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Synthesis, Characterization and Antimicrobial Activities of Mixed Ligand Complexes of Mn(II) and Mn(III) With 5-Chlorosalicylaldehyde and 2-Hydroxyaryl Carbonyl Compounds or β-Diketones

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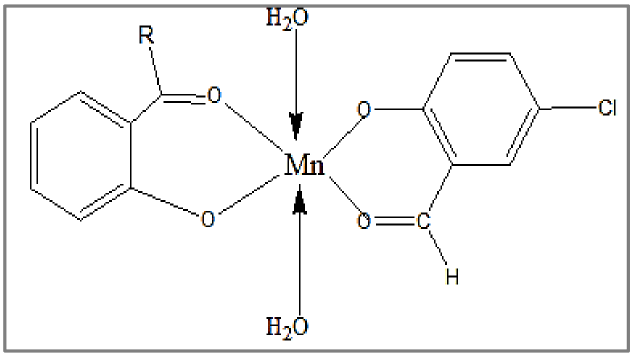
ABSTRACT

Mixed ligand complexes of Mn(II) of the type $[Mn(L)(L')(H_2O)_2]$ *and Mn(III) of the type* $[Mn(L')(L)_2]$, *(HL=5-chlorosalicylaldehyde) and (HL=2-hydroxyacetophenone, 2-hydroxypropiophenone, 2-hydroxy- benzophenone, pentane-2,4-dione, 1-phenylbutane-1,3-dione or 1,3-diphenylpropane-1,3-dione) have been synthesized by the reaction of Manganese(II) acetate and Manganese(III) acetate with a mixture of two different ligands in 1:1:1 and 1:1:2 molar ratios. Physicochemical and spectroscopic methods were used to determine mode of bonding and coordination geometry of newly synthesized mixed ligands complexes of Mn(II) and Mn(III). The electrical conductance studies of the complexes in DMSO (dimethyl sulfoxide) in* 10^{-3}*M concentration indicate their non-electrolytic nature. Magnetic susceptibility measurements revealed paramagnetic nature of the complexes at room temperature. Biological activity of ligands and metal complexes was performed against gram positive bacterial strain Staphylococcus aureus and gram negative bacteria Escherichia coli.*

Graphical Abstract



R= CH_3, C_2H_5, C_6H_5

Mixed lignd complexes of Mn(II) with5-chlorosalicylaldehyde and hap, hpp or hbp.

Keywords: Mixed ligand complexes, Manganese(II) and Manganese(III) complexes, FAB Mass, Antibacterial activities.

INTRODUCTION

Such a rapid progress in the field of coordination chemistry in a short span of time has it origin in the wide applicability in various fields of chemical science, Industry, Biology and analytical chemistry. The coordination chemistry of transition metal has attached the attention of many workers primarily because of their biological importance [1-3].

It is well known fact the activity of drugs is increased when used in the form of metal complexes. Cancer formation and its inhibition both involved chelating, the study of various transition metal complexes as modal for understanding various biochemical process requiring metal atom is very much interesting [4, 5]. Metal complexes play a vital role in metabolic and toxicological function in the biological system. The use of metal complexes as anticancer drug, antimicrobial and antiviral agent and in the treatment of arthritic and inflammation has attracted considerable attention in recent years. Tris complexes [6] $[Mn(acac)_3]$, $[Mn(C_2O_4)_3]$ and few mixed ligand complexes of manganese of the type $[Mn\{PhP(C_2H_4S\text{-}2)_2\}_2]$, $[Mn(mesalim)_2Cl]$ have also been reported [7, 8].

The ability of transition metals to exist in various oxidation states makes them more important industrial and biological catalysts. Goal of the present research proposal is to synthesize and compare the mixed ligand complexes of the metal Mn(II) and Mn(III). Manganese has various oxidation states. The most common oxidation states of Mn are +2, +3, +4, +6 and +7, but +2 oxidation state is the more stable. The +3 oxidation state is known in compounds like manganese(III) acetate, but these are quite powerful oxidizing agents and also prone to disproportionate in solution, forming Mn(II) and Mn(IV).The oxidation of Mn(II) to Mn(III) and Mn(IV) is largely catalyzed by microorganisms (bacteria and fungi) [9]. G. W. Luther [10] has reported work on “Mn(II) Oxidation and Mn(IV) Reduction in the Environment-Two One-Electron Transfer Steps Versus a Single Two-Electron Step”.

A lot of mixed ligand complexes have been synthesized and studied. M. Agrawal *et al.*, [11] synthesized the Fe(III) complexes with β-diketones, hydroxyarylketones and salicylaldehyde with general formula $[Fe(L)_2L']$. These complexes are screened for their bacteriological properties against a gram negative bacterial strain *Escherichia coli* (MTCC 443) and a gram positive bacterial strain *Staphylococcus aureus* (MTCC 96).

In this present work we deal with the compare study of mixed ligand complexes of Mn(III) and Mn(II) with various ligands.

MATERIALS AND METHODS

Materials: 5-chlorosalicylaldehyde (Merck), 5-Bromosalicylaldehyde (Aldrich), 5 nitrosalicylaldehyde (Aldrich), 1-phenylbutane-1,3-dione (sisco-chem), 2-hydroxy-1-naphthaldehyde (Merck) and 1,3-diphenylpropane-1,3-dione (Sisco-chem) were purified by recrystallization from butanol prior to use. Salicylaldehyde (Merck), 2-hydroxyacetophenone (Merck), Pentane-2,4-dione (JohnBaker) and butanol were purified by distillation. Manganese (II) and (III) acetate A.R. was used 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 CarloErba 1108 instrument. Molar conductances were measured at room temperature in DMSO by a Chino make digital conductivity meter (model no-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. Infrared spectra of the complexes were recorded in the region 4000-400cm^{-1} on a SHIMADZU-JAPAN8400S FTIR spectrophotometer using KBr pellets. The FAB mass spectra were recorded on a Jeol SX102/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.

Antibacterial screening: The in vitro antibacterial activities of the ligands and metal complexes were tested by using Muller Hinton agar by well diffusion method against a gram negative bacterial strain *Escherichia coli* (MTCC 443) and a gram positive bacterial strain *Staphylococcus aureus* (MTCC 96). The bacterial strains grown on nutrient agar at 37ºC for 18 h were suspended in a saline solution (0.85% NaCl) and adjusted to a turbidity of 0.5 McFarland standards [108 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 10 mg mL^{-1}. The dissolution of the organic extracts (Methanol) was added 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 (10 mg) was used as a reference standard antibiotic drug.

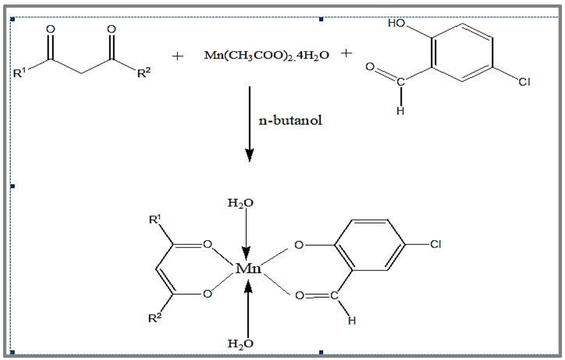
Synthesis of Mixed Ligand Complexes of Manganese

Mixed ligand complexes of Mn(II): To a butanolic solution of $Mn(CH_3COO)_2.4H_2O$ (2.8 mmol, 0.80g. in ~20 mL), a butanolic solution of 5-chlorosalicylaldehyde (0.632 g in ~15mL) and 2-hydroxy acetophenone (0.550 g in ~15 mL) were added with constant stirring. The pH of the solution was raised up to ~7.5 by drop wise addition of 5% aqueous solution of sodium hydroxide with constant stirring. The stirring was continued for 5-6 h. The reaction mixture was kept under reflux for about 4-5 hrs after stirring and then kept at room temperature for about 12 h. The settled solid was filtered, washed with butanol and later with ether to remove stickiness successively and dried properly under reduced pressure. With this same method we synthesize the other complexes of Mn(II) with 5-chlorosalicyl-aldehyde and 2-hydroxypropiophenone, 2-hydroxybenzophenone, pentane-2,4-dione, 1-phenylbutane-1,3-dione or 1,3-diphenylpropane-1,3-dione in 1:1:1 molar ratios.

Mixed ligand complexes of Mn(III): A similar method was adopted to synthesize mixed ligand complexes of $Mn(CH_3COO)_3.2H_2O$ (2.8 mmol, 0.80g. in ~20 mL), with2-hydroxyacetophenone, 2-hydroxypropiophenone, 2-hydroxybenzophenone, pentane-2,4-dione, 1-phenylbutane-1,3-dione or 1,3-diphenylpropane-1,3-dione and 5-chlorosalicylaldehyde in 1:1:2 molar ratios.

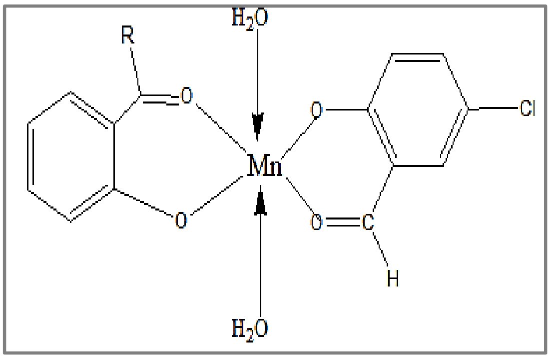
RESULTS AND DISCUSSION

The reactions of manganese (II) acetate tetrahydrate with 5-chlorosalicylaldehyde and β-diketones such as pentane-2,4-dione, 1-phenylbutane-1,3-dione or 1,3-diphenylpropane-1,3-dione in 1:1:1 molar



R^1 CH_3 CH_3 C_6H_5 R^2 CH C_6H_5 C_6H_5

Scheme 1. Mixed ligand complexes of Mn(II) with 5-chlorosalicylaldehyde and acac, bzac or dbzm.

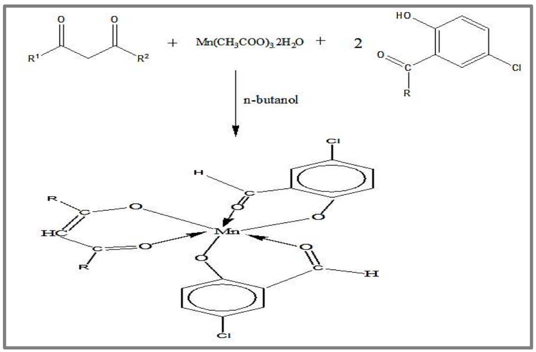


R= CH_3, C_2H_5, C_6H_5

Scheme 2. Mixed lignd complexes of Mn(II) with5-chlorosalicylaldehyde and hap, hpp or hbp.

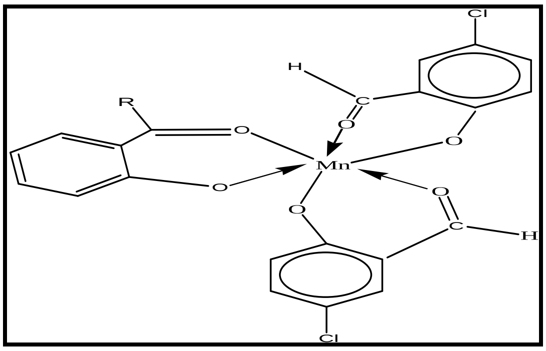
ratios result in the formation of mixed ligand complexes of manganese, scheme 1. Similarly, the other mixed ligand complexes were synthesized with salicylaldehyde and hydroxyarylketones as scheme 2**.**

Mixed ligand complexes of Mn(III) have been prepared by the reaction of manganese(III) acetate with hydoxyarylketones such as 2-hydroxyacetophenone, 2-hydroxypropiophenone or 2-hydroxy benzophenone and 5-chloroosalicylaldehyde in 1:1:2 molar ratios (Scheme 3). Similarly, the other mixed ligand complexes were synthesized with salicylaldehyde and hydroxyarylketones as scheme 4.



R^1 CH_3 CH_3 C_6H_5 R^2 CH_3 CH_3 C_6H_5

Scheme 3. Mixed ligand complexes of Mn(III) with 5-chlorosalicylaldehyde and acac, bzac or dbzm.



R= CH_3, C_2H_5, C_6H_5

Scheme 4. Mixed ligand complexes of Mn(III) with 5-chlorosalicylaldehyde and hap, hpp or hbp.

The resulting complexes are colored solids and octahedral geometry has been proposed for these mixed ligand complexes. The percentage of C, H and Mn agree well with the calculated values corresponding to the respective complexes. The complexes decompose at high temperature on heating. These are sparingly soluble in chloroform, carbon tetrachloride, benzene, nitrobenzene and methanol or most of the organic solvents but completely soluble in DMSO and DMF. Micro analytical data of resulting complexes are presented in table 1.

Table 1. Analyses and Characterization of resulting Mixed Ligand Complexes

S.No.	Complex, Mol. Formula, Mol. Wt.	Colour, Yield (%)	Decomp Temp. (°C)	Analysis % Found (Calculated)		
				C	H	Mn
1.	$[Mn(5\text{-}Clsal)(hap)(H_2O)_2]$ $(C_{15}H_{15}O_6ClMn)$ (383.72)	Yellow (65)	300	46.15 (47.20)	3.25 (3.96)	14.33 (14.39)
2.	$[Mn(5\text{-}Clsal)(hbp)(H_2O)_2]$ $(C_{20}H_{17}O_6ClMn)$ (445.74)	Yellow (48)	305	53.60 (54.13)	3.15 (3.86)	12.10 (12.38)
3.	$[Mn(5\text{-}Clsal)(acac)(H_2O)_2]$ $(C_{12}H_{15}O_6ClMn)$ (347.69)	Dark brown (49)	302	41.15 (41.70)	4.25 (4.37)	15.50 (15.89)
4.	$[Mn(5\text{-}Clsal)(dbzm)(H_2O)_2]$ $(C_{22}H_{20}O_6ClMn)$ (471.82)	Dark brown (75)	302	55.80 (56.13)	4.20 (4.28)	11.15 (11.67)
5.	$[Mn\ (hap)(5\text{-}Clsal)_2]$ $(C_{22}H_{15}O_6Cl_2Mn)$ (504.29)	Dark brown (70)	298	52.88 (52.72)	2.66 (3.02)	10.43 (10.96)
6.	$[Mn(2\text{-}hpp)(5\text{-}Clsal)_2]$ $(C_{23}H_{17}O_6Cl_2Mn)$ (518.31)	Dark brown (52)	298	53.22 (53.62)	2.86 (3.33)	10.65 (10.66)
7.	$[Mn(acac)(5\text{-}Clsal)_2]$ $(C_{19}H_{15}O_6Cl_2Mn)$ (468.26)	Dark brown (50)	302	48.67 (49.06)	3.21 (3.25)	11.80 (11.81)
8.	$[Mn(dbzm)(5\text{-}Clsal)_2]$ $(C_{29}H_{19}O_6Cl_2Mn)$ (592.39)	Dark brown (46)	300	57.89 (58.11)	2.88 (3.25)	9.50 (9.32)

Molar conductance: The molar conductance of the mixed ligand complexes of manganese was measured by preparing their 10^{-3} M solution at room temperature in DMSO solvent. Low value (in the range 15-30 ohm $^{-1}$cm^{2}mol^{-1}) is recorded. The result indicates their non-electrolytic and monomeric nature (Table 2).

Magnetic moment: The observed magnetic moments of the mixed ligand complexes of Mn(III) lies in the range 4.93-5.16 B.M.(Table 2).Which correspond to the high spin d^4(unpaired electron) system. The John-Teller effect, due to an unequal filling of t_2g and eg orbitals yields a distorted octahedral geometry. While the magnetic moments of the complexes of Mn(II) lies in the range 5.60-6.07 B.M. expected for five unpaired electron. This indicates the high spin paramagnetic nature and octahedral geometry. Sun and coworkers [12] have reported magnetic moment 4.1 B.M. for the mixed ligand complexes of the type $[Mn_2Mn(OX)_3(phen)_4](ClO_4)$ (where L= 1,10-phenanthroline). This indicates weak antiferromagnetic spin exchange interaction between Mn(II) and Mn(III) ions.

Table 2. The observed magnetic moments and molar conductance of resulting complexes

S.No.	Complex, Mol.formula, Mol. Weight	Molar conductance ($\Omega^{-1}cm^2mol$)	μ_{eff} (B.M.)
1.	$[Mn(5\text{-}Clsal)(hap)(H_2O)_2]$ ($C_{15}H_{15}O_6ClMn$) (383.72)	28	6.07
2.	$[Mn(5\text{-}Clsal)(hbp)(H_2O)_2]$ ($C_{20}H_{17}O_6ClMn$) (445.74)	21	5.92
3.	$[Mn(5\text{-}Clsal)(acac)(H_2O)_2]$ ($C_{12}H_{15}O_6ClMn$) (347.69)	15	5.84
4.	$[Mn(5\text{-}Clsal)(dbzm)(H_2O)_2]$ ($C_{22}H_{20}O_6ClMn$) (471.82)	18	5.60
5.	$[Mn(5\text{-}Clsal)_2(hap)]$ ($C_{22}H_{15}O_6Cl_2Mn$) (504.29)	27	4.93
6.	$[Mn(5\text{-}Clsal)_2(hpp)]$ ($C_{23}H_{17}O_6Cl_2Mn$) (518.31)	30	5.03
7.	$[Mn(5\text{-}Clsal)_2(acac)]$ ($C_{19}H_{15}O_6Cl_2Mn$) (468.26)	32	5.16
8.	$[Mn(5\text{-}Clsal)_2(dbzm)]$ ($C_{29}H_{19}O_6Cl_2Mn$) (592.39)	19	4.98

Infrared spectra: The IR spectra of Mn(III) and Mn(II) mixed ligand complexes exhibit strong absorption bands in the region 1625-1660 cm^{-1} which may be assigned to coordinated υ(C=O). whereas in free 5-chlorosalicylaldehyde 2-hydroxyacetophenone, 2-hydroxypropiophenone, acetylacetone and benzoylacetone bands at 1680,1650, 1724 and 1724 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.

Bands in the region 1520-1550 cm^{-1} in the mixed ligand complexes may be due to υ(C=C) weak to medium intensity absorption bands in the region 420-450 cm^{-1} which are not present in the free ligand, may be attributed to υ(M-O) vibrations in the case of metal β-diketones. The band in the region 1680-1600 cm^{-1} have been assigned to coordinated C=O groups and those in the region 1580-1500cm^{-1}to C=C stretching mode by Prasad *et al* [13].

A strong band observed in 3100-3000 cm^{-1}region in the spectra of the ligand assigned to υ (OH) (phenolic intramolecular hydrogen bonded with carbonyl oxygen) which is found to have disappeared in the respective complexes, supporting the involvement of phenolic oxygen in bonding with metal ion through deprotonation. This is supported by the low energy shifting [14] of υ(C-O) and appearing at 1450-1398 cm^{-1} in the complexes as compare to free ligand.

The complexes of Mn(II) and Mn(III) can be differentiated with a broad band characteristic to υ(OH) of coordinated water has been observed in the region 3280-3150 cm^{-1}, which further indicated the presence of coordinated water molecules in the Mn(II) complexes. While in Mn(III) complexes this peak is absent (Figure 1 and 2).

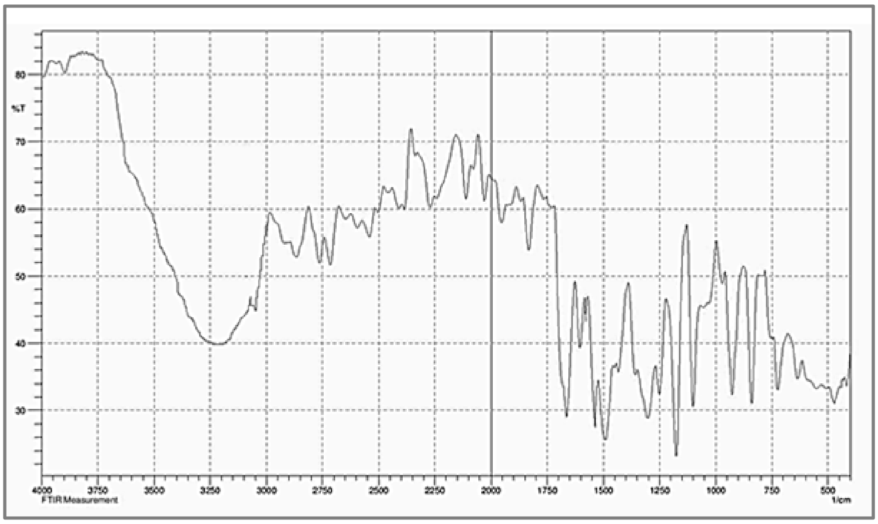


Figure 1. IR spectra of [Mn(5-Clsal)(hap)(H_2O)$_2$].

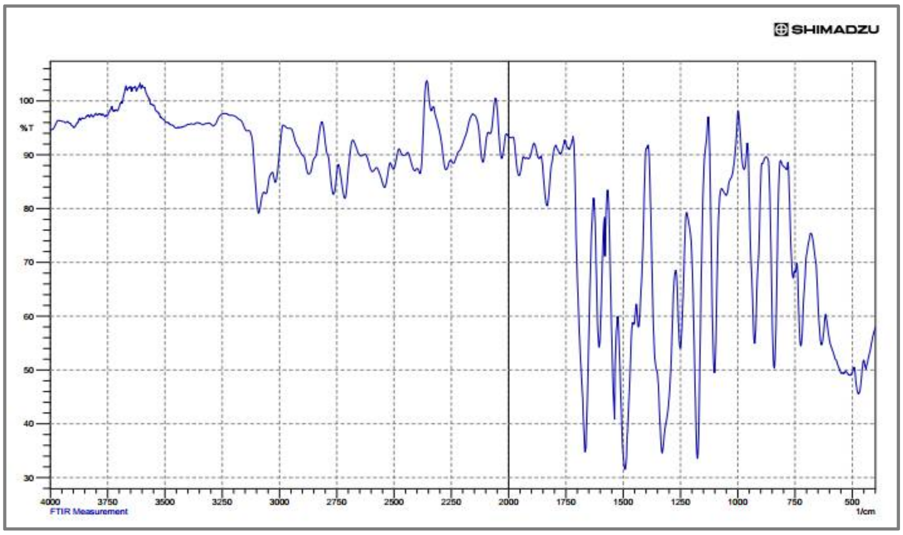


Figure 2. IR spectra of[Mn(hpp)(5-Clsal)$_2$].

FAB mass spectra: FAB mass spectrum of the complexes [Mn(dbzm)(5-Clsal)$_2$] and [Mn(5-Clsal)(hap) (H_2O)$_2$] have been recorded and are reproduced in Fig. The m/z values of the peaks along with their intensities with respect to base peak are shown in table III.

FAB mass spectra of [Mn(dbzm)(5-Clsal)$_2$]: The molecular ion peak [M^+] is observed at m\z 592 (13.88%). Peak at m\z 211 (55.5%) due to the species [Mn(5-Clsal)]$^+$ and m\z 277 (100%) (base peak)is observe due to the species [Mn(dbzm)]$^+$ which could have been formed as the result of the loss of either of the two ligand moieties from the molecular ion.

The peak at m\z 366 (11.11%) due to [Mn(5-Clsal)$_2$]$^+$ and the peak at m\z 502 (22.22%) due to [Mn(dbzm)$_2$]$^+$ have been observed. These peaks can be explained with the help of following reactions:

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

$$MnL_2L'^{+} + L'^{+} \rightleftharpoons MnL_2'^{+} + L_2^{+}$$

The complex exhibit less abundant peaks due to dimeric species [$Mn_2L_2L_2'$].The peak at m\z 884 (5.55%) due to [Mn_2(5-Clsal)$_2$(dbzm)$_2$] is observed. The less intense peak of Mn_2LL_2' and Mn_2L_2L' also observed in the spectra.

FAB mass spectra of [Mn(5-Clsal)(hap)(H_2O)$_2$]: The peak is observed at m\z 347 (75.68%) due to [Mn(5-Clsal)(hap)]$^+$. The complexes show peaks due to the formation of MnL^+ and MnL'^+ species, as a result of the loss of one or the other ligand moiety (Figure 3 and 4). The peak at m\z 209 (60%) due to [Mn (5-Clsal)]$^+$ and at m\z 190 (100%) due to [Mn(hap)]$^+$ are observed. This peak observed as a base peak. Peaks due to the bis complexes MnL_2 and MnL_2' are also observed as a result of the redistribution reactions:

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

For example, peaks at m\z 365 (28%) and 325 (13%) have been noticed due to [Mn(5-Clsal)$_2$]$^+$ and [Mn(hap)$_2$]$^+$ species respectively (Table 3).

Peaks due of ions formally derived from the oligomerisation species occur in the spectra of the complexes, which can be explained as:

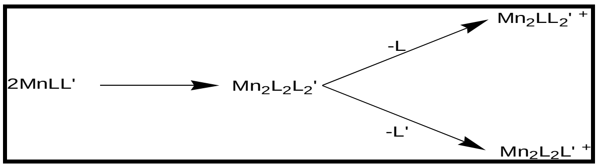


Table 3. Mass spectral data of mixed ligand complexes of Mn(II) and Mn(III) (m/z values and relative Abundances)

S.No.	Ions	[Mn(dbzm)(5-Clsal)$_2$]	[Mn(5-Clsal)(hap)(H_2O)$_2$]
1.	M^+	592 (13.88%)	347 (75.68%)
2.	ML^+	211 (55.5%)	*209 (60%)*
3.	ML'^+	277 (100%)	190 (100%)
4.	ML_2^+	366 (11.11%)	365 (28%)
5.	ML'^+_2	502 (22.22%)	325 (13%)
6.	ML_3^+	519(5.55%)	519(7.33%)
7.	ML'^+_3	724(60.11%)	462(13%)
8.	$Mn_2L_2L_2'$	884(5.55%)	695(5.55%)
9.	Mn_2LL_2'	711(8.33%)	540(5.55%)
10.	Mn_2L_2L'	642(7.00%)	560(5.55%)

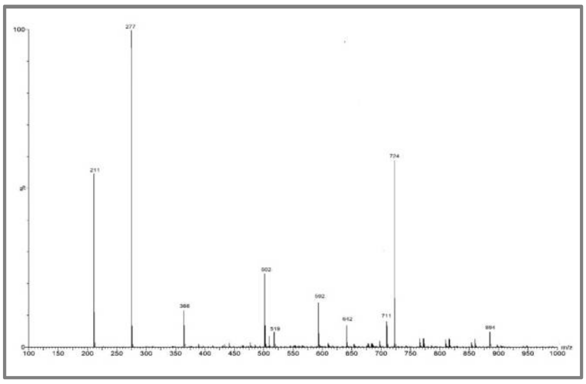


Figure 3. FAB mass spectra of [Mn(dbzm)(5-Clsal)$_2$].

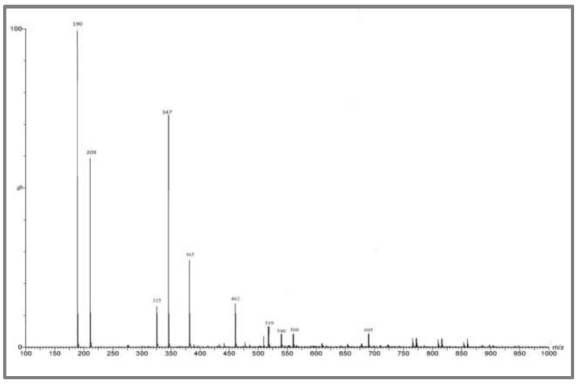


Figure 4. FAB mass spectra of [Mn(5-Clsal)(hap)(H_2O)$_2$].

APPLICATION

Antibacterial screening: Two of the ligands namely 2-hydroxyacetophenone and 1, 3-diphenyl-propane-1, 3-dione and the synthesized mixed ligand complexes $[Mn(5\text{-}Clsal)_2(dbzm)H_2O)_2]$ and $[Mn(5\text{-}Clsal)_2\ (hap)]$ were screened against the bacterial strains. The antimicrobial screening data shows (table 4) that both ligands, 2-hydroxyacetophenone and 1, 3-diphenylpropane-1, 3-dione do not show activity against both the strains of bacteria [15]. It is important to note that the metal chelate exhibits more inhibitory effects towards both of the bacteria than the parent ligand. The complex is much powerful bactericides against *Staphylococcus aureus* and *Escherichia coli*.

The increased activities of the metal chelate as compared to ligands can be explained on the basis of overtone concept [16] and chelation theory [17].

Table 4. Antibacterial activities of the ligands and Manganese metal complexes

Test compound	*E. Coli* Test zone of inhibition (mm)	*S. Aureus* Test zone of inhibition (mm)
2-hydroxyacetophenone (hap)	No activity	No activity
1,3-diphenyl propane1,3-dione	No activity	No activity
$[Mn(5\text{-}Clsal)_2(dbzm)H_2O)_2]$	34	32
$[Mn(5\text{-}Clsal)_2(hap)]$	19	14

CONCLUSION

In present paper, the compare study of the series of mixed ligand complexes of Mn(III) and Mn(II) have been done. All the prepared complexes are high spin, non electrolyte and paramagnetic in nature. Magnetic moments and electronic spectra confirm an octahedral geometry of Mn(II) complexes and distorted octahedral geometry of Mn(III) complexes with John teller distortion. IR spectra support the absence of coordinated water molecules in Mn(III) complexes while presence of coordinated water molecule in Mn(II) 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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REFERENCES

[1]. J. B. Gandhi, N. D. Kulkarani, Study of uranyl complexes with new binucleating ligands involving amide and imine coordinating sites,P*olyhedron*, **1999**, 18, 1735.

[2]. R. J. Prabhaharan, Synthesis, characterization, EXAFS investigation and antibacterial activities of new ruthenium(III) complexes containing tetradentate Schiff base, *Inorg. Biochem.*, **2004**, 98, 2131.

[3]. V. Bachler, G. Olbrich, F. Neese, K. Wieghardt, Theoretical Evidence for the Singlet Diradical Character of Square Planar Nickel Complexes Containing Two *o*-Semiquinonato Type Ligands, *Inorg. Chem.*, **2002**, 41(16), 4179–4193.

[4]. P. Bindu, R. P. Kurup, Thonduparambil, R. Satyakeerty, Epr, cyclic voltammetric and

biological activities of copper(II) complexes of salicylaldehyde N(4)-substituted thiosemicarbazone and heterocyclic bases, *Polyhedron*,**1999**,18, 321.

[5]. M. B. Ferran, S. Capacchi, G. Pelosi, G. Reffo, P. Tarasconi, R. Albertini, S. Pinelli, P. Lunghi, Synthesis, structural characterization and biological activity of helicin thiosemicarbazone monohydrate and a copper(II) complex of salicylaldehyde thiosemicarbazone, *Inorg.chem. Acta*, **1999**, 286, 2096.

[6]. M. M. Ray, J. N. Adhya, D. Biswas, S.N. Poddar, Magnetic Properties of Coordination and Organometallic Transition Metal Compounds Mn(III)-Mn(VII), Mn (oxydation state), *Aust. J. Chem.*, **1966**, 19,1737.

[7]. P. Perez-Lourido, J. Romero, L. Rodriguez, J. A. GarciaVazquez, J. Castro, A. Sousa, J. R. Dilworth and O. R. Nascimento,Photochemical or Thermal Chelate Exchange in the Ruthenium Coordination Sphere of Complexes of the Ru(phen)$_2$L Family (L = Diimine or Dinitrile Ligand**s)**, *Inorg. Chem. Commun.*, **2002**, 5, 337-339.

[8]. M. D. Godbole, E. Grigiotti, P. Zanello, A. M. Mills, A. L. Spek, E. Bouwman,Crystal structure of the mononuclear complex [Mn(mesalim)2Cl] and electrochemical studies of manganese complexes of the ligand Hmesalim, *Inorg. Chem. Acta.*,**2005**, 358, 233-238.

[9]. M. Colleen. Hansel, A. Carolyn. Zeiner, M. Cara. Santelli, M. Samuel. Webb, Mn(II) oxidation by an ascomycete fungus is linked to superoxide production during asexual reproduction, PNAS, **2012**, 109(31) ,12621-12625.

[10]. George W. Luther**,** Manganese(II) Oxidation and Mn(IV) Reduction in the Environment—Two One-Electron Transfer Steps Versus a Single Two-Electron Step *Geomicrobiology Journal*, **2005**, 22,195–203.

[11]. M. Agrawal, N. Jain, Synthesis and Characterization of Mixed Ligand Complexes of Fe (III) with 2-hydroxyacetophenone and Substituted Salicylaldehydes or β-diketones,J. Biol. Chem. Research,**2015**, 32 (2) , 902-913.

[12]. Xian-Ru Sun, Ming-Ming Miao, Peng Cheng, Dai-ZhengLiao, zong-hui Jaing and Gen Lin wang,Syntheses, Structures, Photoluminescence, and Theoretical Studies of d^{10} Metal Complexes of 2,2‘-Dihydroxy-[1,1‘]binaphthalenyl-3,3‘-dicarboxylate, *Transition Metal Chemistry*, **2004**, 21, 270-272.

[13]. R. N. Prasad, M. Agrawal, M. Sharma, Mixed ligand complexes of alkaline earth metals, part-x. Mg(II), Ca(II), Sr(II) And Ba(II) complexes with 5-bromosalicylaldehyde and b-diketones, *J. Chil. Chem. soc.*, **2003**, 48(1) 9707-9717.

[14]. Maurya, P. P. Satel, S. Rajput, Synth, React inorg Met-org chem.Synthesis and characterization of Mixed-Ligand Complexes of Cu(II), Ni(II), Co(II), Zn(II), Sm(III), and U(VI)O$_2$, with a Schiff Base Derived from the Sulfa Drug Sulfamerazine and 2,2′-Bipyridine, **2003**, 33, 801.

[15]. M. Agrawal, G. Kaur and A. khandelwal, Synthesis And Studies Of Mixed Ligand Complexes Of Mn(II) With Salicylaldehyde And Substituted Salicylaldehydes,2-Hydroxyarylcarbonyl Compounds Or β-Diketones, *J. Applicable Chem.*, **2013**, 2(6), 1472-1483.

[16]. N K Singh,S B Singh ,D K Singh & V B Chauhan, Synthesis, characterization and bio;ogical properties of an nicotinoyl-N’-thiobenzoylhydrazine complexes of cobalt(II), nickel(II), copper(II) and zinc(II), Indian j. chem.. **2003**, 42A, 2767-2771.

[17]. Tweedy, B.G. Plant Extracts with Metal Ions as Potential Antimicrobial Agents. Phytopatology, **1964,** 55, 910-918.

Citations of the JOAC

[1]. A. Srivastava, D. Porwal, K. Srivastava, J. Prasad, Electrochemical and Spectral Behaviour of Binary And Mixed Ligand Copper (II) Complexes Involving Various Pyridinedicarboxylic Acids and 2, 9-Dimethyl-1,10-Phenanthroline in Dimethylsulfoxide, *J. Applicable Chem.*, **2017**, 6(5), 941-949.

[2]. K. M. Shwethaw, G. Krishnamurthy, H. S. Bhojya, M. C. Prabhakara, Mixed ligand Co(II) Complexes: Synthesis, Characterization, DNA binding and Photonuclease Studies, *J. Applicable Chem.*, **2018**, 7(4), 873-882.

[3]. P. R.Shirode, P. M. Yeole, Synthesis, Spectroscopic, Thermal and Antimicrobial Studies of Some Transition Metal mixed ligand Complexes of Schiff Base, *J. Applicable Chem*., **2015**, 4 (3), 958-964.

[4]. M. R. Anil Kumar, S. Shanmukhappa, B. E. Rangaswamy, M. Revanasiddappa, Synthesis, Characterization and Antimicrobial Activity of Some Transition Metal Complexes with Schiff Base Ligand, *J. Applicable Chem.,* **2014**, 3(4), 1440-1446.

[5]. P. Mangaiyarkkarasi, S Arul Antony, Synthesis, Characterization And Biological Significance of Some Novel Schiff Base Transition Metal Complexes Derived from 4-Aminoantipyrine And Dihydropyrimidine of Vanillin, *J. Applicable Chem*., **2014**, 3 (3): 997-1006.

[6]. M. Agrawal, R. Karra, N. Jain and G. Baswal, Synthesis and Spectral Studies of Mixed Ligand Complexes of Mn (III) with 1,3-Diphenylpropane-1,3-Dione and B-Diketones, Hydroxyl Aryl Ketones or Substituted Salicylaldehyde, *J. Applicable Chem*., **2017**, 6 (3), 410-416.