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Synthesis, Spectral Characterization, Thermal Studies and Antimicrobial Activity of Cr(III), Mn(III), Fe(III) and VO(IV) Complexes of 2-Hydroxy-5-methylacetophenone Salicyloyl Hydrazone.

Deshmukh SD[1*], Mandlik PR[2]

[1]Lecturer, Department of Chemistry, Government Polytechnic, Amravati India
[2]Associate Professor, Department of Chemistry, Shri Shivaji Science College, Amravati- 444 603, Maharashtra India

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***Corresponding author:** Swati D. Deshmukh

Abstract

2-Hydroxy-5-methylacetophenone salicyloyl hydrazone and its Cr (III), Mn(III), Fe(III) and VO(IV) metal complexes were synthesized. Elemental analyses, molar conductance, magnetic moments, electronic, ^{1}H NMR, mass, IR, ESR spectra and thermal studies (TGA & DTA) were applied for characterization. The complexes are coloured solids, air stable, non-hygroscopic and soluble in DMF and DMSO only. IR spectral studies reveal that ligand act as tribasic tetradentate (ONOO) (enol form) donor towards Cr(III), Mn(III) and Fe(III) and dibasic tridentate (ONO) (keto form) donor towards VO(IV) complex. The molar conductivity data of the complex show them to be non-electrolyte. Magnetic susceptibility measurements favour octahedral coordination for Cr (III) and Fe(III) and square pyramidal coordination for Mn(III) and VO(IV). The complexes were treated for TGA and DTA studies. Thermo-kinetic parameters such as activation energy (Ea), order of reaction (n), entropy change (ΔS), free energy change (ΔF) and apparent entropy change (S*) have been calculated on the basis of TG curve by using the Freeman-Carroll and Sharp-Wentworth methods. ESR spectra of vanadyl complex are recorded and discussed. In addition, the antimicrobial activities of the ligand and its metal complexes were also examined by well diffusion method.

Keywords: Salicyloyl hydrazone, Spectra, TGA, ESR, Antimicrobial activities.

INTRODUCTION

Hydrazones are extensively used as analytical reagents for the determination of various metal ions by using various analytical techniques as they can form stable complexes with most of the transition metal ions [1, 2]. Many researchers have synthesized these compounds as target structures and evaluated their antituberculosis and antitumour activities. Hydrazones and their metal complexes are biologically active compounds. A number of hydrazone derivatives have interesting bioactivity towards anti-bacterial, anti-fungal, anti-convulsant, anti-inflammatory, anti-malarial, analgesic, anti-platelets, anti-tuberculosis and anti-cancer activities [3-5].

In view of the importance of hydrazones and their metal complexes, we report herein the synthesis, spectral characterization and thermal analysis of Cr (III), Mn(III), Fe(III), and VO(IV) complexes of Schiff base ligand derived from the condensation of 2-hydroxy-5-methyl acetophenone and salicyloyl hydrazide and attempt to check their antimicrobial activity.

EXPERIMENTAL

Reagents and materials

All the chemicals used were of 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. Mn $(OAc)_3$. $2H_2O$ was prepared by the oxidation of Mn $(OAc)_2.4H_2O$ using Christen's method [6]. The precursor salicyloyl hydrazide ($C_6H_4(OH)CONHNH_2$) was prepared by the reported procedure [7] 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 M.P. (150^0C).

Physical measurements

C, H, N content of the ligand were determined by Perkin Elmer CHN 2400 elemental analyzer. The metal contents were estimated by standard methods [8].

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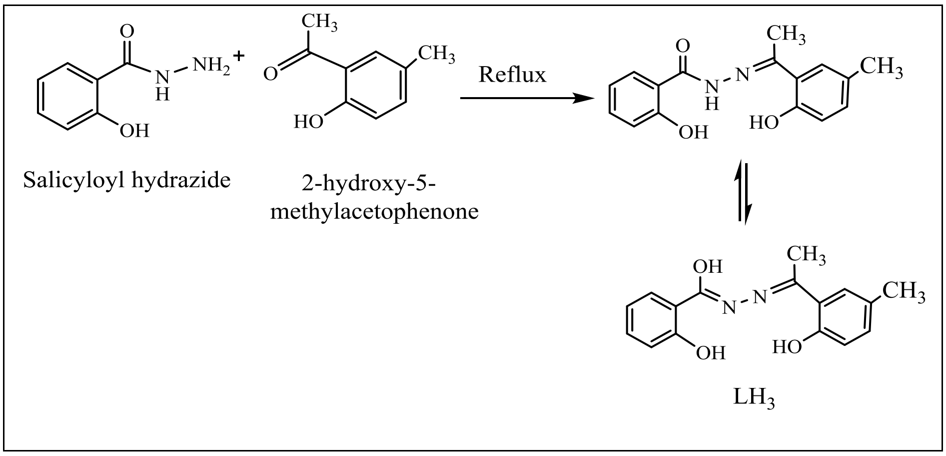
The infrared spectra of the ligand and its complexes were recorded in the range 4000-400 cm^{-1} with a Bruker IF566V KBr and polyethylene medium for manganese complex. ^1H-NMR spectrum of the ligand was recorded in DMSO-d_6 solution on a Bruker 400 FT-NMR spectrophotometer. Thermal analyses were carried out in the temperature range 40-800^oC by heating in air at a rate of 10^0C 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 and calculations were made using computed values of Pascal's constant. The molar conductance of the complexes was determined in DMSO 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 vanadyl complex at room temperature and liquid nitrogen temperature were carried by using JES-FA 200 ESR spectrometer.

Synthesis of salicyloyl hydrazone ligand (LH_3) -

A hot ethanolic solution of salicyloyl hydrazide (1.52 g, 0.01mol) was added to an ethanolic solution of 2-hydroxy-5-methylacetophenone (2.84 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 by ethanol. The purity of the compounds was checked by thin layer chromatography (TLC). It was characterized by elemental analysis, IR, UV, ^1HNMR and mass spectra. Yield 85%, M. P. 210^0C.

^1H-NMR- δ12.86 (2H, S, Phenolic OH), δ11.53 (1H, S, imino NH), δ7.99 - δ6.99 (7H, M, Aromatic proton), δ2.3 (3H, S, methyl, Ar-CH_3), δ2.55 (3H, S, methyl, N=CCH_3) [9]. The schematic representation of synthesis of LH_3 is shown in reaction scheme 1.



Scheme-1: Synthesis of LH_3 ligand

Synthesis of Cr (III), Mn(III), Fe(III) and VO(IV) complexes-

Equimolar quantities (0.02M) of corresponding metal salt and the ligand were dissolved separately in ethanol and refluxed for about 6-8 h in water-bath. The solid products obtained on cooling were filtered off, washed several times by diethyl ether and dried at room temperature over $CaCl_2$.

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. The molar conductance values of 10^{-3} M solution of complexes lie in the range 14.8-24.5 $ohm^{-1}cm^2mol^{-1}$ indicating their non-electrolytic nature.

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

Compound	**Formula wt.**	**Colour**	**Found (Calc.) %**			
			C	**H**	**N**	**M**
$C_{16}H_{16}N_2O_3$	284.31	Yellow	67.50 (67.59)	5.71(5.78)	9.99 (9.85)	-
$[Cr(L)(H_2O)]_2$	702.59	Maroon	14.80 (14.95)	54.70 (54.45)	4.30 (4.13)	8.54 (8.66)
$[Mn(L)]_2$	672.45	Maroon	16.34 (16.68)	57.16 (57.14)	3.90 (4.04)	8.33 (8.47)
$[Fe(L)(H_2O)]_2$	710.29	Black	15.72 (15.83)	54.11 (54.25)	4.26 (4.22)	7.89 (7.77)
$[VO(L)]_2$	698.47	Black	14.59 (14.67)	55.03 (55.14)	4.04 (4.13)	8.02 (8.21)

Infrared spectra

IR group frequencies of diagnostic importance of ligand and its metal complexes are collected in Table 2.

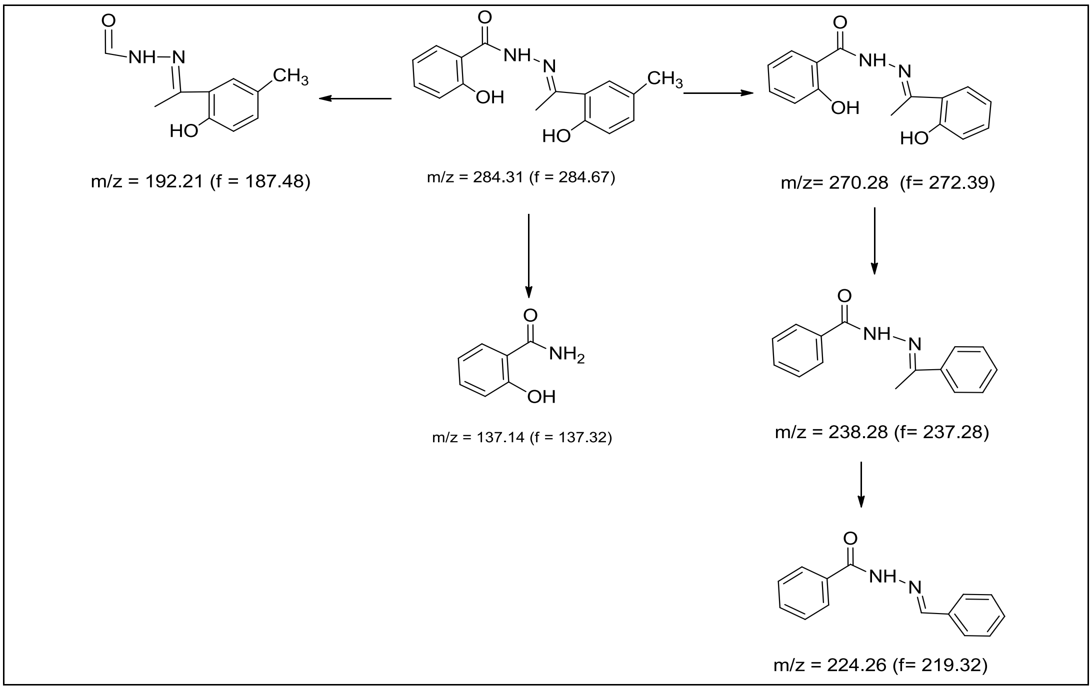
The IR spectrum of free ligand exhibits medium broad band in the region 3269 cm^{-1} due to intramolecular hydrogen bonded OH. This band is absent in the spectra of all the complexes indicating the deprotonation and coordination of the ligand with metal ion through oxygen atom [10-11]. The upward shift of υ(C-O) (phenolic) band at 1287 cm^{-1} of the ligand by 6-21 cm^{-1}and the appearance of a new band at 515-578 cm^{-1} in the spectra of all complexes further supports the involvement of phenolic oxygen in coordination with the metal ions [12]. Also, the increase in shift of the C-O (phenolic) frequency in Cr (III), Mn(III), Fe(III) and VO(IV) attributed to phenolic oxygen bridge formation [13]. The absorption peak for υ(C=N) at 1615 cm^{-1} and υ(N-N) at 975 cm^{-1} in the spectrum of ligand is shifted to a lower frequency by 14-29 cm^{-1}[10] and higher frequency by 5-20 cm^{-1}[14] respectively in the spectra of all the complexes indicating the involvement of azomethine nitrogen in coordination. This is in good agreement with the band observed in the far IR region 462-480 cm^{-1} due to the υ(M-N) stretch. The other bands at 3013 and 1650cm^{-1} in the spectrum of free ligand, assigned due to υ(N-H) and υ(C=O) respectively, disappeared in the spectra of Cr(III), Mn(III) and Fe(III) complexes indicating the destruction of carbonyl moiety and subsequent coordination of enolic oxygen via deprotonation to the metal ion [11]. It is further supported by a new band appearing in the region 1225-1256 cm^{-1} due to υ(C-O) (enolic) mode [11]. Thus, in Cr (III), Mn (III) and Fe(III) complexes the ligand functions in a tribasic tetradentate way bonding through O, O, N and O donor atoms. The positions of υ(N-H) and υ(C=O) bands in the spectrum of VO(IV) complex are almost at the same position as that in the spectrum of ligand suggest the non-involvement of amide oxygen in coordination with metal and the keto form of the coordinated ligand. This indicated the ligand functions as dibasic tridentate ONO donor in this complex. The additional band at 995 cm^{-1} in the is assigned to υ(V=O) mode [11]. The spectra of Cr(III) and Fe(III) complexes display four bands in the region 3393-3433υ(O-H), 1613 δ(H_2O), 813-833 ρ_r(H_2O), 750-756ρ_w(H_2O) suggesting the presence of coordinated water molecules in each of them.

Table-2: IR frequencies of ligand and its metal complexes (cm^{-1})

Compound	**υ(OH) (Hydrogen bonded)**	**υ(C–O) phenolic**	**υ(C=N)**	**υ(N-N)**	**υ(NH)**	**υ(C=O)**	**υ(C–O) enolic**	**M-O**	**M-N**	**H_2O**
LH_3	3269	1287	1615	975	3013	1650	-	-	-	-
[Cr(L)(H_2O)]$_2$	-	1304	1601	995	-	-	1256	578	462	3393, 1613, 813, 750
Mn(L)]$_2$	-	1305	1597	980	-	-	1225	578	465	-
[Fe(L)(H_2O)]$_2$	-	1308	1600	986	-	-	1239	560	488	3433, 1613, 833, 756
[VO(L)]$_2$	-	1303	1586	-	2958	1650	-	515	480	-

Mass Spectra

The mass spectrum of the ligand displays molecular ion peak [M]$^+$ at m/z 284.67; the other important peaks are appeared at 272.48, 237.28, 219.32, 187.18 and 137.32 correspond to fragment ion [$C_{15}H_{14}N_2O_2$]$^+$, [$C_{15}H_{14}N_2O$]$^+$, [$C_{14}H_{12}N_2O$]$^+$, [$C_{10}H_{12}N_2O_4$]$^+$ and [$C_7H_7NO_2$]$^+$. These observed m/z peaks were due to the loss of the fragments of different molecular weights from ligand as proposed in Scheme 2. The mass spectra of Cr(III), Mn(III), Fe(III) and VO(IV) complexes with molecular formula, [Cr(L)(H_2O)]$_2$ (F.W.,702.59), [Mn(L)]$_2$(F.W.,672.45), [Fe(L)(H_2O)]$_2$(F.W.,710.29), [VO(L)]$_2$ (F.W., 698.47) as representative showed the highest mass peak with m/e at 701.6, 673.2, 710 and 695.2 respectively which agree well with the formula weights of these complexes.



Scheme-2: Mass fragmentation pattern of ligand LH_3

Electronic spectra and magnetic moment

The electronic spectrum of $[Cr(L)(H_2O)]_2$ complex shows bands at 615, 481 and 290 nm corresponding to the transitions $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ respectively [11] which are characteristic of six coordinate octahedral geometry. The value of various ligand field parameters is found to be Dq = 1626 cm^{-1}, B = 432 cm^{-1}, β = 0.470 and % covalency = 53. 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 this complex. All these observations suggest that the metal-ligand bond in the complex is covalent in nature [15]. $[Mn(L)]_2$ complex shows bands at 735, 593, 495 and 369 nm. The band at 369 nm is due to charge transfer and the remaining three correspond to $^5B_1 \rightarrow {}^5B_2$, $^5B_1 \rightarrow {}^5A_1$, $^5B_1 \rightarrow {}^5E$ transitions, respectively, with a magnetic moment of 4.73 B.M. suggesting square pyramidal geometry around Mn(III) ion [13]. Fe(III) complex give rise to three absorption bands in octahedral field at 786, 544 and 447 nm corresponding to $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, $^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g}(S) \rightarrow {}^4E_g$, $^4A_{1g}(G)$ transitions. The subnormal magnetic moment 4.95 B.M. is as expected for dimer structure due to strong metal-metal interaction [16]. The electronic spectrum of $[VO(L)]_2$ shows bands at 721, 605, 431 and 343 nm may assign to $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$, $^2B_2 \rightarrow {}^2A_1$ and LMCT, respectively, which are well characteristics for square pyramidal geometry. The magnetic moment value (1.43 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 [17]. The magnetic moments and electronic spectral bands of the complexes are present in Table 3.

Table-3: Electronic spectral data of the complexes

Complex	**Absorption region (nm)**	**Band assignment**	**μ_{eff} B. M.**	**Λ_M $\Omega^{-1}cm^2mol^{-1}$**	**Geometry**
$[Cr(L)(H_2O)]_2$	615	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$	3.51	24.5	Octahedral
	481	$^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$			
	290	$^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$			
$[Mn(L)]_2$	735	$^5B_1 \rightarrow {}^5B_2$	4.73	14.8	Square pyramidal
	593	$^5B_1 \rightarrow {}^5A_1$			
	495	$^5B_1 \rightarrow {}^5E$			
	369	LMCT			
$[Fe(L)(H_2O)]_2$	786	$^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$	4.95	18.3	Octahedral
	544	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$			
	447	$^6A_{1g}(S) \rightarrow$ 4Eg, $^4A_{1g}(G)$			
$[VO(L)]_2$	721	$^2B_2 \rightarrow {}^2E$	1.43	22.6	Square pyramidal
	605	$^2B_2 \rightarrow {}^2B_1$			
	431	$^2B_2 \rightarrow {}^2A_1$			
	343	LMCT			

Thermal analysis

Thermal behaviour and decomposition pattern of the metal complexes was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves. Thermogravimetric studies of the ligand, Mn (III) and VO (IV) complexes showed that the complex decomposes in two stages whereas the Cr (III) and Fe (III) complexes decomposed in three stages. In the present investigation, no weight loss is observed in Mn (III) and VO (IV) complexes upon heating till ~300^{0}C, and thus ruling out the presence of lattice as well as coordinated water molecules. The corresponding peaks in their DTAs is observed at 355^{0}C, 515^{0}C and 680^{0}C (exothermic) for Mn(III) complex and at 315^{0}C, 430^{0}C and 515^{0}C (exothermic) for VO(IV) complex corresponds to partial and complete removal of ligand moiety in two steps. In Cr (III) and Fe(III) complexes, no weight loss is observed upto 160^{0}C corresponds to the absence of lattice water molecules. The further weight loss in the range 160-250^{0}C in Cr(III) and 180-260^{0}C in Fe(III) complex are attributable to removal of two coordinated water molecules (% weight loss obs./calcd.: Cr(III): 5.24/5.13); Fe(III): 5.11/5.07) respectively. The thermograms of Cr(III) and Fe(III) show exothermic peak at 190^{0}C and 205^{0}C which supports to the removal of two coordinated water molecules respectively. Further, the Cr(III) and Fe(III) complexes show rapid weight loss in the range 251-320^{0}C and 261-450^{0}C in support of DTA peak at 270^{0}C and 295^{0}C (exothermic) indicative of decomposition of free part of the coordinated ligand. A gradual weight loss above 330^{0}C and 460^{0}C was accompanied by degradation of coordinated part of ligand in Cr(III) and Fe(III) complex showing DTA peak at 380^{0}C, 485^{0}C (exothermic) and 498^{0}C, 510^{0}C, 600^{0}C (exothermic). Finally, horizontal curves are observed corresponding to the final pyrolysis product metal oxides. From TGA curve, thermo-kinetic parameters such as activation energy (Ea), order of reaction (n), entropy change (ΔS), free energy change (ΔF) and apparent entropy change (S*) have been calculated by using the Freeman-Carroll and Sharp-Wentworth methods and the results are given in Table 4. According to the half decomposition temperature the relative thermal stability found to be as Mn (III) > VO (IV) > Cr (III) > Fe(III) > LH_3.

Table-4: Thermoanalytical results of the compounds

Complex	**Half decomTemp. (^{0}C)**	**STEp**	**Decom. Temp. (^{0}C)**	**Ea (k/J)**		**(n)**	**-ΔS (J/mol/K)**	**ΔF (kJ/ mol)**	**S* (kJ)**	**DTA Peak Temp. (^{0}C)**
				FC*	**SW****					
LH_3	220^{0}C	I	105^{0}C-350^{0}C	10.77	10.99	0.95	-224.83	81.14	-32.60	105^{0}C, 190^{0}C
$[Cr(L)(H_2O)]_2$	350^{0}C	I	160^{0}C-250^{0}C	13.75	17.21	0.92	-285.92	103.24	-37.87	190^{0}C
		II	251^{0}C-320^{0}C	69.63	60.24		-324.18	170.82	-39.49	270^{0}C
		III	321^{0}C-515^{0}C	14.21	30.22		-314.12	112.52	-37.90	380^{0}C, 485^{0}C
$[Mn(L)]_2$	515^{0}C	I	295^{0}C-515^{0}C	5.30	17.23	0.90	-287.88	95.40	-33.06	355^{0}C, 515^{0}C
		II	516^{0}C-680^{0}C	69.46	60.68		-328.61	172.31	-35.63	680^{0}C
$[Fe(L)(H_2O)]_2$	340^{0}C	I	180^{0}C-260^{0}C	10.27	13.52	0.92	-271.17	95.14	-33.30	205^{0}C
		II	261^{0}C-450^{0}C	5.96	21.16		-310.66	103.19	-32.76	295^{0}C
		III	451^{0}C-600^{0}C	77.22	65.45		-317.45	176.58	-35.32	498^{0}C, 510^{0}C, 600^{0}C
$[VO(L)]_2$	421^{0}C	I	295^{0}C-370^{0}C	5.17	21.16	0.90	-332.78	109.33	-33.34	315^{0}C
		II	371^{0}C-470^{0}C	25.76	18.97		-312.76	123.65	-34.95	430^{0}C, 515^{0}C

ESR spectra

The ESR spectra of the VO (IV) complex were provide useful information of metal ion environment in complexes. The observed spectral parameter for VO(IV) complex is: $g_\perp = 2.0964$, $g_\parallel = 1.9987$ suggest that the resulting complex is covalent and characteristics of square pyramidal geometry. The vanadium complex shows well resolved axial anisotropy with $g_\parallel < g_\perp$a relationship characteristic of an axially compressed $(dxy)^1$ configuration. This indicates that the unpaired electron is present in d_{xy} orbital [18]. The ESR spectral parameters of the Cu (II) and VO (IV) complexes are listed in Table 5. The figure 1 (a to b) depicts the ESR spectrum of VO (IV) complex at RT and LNT.

Table-5: ESR spectral data of the VO (IV) complexes

Complexes	Spectral Parameters			
	$g_{\|}$	$g_{\perp}$	/g/	G
VO(IV)	1.9987	2.0964	2.0639	_

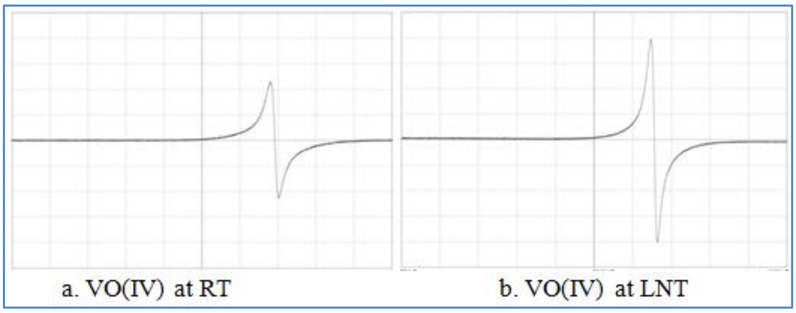
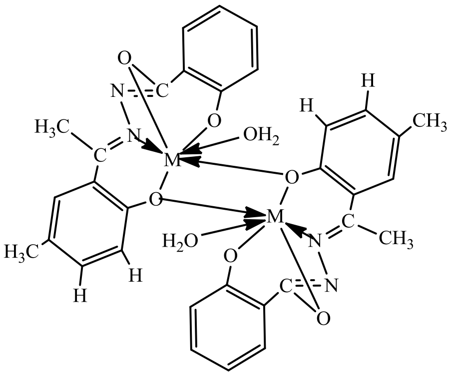

a. VO(IV) at RT
b. VO(IV) at LNT

Fig-1(a-b): ESR spectra of VO (IV) complex at RT and LNT

On the basis of the above spectroscopic, elemental analysis, molar conductance, magnetic moment and thermal analysis, the proposed structures of complexes are shown in Fig. 2.


M = Cr(III), Fe(III)

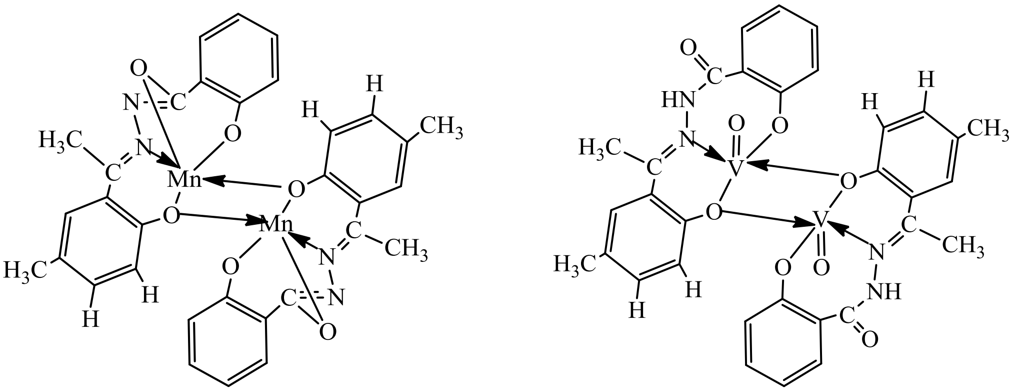


Fig-2: Suggested structures of the salicyloyl hydrazone complexes

Antimicrobial activity

Evaluation of antimicrobial activity of the ligand and all compounds were carried out against *Staphylococcus aureus, Streptococcus pneumoniae, Escherichia coli* and *Klebsiella pneumoniae*. It is observed that, the ligand is inactive against gram-positive as well as gram-negative bacteria. The Cr (III) and Mn(III) complexes exhibited moderate activities against all the bacteria with zone of inhibition in the range 13-18 mm (gram-positive) and 17-22 mm (gram-negative). The VO(IV) complex shows no activity against *S. aureus* and *S. pneumoniae* and moderate activity against gram-negative bacteria with zone of inhibition in the range 18-20 mm. The Fe(III) complex are active against gram-positive bacteria with zone of inhibition in the range 13-16 mm and show no activity towards gram-negative bacteria. From the % Activity data, it is observed that Mn(III) complex shows highest activity among all complexes towards all bacteria. The antimicrobial investigation data are summarized in the table6.

Table-6: Antimicrobial activity of ligand and its complexes

Ligand and its complexes	**Diameter of inhibition of zone (in mm)^a**				**% Activity index**			
	S. aureus	***S. pneumoniae***	***E. coli***	***K. Pneumoniae***	***S. aureus***	***S. pneumoniae***	***E. coli***	***K. Pneumoniae***
LH_3	-	-	-	-	-	-	-	-
Cr(III)	15	14	17	20	52	61	45	59
Mn(III)	17	15	18	22	59	65	47	58
Fe(III)	15	13	-	-	52	57	-	-
VO(IV)	-	-	18	20			47	59
DMSO	-	-	-	-	-	-	-	-
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								

CONCLUSION

Cr(III), Mn(III), Fe(III) and VO(IV) complexes of 2-hydroxy-5-methylacetophenone salicyloyl hydrazone have been synthesized and characterized on the basis of elemental analysis, infrared, electronic and electron spin resonance spectra, conductance and magnetic susceptibility at room temperature. Elemental analysis shows 1:1 metal-ligand stoichiometry. Infrared spectra suggest the tribasic tetradentate (ONOO) (enol form) donor towards Cr(III), Mn(III) and Fe(III) and dibasic tridentate (ONO) (keto form) donor towards VO(IV) complex. The complexes exhibit subnormal magnetic moments (μ_{eff} = 3.51, 4.73, 4.95, 1.43 B.M. respectively for Cr(III), Mn(III), Fe(III) and VO(IV) complexes) due to anti-ferromagnetic exchange. On the basis of magnetic and spectral data, dimeric octahedral (Cr(III), Fe(III)) and square pyramidal (Mn(III) and VO(IV)) structures are suggested. TG and DTA studies also guide to thermodynamic, kinetic and reactivity behaviour of compounds and metal-ligand interaction.

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