *S. aureus* with zone of inhibition 23 mm. The Cu(II) complex also found most effective towards *S. pneumoniae* with zone of inhibition 20 mm. Among gram-negative bacteria, the Co(II), Ni(II), Cu(II) and Zr(IV) displays promising antibacterial activities with zone of inhibition in the range 24-33 mm. The result reveals that the activity of the metal complexes becomes more pronounced when coordinated with metal ions. The % Activity index data indicates highest activity 79% and 87% for Cu(II) complex against *S. aureus* and *S. pneumoniae* respectively and 87% and 88 % for Zr(IV) complex against *E. coli* and *K. Pneumoniae* respectively. The zone of inhibition and % activity index of the ligand and its complexes are given in the table 6.

Table 6- Antimicrobial activity of ligand and its complexes.

Ligand and its complexes	Diameter of inhibition of zone (in mm) ^a				% Activity index			
	<i>S. aureus</i>	<i>S. pneumoniae</i>	<i>E. coli</i>	<i>K. Pneumoniae</i>	<i>S. aureus</i>	<i>S. pneumoniae</i>	<i>E. coli</i>	<i>K. Pneumoniae</i>
LH ₃	-	8	-	15	-	35	-	44
[Co(LH)] ₂	18	16	32	28	62	70	84	82
[Ni(LH)] ₂	20	18	30	24	69	78	79	71
[Cu(LH)] ₂	23	20	32	25	79	87	84	74
[Zr(LH)] ₂	22	17	33	30	76	74	87	88
Antibiotic (Standard)	29	23	38	34	100	100	100	100

—: no activity, ^a values, including diameter of the well (8mm), are means of three replicates

V. CONCLUSION

In the present study, the Schiff base derived from the condensation between salicylaldehyde and salicyloyl hydrazone is a versatile ligand since it formed mono nuclear Zr(IV) and binuclear complexes of octahedral and square planar geometries respectively. The synthesized Schiff base and its metal complexes have been confirmed by the analytical data, IR, electronic, mass spectrometry, ¹H NMR, ESR spectral data, molar conductance, magnetic moments and thermal studies.

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