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Synthesis And Studies Of Mixed Ligand Complexes Of Mn(II) With Salicylaldehyde And Substituted Salicylaldehydes,2-Hydroxyarylcarbonyl Compounds Or β-Diketones

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ABSTRACT

Mixed ligand complexes of Mn(II) of the type $[MnLL'(H_2O)_2]$, *(where HL = salicylaldehyde and HL' = 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, 2-hydroxyacetophenone, 2-hydroxypropiophenone, 2-hydroxybenzophenone, pentane-2,4-dione, 1-phenylbutane-1,3-dione or 1,3-diphenylpropane-1,3-dione) have been synthesized by the reactions of manganese(II) acetate with a mixture of two different ligands in 1:1:1 molar ratios. The solid complexes were separated, filtered, washed with butanol and ether successively and dried under reduced pressure. The resulting complexes have been characterized by elemental analyses, molar conductances, magnetic moments, electronic spectra, IR spectra, FAB mass spectra and thermo gravimetric analysis. At the same time, above mentioned complexes were studied for in vitro antimicrobial properties and found to be more potent bactericides than parent ligands. Octahedral geometry has been proposed for the mixed ligand complexes.*

Keywords: Mixed ligand complexes, FAB mass spectra, octahedral geometry, thermo gravimetric analysis, antimicrobial properties.

INTRODUCTION

Interest in the chemistry of mixed ligand complexes has increased in recent decades, because of wide applications of these coordination complexes in various fields. Mixed ligand complexes appear in biological fluids, create specific structures and manifest themselves as enzyme-metal ion-substrate complexes[1, 2]. These are suitable precursors for the selective CVD of high purity metals[3,4] and have been used in the analysis of semiconductor materials. Many of the inorganic medicinal compounds are mixed ligand complexes[5].

Various oxidation states of manganese and the wide applications of its mixed ligand complexes in biological and industrial fields are gaining popularity in the chemistry nowadays. Tanaka[6] have been synthesized Bis-[5-(p-sulfophenylazo)salicylaldehyde] metal chelates (IV) of copper, nickel, cobalt and manganese. Rani et al.[7] prepared and characterized Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of a new multidentate oxygen nitrogen donor,bis(N-salicylidene)-2,3-dihydrazino-1,4-quinoxaline. A new chiral amino acid Schiff base ligand (Salarg) and its metal complex (Mn-Salarg) have been synthesized using L-Arginine, a naturally occurring chiral diamine with two kinds of asymmetric α-, ε-

NH_2 groups by Roy[8]. The complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with a potentially tridentate schiff base (formed by the condensation of 2-amino-3-carboxyethyl-4,5-dimethylthiophene with salicylaldehyde) have been synthesized and characterized by Daniel et al[9]. Niasari et al[10] have been prepared complexes of transition metals, Mn(II), Co(II), Ni(II) and Cu(II) with tetradentate schiff base ligand, N,N'-bis(salicylidene)phenulene-1,3-diamine. Mashaly and co-workers[11] have synthesized complexes of the transition metal ions Cu(II), Ni(II), Zn(II) with schiff base ligand 1,4-di (hydroxybenzylidene)thiosemicarbazide. Mixed ligand complexes with the general formula $[M(BT)(BI)_2X_2]$, [where BT=benzotriazole, BI=benzimidazole, X=SCN and M=Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Pd(II)] have been investigated by Shaker[12]. Earlier, mixed ligand complexes of Ni(II), Cu(II), Zn(II), Cr(II), Co(II) and alkaline earth metals with substituted salicylaldehyde have been reported from our laboratory[13-16].

MATERIALS AND METHODS

Materials: 5-Bromosalicylaldehyde (Aldrich),5-nitrosalicylaldehyde(Aldrich),2-hydroxybenzophenone (Aldrich),1-phenyl butane-1,3-dione(sisco-chem) and 1,3-diphenylpropane-1,3-dione (sisco-chem) were purified by recrystallisation from hot ethanol prior to use. Salicylaldehyde (Merck), 2-hydroxyacetophenone (John Baker), 2-hydroxypropiophenone (Fluka), pentane-2,4-dione(K. Light) and n-butanol were purified by distillation. $Mn(CH_3COO)_2.4H_2O$ (Fluka) A. R. was used as supplied.

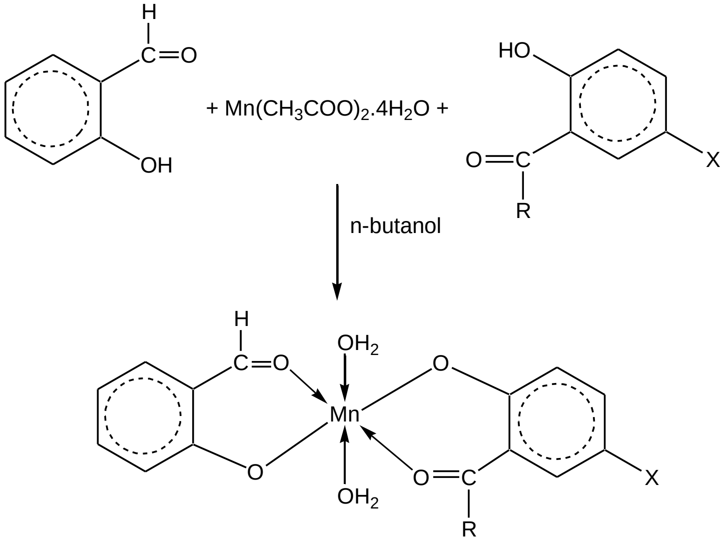
Analytical methods and physical measurements: Manganese was estimated volumetrically by EDTA using Eriochrome black-T as an indicator[17]. Nitrogen was determined by Kjeldahl's method. Carbon and hydrogen analyses were carried out on a Heraeus Carlo Erba 1108 instrument. Molar conductances were measured at room temperature in DMSO by a digital conductivity meter-NDC-736. Magnetic measurements were carried out using MSB MK1 Magnetic Susceptibility Balance, Sherwood Scientific. Electronic spectra were recorded in DMSO in the range of 200nm-800nm on a SYSTRONICS UV-VIS Spectrophotometer using distilled water as a reference. Infrared spectra of the complexes were recorded in the region 4000-400cm^{-1} on a SHIMADZU-JAPAN 8400S FTIR spectrophotometer using KBr pellets. The FAB mass spectra were recorded on a Jeol SX 102/DA-600 mass spectrometer/Data System using Argon/Xenon (6kV, 10mA) as the FAB gas. The accelerating voltage was 10kV and spectra were recorded at room temperature. m-Nitrobenzyl Alcohol (NBA) was used as the matrix. Thermogravimetric analysis were performed on Mettler Toledo star SW 701 instrument in the range 57.4-689^{o}C with the heating rate 10^{o}C per minute.

Antibacterial screening: The *in vitro* antibacterial activities of the ligands and metal complexes were tested by using Muller Hinton agar by well diffusion method[18] against a gram positive bacterial strain *Staphylococcus aureus* (ATCC 29213) and a gram negative bacterial strain *Escherichia coli* (ATCC 25922). The bacterial strains grown on nutrient agar at 37ºC for 18 hours were suspended in a saline solution (0.85% NaCl) and adjusted to a turbidity of 0.5 McFarland standards [10^8 colony forming units (CFU) ml^{-1}]. The suspension was used to inoculate 90 mm diameter Petri plates. Wells (6 mm diameter) were punched in the agar with the help of a sterile metallic borer and filled with 100 µl of the test extract of the concentration 5 mg mL^{-1}. The dissolution of the organic extracts (Methanol) was aided by DMSO which did not affect the growth of microorganisms, in accordance with our control experiments. Plates were incubated in air at 37ºC for 24 h. Antibacterial activities were evaluated by measuring diameters of the inhibition zone in millimeters carefully. DMSO was taken as control for the methanol extracts and ciprofloxacin (5mg) was used as a reference standard antibiotic drug.

Synthesis of Mixed Ligand Complexes of Manganese(II): To a solution of $Mn(CH_3COO)_2.4H_2O$ (6.12 mmol, 1.5g in ~10mL butanol), salicylaldehyde (6.12 mmol, 0.747g in ~25mL butanol) and 5-bromo salicylaldehyde (6.12 m mol, 1.23g in ~25mL butanol) were added with constant stirring. The reaction mixture was stirred for about 15-20 minutes. The pH of the solution was raised up to ~8.0 by drop wise addition of 5% aqueous solution of sodium hydroxide with constant stirring. The reaction mixture was stirred for 5-6 hours. The reaction mixture was kept in the refrigerator for about 30-35 days. The settled solid was filtered, washed with butanol and later with ether to remove stickiness and dried properly under reduced pressure. A similar method was adopted to synthesize mixed ligand complexes of Mn(II) with salicylaldehyde and 5-nitrosalicylaldehyde, 2-hydroxyacetophenone, 2-hydroxypropiophenone,2-hydroxy benzophenone, pentane-2,4-dione, 1-phenylbutane-1,3-dione or 1,3-diphenylpropane-1,3-dione.

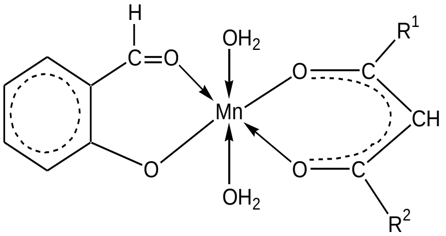
RESULTS AND DISCUSSION

The reactions of manganese (II) acetate tetrahydrate with salicylaldehyde and 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, 2-hydroxyacetophenone, 2-hydroxypropiophenone or 2-hydroxybenzophenone in 1:1:1 molar ratios result in the formation of mixed ligand complexes of manganese ,scheme 1. Similarly, the other mixed ligand complexes were synthesized with salicylaldehyde and β-diketones as scheme 2**.**



Where R= -H, X= -Br ; R= -H, X= -NO$_2$; R= -CH$_3$, X= -H ; R= -C$_2$H$_5$, X= -H ; R= -C$_6$H$_5$, X= -H

Scheme 1: Synthesis of mixed ligand complexes of Manganese(II) with sal and 5-Brsal, 5-NO$_2$sal, hap, hpp or hbp



Where R^1 = -CH$_3$, R^2 = -CH$_3$; R^1 = -CH$_3$, R^2 = -C$_6$H$_5$; R^1 = -C$_6$H$_5$, R^2 = -C$_6$H$_5$

Scheme 2: Mixed ligand complexes of Manganese(II) with sal and β-diketones

Table 1 . Characterization data for the mixed ligand complexes of Mn(II) Complex

S. No.	Complex Molecular Formula Molecular Weight	Color Yield (%)	Decomposition temperature (^{o}C)	Found (Calculated) %			
				Mn	C	H	N
1.	[Mn(sal)(5-Brsal)(H_2O)$_2$] $C_{14}H_{13}O_6$MnBr, 411.900	Dark-brown (44.95)	198	13.19 (13.34)	39.66 (40.79)	2.94 (3.18)	-
2.	[Mn(sal)5-NO_2sal)(H_2 O)$_2$ $C_{14}H_{13}O_8$MnN, 377.983	Yellow (45.75)	260	13.64 (14.53)	43.42 (44.45)	3.21 (3.47)	3.502 (3.71)
3.	[Mn(sal)(hap)(H_2O)$_2$] $C_{15}H_{16}O_6$Mn, 347.225	Light-brown (49.24)	156	15.26 (15.82)	49.89 (51.88)	4.22 (4.64)	-
4.	[Mn(sal)(hpp)(H_2O)$_2$] $C_{16}H_{18}O_6$Mn, 361.038	Brown (31.87)	230	14.81 (15.21)	52.26 (53.18)	4.97 (5.02)	-
5.	[Mn(sal)(hbp)(H_2O)$_2$] $C_{20}H_{18}O_6$Mn, 409.042	Dark-brown (43.88)	246	13.13 (13.43)	57.91 (58.68)	4.21 (4.43)	-
6.	[Mn(sal)(acac)(H_2O)$_2$] $C_{14}H_{19}O_8$Mn, 370.234	Brown (44.79)	168	14.32 (14.73)	53.85 (54.69)	4.69 (4.86)	-
7.	[Mn(sal)(bzac)(H_2O)$_2$] $C_{17}H_{18}O_6$Mn, 373.039	Dirty-yellow (63.17)	260	12.36 (12.63)	60.25 (60.68)	4.48 (4.63)	-
8.	[Mn(sal)(dbzm)(H_2O)$_2$] $C_{22}H_{20}O_6$Mn, 435.060	Brown (65.44)	206	14.13 (14.34)	58.79 (58.97)	3.72 (3.96)	-

The resulting mixed ligand complexes are obtained in 44-65% yields as brown solid except [Mn(sal) (5-NO_2 sal)(H_2O)$_2$], which is yellow in color. The data of C, H, N and Mn analyses agree well with the calculated values corresponding to the respective complexes. The complexes decompose at high temperature on heating. All the physical data are shown in table 1. These are insoluble in water or most of the organic solvents like methanol, benzene and carbon tetrachloride but soluble in DMSO and DMF.

Molar conductances*:* Molar conductances (Λ_m) of 10^{-3} solutions of the complexes in DMSO (table 2) lie in very low range 4.8-18.8 $\Omega^{-1}cm^2mol^{-1}$ supporting their non-electrolytic behaviour[19] .

Magnetic moments*:* The μ_{eff} values for the complexes are observed (table 2) in the range 5.60 to 6.01 B.M. as expected for five unpaired electrons. These values indicate that the complexes are high spin paramagnetic; it lies within the octahedral range which is very close to spin value 5.90 B.M. as the ground term is $^6A_{1g}$ and thus supports the octahedral geometry[20]. Siddappa *et al*.[13] have reported Mn(II) high spin complex having an octahedral geometry with 5.65 B.M. magnetic moment.

Table 2. Molar Conductance & Magnetic moments of mixed ligand complexes of Mn(II)

Complex no.	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$)	μ_{eff} (B.M.)
1	16.9	5.72
2	18.8	5.73
3	5.7	5.61
4	4.8	5.71
5	15.4	5.98
6	10.9	5.60
7	11.0	5.73
8	15.6	6.01

Electronic spectra*:* Spectrum of[Mn(sal)(5-Brsal)$(H_2O)_2$] has been recorded in figure 1.

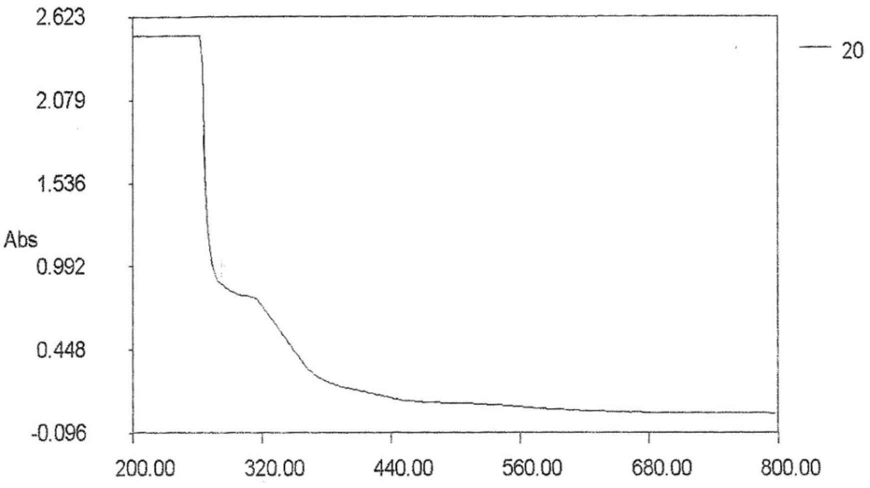


Figure 1: Electronic spectrum of [Mn(sal)(5-Brsal)$(H_2O)_2$]

The absorption bands are observed at 295nm (33898cm^{-1}), 320nm (31250cm^{-1}) and 394nm (25400cm^{-1}) corresponding to $^6A_{1g}\rightarrow{}^4E_g(G)$ (v_3), $^6A_{1g}\rightarrow{}^4T_{2g}(G)$ (v_2) and $^6A_{1g}\rightarrow{}^4T_{1g}(G)$ (v_1) transitions respectively. Deshmukh et al.[22] have observed three bands at 15125, 24032 and 23225cm^{-1} in case of d^5 Fe(III) complex belong to $^6A_{1g}\rightarrow{}^4T_{1g}$, $^6A_{1g}\rightarrow{}^4T_{2g}$ and $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}$ transitions respectively indicating octahedral geometry. Vashi et al.[23] have reported absorption bands at 15856, 18755, 24548cm^{-1} corresponding to $^6A_{1g}\rightarrow{}^4T_{1g}(G)$, $^6A_{1g}\rightarrow{}^4T_{2g}(G)$ and $^6A_{1g}\rightarrow{}^4E_g$, $^4T_{1g}(G)$ electronic transitions respectively for Mn(II) high spin octahedral complexes. v_2/v_1 ratio is 1.230 for the complex. The Racah Parameter (B') for the complexes is 736.8cm^{-1}, is less than free ion value (B=860cm^{-1}) suggesting a considerable orbital overlap and delocalization of electrons on the metal ion. The nephelauxetic ratio (β) for the complex is less than one (0.857), suggesting partial covalency in the metal ligand bond. All these values suggest the high spin octahedral geometry around the metal ion and are in accordance with the reported values in literature[24].

Infra red spectra*:* Attempts have been made to identify some important bands which furnish information regarding the mode of binding. IR spectra of [Mn(sal)(5-Brsal)$(H_2O)_2$] and [Mn(sal)(dbzm)$(H_2O)_2$] have been recorded in figures 2 and 3 respectively. In free salicylaldehyde, 5-bromosalicylaldehyde, 2-hydroxyaceto phenone, 2-hydroxypropiophenone, 2-hydroxybenzophenone, acetylacetone, benzoylacetone and dibenzoyl - methane bands at 1680, 1670, 1660, 1650, 1640, 1724, 1724 and 1806cm^{-1} respectively have been reported due to *ν*(C=O)[25,26], whereas metal complexes show strong absorption bands in the region 1650-1600cm^{-1} may be assigned to coordinated ν(C=O) bond. Such a shifting of ν(C=O) to lower wave number suggest the coordination of C=O group of the ligand to the metal ion. Bands in the region 1560-1540cm^{-1} may be attributed to ν(C=C).

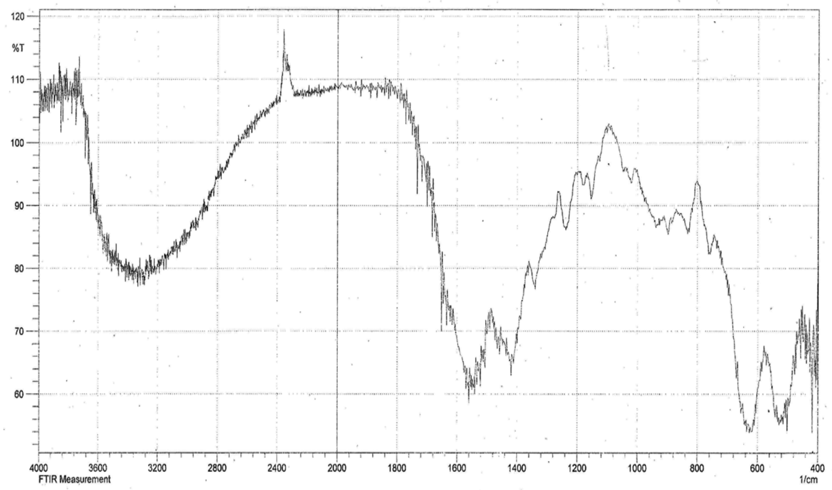


Figure 2: IR spectrum of [Mn(sal)(5-Brsal)(H_2O)$_2$]

Similar bands have been observed in the mixed ligand complexes of Co(II) with 5- nitrosalicylaldehyde and β-diketones, hydroxyaryl aldehydes or ketones in the region of 1664-1604 and 1556-1512cm^{-1} for ν(C=O) and ν(C=C) respectively by Prasad et al[27]. Absorption bands in the region 1475-1420cm^{-1} may be assigned to *ν*(C-O).

A broad band in the region 3400-3175cm^{-1} observed in the spectra of the complexes suggests the presence of coordinated water molecule. A similar broad band has been assigned to coordinated water molecule in the region 3519-3373cm^{-1} by Gudasi et al[19]. The ν(M-O) bond formation in the complexes have been confirmed by the presence of absorption bands at 475-420cm^{-1}, which are not seen in free ligands. Bands have been observed in the region (454cm^{-1}) for the confirmation of similar bond by Wahed et al[28].

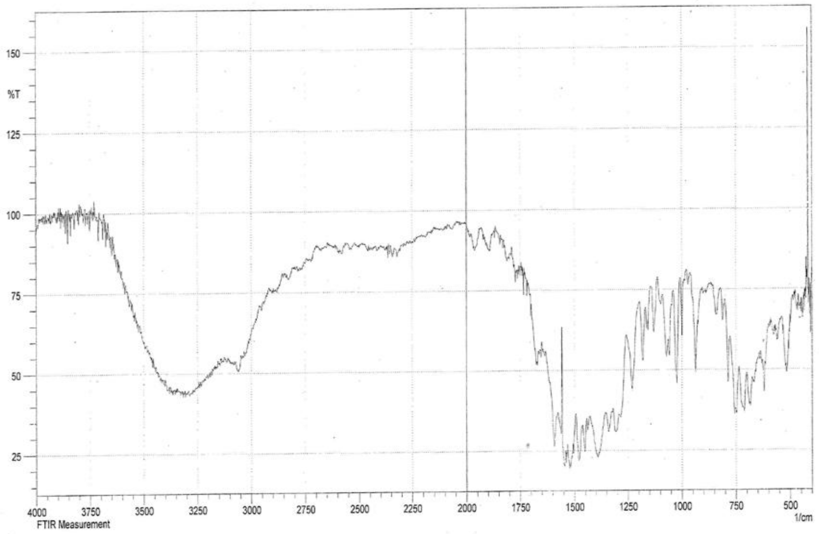
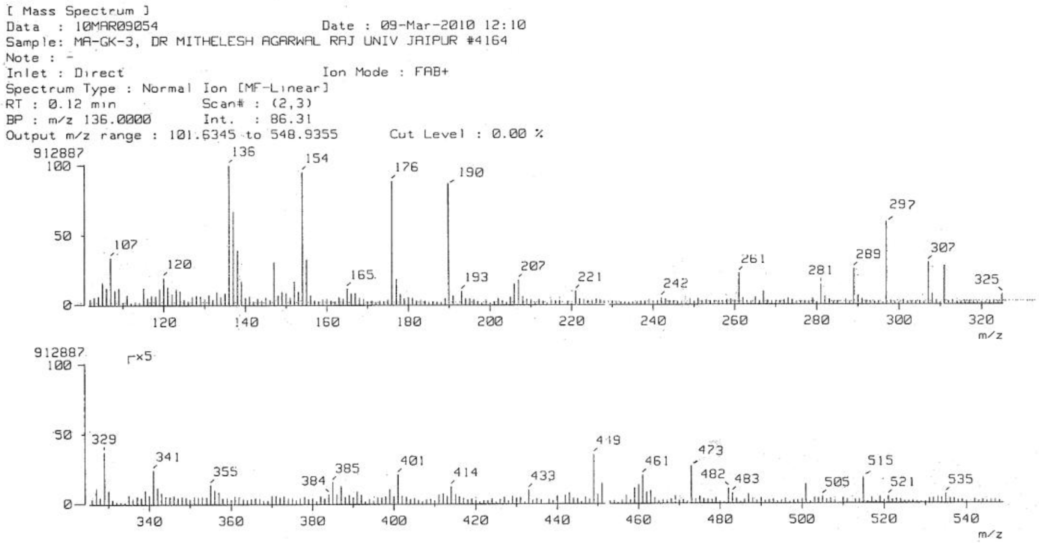


Figure 3: IR spectrum of [Mn(sal)(dbzm)(H_2O)$_2$]

Fast atom bombardment mass spectra*:* The FAB mass spectra of two complexes [Mn(sal)(hap)] I, [Mn(sal)(dbzm)] II have been reproduced in figure 4 and 5. The *m/z* values of the peaks along with their intensities relative to the base peak are given in table 3. Peaks at *m/z* 136, 137, 154, 289, 307 are due to NBA matrix in the absence of any metal ions. Complex I and II show base peak at *m/z* 136 and *m/z* 154 respectively**.** Both complexes exhibit molecular ion $[M]^+$ peak (I *m/z* 311, 27.78%, II *m/z* 399, 13.89%). Peak due to specie $[MnL'O]^+$ is observed at *m/z* 206(13.89%) and 294(63.89%) in complex I and II respectively. In addition, peaks are also observed due to the formation of MnL^+ and MnL'^+ species, which are formed as a result of the loss of one or the other ligand moiety. A very intense peak can be seen for the complexes at *m/z* 176 due to MnL^+ specie (I 88.89%, II 91.67%). The peaks corresponding to MnL'^+, which would have resulted by the loss of salicylaldehyde moiety are observed, e.g. in complex I, at *m/z* 190(86.11%) due to $Mn(hap^+)$ and in complex II, at *m/z* 278(52.78%) due to $Mn(dbzm)^+$. On comparing the intensities of $Mn(hap)^+$ and $Mn(sal)^+$ ions suggests that $Mn(sal)^+$ is more stable than $Mn(hap)^+$ which may be due to the more planarity of the chelate ring in $Mn(sal)^+$ ion as compared to $Mn(hap)^+$, in which the methyl group disturbs the planarity of the chelate ring. Thus the loss of 2-hydroxyacetophenone moiety is more favorable and hence it may be concluded that salicylaldehyde is more strongly bounded to the manganese atom than 2-hydroxyacetophenone ligand[29]. Peaks corresponding to symmetrical bis-complexes MnL_2 and MnL'_2 are also observed as a result of the redistribution reactions:



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[ Mass Spectrum ]
Data   : 10MAR09054                    Date : 09-Mar-2010 12:10
Sample: MA-GK-3, DR MITHELESH AGARWAL RAJ UNIV JAIPUR #4164
Note : -
Inlet : Direct                         Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.12 min          Scan# : (2,3)
BP : m/z 136.0000      Int.  : 86.31
Output m/z range : 101.6345 to 548.9355      Cut Level : 0.00 %
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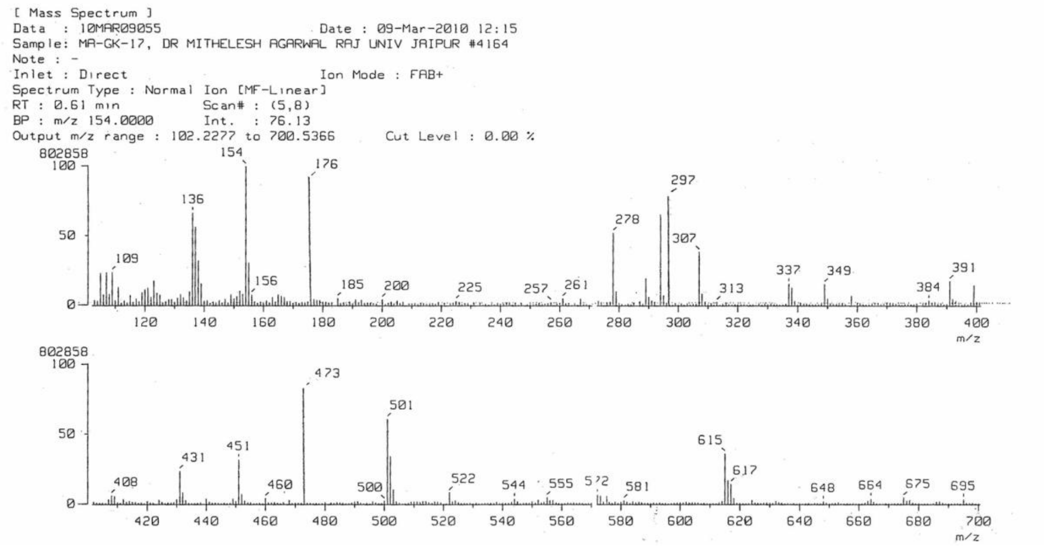
Figure 4: FAB mass spectrum of $[Mn(sal)(hap)(H_2O)_2]$

$$MnLL' \xrightarrow{-L'} MnL^+$$

$$MnLL' \xrightarrow{-L} MnL'^+$$

$$2MnLL' \rightleftharpoons MnL_2 + MnL'_2$$

For example, peaks are observed due to $Mn(hap)_2^+$ at *m/z* 325(5.56%) in complex I and due to $Mn(dbzm)_2^+$ at *m/z* 501(61.11%) in complex II, whereas peak due to $Mn(sal)_2^+$ is noticed at *m/z* 297(I 58.33%, II 77.78%) in both of the complexes .



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[ Mass Spectrum ]
Data   : 10MAR09055                         Date : 09-Mar-2010 12:15
Sample: MA-GK-17, DR MITHELESH AGARWAL RAJ UNIV JAIPUR #4164
Note : -
Inlet : Direct                              Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.61 min          Scan# : (5,8)
BP : m/z 154.0000      Int.   : 76.13
Output m/z range : 102.2277 to 700.5366      Cut Level : 0.00 %
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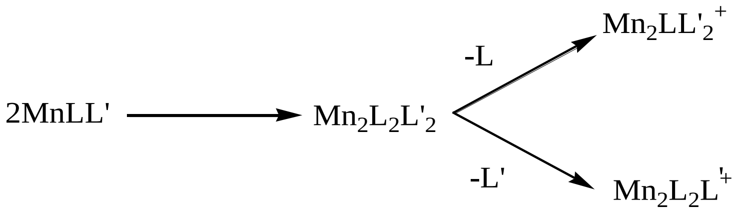
Figure 5 . FAB mass spectrum of $[Mn(sal)(dbzm)(H_2O)_2]$

Table 3 . Mass spectral data of mixed ligand complexes of Mn(II) (*m/z* values and relative abundance)*m/z* (relative abundance %)

Ions	**$[Mn(sal)(hap)]^+$** **I**	**$[Mn(sal)(dbzm)]^+$** **II**
M^+	311 (27.78 %)	399 (13.89%)
$[MnL'O]^+$	206 (13.89 %)	294 (63.89 %)
MnL^+	176 (88.89 %)	176 (91.67 %)
MnL'^+	190 (86.11 %)	278 (52.78 %)
MnL_2^+	297 (58.33 %)	297 (77.78 %)
MnL'_2^+	325 (5.56 %)	501 (61.11 %)
$Mn_2L_3^+$	473 (26.39 %)	473 (83.33 %)
$Mn_2L'_3^+$	515 (18.06 %)	–
$[Mn_2L_2L']^+$	487 (5.56 %)	575 (5.56 %)
$[Mn_2LL'_2]^+$	501 (13.89 %)	677 (2.78 %)

HL = salicylaldehyde, HL' = 2-hydroxyacetophenone (hapH) or dibenzoylmethane (dbzmH). All the fragments have been denoted as positive ions irrespective of whether they are odd or even electron species.

Peaks due to ions formally derived from the oligomeric species such as $Mn_2L_3^+$ and $Mn_2L'_3^+$ are also observed. Both the complexes exhibit a peak at *m/z* 473 (I 26.39%, II 83.33%) due to specie $Mn_2(sal)_3^+$. The complex I shows a peak at *m/z* 515(18.06%) corresponding to $Mn_2(hap)_3^+$. The spectra of both of the complexes exhibit peaks due to $[Mn_2LL'_2]^+$ and $[Mn_2L_2L']^+$ ions, which might have been formed by the loss of either of the two ligand moieties from the dimeric species.



Peaks of low intensities are seen at m/z 487(5.56%) due to dimeric specie $[Mn_2(sal)_2(hap)]^+$ and at *m/z* 501(13.89%) due to $[Mn_2(sal)(hap)_2]^+$ specie in complex I and at *m/z* 575(5.56%) and 677(2.78%) due to $[Mn_2(sal)_2(dbzm)]^+$ and $[Mn_2(sal)(dbzm)_2]^+$ species respectively in II. Thus, the mass spectral studies confirm the proposed structures and formulae of the complexes.

Thin Layer Chromatography*:* TLC of all the synthesized mixed ligand complexes were performed on silica gel G using chloroform petroleum ether (1:1) as a mobile phase and the retention times were compared to those of the corresponding bis-complexes. The result shown in table 4 indicates that these complexes are mixed ligand complexes rather than a mixture of the two corresponding bis-complexes.

Table 4.R_f data for the some bis & mixed ligand Complexes of Mn(II)

S.No.	**complexes**	**R_f values**
1	$[Mn(sal)_2(H_2O)_2]$	0.51
2	$[Mn(hap)_2(H_2O)_2]$	0.55
3	$[Mn(sal)(hap)(H_2O)_2]$	0.53
4	$[Mn(hpp)_2(H_2O)_2]$	0.57
5	$[Mn(sal)(hpp)(H_2O)_2]$	0.55
6	$[Mn(acac)_2(H_2O)_2]$	0.61
7	$[Mn(sal)(acac)(H_2O)_2]$	0.56
8	$[Mn(bzac)_2(H_2O)_2]$	0.54
9	$[Mn(sal)(bzac)(H_2O)_2]$	0.52

Thermo gravimetric analysis*:* It seemed of interest to evaluate the effect of heating on the thermal stability of the prepared complexes. The TG curve has been recorded for the mixed ligand complex $[Mn(sal)(dbzm)(H_2O)_2]$. The weight loss with temperature is shown in the table 5 . The results showed that the complex was thermally decomposed in three successive decomposition steps within the temperature range 140-689°C. The first decomposition step (obs. = 8.42%, cal. = 8.27%) within the temperature range 140-280°C, is reasonably accounted for the removal of two coordination water molecules, which confirms the presence of two coordinated water molecules in the metal complex. El-Wahed et al[28] have also reported the loss of coordinated water molecules in the temperature range 150-300°C in a sulfasalazine manganese(II) complex of the type $[Mn(SuzH)(H_2O)_4].2H_2O$.

Table 5. Thermal data of $[Mn^{II}(sal)(dbzm)(H_2O)_2]$

Complex	**Steps**	**Temp. range (°C)**	**TG weight loss (%)**		**Assignments (Mass)**
			Cal.	**Obs.**	
$[Mn(sal)(dbzm)(H_2O)_2]$	1 2 3	140-280 280-400 400-689	8.27 37.93 37.48	8.42 37.87 36.82	2 H_2O(36) sal+CO_2(165.027) Rest of dbzm leaving MnO (cal.=16.32%, obs.=16.83%)

The second step is found between the temperature range 280-400°C (obs. = 37.87%, cal. = 37.93%), may be attributed to the liberation of salicylaldehyde ligand moiety and one molecule of CO_2, suggesting the decomposition of the dibenzoylmethane ligand. The decomposition of the rest of the complex molecule ended with a final oxide of MnO in the third step within the temperature range 400-689°C (obs. = 16.83%, cal. = 16.32%).

APPLICATIONS

Antibacterial screening*:* Two of the ligands namely salicylaldehyde and 2-hydroxyacetophenone and one of the synthesized mixed ligand complex [Mn(sal)(hap)(H_2O)$_2$] were screened against the bacterial strains. The antimicrobial screening data shows (table 6) that salicylaldehyde and the metal complex exhibit antimicrobial properties against both bacterial strains, whereas 2-hydroxyacetophenone does not show activity against both the strains.

It is important to note that the metal chelate exhibits more inhibitory effects towards both of the bacteria than the parent ligands. Similar results have been previously reported by Jain et al.[30] for some Mn(II) complexes derived from different sulpha drugs and heterocyclic ketones. Neelakantan and co-workers[31] have also reported the similar observations for mixed ligand complexes of the type ML'B, ML_2'' and M_2L'', (where M(II)= Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), HL'= o-vanillidene-2-aminobenzothiazole, B= phen and HL''= o-vanillidene-2-amino-N-(2-pyridyl)-benzene sulfonamide). From table 6, it is clear that the zone of inhibition is much larger for metal complexes against both bacterial strains than the parent ligands. Moreover, the complex is much powerful bactericides against *Staphylococcus aureus* rather than *Escherichia coli.*

The increased activities of the metal chelate as compared to ligands can be explained on the basis of chelation theory. According to chelation theory[32], chelation tends to make the ligand act as more powerful and potent bactericidal agents, thus killing more of the bacteria than the ligand. It is observed that in a complex, the positive charge of the metal is partially shared with the donor atoms present in the ligands, and there may be π-electron delocalization over the whole chelating ring.

Table 6 .Antibacterial activities of the ligands and manganese metal complexes

S. No.	Test compound	***E. Coli*** **Test zone of inhibition (mm)**	***S. Aureus*** **Test zone of inhibition (mm)**
1	Salicylaldehyde (sal)	33	32
2	2-hydroxyacetophenone (hap)	No activity	No activity
3	[Mn(sal)(hap)(H_2O)$_2$]	35.6	36
4	Ciprofloxacin	31	31

This increases the lipophilic character of the metal chelate and favors its permeation through the lipoid layer of the bacterial membranes and blocks the metal bonding sites on the enzymes of micro-organism. These complexes also disturb the respiratory processes of the cell and thus block the synthesis of protein, which restricts further growth of the organism. There are other factors which also increase the activity, which are solubility, conductivity, and bond length between the metal and the ligand. Moreover,

Tweedy's[33] overtone's concept of cell permeability is also important in this contrast. According to this concept, the lipid membrane that surrounds the cell, favors the passage of only lipid-soluble material, due to which liposolubility is also an important factor that controls the antibacterial activity of the compound.
Interestingly, it has been also observed from the study of antibacterial zone of inhibition data that the complex is much potent bactericide than the standard control ciprofloxacin against *Staphylococcus aureus* and *Escherichia coli*. Similar results have been reported by Chordia and Chaturvedi[34] for mixed ligand complexes of diorganotin(IV) of the type [PhCOCHCOPh] R_2Sn-[SSH(S)POR'], (where R = Me, Bu, Ph; R' = Me,Et,Pr^i,Bu^i, Ph).

CONCLUSIONS

In the light of the above discussion, an octahedral geometry for Mn(II) complexes are proposed. All the complexes are non-electrolyte and high spin paramagnetic in nature. Magnetic moments and electronic spectra confirm an octahedral geometry of the complexes. IR spectra and thermo gravimetric analysis support the presence of coordinated water molecules in the complexes. Mass spectral study further confirms the proposed structure of the complexes. The complexes are biologically active and exhibit enhanced antibacterial activities as compared to their parent ligands, hence further study of these complexes could lead to interesting results.

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