



Synthesis, spectroscopic characterization and biological screening of mixed ligand complexes of Mn(II) with 2-hydroxybenzophenone and β -diketones or substituted salicylaldehyde

Dr. Rashmi Gaur ¹, Dr. Manish Rao Ambedkar ²

Department of Chemistry, University of Rajasthan, Jaipur, India. ¹

Department of Chemistry, M.M.H. (P.G.) College Ghaziabad, India. ²

Ch. Charan Singh University, Meerut, India. ²

Abstract

Some new mixed ligand complexes have been synthesized by the reaction of Manganese (II) acetate tetra hydrate with 2-hydroxybenzophenone/(hbp) and β -diketones or substituted salicylaldehyde in 1:1:1 molar ratios and produced complexes of manganese with general formula $[Mn(hbp)(L')(H_2O)_2]$ here HL' = Pentane-2,4-dione/(acac), 1-phenylbutane-1,3-dione/(bzac), 1,3-diphenylpropane-1,3-dione/(dbzm), 2-hydroxybenzaldehyde/(Sal), 5-Bromo-2-hydroxybenzaldehyde/(5-BrSal), 5-Chloro-2-hydroxybenzaldehyde/(5-ClSal) and 5-Nitro-2-hydroxybenzaldehyde/(5-NO₂Sal). For the determination of bonding and coordination geometry of newly synthesized complexes, physiochemical and spectroscopic methods were used. The electric conductance and magnetic susceptibility revealed their non electrolytic and paramagnetic nature. The mixed ligand complexes were also tested for E. Coil and Staphylococcus aureus.

Keywords: Mixed ligand complexes, Manganese (II), FAB Mass, UV, IR spectra of Mn(II), Antimicrobial Activity.

Introduction:

D block elements ions definitely exist as metal complexes in organic framework by cooperation with various atoms having gathering equipped for complexation or chelation. Then again metals are associated with such a large number of essential biological reactions that life as we probably am aware, couldn't exist without coordination compounds. In addition mixed ligand complexes are seen in organic framework in the intermediate chemical reaction with metal particles, which are essential to comprehend the separate chemistry¹⁻⁶.

The mixed ligand complexes of transition metals are very important in different field of chemistry like photochemistry, analytic chemistry and magneto chemistry etc⁷⁻⁹. More interestingly, the emergence of mixed ligand chemistry has brought a revolutionary new era for the progress of medicinal and clinical chemistry these days. These ligands and their metal chelates are being widely used as chemical drugs in the area of antitumor, anti-inflammatory, analgesic, antimalarial, antibacterial, antifungal, antiviral, anti-epileptic, cardiovascular agents and magnetic resonance¹⁰⁻¹¹.

The coordination chemistry of manganese has studied in inorganic biochemistry as an interested field. The magnetic properties, diverse catalytic activity of such compounds are now being explored for its biological importance. Recently a few reports on the antimicrobial activity of Mn(II) complexes were studied.

In the present work, we describe the synthesis, characterization and antimicrobial activity of mixed ligand complexes of Mn(II) with hydroxybenzophenone, β -diketones and 2-hydroxybenzaldehyde. The reared complexes have also been tested in-vitro to assess their antibacterial activities against some common reference bacteria.

MATERIALS AND METHODS

Materials: 5-Chloro-2-hydroxybenzaldehyde (Merck), 5-Bromo-2-hydroxybenzaldehyde (Aldrich), 5 nitro-2-hydroxybenzaldehyde (Aldrich), 1-phenylbutane-1,3-dione (Sisco-chem) and 1,3-diphenylpropane-1,3-dione (Sisco-chem) were purified by recrystallization from butanol prior to use. 2-hydroxybenzaldehyde (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 4000-400 cm^{-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 grow on nutrient agar at 37°C 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 37°C 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 Mn(II)

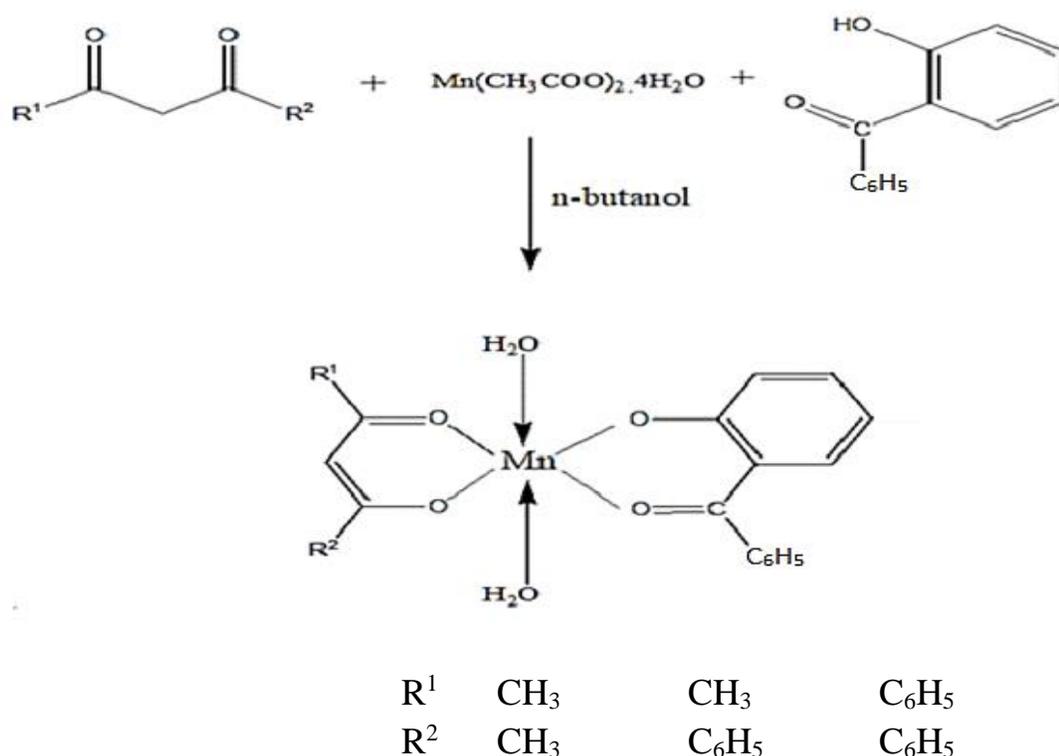
We add Mn(CH₃COO)₂.4H₂O (2.8mmol, 0.80g. dissolved in ~20ml butanolic solution), 2-hydroxybenzophenone (hbp) (0.64 g. in ~15 ml) and 2-hydroxybenzaldehyde (salicylaldehyde = 0.400 g. ~15 ml) and stir constantly. Now 5% aqueous solution of NaOH was added dropwise to raise the pH of the solution to ~7 to 8. The stirring was constantly for five to six hours. The reaction mixture refluxed for about four to five hours in the wake of mixing and afterward holds at room temperature for around 12 hrs. The

settled solid was separated, washed with butanol and later with ether to expel progressively and dried appropriately under reduced pressure.

To integrate Mixed ligand complexes of Mn(II) and hbp with Pentane-2,4-dione/(acac), 1-phenylbutane-1,3-dione, 1,3-diphenylpropane-1,3-dione, 5-Bromo-2-hydroxybenzaldehyde, 5-Chloro-2-hydroxybenzaldehyde or 5-Nitro-2-hydroxybenzaldehyde in 1:1:1 molar proportions a similar technique was adopted.

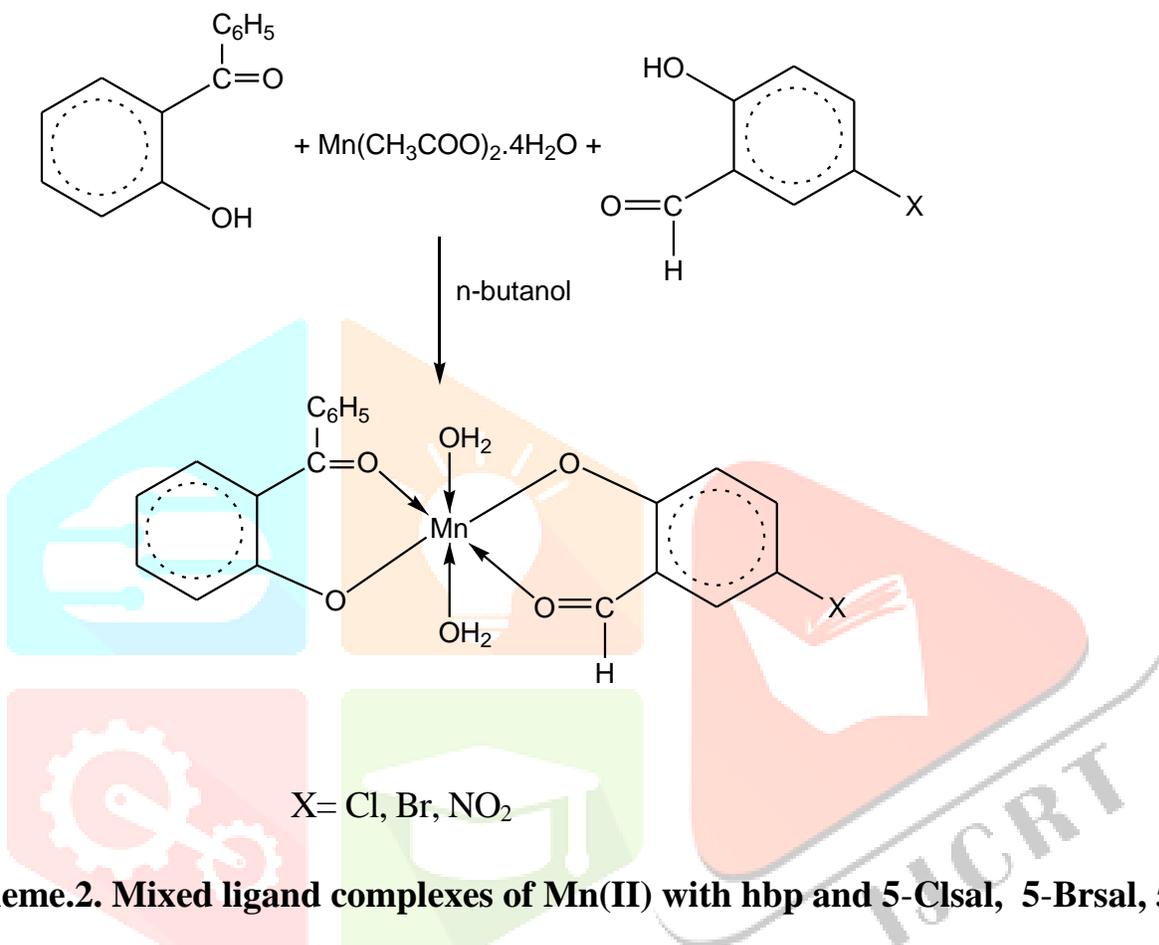
Result and Discussion:

Manganese (II) acetate tetrahydrate react with 2-hbp and β -diketones such as acac, bzac or dbzm in 1:1:1 molar ratios and produce complexes of manganese with general formula $[\text{Mn}(\text{hbp})(\text{L}')(\text{H}_2\text{O})_2]$.



Scheme.1. Mixed ligand complexes of Mn(II) with 2- hydroxybenzophenone and acac, bzac or dbzm

The same processor used for synthesized the other mixed ligand complexes with the reation of hydroxybenzophenone with 2-hydroxybenzaldehyde, and derivatives of 2-hydroxybenzaldehyde in 1:1:1 molar ratios.



Scheme.2. Mixed ligand complexes of Mn(II) with hbp and 5-Cl₂sal, 5-Br₂sal, 5-NO₂sal

The resulting complexes are green solids. The complexes decompose at high temperature on heating but don't melt. These are insoluble in CHCl₃, CCl₄, C₆H₆, C₆H₅NO₂ and CH₃OH or most of the organic solvents but completely soluble in Dimethyl sulfoxide and Dimethylformamide.

Table 1. Analytical data of resulting complexes are presented

S. N.	Complex, Mol. Formula, Mol. Wt.	Colour, Yield (%)	Decom p Temp. (°C)	Analysis % Found (Calculated)		
				C	H	Mn
1.	[Mn(hbp)(sal)(H ₂ O) ₂] (C ₂₀ H ₁₈ O ₆ Mn) (409.3)	Dark brown (60)	295	46.15 (58.69)	3.25 (4.43)	14.33 (13.42)
2.	[Mn(hbp)(5-Brsal)(H ₂ O) ₂] (C ₂₀ H ₁₇ O ₆ MnBr) (488.4)	Yellow (58)	300	47.60 (49.21)	4.15 (3.50)	12.10 (11.25)
3.	[Mn(hbp)(hap)(H ₂ O) ₂] (C ₂₁ H ₂₀ O ₆ Mn) (423.3)	Dark brown (45)	305	51.15 (59.58)	3.25 (4.76)	12.50 (12.98)
4.	[Mn(hbp)(acac)(H ₂ O) ₂] (C ₁₈ H ₂₀ O ₆ Mn) (387.3)	Dark brown (60)	300	40.80 (55.82)	4.20 (5.21)	15.15 (14.19)
5.	[Mn(hbp)(bzac)(H ₂ O) ₂] (C ₂₃ H ₂₂ O ₆ Mn) (449.4)	Dark brown (65)	295	47.88 (61.48)	3.66 (4.93)	13.43 (12.23)
6.	[Mn(hbp)(dbzm)(H ₂ O) ₂] (C ₂₈ H ₂₄ O ₆ Mn) (511.4)	Yellow (65)	305	55.5 (65.76)	4.30 (4.73)	11.30 (10.71)

Molar conductance

The molar conductance of the complexes of manganese was calculated by preparing their 10^{-3} M sol. at room temp in DMSO solvent. Mn(II) complexes are observed in the range 5-20 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$). The result indicates their non-electrolytic and monomeric nature. (Table 2). The low value indicates that there is no any dissociation of the complexes in DMSO. The mixed ligand complexes of Nickel, Cupper and Iron with Schiff bases have been prepared by D. Lakhe *et al*¹². The molar conductance values (12.24-13.60) $\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^2$) for 10^{-3} M solutions in DMF point out that the nature of metal complexes are non-electrolytic

Magnetic moment:

The magnetic measurement of the complexes of Mn(II) lies in the range 5.75-6.05 B.M. expected for five unpaired electron. This indicates the high spin paramagnetic nature and octahedral geometry.

Table 2. Molar conductance and Magnetic Moment of Mixed Ligand complexes of $[\text{Mn}(\text{hbp})(\text{L}')(\text{H}_2\text{O})_2]$

S.N.	Complex, Mol.formula, Mol. Weight	Molar conductance ($\text{ohm}^{-1}\text{cm}^2 \text{mol}$)	Magnetic Moment (μ_{eff})(B.M.)
1.	$[\text{Mn}(\text{hbp})(\text{sal})(\text{H}_2\text{O})_2]$ ($\text{C}_{20}\text{H}_{18}\text{O}_6\text{Mn}$) (409.3)	15	5.90
2.	$[\text{Mn}(\text{hbp})(5\text{-Brsal})(\text{H}_2\text{O})_2]$ ($\text{C}_{20}\text{H}_{17}\text{O}_6\text{MnBr}$) (488.4)	7	5.75
3.	$[\text{Mn}(\text{hbp})(\text{hap})(\text{H}_2\text{O})_2]$ ($\text{C}_{21}\text{H}_{20}\text{O}_6\text{Mn}$) (423.3)	5.8	6.04
4.	$[\text{Mn}(\text{hbp})(\text{acac})(\text{H}_2\text{O})_2]$ ($\text{C}_{18}\text{H}_{20}\text{O}_6\text{Mn}$) (387.3)	9	5.90

5.	[Mn(hbp)(bzac)(H ₂ O) ₂] (C ₂₃ H ₂₂ O ₆ Mn) (449.4)	12	5.87
6.	[Mn(hbp)(dbzm)(H ₂ O) ₂] (C ₂₈ H ₂₄ O ₆ Mn) (511.4)	20	5.75

Electronic spectra

Electronic Spectrum of [Mn(hbp)(Sal)(H₂O)₂] has been recorded in Dimethylformamide in the range 200-800 nm using distilled water as a reference in fig 1.

The spectra of the complex displayed absorption bands at 300nm (33333cm⁻¹), 350nm (28571cm⁻¹), 425nm (23529cm⁻¹), which belongs to ⁶A_{1g} →⁴E_g(G)(v₃), ⁶A_{1g} →⁴T_{2g}(G) (v₂) and ⁶A_{1g} →⁴T_{1g}(G) (v₁) transitions correspondingly. Hosny *etal* have observed bands at 25000, 31000 and 37000cm⁻¹ assignable to intraligand and charge transfer transitions for high spin Mn(II) complexes. Suresh *etal* have assigned a band at 25510cm⁻¹ for ⁶A_{1g} →⁴T_{2g}(G) transition for d⁵ Mn(II) octahedral complex.

The spectra of Cobalt complex show two bands at 15923 cm⁻¹ and 19894 cm⁻¹ as a result of ⁴T_{1g}(F) →⁴A_{2g}(F) (v₂) and ⁴T_{1g}(F) →⁴T_{2g}(P) (v₃) transitions correspondingly.¹³

Table 3. Electronic spectral data (cm⁻¹) of the mixed ligand complexes

S.N.	Complex	Transitions (Cm ⁻¹)		
		⁶ A _{1g} → ⁴ T _{1g} (G) (v ₁)	⁶ A _{1g} → ⁴ T _{2g} (G) (v ₂)	⁶ A _{1g} → ⁴ E _g (G) (v ₃)
1.	[Mn(hbp)(sal)(H ₂ O) ₂]	23529	28571	33333
2.	[Mn(hbp)(5-Brsal)(H ₂ O) ₂]	21141	25000	26455
3.	[Mn(hbp)(hap)(H ₂ O) ₂]	20618	24390	26455
4.	[Mn(hbp)(acac)(H ₂ O) ₂]	20833	24600	26809
5.	[Mn(hbp)(bzac)(H ₂ O) ₂]	21053	24691	26666
6.	[Mn(hbp)(dbzm)(H ₂ O) ₂]	20833	24820	26550

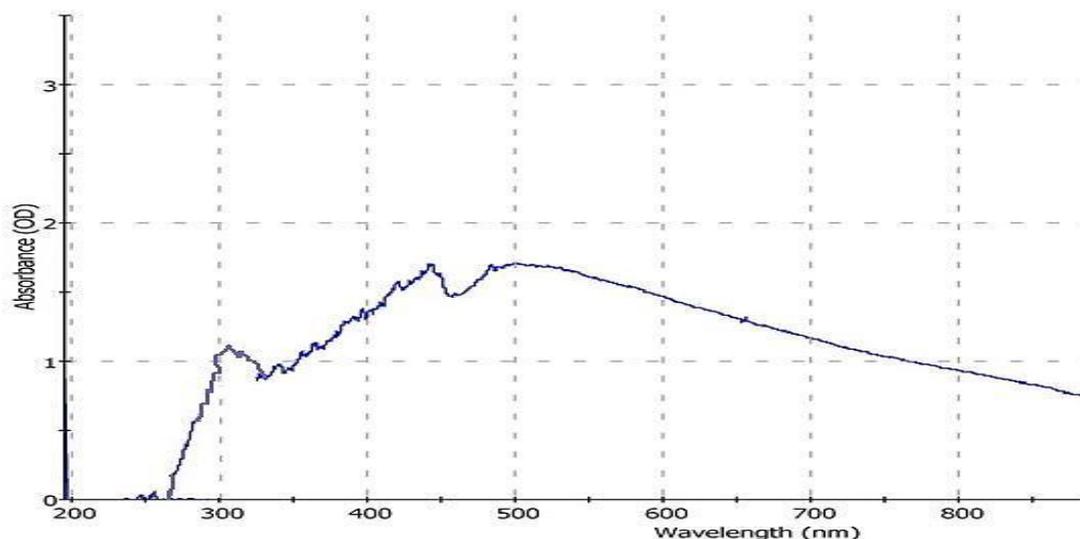


fig 1. Electronic spectra of [Mn(hbp)(sal)(H₂O)₂]

Infrared Spectra

The Infrared absorption bands of Mn(II) mixed ligand complexes [Mn(hbp)(sal)(H₂O)₂] has been reproduced in Fig 2.

Many vibrations of different intensities observed in the region 4000-400 cm⁻¹ in IR spectra. Bands occurred in the region of 3330-3100, 1655-1590, 1555-1520, 1470, 1390 and 450-420 cm⁻¹ have been represented in the current case. The strong bands displayed in 3200-3000 cm⁻¹ range in the spectra of the ligands, introduced to ν(OH) (phenolic, intramolecular hydrogen bonded with carbonyl oxygen), which were not present in the particular complexes in that way this explain the bonding of phenolic oxygen with metal ion through deprotonation. In free hydroxyarylketones, β-diketones and salicylaldehyde ligands bands have been reported at 1680-1800 cm⁻¹ due to ν(C=O). A low energy shifting of ν(C=O) at 1490, 1390 cm⁻¹ in the mixed ligand supports the chelation of these ligands to the metal atom.

Patange and coworkers¹⁴ explained that coordinated H₂O v(OH) band displayed a broad band in the range 3300-3100 cm⁻¹, which further supports the attendance of coordinated H₂O molecules in the complexes

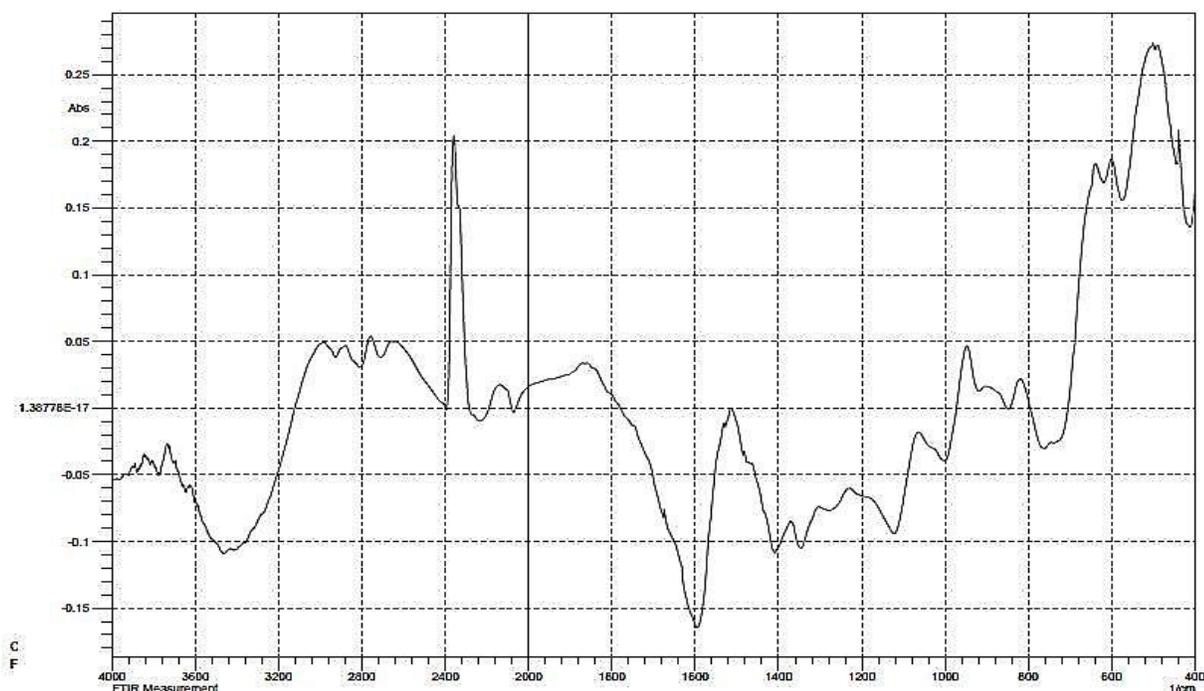


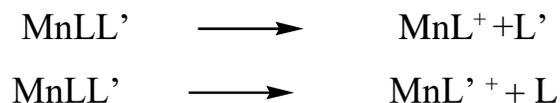
Fig 2. IR spectrum of [Mn^{II}(hbp)(sal)(H₂O)₂]

FAB mass spectral study

FAB mass spectrum of [Mn(hbp)(5-BrSal)(H₂O)₂] and [Mn(hbp)(acac)(H₂O)₂] have been recorded. The data of peaks are described in table 4.

The peak is observed at m/z 452 (18.75%) and 351(20.55%) due to ion [Mn(hbp)(5-BrSal)]⁺ and [Mn(hbp)(acac)]⁺ in complexes I and II respectively. This is called molecular ion peak. Complexes show their molecular ion (M⁺) peak of low intensity.

The complexes show peaks as a result of synthesis of MnL⁺ and MnL⁺ species, due to the isolation of one or the other ligand. The first complex show the peak at m/z 255 (35%) because of [Mn(5-BrSal)]⁺ and at m/z 254 (100%) due to [Mn(hbp)]⁺. This peak observed as a base peak. And complex II exhibit the peak at m/z 155 (100%) due to [Mn(acac)]⁺ and at m/z 255 (60%) due to [Mn(hbp)]⁺. These peaks can be explained as:

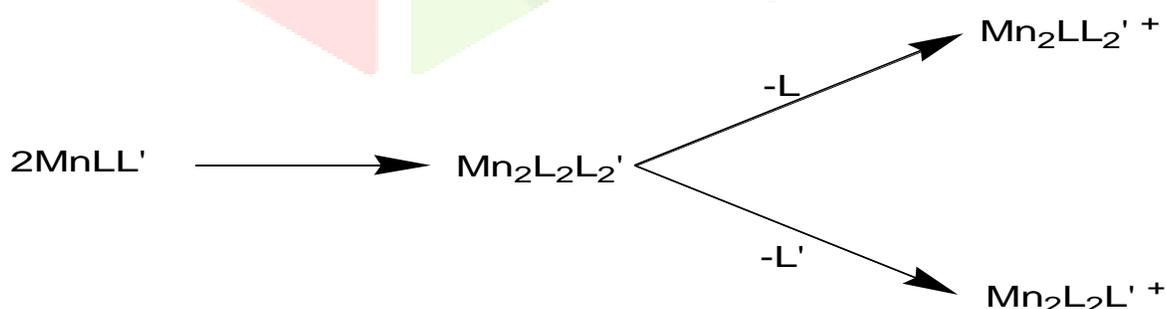


Peaks due to the bis complexes MnL_2 and MnL_2' are also noticed due to the redistribution reactions:



i.e., in first complex peaks at m/z 456 (10.50%) and 453 (24%) have been noticed due to $[\text{Mn}(5\text{-Brsal})_2]^+$ and $[\text{Mn}(\text{hbp})_2]^+$ species respectively, whereas complex II exhibit peaks at m/z 453 (16.80%) and 254 (25%) due to $[\text{Mn}(\text{hbp})_2]^+$ and $[\text{Mn}(\text{acac})_2]^+$ species respectively.

Peaks resultant from the oligomerisation species take place in the spectra of the complexes. peaks at m/z 708(9.75%) and 712(5.50%) have been noticed in complex I due to $[\text{Mn}_2(5\text{-Brsal})(\text{hbp})_2]^+$ and $[\text{Mn}_2(\text{hbp})(5\text{-Brsal})_2]^+$ species respectively. Complex II show the peak due to $[\text{Mn}_2(\text{hbp})(\text{acac})_2]^+$ and $[\text{Mn}_2(\text{acac})(\text{hbp})_2]^+$ at m/z 510(9.75%) and 608(7.50%) respectively. which can be explained as:



Complex I exhibits peaks due to $[\text{Mn}_2(5\text{-Brsal})_3]^+$ at m/z (715, 10.87%) and due to $[\text{Mn}_2(\text{hbp})_3]^+$ at m/z (702, 6.85%). Complex II show this peak at m/z (408, 15.11%) because of $[\text{Mn}_2(\text{acac})_3]$. Appearance of peaks due to these Mn_2L_3^+ and $\text{Mn}_2\text{L}_3'^+$ ions can be described with this manner:

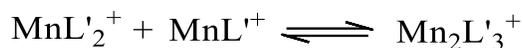
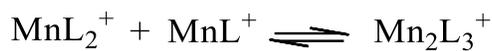


Table 4: Mass spectral data of manganese mixed ligand complexes [Mn(hbp)(5-Brsal)(H₂O)₂] and [Mn(hbp)(acac)(H₂O)₂] (m/z values and relative abundances)

S.N.	Ions	[Mn(hbp)(5-Brsal)(H ₂ O) ₂]	[Mn(hbp)(acac)(H ₂ O) ₂]
1.	M ⁺	452 (18.75%)	351(20.55%)
2.	ML ⁺	254 (100%)	255 (60%)
3.	ML' ⁺	255 (35%)	155(100%)
4.	ML' ⁺ -Br	175(25%)	—
4.	ML ₂ ⁺	453 (24%)	453 (16.80%)
5.	ML' ₂ ⁺	456 (10.50%)	254 (25%)
6.	M ₂ L ₃ ⁺	(702, 6.85%)	702(8.50%)
7.	M ₂ L' ₃ ⁺	(715, 10.87%)	(408, 15.11%)
8.	Mn ₂ L ₂ L' ₂	910 (5.00%)	844(5.55%)
9.	Mn ₂ LL' ₂	712(5.50%)	510(9.75%)
10.	Mn ₂ L ₂ L'	708(9.75%)	608(7.50%)

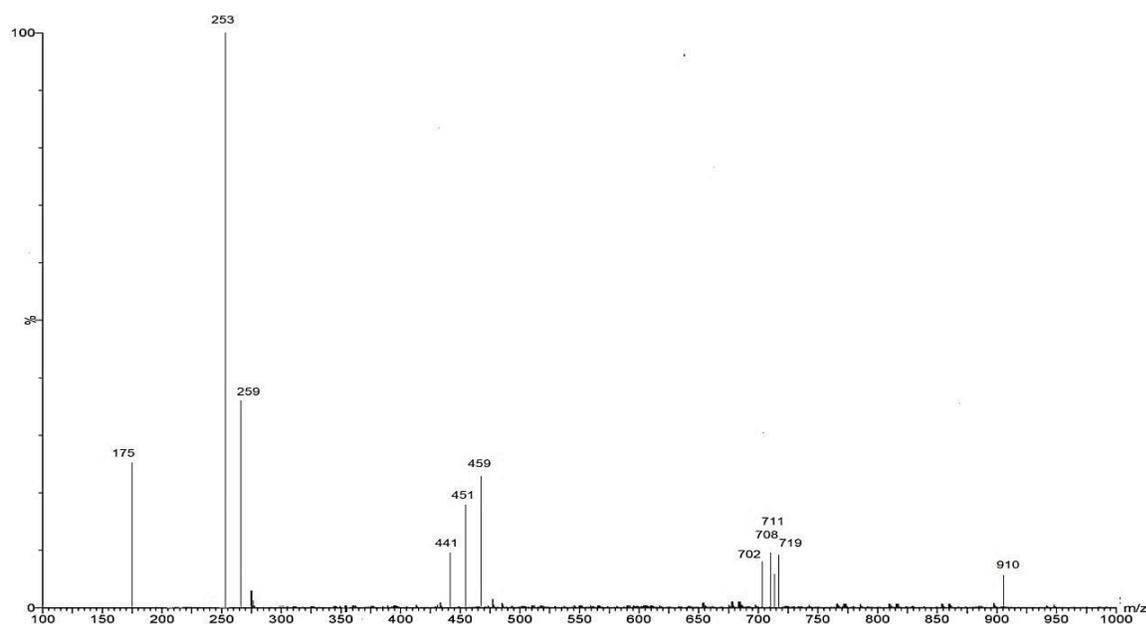


Fig 3. FAB MASS spectra of [Mn(hbp)(5-Brsal)(H₂O)₂]

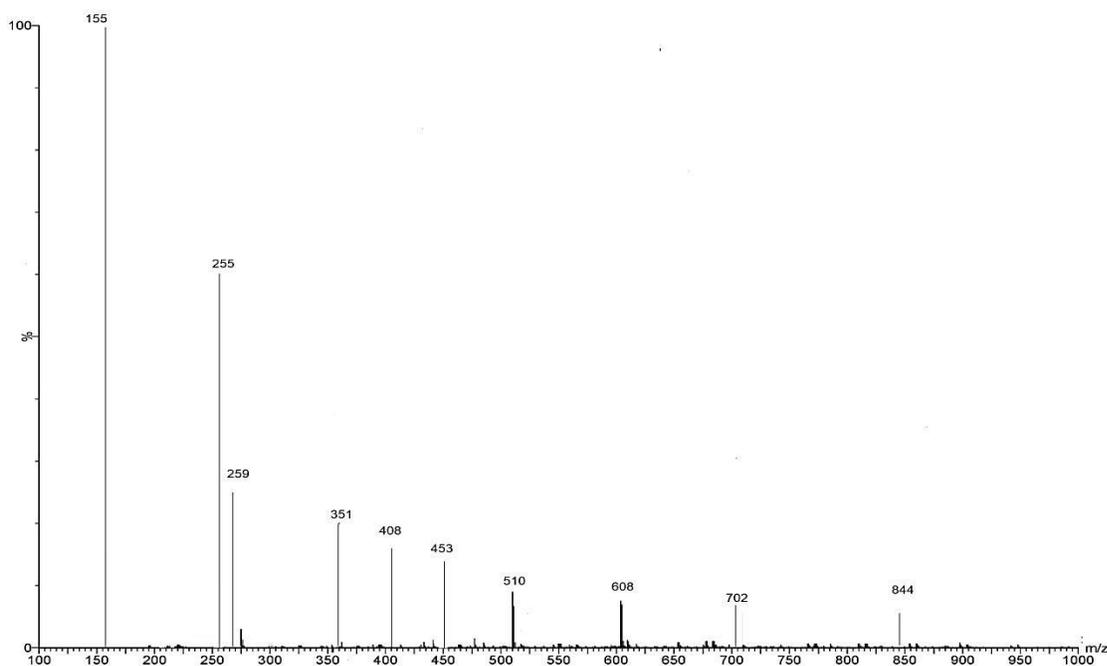


Fig 4. FAB MASS spectra of $[\text{Mn}(\text{hbp})(\text{acac})(\text{H}_2\text{O})_2]$

Antibacterial screening

Antibacterial screening of hbp and the metal complexes have been determined against bacteria *E. coli*, and *Staphylococcus aureus* are given in (Table 5 and fig 5). A relative study of the reference ciprofloxacin, parent ligands and the M complexes exhibited that some free ligands and all the tested complexes show positive effect against both the strains.

The comparison of the biological activities of the parent ligands, synthesized metal complexes and known antibiotic shows that the free ligand 5-NO₂sal, 5-chlorosalicylaldehyde and hydroxybenzophenone are occur to be active against both the bacteria, whereas 2-hydroxyacetophenone and 2-hydroxypropiophenone are not active against both the strains. More interestingly 2-hbp is much active even than standard ciprofloxacin. all the tested complexes show antibacterial activity against both the bacteria. The free ligands and

complexes show higher antibacterial effect against *S. aureus* as compared to *E. coli* and that of the standard antibacterial agent also. Same report have been noticed by Chordia and Chaturvedi¹⁵ for the complexes of diorganotin(IV) with formula $[\text{PhCOCHCOPh}]R_2\text{Sn}[\text{SSH}(\text{S})\text{POR}']$. The result explains that the complexes are much potent bactericides than ligands.

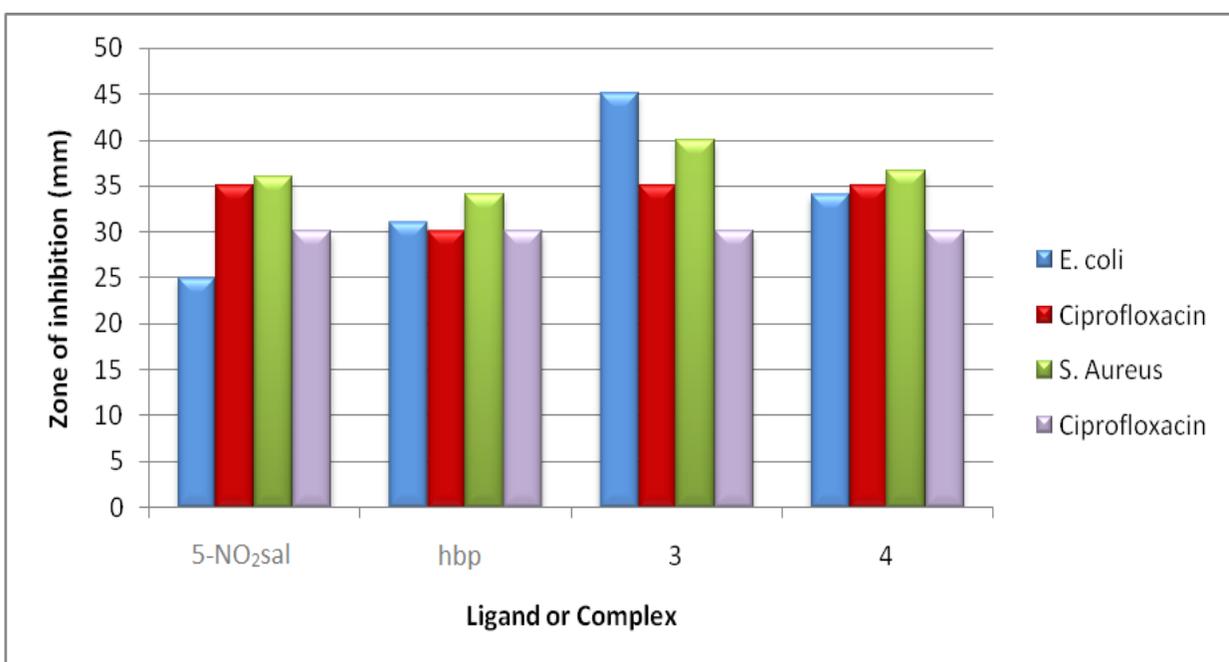


Fig. 5. The data of zone of inhibition of the ligands and their metal complexes

Table 5. Zone of inhibition (mm) of the ligands and their metal complexes

S. No.	Compounds	<i>E.Coli</i> Test zone	Ciprofloxacin control zone	<i>S.Aureus</i> Test zone	Ciprofloxacin control zone
1.	5-nitrosalicylaldehyde	25	35	36	30
2.	2-hydroxybenzophenone	31	30	34	30
3.	$[\text{Mn}(\text{hbp})(5\text{-Brsal})(\text{H}_2\text{O})_2]$	45	35	40	30
4.	$[\text{Mn}(\text{hbp})(\text{acac})(\text{H}_2\text{O})_2]$	34	35	36.6	30

Conclusion:

In present paper, the series of mixed ligand complexes of Mn(II) have been synthesized. All the prepared complexes have an octahedral geometry, high spin, non electrolyte and paramagnetic in nature. IR spectra 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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