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Synthesis And Spectral Studies of Mixed Ligand Complexes of Mn(III) With 2-Hydroxypropiophone And Substituted Salicylaldehyde or β -Diketones

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ABSTRACT

A series of mixed ligand complexes of Mn (III) having the general formula [MnL_2L'] (where HL= 2-hydroxypropiphenone and HL' = 5-bromosalicylaldehyde, 5-chlorosalicylaldehyde, pentane-2,4- dione, 1-phenylbutane-1,3-dione, or 1,3-diphenylpropane-1,3-dione) have been synthesized by the reactions of Mn(III) acetate with a mixture of two different ligands. The resulting complexes have been characterized by elemental analyses, molar conductance, magnetic moments, IR, FAB mass spectra and antibacterial activities. Octahedral geometry has been proposed for the prepared mixed ligand complexes.

Keywords: Mixed ligand complexes, Mn (III), IR Spectra, conductivity, magnetic moments and FAB mass spectra.

INTRODUCTION

In the last decade, special interest has been devoted to Mn-complexes[1-4] as they do not lead to Fenton chemistry that induces pro-oxidant effects by the production of the reactive hydroxyl radical. Indeed, to date, a large variety of Mn-derivatives have been reported for their ability to react with superoxide in non-cellular conditions (labeled herein as in vitro), either as a true SOD mimic with catalytic activity or as a stoichiometric scavenger[5,6]. Recently, some differences have been evidenced between intrinsic SOD mimic Mn-complexes' activities evaluated in vitro, and there in cellular in vivo efficiency, that were assigned to a differential cell-location[7]. Manganese is required in living systems to perform diverse redox functions including water splitting by photosynthetic enzymes[8-11]. Coordination compounds of manganese involve in several enzymes that participate in the chemistry of reactive oxygen species, such as Mn catalase[12], Mn superoxidase dismutase[13], Mn ribonucleotide reductase[14], the oxygen evolving complex (OEC)[15,16], or, in particular the Mn peroxidase that protects cells against hydrogen peroxide induced. The presence of transition metals in human blood plasma indicates their importance in the mechanism for accumulation, storage and transport of transition metals in living organisms[17-19]. Few novel mixed ligand complexes of Mn(III) of general formula $[Mn(\beta\text{-diketone})_2X]_2(en)$; β-diketones are acetylacetone, benzoylacetone, dibenzoylmethane; X = NCS^-, N_3^-, Cl^-, Br^- and en = ethylenediamine have been synthesised[20]. Gorkum *et al*[21] have been synthesized Mn(III) complexes of the formula [Mn(papy)(acac)] (H_2papy = N-(2-hydroxybenzyl)-N-(2-picolyl)-glycine; Hacac = acetylacetone). The mixed ligand mononuclear complex $[Mn(bipy)(HPMFP)(OAc)]ClO_4$ was synthesized by reaction of

$Mn(OAc)_3 \cdot 2H_2O$ with HPMFP and 2,2'-bipyridyl. The corresponding Schiff base complexes were prepared by condensation of $[Mn(bipy)(HPMFP)(OAc)]ClO_4$ with ethylenediamine, ethanolamine and glycine (where HPMFP= 1-phenyl-3methyl-4-formyl-2-pyrazolin-5one, bipy=2,2'-bipyridyl)[22]. The complex $[Mn(dbm)_2(py)_2](ClO)_4]$ (where dbm = anion of 1,3-diphenyl-1,3-propanedione (dibenzoylmethane), py = pyridine) was synthesized and characterized by Aromi et al [23].

Keeping in view the importance of Mn (III) complexes, we have undertaken the systematic study of the preparation and characterization of Mn (III) complexes with 2-hydroxypropiophone and substituted salicylaldehyde or β-diketones during the present investigations.

MATERIALS AND METHODS

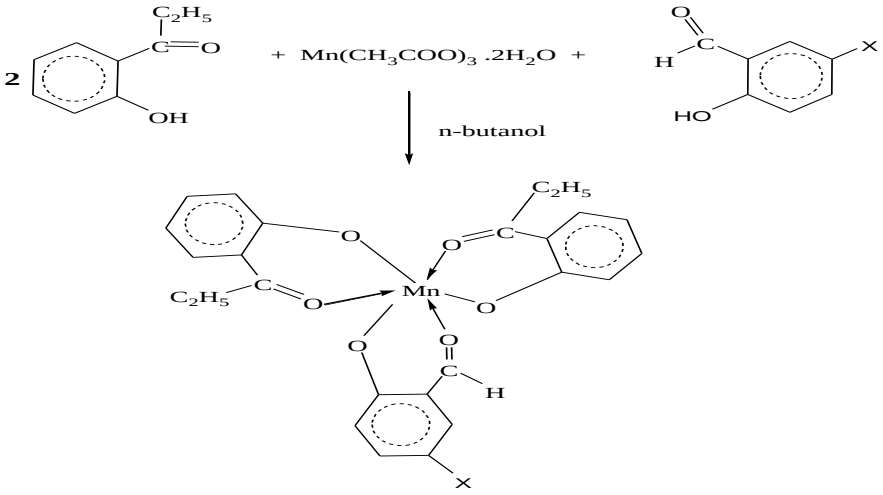
Chemicals: 1,3-Diphenylpropane-1,3-dione (sisco-chem.), 1-phenylbutane-1,3-dione (fluka), 5-chlorosalicylaldehyde (Lancaster) and 5-bromosalicyladehyde (Aldrich) were purified by re-crystallization from ethanol, 2-hydroxyacetophenone (John Baker), 2-hydroxypropiophenone (fluka) and butanol were purified by distillation before use. Mn $(CH_3COO)_3$. $2H_2O$ (Aldrich) was used of AR grade as supplied.

Analytical methods and physical measurements: Manganese was estimated volumetrically by EDTA using Eriochrome Black-T as an indicator. Carbon and hydrogen analyses were carried out on a Heraeus Carlo Erba 1108 instrument. Molar conductances were measured at room temperature in DMF by a systronic direct reading 304-conductivity meter using a glass cell having a cell constant of 1.0 cm^{-1}. Magnetic measurements were carried out at room temperature (~300k) on a Gouy balance using $Hg[Co(NCS)_4]$ as a calibrant. IR spectra of the complexes (KBr) were recorded in the region 400-4000 cm^{-1} on a Nicolet magna 550 FTIR spectrophotometer. The FAB mass spectra were recorded on JEOL SX 102/DA-6000 mass spectrometer/Data system using Argon/xenon (6 KV, 10mA) as the FAB gas. 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).

Synthesis of mixed ligand complexes of Mangnese (III): Take butanolic solution of Manganese (III) acetate (0.539 gm in 20 ml butanol) and stirred about 5 minutes. The color of the solution was dark brown. Then added 2-hydroxypropiophenone (0.603 gm in 15 ml butanol) and 5-chlorosalicylaldehyde (0.310 gm in 15 ml butanol) with continuous stirring at room temperature. A clear solution was obtained; the pH of the reaction mixture was raised to ~8.5 by adding 5% NaOH solution drop wise with constant stirring. The pH was measured with the help of a pH paper and stirring was continued for another 4-5 hrs. The solid complex was filtered, washed with butanol successively and dried under reduced pressure.

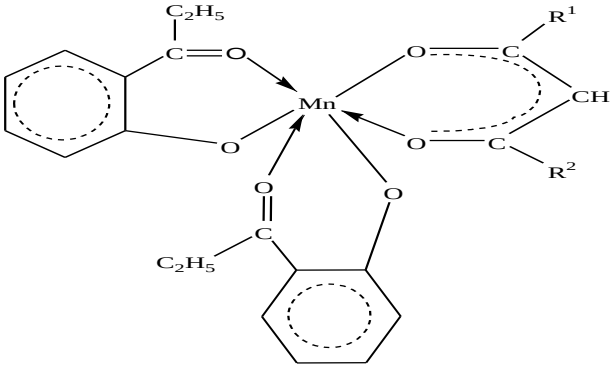
RESULTS AND DISCUSSION

Mixed ligand complexes of Mn (III) have been synthesized by the reactions of Manganese (III) acetate with 2-hydroxypropiophenone and 5-bromosalicylaldehyde or 5-chlorosalicyldehyde in 1:2:1 molar ratios result in the formation of mixed ligand complexes (**Scheme 1**).



Scheme 1: Synthesis of mixed ligand complexes of Mn (III) (X = Br, Cl)

The mixed ligand complexes with 2-hydroxypropiophenone and β-diketones such as acetylacetone, benzoylacetone or dibenzoylmethane have been synthesized by the similar procedure (**Scheme 2**).



R^1	R^2
$-CH_3$	$-CH_3$
$-CH_3$	$-C_6H_5$
$-C_6H_5$	$-C_6H_5$

Scheme 2: Mixed ligand complexes of Mn (III)

The resulting Mn (III) complexes are dark brown solids. They do not melt on heating but decomposed at high temperature. They are insoluble in chloroform, carbon tetrachloride, benzene and methanol but soluble in DMSO and DMF. The properties and analyses of the complexes are recorded (**Table 1)**.

Table 1. Analysis and characteristics of mixed ligand complexes of $[Mn^{III}(hpp)_2L]$

S. No	Complexes Molecular formula, Mol. Wt.	Colour and Decomposition temp. (°C)	Yield (%)	Analysis % Found (Calcd.)		
				C	H	Mn
1.	$[Mn(2\text{-hpp})_2(5\text{-Brsal})]$ $C_{25}H_{22}O_6BrMn$ 553.2873	Dark brown 220	32	54.12 (54.27)	3.67 (4.00)	9.61 (9.92)

2.	$[Mn(2\text{-}hpp)_2(5\text{-}Clsal)]$ $C_{25}H_{22}O_6ClMn$ 508.836	Dark brown 218	27	58.98 (59.01)	3.88 (4.35)	10.82 (10.79)
3.	$[Mn(2\text{-}hpp)_2(2\text{-}hap)]$ $C_{26}H_{25}O_6Mn$ 488.418	Dark brown 225	37	63.70 (63.93)	4.87 (5.15)	11.21 (11.24)
4.	$[Mn(2\text{-}hpp)_2(acac)]$ $C_{23}H_{25}O_6Mn$ 452.382	Dark brown 208	24	59.78 (61.06)	5.72 (5.56)	12.48 (12.14)
5.	$[Mn(2\text{-}hpp)_2(bzac)]$ $C_{28}H_{27}O_6Mn$ 514.4561	Dark brown 212	25	65.01 (65.37)	5.01 (5.28)	10.61 (10.67)
6.	$[Mn(2\text{-}hpp)_2(dbzm)]$ $C_{33}H_{29}O_6Mn$ 576.5274	Dark brown 215	43	68.53 (68.75)	4.89 (5.06)	9.49 (9.52)

Conductivity Measurement : The molar conductance of the complexes determined at concentration of $1x10^{-3}$ M at room temperature in DMSO are very low ranging 13-26 Mho $Cm^2.mol^{-1}$ showing their non electrolytic nature (**Table 2).**

Table 2. Magnetic moments, molar conductances and absorption bands (Cm^-) in the IR Spectra of mixed ligand complexes of Mn(III)

S. No.	**Complexes**	**Magnetic moment (B.M.)**	**Molar conductance $\Omega^{-1}cm^2mol^{-1}$**	**IR Bands**		
				C=C	**C=O**	**M-O**
1.	$[Mn(2\text{-}hpp)_2(5\text{-}Brsal)]$	5.13	26	1437-1550	1620-1850	455-590
2.	$[Mn(2\text{-}hpp)_2(5\text{-}Clsal)]$	4.31	24	1517-1546	1610-1650	497-528
3.	$[Mn(2\text{-}hpp)_2(2\text{-}hap)]$	4.12	13	1540-1555	1600-1680	420-510
4.	$[Mn(2\text{-}hpp)_2(acac)]$	4.93	17	1520-1610	1620-1724	413-580
5.	$[Mn(2\text{-}hpp)_2(bzac)]$	4.82	19	1497-1580	1610-11724	412-567
6.	$[Mn(2\text{-}hpp)_2(dbzm)]$	5.16	16	1514-1542	1610-1806	497-557

Magnetic moment: The μ_{eff} values for the complexes are observed in the range 4.12-5.16 B.M (**Table 2**) as expected for four unpaired electrons. These values indicate that the complexes are high spin paramagnetic. Cakic *et al[*24] have reported magnetic moment for the complexes of the type $[Mn(C_5H_7O_2)_2L]$ {where L= -OCO-CH-COOH} in the range of 4.76-4.9 B.M. This corresponds to four unpaired electrons typical of the d^4 system. It is supported that in the mixed ligand complexes the ligand have localized π-bonds and do not favour the electron pairing. The John-Teller effect, due to unequal filling up to t_2g and eg orbitals, gives a distorted octahedral geometry in complexes. Magnetic moment value of the Mn(III) salen complexes have been reported in the range 4.5-5.3 B.M. by Kurahashi, T. and Fujii, H[26]. Which represent the presence of four unpaired electrons in Mn(III) complexes.

IR Spectra: The mixed ligand complexes exhibit strong absorption band in the region 1626-1806 cm^{-1} which may be assigned to the coordinated υ(C=O) whereas in free 5-chlorosalicylaldeyde, 5bromosalicylaldehyde, 2-hydroxyacetophenone, 2-hydroxypropiophenone, acetylacetone, benzoylacetone and dibenzoylmethane bands at 1626, 1650, 1680, 1640, 1724, 1724, 1806 cm^{-1} respectively have been reported due to υ(C=O). Thus the shifting of υ(C=O) to lower wave number side in the mixed ligand

complexes supports the chelation of these ligands to the metal atom. Cakic[24] and co-workers have reported similar bands due to υ(C=O) at 1651 cm^{-1} in $[Mn(C_5H_7O_2)_2L]$ (where L=hydroxylaminmaleate). Band in the region 1514-1595 cm^{-1} in the mixed ligand complexes may be due to υ(C=C). In the spectra of the mixed ligand complexes ,weak to medium, intensity absorption bands in the region 412-590 cm^{-1} which are not presented in the free ligands, may be attributed to υ(Mn=O) vibrations. Similar bands in the region have been assigned to υ(M-O) vibrations in case of metal β-diketonates by Nakamato *et al[*25]. The bands at 417, 482, 613, 654, 689 cm^{-1}, assigned to Mn-O vibrations. A broad bond appears at 2598-2764 cm^{-1}, which may be attributed to C-H* str **(Table 2, Fig 1 &2)**

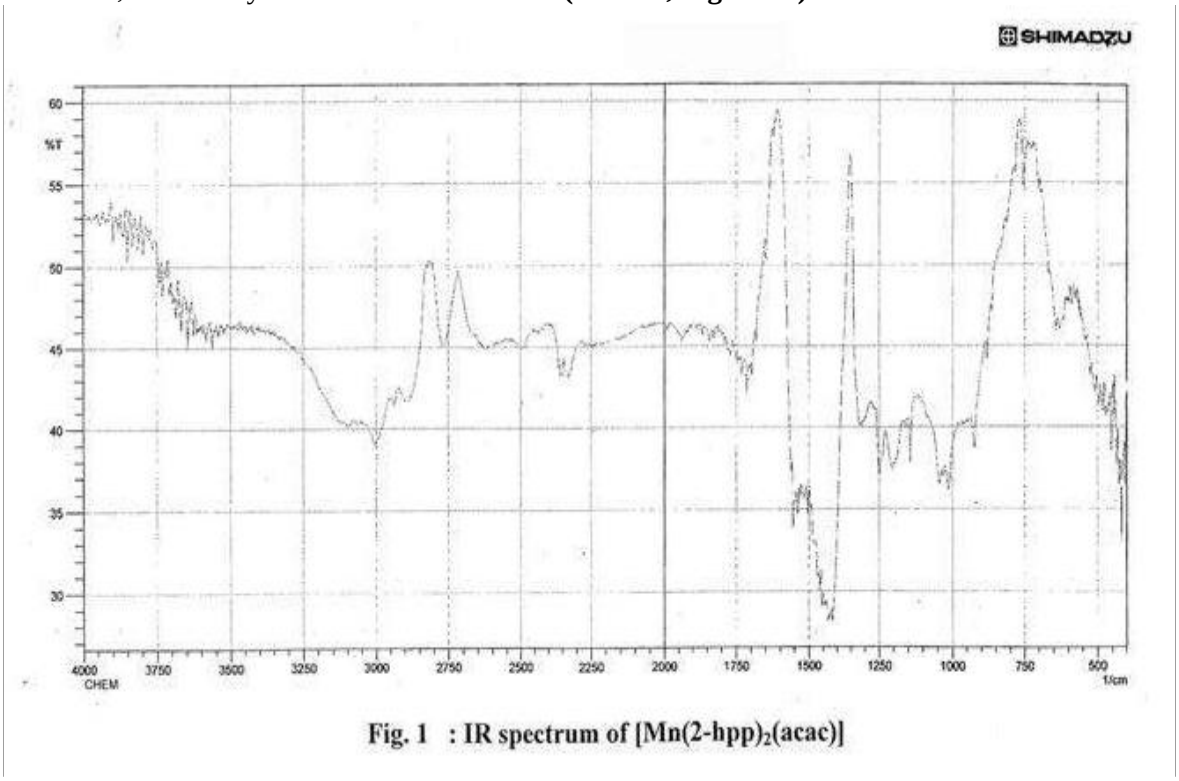


Fig. 1 : IR spectrum of $[Mn(2\text{-}hpp)_2(acac)]$

FAB Mass Spectra: FAB mass spectra of two complexes $[Mn(2\text{-}hpp)_2(2\text{-}hap)]$ (I) and $[Mn(2\text{-}hpp)_2(dbzm)]$ (II) have been recorded and the spectra of both complexes are reproduced in **Fig. 3** and **Fig. 4.** The m/z values of the peaks along with their intensities relative to the base peak are given in **Table 3**. Both the complexes exhibit molecular ion (M^+) peaks, $[Mn(2\text{-}hpp)_2(2\text{-}hap)]^+$ (m/z 488, 26.31%), $[Mn(2\text{-}hpp)_2(dbzm)]^+$ (m/z 576, 5.26%). In both complexes peaks due to MnL_2^+ and MnL'^+ are also observed due to the formation of such species as a result of the loss of the other ligand moiety.

$$MnL_2L'^+ \rightleftharpoons MnL_2^+ + L'$$

$$MnL_2L'^+ + L' \rightleftharpoons MnL'^+_2 + L_2$$

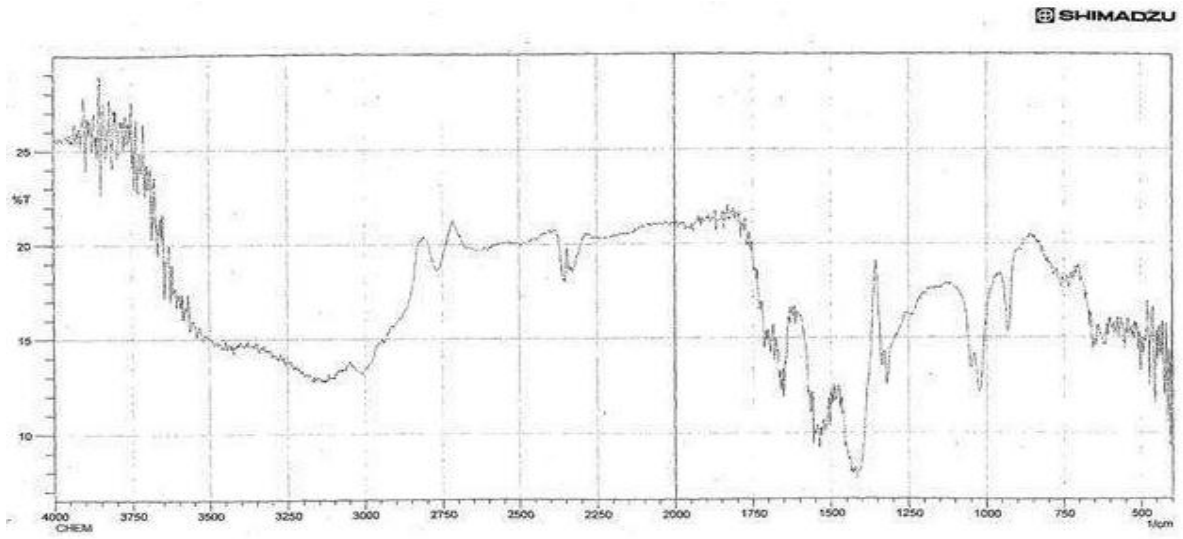


Fig. 2 : IR spectrum of [Mn(2-hpp)$_2$(5-Brsal)]

The peak is observed at m/z 353 due to the species $[Mn(2\text{-hpp})_2]^+$ which is formed by the loss of other ligand moiety (L') from the molecular ion (M^+) in the complexes I and II. Quite intense peak is observed at m/z 325(47.36%) due to formation of $[Mn(2\text{-hap})_2]^+$ in complex I whereas in complex II base peak is observed at 501(100%) due to $[Mn\ (dbzm)_2]^+$ species. Further loss of 2-hpp moiety from $[Mn(2\text{-hpp})_2]^+$ gives $[Mn(2\text{-hpp})]^+$ which exhibits strong peak at m/z 204 (42.10%) in complex (I), while less intens peak at 204 (5.26%) is observed in complex II. Removal of 2-hydroxypropiophenone moiety from the molecular ion (M^+) results in the formation of MnL' which exhibits quite intense peaks in complex (I) (m/z 190, 21.05%) and II (m/z 278, 52.6%). The formation of such species can be explained as follows:

$$MnL_2L'^{+} \xrightarrow{-L} MnLL'^{+} \xrightarrow{-L} MnL'^{+}$$

$$Mn(2\text{-hpp})_2L'^{+} \xrightarrow{-2\text{-hpp}} Mn(2\text{-hpp})L'^{+} \xrightarrow{-2\text{-hpp}} MnL'^{+}$$

Both complexes exhibit less abundant peaks due to dimeric species $[Mn_2L_2L_2']^+$. Thus in complex I , peak at m/z 678 (15.78%) due to $[Mn_2(2\text{-hpp})_2(2\text{-hap})_2]^+$, in complex II peak at m/z 854 (15.78%) due to $[Mn_2(2\text{-hpp})_2(dbzm)_2]^+$ are observed. The spectra of both 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.

$$Mn_2L_2L'_2{+} \xrightarrow{-L'} Mn_2L_2L'^{+}$$

$$Mn_2L_2L'_2{+} \xrightarrow{-L} Mn_2LL_2'^{+}$$

The peaks due to such polymeric ions are observed; in complex I, quite intense peak at m/z 529 (42.10%) due to $[Mn_2(2\text{-hpp})(2\text{-hap})_2]^+$, however in complex II, less intense peak at m/z 705 (2.63%) due to $[Mn_2(2\text{-hpp})(dbzm)_2]^+$. Similarly peak at m/z 543(15.78%) due to $[Mn_2(2\text{-hpp})_2(2\text{-hap})]^+$, and at m/z 631(2.63%) due to $[Mn_2(2\text{-hpp})(dbzm)_2]^+$ are shows in complex I and II respectively. Both complexes exhibit the peaks at m/z 55 (I 15.78%, II 2.63%) due to $[Mn(2\text{-hpp})_3]^+$. Similarly, complex I exhibit peak at m/z 405 (21.05%) due to $[Mn(2\text{-hap})_3]^+$, and complex II at m/z 779(31.57%) due to $[Mn(dbzm)_3]^+$ species. Appearance of peaks due to these $Mn_2L_3^+$ and $Mn_2L'_3^+$ ions can be explained with the help of the following reactions.

$$MnL_2^+ + MnL^+ \rightleftharpoons Mn_2L_3^+$$

$$MnL'^{+}_{2} + MnL'^{+} \rightleftharpoons Mn_2L'^{+}_{3}$$

Table 3. Mass spectral data of mixed ligand complexes of Mn(III) (M/z values and relative abundances)

Ions	$[Mn_2(2\text{-hpp})(2\text{-hap})_2]^+$	$[Mn_2(2\text{-hpp})_2(2\text{-dbzm})]^+$
$MnL_2L'^+$	488(26.31%)	576(5.26%)
MnL^+	204(42.10%)	204(2.26%)
MnL'^+	190(21.05%)	278(52.6%)
MnL_2^+	353(36.84%)	353(5.26%)
$MnL_2'^+$	325(47.36%)	501(100%)
MnL_3^+	502(21.05%)	502(63.15%)
$MnL_3'^+$	460(26.31%)	724(68.42%)
$Mn_2L_3^+$	557(15.78%)	557(2.26%)
$Mn_2L'^+_3$	515(21.05%)	779(31.57%)
$MnL_2L_2'^+$	678(15.78%)	854(1`5.78%)
$Mn_2L_2L'^+$	543(15.78%)	631(2.63%)
$Mn_2LL_2'^+$	529(42.10%)	705(5.26%)
$Mn_2L_3L'^+$	692(26.31%)	835(31.57%)
Mn_2L_3'-CO	487(6.13%)	-
Mn_2L_2L'-CO	-	603(5.12%)
Mn_2L_2L'-CH_3	528(4.27%)	-
Mn_2L_2L'-$H_2C_2O_2$	-	573(2.13%)

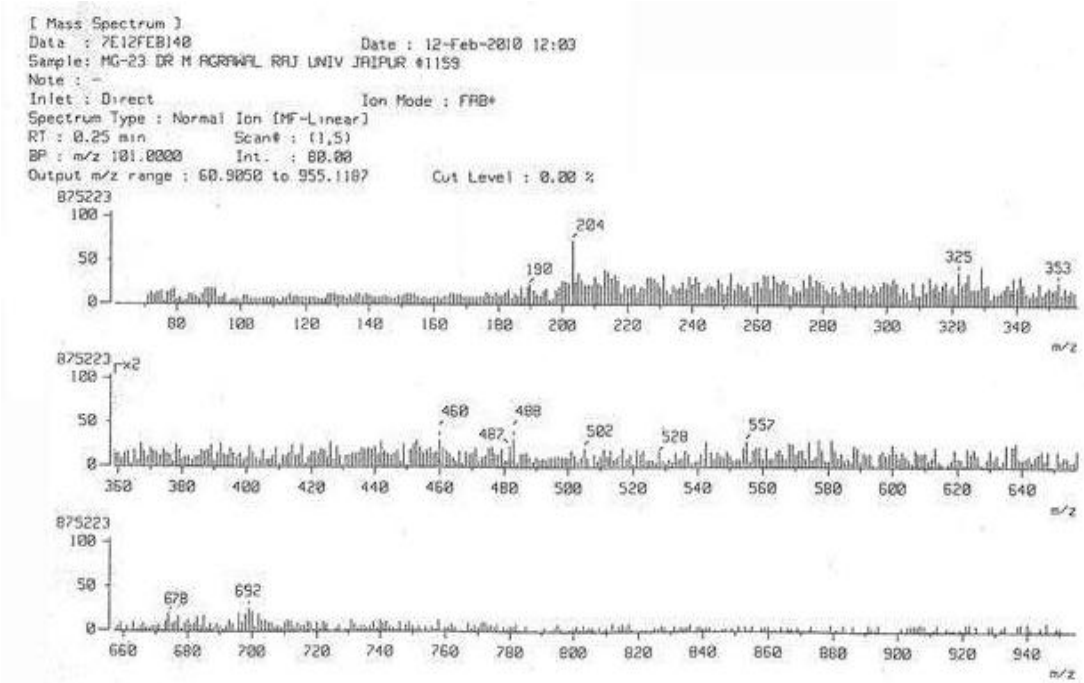


Fig. 3 : FAB mass spectrum of $[Mn(2\text{-hpp})_2(2\text{-hap})]$

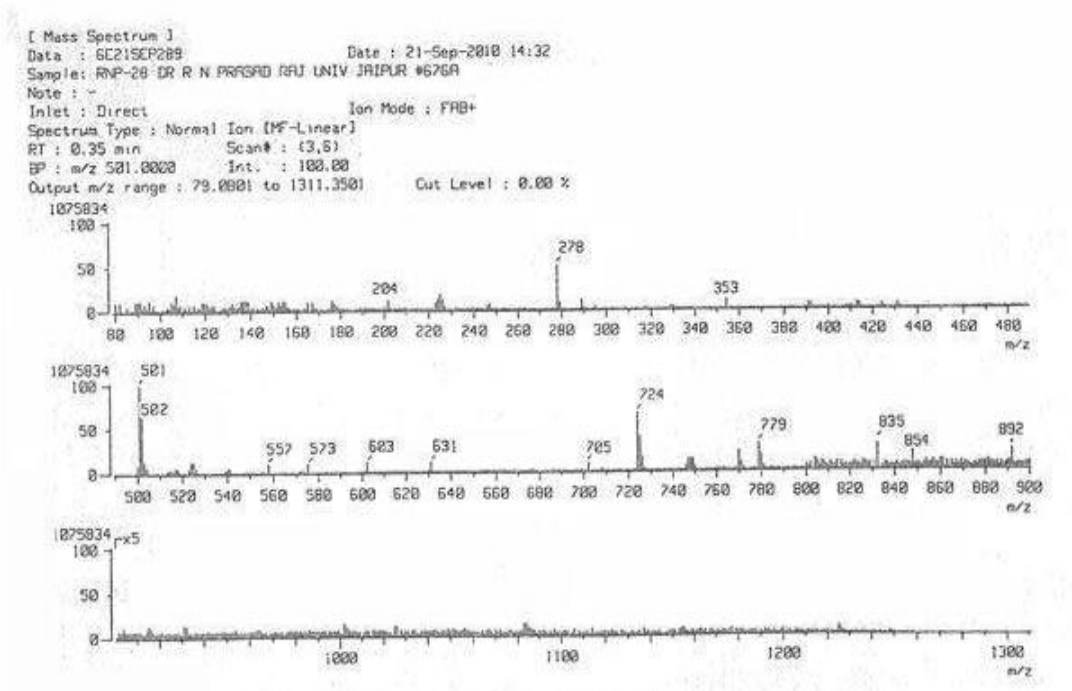


Fig. 4 : FAB mass spectrum of [Mn(2-hpp)$_2$(dbzm)]

APPLICATIONS

Antibacterial screening: Two of the ligands namely 2-hydroxypropiophenone and 2-hydroxyacetophenone and one of the synthesized mixed ligand complex [Mn(hpp)$_2$(hap)(H$_2$O)$_2$] were screened against the bacterial strains. The antimicrobial screening data shows (**Table 4**) that the metal complex exhibit antimicrobial properties against both bacterial strains, whereas 2-hydroxypropiophenone and 2-hydroxyacetophenone do 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. From **Table 4**, 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[27], 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. This increases the lypophilic 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, solubility, conductivity, and bond length between the metal and the ligand. Moreover, Tweedy's[28] 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 lyposolubility 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[29] 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). M.Agrawal et al also find similar results for mixed ligand complexes of manganese with salicylaldehyde and 2-hydroxyacetophenone [30]

Table 4 - 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	2-hydroxypropiophenone (hpp)	No activity	No activity
2	2-hydroxyacetophenone (hap)	No activity	No activity
3	$[Mn(hpp)_2(hap)(H_2O)_2]$	35.6	36
4	Ciprofloxacin	31	31

CONCLUSIONS

In the light of the above discussion, an octahedral geometry for Mn (III) complexes is proposed. All the complexes are non-electrolyte and high spin paramagnetic in nature. In the IR spectra of the complexes, shifting of ν(C=O) to lower wave number side supports the chelation of the ligand to the metal atom and also support the absence 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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