



SYNTHESIS, SPECTROSCOPIC AND THERMAL STUDIES OF CO(II), NI(II), CU(II), CR(III), MN(III), FE(III), VO(IV) AND ZR(IV) COMPLEXES WITH O-VANILINE SALICYLOYL HYDRAZONE AND THEIR ANTIMICROBIAL ACTIVITY

S.D. Deshmukh^a, V.A. Sadafale^b, P.R. Mandlik^{a,b,*}

^aDepartment of Chemistry, Government Polytechnic, Amravati- 444603, India

^{a,b,*}Department of Chemistry, Shri Shivaji Science College, Amravati- 444603, India

ABSTRACT

In the present study, Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III), VO(IV) and Zr(IV) complexes of o-vaniline salicyloyl hydrazone (VSH) have been synthesized and characterized by elemental analyses, molar conductance, magnetic moments, electronic, ¹H NMR, mass, infrared spectra, and thermal studies. All the complexes were colored, stable in air and non-electrolyte in nature. On the basis of various studies proposed geometries are square planer for Co(II), Ni(II) and Cu(II), octahedral for Cr(III), Fe(III) and Zr(IV) and square pyramidal for Mn(III) and VO(IV) complexes. The complexes were found to have compositions [M(LH)]₂ where M = Co(II), Ni(II), Cu(II), [M(L)(H₂O)]₂ where M = Cr(III) and Fe(III), [M(L)]₂ where M = Mn(III) and VO(IV), [Zr(LH)₂]. The thermal analysis supports the presence or absence of water molecule in or outside the coordination sphere. The ligand and its metal complexes were screened for their antimicrobial activity against Staphylococcus aureus and Streptococcus pneumoniae as gram positive bacteria and Escherichia coli and Klebsiella pneumoniae as gram negative bacteria by agar well diffusion method.

Keywords: Salicyloyl hydrazone metal complexes, electronic, magnetic moment, molar, conductance, thermal analysis, antimicrobial activity

1. Introduction

In the Schiff base family, hydrazones are special group of compounds having the >C=N-N=C< linkage. Hydrazones are prepared

by refluxing the appropriate substituted hydrazine/hydrazide with aldehydes and ketones in solvent like methanol, ethanol etc. (Al Zoubi, Kandil and Chebani, 2011, Vora, Patel, Patel and Dholakia, 2012). The presence of two interlinked nitrogen atoms distinguished hydrazones from other members of this family and characterized by the tri-atomic grouping C=N-N in their molecules. Acyl, aroyl and heteroaryl hydrazones of carbonyl compounds has an additional donor site; coordinate to a metal ion via phenolate- or enolate-O, imine-N and deprotonated amide-O atoms producing mono, di and polynuclear metal complexes. This makes them good polydentate and flexidentate chelating agent and they can form a variety of complexes with various transition and inner transition metals. Another interesting feature of hydrazones is their tautomeric ability. The keto-enol (amido-iminol) tautomerism is shown by hydrazones due to the -NH-C=O functional group present in it. In solid state, they exist in keto (amido) form but in solution, they exist as an equilibrium mixture of keto and enol (iminol) forms. In spite of good chelating ability, hydrazones exhibit biological activities in the treatment of several diseases (Monfareda, Pouralimardana and Janiak, 2007, Agrawal, Jain and Chand, 2002, Iskander, El-Sayed, Salem, Haase, Linder and Foro, 2004), also act as plant growth regulators, sterilants for houseflies, herbicides, insecticides, nematocides, rodenticides, among other applications.

The aim of the present study was to prepare, characterize and determine the antimicrobial activity of Schiff base complexes derived from salicyloyl hydrazone and o-vaniline.

2. Experimental

2.1. Reagents and materials

All the chemicals used were analytical reagent grade and solvents were dried and distilled before use according to standard procedure. Metal salts were purchased from Merck, Sigma-Aldrich and S.D. Fine and were used as received. $Mn(OAc)_3 \cdot 2H_2O$ was prepared by the oxidation of $Mn(OAc)_2 \cdot 4H_2O$ using Christen's method (Christensen, 1901). The precursor salicyloyl hydrazide ($C_6H_4(OH)CONHNH_2$) was prepared by the reported procedure (Singh, Srivastava, Narang and Singh, 1999) 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. $150^\circ C$

2.2. Physical measurements

C, H, 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} in KBr pellet on a Shimadzu spectrophotometer. 1H -NMR spectra

of the ligand were recorded in DMSO- d_6 solution on a EM-360, 60 MHz NMR spectrometer. Thermal analysis of complexes was carried out by heating in air at a rate of $10^\circ C$ 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. The molar conductance of the complexes was determined in dimethylsulphoxide using solution of about 10^{-3} mol concentration. The electronic spectra of the ligand and complexes were recorded on a shimadzu UV/Vis spectrophotometer in the region 200-1100 nm.

2.3. Synthesis of salicyloyl hydrazone ligand (LH_3)

A hot ethanolic solution of salicyloyl hydrazide (1.52 g, 0.01 mol) was added to an ethanolic solution of o-vaniline (1.52 g, 0.01 mol). The reaction mixture was refluxed in a water-bath for 4-6 hours. The yellow coloured product was filtered off and recrystallized from ethanol. Yield 85%, M. P. $180^\circ C$.

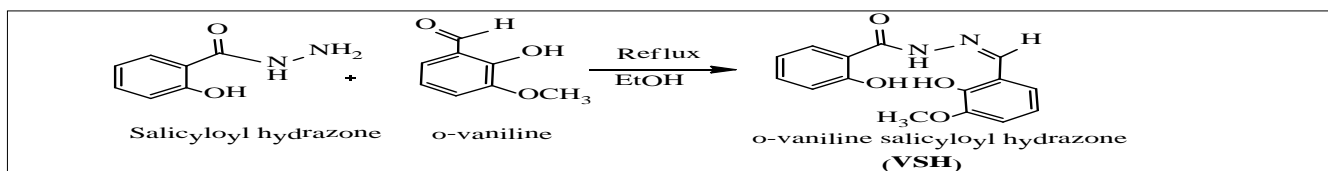


Fig.1- Synthesis of LH_3 ligand

2.4. Synthesis of Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III) and VO(IV) 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 $CaCl_2$.

2.5. Synthesis of Zr(IV) complex

Zirconyloxychloride 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.

3. Results and Discussion

The analytical data of the ligand and its metal complexes are consistent with proposed molecular formula listed in Table 1. 1HNMR spectrum of the ligand shows signals at $\delta 10.07$ (phenolic OH, br, 2H), $\delta 11.43$ (Imino NH, s, 1H), $\delta 6.95 - \delta 7.95$ (7H, m, Aromatic proton), $\delta 3.79$ (3H, s, methyl, Ar-OCH₃), $\delta 8.96$ (1H, s, azomethine HC=N) (Jayaramudu and Reddy, 1999).

All the metal complexes are coloured, solid and stable towards air and moisture at

room temperature. Analytical data show that all the metal complexes have 1:1 (metal: ligand) stoichiometry except Zr(IV) complex having 1:2 stoichiometry. It also appears that ligand enolize and deprotonate during complexation with Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III) and Zr(IV) complexes. All the metal

complexes are insoluble in water and common organic solvents but soluble in coordinating solvents like DMF and DMSO. The molar conductance values of 10^{-3} m solutions of complexes lie in the range 7.62-23.4 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ indicating the non-electrolytic nature of all the complexes.

Table 1: Analytical and physical data of ligand and its metal complexes-

Proposed composition of the complexes	Formula Weight	Colour	Time of Reflux	M% Found	C% (Calcd.)	H% (Calcd.)	N% Found (Calcd.)	Found (Calcd.)
[Co(LH) ₂]	686.03	Brown	6 h	17.17	(17.28)	52.49	(52.52)	3.52 (3.77) 8.16 (8.63)
[Ni(LH) ₂]	685.92	Brown	6 h	17.11	(17.18)	52.53	(52.48)	3.53 (3.48) 8.17 (8.51)
[Cu(LH) ₂]	695.63	Green	6 h	18.27	(18.36)	51.80	(51.67)	3.48 (3.61) 8.05 (8.20)
[Cr(L)(H ₂ O) ₂]	706.54	Maroon	6h	14.72	(14.68)	51.00	(51.20)	3.71 (3.58) 7.93 (7.98)
[Mn(L) ₂]	676.39	Orange	6 h	16.24	(16.46)	53.27	(53.20)	3.28 (3.22) 8.28 (8.36)
[Fe(L)(H ₂ O) ₂]	714.24	Black	8 h	15.64	(15.45)	50.45	(50.70)	3.67 (3.84) 7.84 (7.37)
[VO(L) ₂]	702.42	Black	6 h	14.50	(14.98)	51.30	(51.44)	3.44 (3.56) 7.98 (7.68)
[Zr(LH) ₂]	659.76	Yellow	6 h	13.83	(13.99)	54.61	(54.78)	3.67 (3.49) 8.49 (8.56)

3.1. Infrared spectral studies of ligand and its complexes

The IR spectrum of free ligand exhibits medium broad band in the region 3367 cm^{-1} due to intramolecular hydrogen bonded OH. This band is absent in the spectra of all complexes indicating the deprotonation of ligand with metal through oxygen atom via coordination (Dey, Bandopadhyay, Bhattacharya and Chakraborty, 1996). The upward shift of $\nu(\text{C}-\text{O})$ (phenolic) band at 1303 cm^{-1} of the ligand by $12-38\text{ cm}^{-1}$ (Aranha, Santos, Romera and Dockal, 2006) and the appearance of a new band at $547-578\text{ cm}^{-1}$ in the spectra of all complexes further supports the involvement of phenolic oxygen in coordination. The increase in shift of the C-O (phenolic) frequency in Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III) and VO(IV) attributed to phenolic oxygen bridge formation (Malhotra, Kumar, Singal and Dhindsa, 2000). The absorption peak for $\nu(\text{C}=\text{N})$ at 1620 cm^{-1} and $\nu(\text{N}-\text{N})$ at 964 cm^{-1} in the ligand is shifted to a lower frequency by $18-23\text{ cm}^{-1}$ (Ghosh, 2006) and higher frequency by $15-26\text{ cm}^{-1}$ (Singh and Katiyar, 2008) respectively in all complexes due to coordination of azomethine nitrogen. This is in agreement with the band observed in the far IR region $428-478\text{ cm}^{-1}$ due to the $\nu(\text{M}-\text{N})$ stretch. The other bands at 3367 and 1651 cm^{-1} of the free ligand, assigned due to $\nu(\text{N}-\text{H})$ and $\nu(\text{C}=\text{O})$ respectively, disappeared in the spectra of

Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III) and Zr(IV) complexes indicating the destruction of carbonyl moiety and subsequent coordination of enolic oxygen via deprotonation (Baligar and Revankar, 2006). It is further supported by a new band appearing in the region $1242-1253\text{ cm}^{-1}$ due to $\nu(\text{C}-\text{O})$ (enolic) mode (Ghosh, Roy, Bhattacharya and Banerjee, 2005). In Co(II), Ni(II), Cu(II), and Zr(IV) complexes the broad band at $2850-2950\text{ cm}^{-1}$ corresponds to $\nu(\text{OH})$ vibration indicates uncoordinated phenolic group. Thus, in Co(II), Ni(II), Cu(II) and Zr(IV) complexes the ligands function in dibasic tridentate bonding through O, N and O donor atoms and Cr(III), Mn(III) and Fe(III) complexes in tribasic tetradentate bonding through O, O, N and O donor atoms. The presence of these two bands almost at the same position in VO(IV) complex suggest the non-involvement of amide oxygen in the coordination and the keto form of coordinated ligand in this complex. Thus in this complex the ligand functions in a dibasic tridentate bonding through O, N and O atoms. The spectra of Cr(III) and Fe(III) complexes display four bands in the region $3456-3475\text{ cm}^{-1}$ $\nu(\text{O}-\text{H})$, 1627 cm^{-1} $\delta(\text{H}_2\text{O})$, $829-833\text{ cm}^{-1}$ $\nu(\text{H}_2\text{O})$, $752-760\text{ cm}^{-1}$ $\nu(\text{H}_2\text{O})$ suggesting the presence of coordinated water molecule in each of them. The additional bands at 987 cm^{-1} in the spectra of VO(IV) complex is assigned to $\nu(\text{V}=\text{O})$ mode (Prasanna and Kumar, 2013).

Table 2: Infrared spectral data (cm⁻¹) of the ligand and its metal complexes-

Compound	$\nu(\text{OH})$ (Hydrogen bonded)	$\nu(\text{C-O})$ phenolic	$\nu(\text{C=N})$ enolic	$\nu(\text{N-N})$	$\nu(\text{NH})$	$\nu(\text{C=O})$	$\nu(\text{C-O})$	M-O	M-N
[Co(LH)] ₂	-	3367	1303	1620	964	3221	1651	-	-
[Ni(LH)] ₂	1320	1602	990	-	-	1242	578	435	
[Cu(LH)] ₂	1338	1602	980	-	-	1249	567	462	
[Cr(L)(H ₂ O)] ₂	1321	1597	979	-	-	1249	555	459	
[Mn(L)] ₂	1342	1604	990	-	-	1242	547	455	
[Fe(L)(H ₂ O)]	1338	1600	983	-	-	1252	555	478	
[VO(L)] ₂	1315	1597	-	3232	1651	-	555	462	
[Zr(LH)] ₂	1332	1603	981	-	-	1253	563	428	

3.2. Mass Spectral studies of Schiff base and its complexes

The FAB mass spectra of the all compounds were recorded. All the spectra exhibited parent peaks due to respective molecular ions (M⁺). The proposed molecular formula of these compounds was confirmed by comparing their molecular formula weights with m/z values. The molecular ion peak obtained were as follows: m/z 286.41 (ligand), 688.90 (Co(II) complex), 684.87 (Ni(II) complex), 691.90 (Cu(II) complex), 706.82 (Cr(III) complex), 678.96 (Mn(III) complex), 713.12 (Fe(III) complex), 701.22 (VO(IV) complex) and 657.07 (Zr(IV) complex). These data are in good agreement with the proposed molecular formula for these complexes, i.e., [M(LH)]₂, where M = Co(II), Ni(II) and Cu(II), [M(L)(H₂O)]₂ where M = Cr(III), Fe(III), [M(L)]₂ where M = Mn(III) and VO(IV), [Zr(LH)]₂. In addition to molecular ion peak, the spectra exhibited peaks assignable to various fragments arising from the thermal cleavage of the complexes. The peak intensity suggested the stability of the fragments.

3.3. Electronic spectra, magnetic moment and molar conductance of metal complexes-

The magnetic moments and electronic spectral bands of the complexes are listed in Table 3. The electronic spectrum of [Co(LH)]₂ shows bands at 361 and 517 nm assigned for INCT and ¹A_{1g}→¹B_{1g} respectively in square planer geometry (Singh, Singh and Katiyar, 2009). The subnormal magnetic moment 2.11 is as expected for dimer structure due to strong metal-metal interaction. In [Ni(LH)]₂ complex well-defined bands observed at 520, 739 and 789 nm are assigned to ¹A_{1g}→¹A_{2g}, ¹A_{1g}→¹B_{2g} and ¹A_{1g}→¹E_g respectively in a square planer configuration (Singh, Katiyar and Singh, 2008). The complex is of diamagnetic nature. The electronic spectrum of the green [Cu(LH)]₂ complex exhibit three bands at 348, 539 and

645 nm corresponding to INCT, ²B_{1g}→²A_{1g} and ²B_{1g}→²E_g transitions in a square planer geometry (Mohan, Kumar and Kumar, 1987). The magnetic moment value 1.33 B.M recorded for the Cu(II) complex lies within the permissible range recorded for one unpaired electron. The electronic spectrum of [Cr(L)(H₂O)]₂ complex shows bands at 618, 482 and 295 nm corresponding to the transitions ⁴A_{2g}(F)→⁴T_{2g}(F), ⁴A_{2g}(F)→⁴T_{1g}(F) and ⁴A_{2g}(F)→⁴T_{1g}(P) respectively (Hassan, Zayed, Elkholy, Moustafa and Mohamed, 2013) which are characteristic of six coordinate octahedral geometry. The ligand field parameters 10Dq and B have been calculated for Cr(III) complex. The Racah inter-electron repulsion parameter B observed for Cr(III) complex is less than that of the free ion. The nephelauxetic parameter β = B/B' is less than one in these complex. All these observations suggest that the metal-ligand bond in the complex is covalent in nature. The Racah inter-electron repulsion parameter (B) and nephelauxetic parameter (β) for Cr(III) complex (B = 406 cm⁻¹, β = 0.442) suggest that considerable amount of covalent character of the M-L bond in them (Dutta and Hossain, 1985). [Mn(L)]₂ complex shows bands at 731, 596, 504 and 364 nm. The band at 364 nm is due to charge transfer and the remaining three correspond to ⁵B₂→⁵B₂, ⁵B₁→⁵A₁, ⁵B₁→⁵E transitions, respectively, with a magnetic moment of 4.62 B.M. suggesting square pyramidal geometry of ligand around Mn(III) ion (Mandlik, More and Aswar, 2003). Fe(III) complex give rise to three absorption bands in octahedral field at 720, 521 and 450 nm corresponding to ⁶A_{1g}(S)→⁴T_{1g}(G), ⁶A_{1g}(S)→⁴T_{2g}(G) and ⁶A_{1g}(S)→⁴E_g, ⁴A_{1g}(G) transitions. The subnormal magnetic moment 4.87 B.M. is as expected for dimer structure due to strong metal-metal interaction (Mandlik, More and

Aswar, 2003). The electronic spectrum of [VO(L)]₂ shows bands at 735, 597, 437 and 346 nm may assign to ²B₂→²E, ²B₂→²B₁, ²B₂→²A₁ and LMCT, respectively, which are well characteristics for square pyramidal geometry. The magnetic moment value (1.49 B.M.) measured is lower than the reported, this may

support the presence of vanadyl complex in a binuclear with strong interaction between two vanadium ions (Mandlik, More and Aswar, 2003). The electronic spectra of Zr(IV) complex show a single broad band at 419 nm, which may be assigned due to LMCT (Abou-Hussein and Linert, 2012).

Table 3: Electronic spectra, magnetic moment and molar conductance data of metal complexes-

Complex	Electronic spectral bands (nm)	μ^{eff} (B.M)	Geometry	Molar conductance $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$
[Co(LH)] ₂	361, 517	2.11	Square planer	7.62
[Ni(LH)] ₂	520, 739, 789		Dia. Square planer	10.57
[Cu(LH)] ₂	348, 539, 645	1.33	Square planer	9.25
[Cr(L)(H ₂ O) ₂] ₂	618, 482, 295	3.48	Octahedral	20.2
[Mn(L)] ₂	731, 596, 504, 364	4.62	Square pyramidal	18.8
[Fe(L)(H ₂ O) ₂] ₂	720, 521, 450	4.87	Octahedral	23.4
[VO(L)] ₂	735, 597, 437, 346	1.49	Square pyramidal	10.6
[Zr(LH) ₂]	419	Dia.	Octahedral	13.6

3.4. Thermal analysis

An analysis of TG curves of the ligand and its metal complexes (Fig.2) shows that the Cr(III) and Fe(III) complexes decompose three stages while Co(II), Ni(II), Cu(II), Mn(III), VO(IV) and Zr(IV) complexes in two stages. The presence of water molecule (coordinated) in Cr(III) and Fe(III) complexes suggested from IR spectra is confirmed by the weight-loss observed in the first decomposition step of these complexes. The Cr(III) and Fe(III) complexes are stable upto 140°C indicating absence of lattice water molecule and lose their weights 140°C-260°C corresponding to two coordinated water molecule (% weight loss obs./calcd.: Cr(III) : 5.32/5.10; Fe(III) : 5.26/5.04). The Co(II), Ni(II), Cu(II), Mn(III), VO(IV) and

Zr(IV) complexes are stable upto ~300°C indicating the absence of any water molecule. A rapid loss in weights is observed in the temperature range 300°C-460°C, indicative of decomposition of free part of the coordinated ligand. A gradual increase in temperature above ~460°C was accompanied by degradation of coordinated part of ligand. The thermal data for each decomposition step have been evaluated using Freeman-Carroll and Sharp-Wentworth method (Ahmed, Hassan, Gumma, Mohamed and Eraky, Kavitha and Reddy, 2014) of the compounds is given in Table 4. On the basis of half decomposition temperature the thermal stability order of compounds was found to be

Zr(IV) > Ni(II) > Mn(III) > Cr(III) > VO(IV) > Cu(II) = Fe(III) > Co(II) > Ligand

Table 4: Thermal decomposition data of Ligand (LH₃) and metal Complexes.

Complex	Half decomp. Temperature (°C)	Step	Decomposition Temperature (°C)	Activation Energy (kJ mole ⁻¹)	Overall Order of Reaction	Entropy Change (-ΔS)	Free Energy Change (-ΔG)	Apparent Entropy Change
VSH (LH ₃)	220°C	I	160°C-400°C	17.02	16.62	0.92	-277.59	103.90
[Co(LH)] ₂	390°C	I	260°C-420°C	36.36	32.24	1.00	-189.99	95.82
		II	421°C-600°C	24.44	22.62	-313.99	122.72	-34.9
[Ni(LH)] ₂	490°C	I	260°C-400°C	74.14	68.68	0.93	-249.66	152.28
		II	401°C-600°C	28.01	38.21	-259.09	109.10	-29.6
[Cu(LH)] ₂	410°C	I	260°C-400°C	22.88	17.11	0.96	-207.75	87.90
		II	401°C-600°C	33.46	17.63	-321.55	134.10	-28.9
[Cr(L)(H ₂ O)] ₂	445°C	I	160°C-240°C	9.31	13.31	0.95	-321.35	109.89
		II	241°C-380°C	13.53	17.12	-309.39	110.37	-29.76
		III	381°C-600°C	7.93	18.45	-325.28	109.74	-29.23
[Mn(L)] ₂	470°C	I	260°C-400°C	25.27	22.34	1.00	-230.43	97.39
		II	421°C-540°C	8.94	8.74	-320.18	109.15	-28.23
[Fe(L)(H ₂ O)] ₂	410°C	I	160°C-240°C	8.88	16.48	0.95	-333.58	119.29
		II	241°C-400°C	46.86	58.24		-256.13	127.08
		III	401°C-600°C	28.41	14.69	-327.78	131.00	-28.24

[VO(LH) ₂]	420 ⁰ C	I260 ⁰ C-400 ⁰ C	20.0031.1	0.90	-220.0688.88	-30.25
	II401 ⁰ C-600 ⁰ C	8.79	18.47	-337.53	114.43	-29.43
[Zr(LH) ₂]	590 ⁰ C	I260 ⁰ C-400 ⁰ C	46.6136.16	0.90	-269.42	130.93
	II401 ⁰ C-640 ⁰ C	23.7917.49		-301.48	118.15-24.40	

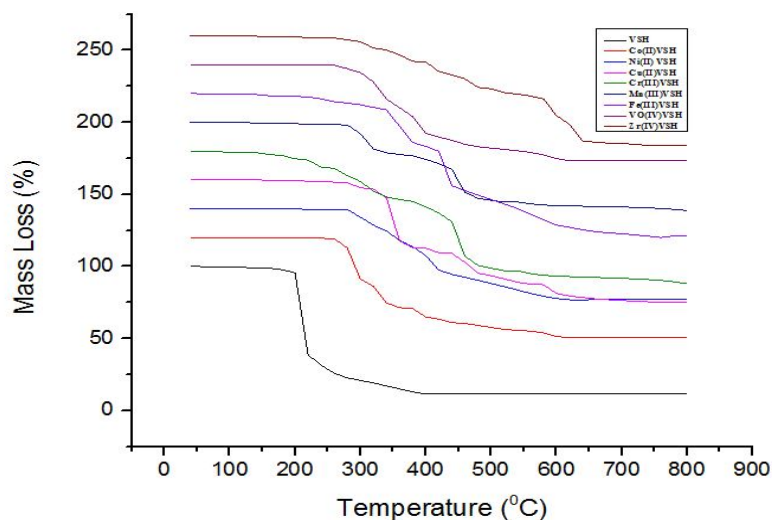


Fig. 2- Thermograms of ligand (LH₃) and its complexes.

3.5. Antibacterial Activity

In vitro antibacterial activity of the ligand, its complexes and standard antibacterial agent against two gram-positive bacteria (*Staphylococcus aureus*, *Streptococcus pneumoniae*) and two gram-negative bacteria (*Escherichia coli*, *Klebsiella pneumoniae*) were carried out. Ligand shows no activity against *S. aureus*, *S. pneumoniae* and *E. coli* and lower activity against *K. Pneumoniae* with zone of inhibition 11 mm. An inhibition zone for gram-positive bacteria is found in the range of 15-24 mm, for gram negative bacteria 11-33 mm. It is observed that Zr(IV) complex are very effective against *S. aureus* and *S. pneumoniae* with highest zone of inhibition 24 and 18 mm respectively while it shows no activity against gram-negative bacteria. The Co(II) complex are more effective against *E. coli* and *K. Pneumoniae* with the zone of inhibition 33 and 30 mm respectively while it shows no activity against gram-positive bacteria. The Cr(III) and Mn(III) complexes are inactive towards gram-positive and gram-negative bacteria

respectively, and also, Cr(III) complex shows higher activity with zone of inhibition 30 and 28 mm for *E. coli* and *K. pneumoniae* and Mn(III) shows higher activity with zone of inhibition 18 and 16 mm for *S. aureus* and *S. pneumoniae* respectively. The Ni(II), Cu(II), Fe(III) and VO(IV) complexes are found to be bacteriocidal against all the bacterial strains with a zone of inhibition in the range 15-32 mm, 18-28mm, 17-30 mm and 18-32 mm respectively. Thus ligand exhibit a bacteriostatic behaviour against all the bacterial strains except *K. pneumoniae* and the activity of the ligand was found to be enhanced on complexation with metal ions. The % activity index data indicates highest activity 83% for Zr(IV) complex against *S. aureus*, 78% for Ni(II), VO(IV) and Zr(IV) complexes against *S. pneumoniae*, 87% for Co(II) against *E. coli* and 88% for Co(II) complex against *K. Pneumoniae* compared with standard antibiotic 100%. The inhibition effect and % activity index of the ligand VSH and its complexes are summarized in Table 5.

Table 5: Antibacterial activity of ligand and their complexes through agar well diffusion method.

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>
VSH	-	-	11	-	-	-	32
Co-VSH	-	33	30	-	-	87	88
Ni-VSH	16	15	32	26	55	65	84

Cu-VSH 18	1828	26	62	78	74	76	
Cr-VSH -	-	30	28-	-79	82		
Mn-VSH 18	16	-	-	62	70	-	-
Fe-VSH 18	1730	27	62	74	79	79	
VO-VSH 19	1832	26	66	7884	76		
Zr-VSH 24	18	-	-	83	78	-	-
DMSO -	--	--	-	-	-		
Antibiotic (Standard)		29	2338	34	100	100	100 100

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

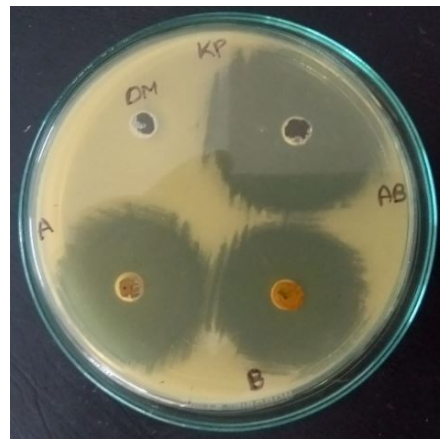
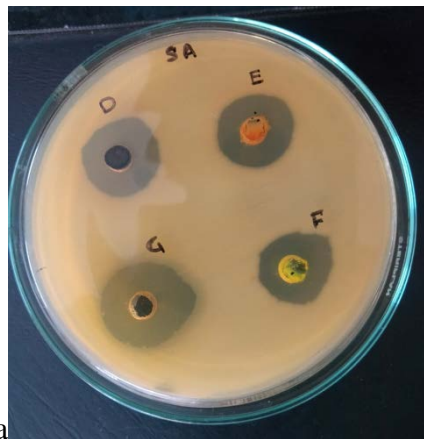


Fig. 3 - (a) Zone of inhibition of growth of *S. aureus*; (b) Zone of inhibition of growth of *K. pneumoniae*.

4. Conclusion

In the present study, Schiff base and metal complexes were synthesized and characterized by elemental analyses, molar conductance, magnetic moments, electronic, ¹H NMR, mass, infrared spectra, and thermal studies. With the help of aforementioned techniques, all the complexes except Zr(IV) complex are binuclear showing subnormal magnetic moments probably due to metal-metal interaction and super exchange phenomena. The coordination compounds show significant enhanced antimicrobial activities as compared to the free Schiff base. Therefore, these compounds can be further used in pharmaceutical industry as antimicrobial agents.

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