



Spectroscopic Analysis And Antibacterial Evaluation of Some Mixed Ligand Complexes of Zn(II)

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ABSTRACT

Mixed ligand complexes of Zn(II) with 5-nitrosalicylaldehyde (HL) as primary ligand and various secondary ligands (L') like salicylaldehyde, substituted salicylaldehyde, 2-hydroxyaryl ketones or β -diketones have been synthesized in 1:1:1 molar ratios. The resulting complexes have been characterized by various physical and spectral studies. From the analytical and spectral data the stoichiometry of these complexes have been found to be $[M(L)(L')(H_2O)_2]$. It has been found that complexes exhibited octahedral geometry. At the same time, above mentioned complexes and ligands were studied for in vitro antimicrobial properties and found to be more potent bactericides than parent ligands.

Keywords: Mixed ligand complexes, β -diketones, octahedral geometry, antimicrobial properties.

INTRODUCTION

Over the last few years, the chemistry of β -diketones and hydroxyaryl aldehydes or ketones containing compounds has become an active area of research. The coordination compounds of transition metal (II) ions with ligand containing oxygen donor atoms have been the subject of greatest interest due to containing chelate groups and provide the extra stability of complexes [1]. The structural characterization of mixed ligand complexes may be interesting due to various ratios of coordination like 1:1, 1:2, 1:3 etc. Moreover many biological important mixed ligand transition metal complexes have been reported in the literature possessing antimicrobial [2], anti-inflammatory [3] and anti cancer[4] activities. The fact that zinc together with copper, magnesium, iron, chromium, nickel and manganese are essential metallic elements and displays great biological activity when associated with certain metal protein complexes, participating in oxygen transport[5], electronic transfer reactions[6], or the storage of ions has also created massive interest in the study of system containing metals.

Previously a number of biologically important metal complexes have been reported by our group. In order to broaden the scale of investigations on first series transition metal mixed ligand complexes of salicylaldehyde and substituted salicylaldehyde, 2-hydroxyaryl carbonyl compounds or β -diketones, we have synthesized, structurally characterized and determined biological activities of mixed ligand complexes of Zn(II) with 5-nitrosalicylaldehyde and hydroxyaryl aldehydes or ketones or β -diketones like $[Zn(5\text{-nitrosal})(L')(H_2O)_2]$ and results have been reported.

MATERIALS AND METHODS

Materials: $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (Merck) was used of A.R. grade. The ligands 5-bromo-salicylaldehyde (Himedia), 5-nitrosalicylaldehyde (Aldrich), 5-chlorosalicylaldehyde (Himedia), 2-hydroxy-1-naphthaldehyde (Fluka), 2-hydroxybenzophenone (Aldrich), 1-phenylbutane-1,3-dione (Himedia) and 1,3-diphenylpropane-1,3-dione (Merck) were purified by recrystallization from hot ethanol prior to use. Salicylaldehyde (Merck), 2-hydroxyacetophenone (Aldrich), 2-hydroxy-propiofenone (Fluka), Pentane-2,4-dione (K.Light) and ethanol were purified by distillation.

Analytical methods and physical measurements: Zinc was estimated volumetrically [7] by EDTA using Eriochrome black-T as an indicator. Nitrogen was determined by Kjeldahl's method. Carbon and hydrogen analysis 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 EC Double Beam UV-VIS Spectrophotometer using distilled water as a reference. Infrared spectra of the complexes were recorded in the region $4000\text{-}400\text{cm}^{-1}$ on a SHIMADZU-JAPAN 8400S FTIR spectrophotometer using KBr pellets. ^1H NMR spectra were recorded in DMSO-D_6 on a Jeol AL-300 at 300 MHz using TMS as reference. The ESI mass spectra were recorded on a MICROMASS QUATTRO II triple ionization mass spectrometer. Thermo gravimetric analysis were performed on Mettler Toledo star SW 701 instrument in the range $57.4\text{-}689^\circ\text{C}$ with the heating rate 10°C per minute.

Antibacterial Assay (Paper Disc Diffusion Method): This method was used to study the antibacterial activity of the complexes and their corresponding ligands against E.coli, Entrococii, Staphylococii and Straptococii pathogenic bacteria. In this method, 0.1 mL of inoculums of the test organism was spread uniformly on the surface of the agar medium in a petri plate by using a spreader. The sterilized Whatmann filter paper discs of 5 mm diameter were dipped into the 200 ppm solution of the complexes in DMSO and then were placed on the surface of the agar. Up to four discs in each plate were used. The plates were incubated at 37°C for 24 h. During incubation, the complex diffuses from the filter paper into agar. The activity of the complexes was assessed by measuring the diameter of the inhibited zone in millimeters (mm) carefully. The results were compared against those of control standard antibiotic drug Ciprofloxacin which was screened simultaneously. Ciprofloxacin has a definite value for each strain but the zone of inhibition may vary according to the experimental conditions as temperature, pH of the media and other factors. So it becomes essential to incorporate a positive control with each sample and each micro-organism. This is the reason, why a corresponding plate is set for ciprofloxacin for each sample with each bacterial strain. Solvent DMSO, used as blank, was also run to know its activity.

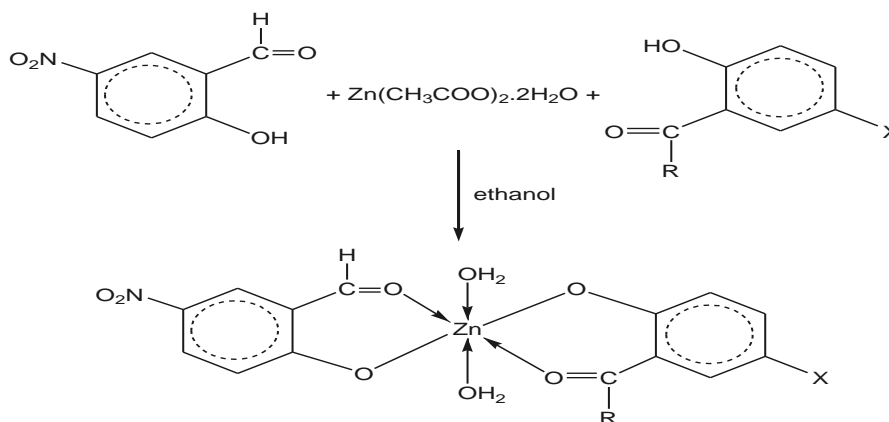
Synthesis of mixed ligand complexes of Zn (II): To an ethanolic solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.500gm in ~10ml ethanol), an ethanolic solution of 5-nitrosalicylaldehyde (0.3807gm in ~10mL ethanol) and salicylaldehyde (0.278gm dissolved in ~10mL ethanol) were added with constant stirring on magnetic stirrer. The reaction mixture was stirred for about 2 h and color of the solution was pale yellow. The pH of the solution was raised up to ~6.5 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 stand for 1-2 days. The settled solid was filtered, washed with ethanol and dried properly under reduced pressure. A similar method was adopted to synthesize mixed ligand complexes of Zn (II) with 5-nitrosalicylaldehyde and 5-bromoalicylaldehyde, 5-chlorosalicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-hydroxyaceto -phenone, 2-hydroxypropiofenone, 2-hydroxybenzophenone, Pentane-2,4-dione, 1-phenyl -butane-1,3-dione or 1,3-diphenylpropane-1,3-dione.

Table 1. Analysis and characteristics of the mixed ligand complexes $[Zn(L)(L')(H_2O)_2]$

S.No.	Complex, mol .wt.,mol formula	Colour, yield (%)	Analysis% found (Calcd.)			
			C	H	N	Zn
1	$[Zn(5-NO_2sal)(sal)(H_2O)_2]$ 388.63, $C_{14}H_{13}O_8NZn$	Yellow-orange (60.11)	42.91 (43.49)	2.56 (2.86)	3.47 (3.62)	16.27 (16.91)
2	$[Zn(5-NO_2sal)(5-Brsal)(H_2O)_2]$ 467.53, $C_{14}H_{12}O_8NZnBr$	Pale-yellow (61.47)	35.69 (36.12)	2.06 (2.16)	2.89 (3.00)	13.98 (14.04)
3	$[Zn(5-NO_2sal)(5-Clisal)(H_2O)_2]$ 424.06, $C_{14}H_{12}O_8NZnCl$	Yellow (63.25)	39.01 (39.88)	2.54 (2.85)	3.02 (3.30)	15.08 (15.41)
4	$[Zn(5-NO_2sal)(2-hnp)(H_2O)_2]$ 438.65, $C_{18}H_{15}O_8NZn$	Light yellow (71.18)	49.03 (49.51)	2.88 (3.00)	3.14 (3.20)	14.20 (14.97)
5	$[Zn(5-NO_2sal)(2-hap)(H_2O)_2]$ 402.67, $C_{15}H_{15}O_8NZn$	Brown-red (88)	44.05 (44.85)	3.21 (3.51)	3.11 (3.49)	16.08 (16.28)
6	$[Zn(5-NO_2sal)(2-hpp)(H_2O)_2]$ 416.70, $C_{16}H_{17}O_8NZn$	Light yellow (45)	45.99 (46.11)	4.05 (4.11)	3.07 (3.33)	15.21 (15.69)
7	$[Zn(5-NO_2sal)(2-hbp)(H_2O)_2]$ 464.74, $C_{20}H_{17}O_8NZn$	Yellow (57)	51.23 (51.68)	3.25 (3.68)	3.00 (3.01)	13.98 (14.07)
8	$[Zn(5-NO_2sal)(acac)(H_2O)_2]$ 366.64, $C_{12}H_{15}O_8NZn$	Brown (60)	44.02 (44.13)	3.92 (4.12)	3.50 (3.82)	17.28 (17.83)
9	$[Zn(5-NO_2sal)(bzac)(H_2O)_2]$ 428.71, $C_{17}H_{17}O_8NZn$	Orange-yellow (45)	47.25 (47.6)	3.58 (3.99)	3.14 (3.26)	15.02 (15.25)
10	$[Zn(5-NO_2sal)(dbzm)(H_2O)_2]$ 490.78, $C_{22}H_{19}O_8NZn$	Light-yellow (66)	53.50 (53.83)	3.65 (3.90)	2.63 (2.85)	13.02 (13.32)

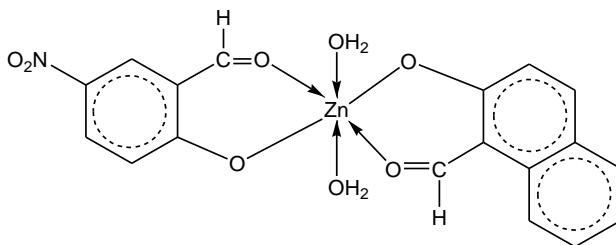
RESULTS AND DISCUSSION

Mixed ligand complexes of Zn (II) have been prepared by the reaction of Zinc (II) acetate dihydrate with 5-nitrosalicylaldehyde and salicylaldehyde, 5-bromosalicylaldehyde, 5-chlorosalicylaldehyde, 2-hydroxyacetophenone, 2-hydroxypropiophenone or 2-hydroxybenzophenone in 1:1:1 molar ratios result in the formation of mixed ligand complexes.

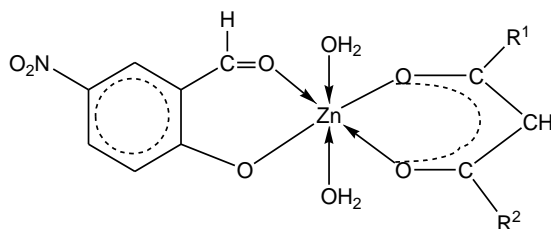


Scheme 1: Synthesis of mixed ligand complexes of Zn(II) with 5- NO_2sal and sal, 5-Brsal, 5-Clisal, hap, hpp or hbp
 R= -H, X= -H; R= -H, X= -Br; R= -H, X= -Cl; R= - CH_3 , X= -H; R= - C_2H_5 , X= -H; R= - C_6H_5 , X= -H

Similarly, the other mixed ligand complexes were synthesized with 5-nitrosalicylaldehyde and 2-hydroxy-1-naphthaldehyde or β -diketones as (Scheme 1.1 and 1.2) respectively.



Scheme 1.1: Mixed ligand complex $[Zn(5-NO_2sal)(hnp)(H_2O)_2]$



Scheme 1.2: Mixed ligand complexes of Zn(II) with 5-NO₂sal and β -diketones (acac, bzac & dbzm)

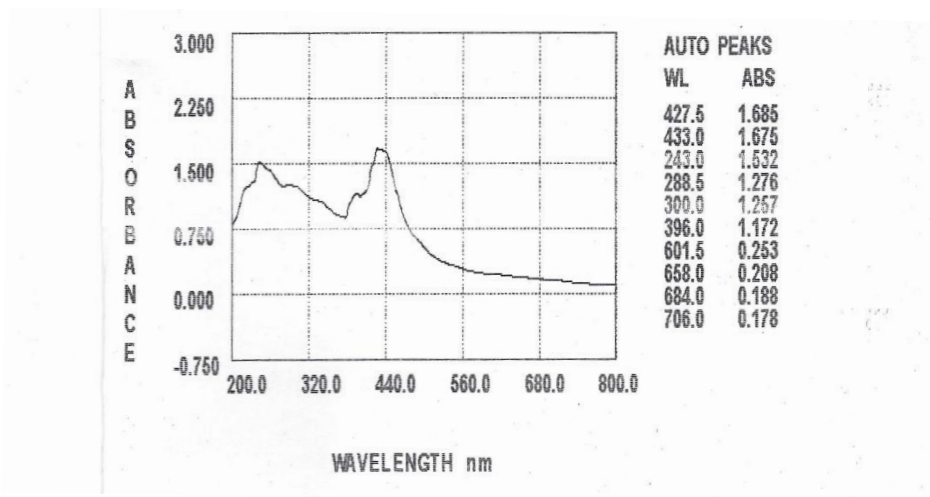
Micro-analysis: All resulting complexes are light yellow solids except $[Zn(5-NO_2sal)(2-hap)(H_2O)_2]$ which is brown-red in color and moisture stable amorphous solid which decomposes without melting. The elemental analysis data (**Table-1**) of mixed ligand complexes $[M:L:L']$ show the formation in 1:1:1 molar ratio. It has been found that the theoretical values are in good agreement with the found values. These are insoluble in water and common organic solvents like methanol, benzene, chloroform and carbon tetrachloride but soluble in DMSO and DMF.

Molar conductance measurements: Molar conductances (Λ_m) of the complexes in DMF (10^{-3} M solutions at 25°C) are observed in the range 20.01-49.05 $\Omega^{-1}cm^2mol^{-1}$ (**Table-3**) indicated that they all are non-electrolytic and monomeric in nature. Zahid *et al.* [8] have found molar conductivity in between 26-35 $\Omega^{-1}cm^2mol^{-1}$ for the complexes of Cu(II), Ni(II), Co(II), and Zn(II) indicating that all the metal complexes are non electrolytic in nature.

Magnetic moment and Electronic spectra: All the complexes of Zinc are diamagnetic [9] in nature and shows no any d-d transitions which further shows absence of empty d orbital in Zn (II). The electronic spectral data of free ligands and Zn (II) complexes were recorded (**Table-2**). The maximum absorption appears at 41322-40984 cm^{-1} (1.475 absorbance) in all free ligands which is attributed to O=C-C=C-OH chromophore of the ring in salicylaldehyde and substituted salicylaldehyde or β -diketones (acac, bzac and dbzm) ligands. The spectra recorded for all the complexes shows a band between 40984-40786 cm^{-1} region which showed lower values than ligands indicating that chromophore modified by the interaction with metallic ion as in (fig-1) spectrum of $[Zn(5-NO_2sal)(acac)(H_2O)_2]$. Such type of bands in spectra of ligands and their complexes of Zn and Cd have been found by A.I.El-Said *et al* [10]. The maximum absorption bands at 30,769 cm^{-1} for ceftriaxone ligand chromophore which are lowered in complexes of Zn (II) and Cd (II) at 28,818-29,761 cm^{-1} region indicating that chromophore modified by the interaction with metallic ion. The band recorded for all complexes at 23810-21645 cm^{-1} is attributed to charge transfer and is mainly due to M→L transitions. The peaks above 25253 cm^{-1} region is due to intraligand transition. There are two broad bands in region 25253-27624 cm^{-1} and 40984-40786 cm^{-1} could be ascribed to intraligand transition band in metal ligand complexes.

Table 2: Electronic spectral data of the mixed ligand complexes $[\text{Zn}(\text{L})(\text{L}')(\text{H}_2\text{O})_2]$

S.N.	Complex	ν_{max} (cm^{-1})	Assignments
1	$[\text{Zn}(5\text{-NO}_2\text{sal})(\text{sal})(\text{H}_2\text{O})_2]$	40983 37415 26252	Intra ligand transition Intra ligand transition M→L transition
2	$[\text{Zn}(5\text{-NO}_2\text{sal})(5\text{-Brsal})(\text{H}_2\text{O})_2]$	40322 35252 27834	Intra ligand transition Intra ligand transition M→L transition
3	$[\text{Zn}(5\text{-NO}_2\text{sal})(5\text{-Clsal})(\text{H}_2\text{O})_2]$	40532 37316 27391	Intra ligand transition Intra ligand transition M→L transition
4	$[\text{Zn}(5\text{-NO}_2\text{sal})(2\text{-hnp})(\text{H}_2\text{O})_2]$	40983 35252 27551	Intra ligand transition Intra ligand transition M→L transition
5.	$[\text{Zn}(5\text{-NO}_2\text{sal})(2\text{-hap})(\text{H}_2\text{O})_2]$	39852 37421 27624	Intra ligand transition Intra ligand transition M→L transition
6.	$[\text{Zn}(5\text{-NO}_2\text{sal})(2\text{-hpp})(\text{H}_2\text{O})_2]$	40271 35252 26645	Intra ligand transition Intra ligand transition M→L transition
7	$[\text{Zn}(5\text{-NO}_2\text{sal})(2\text{-hbp})(\text{H}_2\text{O})_2]$	40152 36325 25252	Intra ligand transition Intra ligand transition M→L transition
8.	$[\text{Zn}(5\text{-NO}_2\text{sal})(\text{acac})(\text{H}_2\text{O})_2]$	40152 36252 27094	Intra ligand transition Intra ligand transition M→L transition
9.	$[\text{Zn}(5\text{-NO}_2\text{sal})(\text{bzac})(\text{H}_2\text{O})_2]$	40983 35252 27624	Intra ligand transition Intra ligand transition M→L transition
10.	$[\text{Zn}(5\text{-NO}_2\text{sal})(\text{dbzm})(\text{H}_2\text{O})_2]$	39052 34596 25134	Intra ligand transition Intra ligand transition M→L transition

**Fig.1-** UV-VIS spectrum of mixed ligand complex $[\text{Zn}(5\text{-NO}_2\text{sal})(\text{acac})(\text{H}_2\text{O})_2]$

Infrared spectra: Infrared spectra of ligands show a broad band centered at around $2950\text{-}3090\text{ cm}^{-1}$ due to free phenolic hydroxyl group in free ligands [11] which disappeared in spectra of their complexes (Table-3) indicating the coordination of ligands in complexes through phenolic oxygen moiety as shown

in scheme 1. The ligands show a medium intensity band at around $1150\text{-}1290\text{cm}^{-1}$ due to phenolic =C-O group; is shifted to higher region or downfield at around $1300\text{-}1395\text{cm}^{-1}$ in complexes further indicating the coordination in complexes through phenolic oxygen moiety. The spectra of the complexes show broad diffused band in the region at around $3200\text{-}3420\text{cm}^{-1}$ due to $\nu(\text{OH})$ of the coordinated water molecules which are absent in ligands as shown in spectrum of $[\text{Zn}(5\text{-NO}_2\text{sal})(2\text{-hnp})(\text{H}_2\text{O})_2]$ (Fig.2).

In present work, the IR spectra of the complexes exhibit strong absorption bands in the region $1600\text{-}1700\text{cm}^{-1}$ and $1400\text{-}1510\text{cm}^{-1}$ which may be assigned to coordinated $\nu(\text{C=O})$ and $\nu(\text{C=C})$ respectively. The $\nu(\text{C=O})$ bands in ligands show at $1640\text{-}1806\text{cm}^{-1}$. The $\nu(\text{C=O})$ bands of the complexes are observed in the lower wave number side as compared to free ligands [12-14] confirming the coordination of $\nu(\text{C=O})$ group to the Zinc atom.

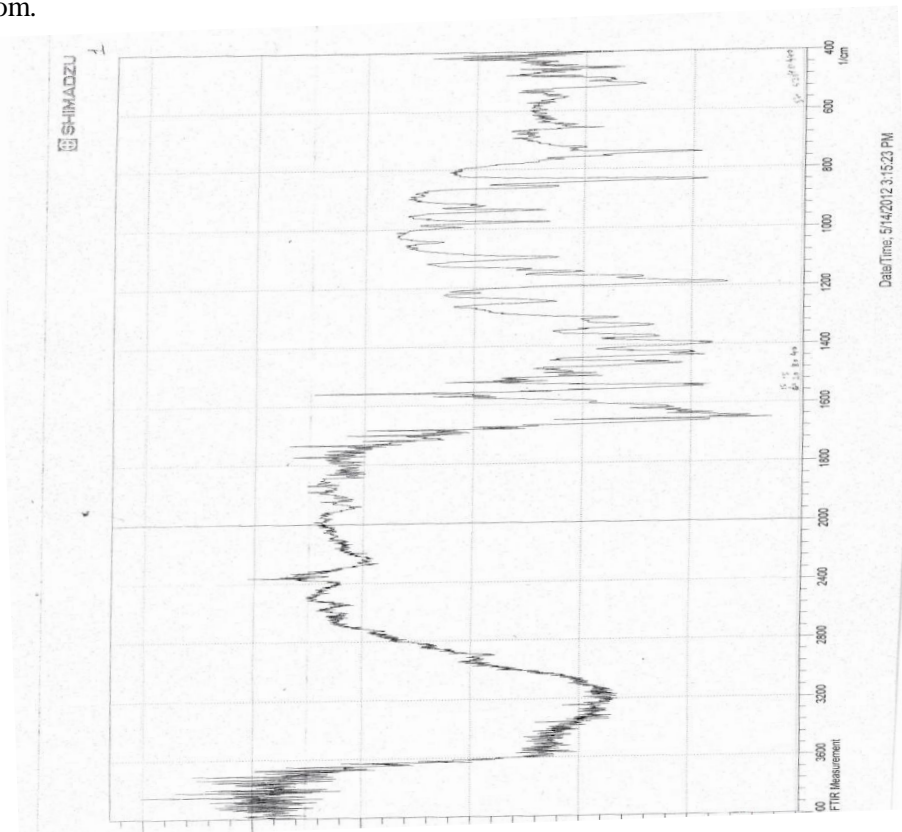


Fig.2- IR Spectrum of mixed ligand complex $[\text{Zn}(5\text{-NO}_2\text{sal})(2\text{-hnp})(\text{H}_2\text{O})_2]$

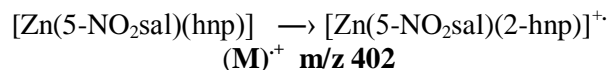
Surati *et al.*[15] have reported the lowering of coordinated $\nu(\text{C=O})$ at 1637cm^{-1} in complexes as compared to ligands (1671cm^{-1}) and stretching $\nu(\text{C-O})$ at $1350\text{-}1345\text{cm}^{-1}$ in $[\text{Mn}(\text{PMFP})(\text{Bipy})(\text{OAc})]\text{ClO}_4$ and $[\text{Mn}(\text{PMFP-Me})(\text{Bipy})(\text{OAc})]\text{ClO}_4$ complexes. Bands due to $\nu(\text{C=C})$ in the range of $1574\text{-}1543\text{cm}^{-1}$ in the Mn(III) complexes of the type $[\text{Na}[\text{Mn}(\text{L}1\text{-}6)_2].n\text{H}_2\text{O}]$ with schiff bases (obtained by the condensation of 2-hydroxy-1-naphthaldehyde with glycine, L-alanine, L-phenyl -alanine, L-histidine, L-tryptophen and L-threonine have been assigned by Sakiyan *et al*[16]. Bands have been observed for mixed ligand complexes of Co(II) with 5-nitrosalicylaldehyde and β -diketones, hydroxyarylaldehydes or ketones in the region of $1664\text{-}1604$ and $1556\text{-}1512\text{cm}^{-1}$ for $\nu(\text{C=O})$ and $\nu(\text{C=C})$ respectively by Prasad *et al* [17]. A broad band has been assigned to coordinated water molecule in the range of $3519\text{-}3373\text{cm}^{-1}$ by Gudasi *et al*[18] in the spectra of Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) complexes of a new tetradentate ligand N-(salicylidene) nitrosophenylglycine (H_2snp). They have been also assigned $\nu(\text{C-O})$ bands in these complexes in the region of $1263\text{-}1231\text{cm}^{-1}$ and $\nu(\text{M-O})$ at 516 and 454cm^{-1} .

Table 3: Conductances and IR bands of the mixed ligand complexes [Zn(L)(L')(H₂O)₂]

S. No	Complexes	Conductance $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	$\nu_{\text{C=C}}$	$\nu_{\text{C=O}}$	$\nu_{(\text{O-H})}$ in (Coordi - H ₂ O)	$\nu_{(\text{C-O})}$	$\nu_{\text{M-O}}$
1	[Zn(5-NO ₂ sal)(sal)(H ₂ O) ₂]	20.01	1400	1600	3420	1340	490
2	[Zn(5-NO ₂ sal)(5-Brsal)(H ₂ O) ₂]	35.06	1500	1665	3300	1345	495
3	[Zn(5-NO ₂ sal)(5-Clisal)(H ₂ O) ₂]	30.1	1510	1660	3310	1340	492
4	[Zn(5-NO ₂ sal)(2-hnp)(H ₂ O) ₂]	40.08	1440	1650	3200	1395	505
5.	[Zn(5-NO ₂ sal)(2-hap)(H ₂ O) ₂]	39.10	1490	1610	3360	1330	480
6.	[Zn(5-NO ₂ sal)(2-hpp)(H ₂ O) ₂]	40.45	1490	1600	3200	1355	518
7	[Zn(5-NO ₂ sal)(2-hbp)(H ₂ O) ₂]	49.01	1470	1610	3210	1350	510
8.	[Zn(5-NO ₂ sal)(acac)(H ₂ O) ₂]	45.51	1490	1650	3420	1300	480
9.	[Zn(5-NO ₂ sal)(bzac)(H ₂ O) ₂]	40.17	1495	1700	3420	1335	485
10.	[Zn(5-NO ₂ sal)(dbzm)(H ₂ O) ₂]	38.13	1483	1665	3360	1312	520

¹H NMR Spectral studies: ¹H NMR spectra for all complexes [Zn (5-NO₂sal) (L') (H₂O) ₂] and free ligands were recorded in DMSO-D₆ by taking TMS as internal reference. In free primary ligand 5-nitrosalicylaldehyde the aldehydic CH proton gives a signal at 10.34 ppm which is shifted in the mixed ligand complexes and appears at upfield 9.64 to 9.51ppm. This confirms the coordination of the C=O group of the aldehyde to metal atom. All the free ligands show a signal at 10.80-17.0ppm due to phenolic –OH group but in the spectra of Zn(II) complexes the signal due to -OH group disappeared indicating their involvement in coordination via deprotonation. This was also supported by the infrared spectral studies. The multiplets appearing at 6.38-8.4 ppm for all ligands corresponds to the protons of aromatic ring except acetylacetone in which phenyl ring is absent. These multiplets are shifted in the mixed ligand complexes and appears at upfield 6.0 to 8.0 ppm due to coordination of metal atom. Including secondary ligands like 2-hydroxyarylaldehyde or ketones, there is also a series of β-diketones such as acetylacetone (acac), benzoylacetone (bzac) and dibenzoylmethane(dbzm). In free β-diketones the resonance due to CH₃ and CH protons signals have been reported at 5.54-6.80 ppm and 1.99-2.25ppm respectively but these signals are observed at upfield 1.78-1.91ppm in the mixed ligand complexes of these ligands and confirm the coordination of these ligands to Zn metal in enolic form. Similar upfield shift have been reported for [Mg (5-Brsal) (acac)(H₂O)₂] by Prasad *et al* [19]. According to Recca *et al* [20] appearing of CH signals of β-diketones in a region very close to that of aromatic proton supports the psuedoaromatic character of the ring involving the metal atom in the β-diketones ligands.

ESI Mass spectral studies: The graphical representation of mass spectrum of complex [Zn(5-NO₂sal)(2-hnp)] (Fig.3), is constructed by plotting mass charge ratio (m/z) versus relative abundance or % of base peak is the most intense peak in spectrum which can be seen at m/z 164.2(100%) due to 5-nitrosalicylaldehyde moiety. Molecular ion peak or positive ion peak at m/z 402(12%) represents the intact complex less one electron which is knocked out by the impacting beam.



The molecular ion subsequently produce a series of fragment ions as shown for complex (Fig.3). The spectrum establishes that a M-1 peak at m/z 401 (3.8%) is formed by the loss of a hydrogen atom from any aromatic ring.

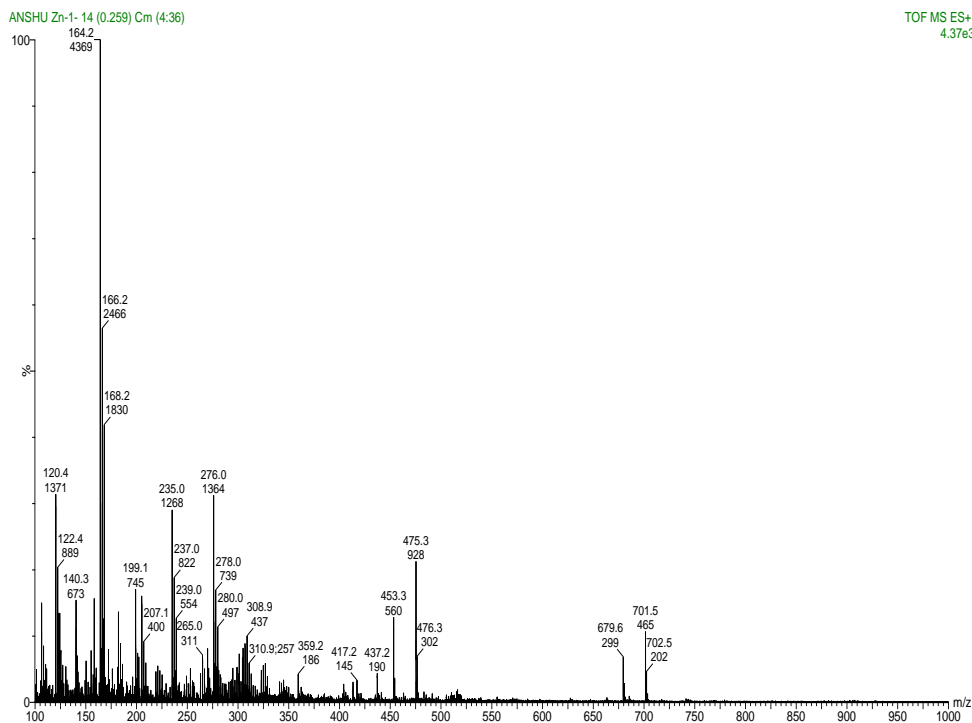
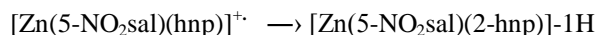
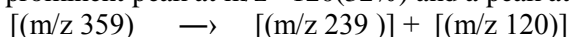


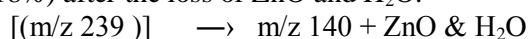
Fig.3- ESI mass spectrum of $[\text{Zn}(5\text{-NO}_2\text{sal})(2\text{-hnp})]$



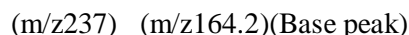
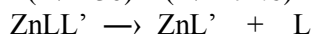
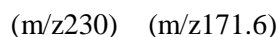
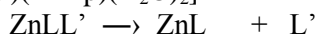
A peak can be seen at m/z 359(7%) due to loss of both arylaldehydic moiety from both ligands in complex. The primary ligand 5- NO_2sal leaves their oxygen of hydroxyl group attach to Zn and depart rest moiety $[\text{C}_6\text{H}_2\text{NO}_2]^+$ shows a prominent peak at m/z =120(32%) and a peak at m/z 239(15%) due to-



Peak can be seen at m/z 140(18%) after the loss of ZnO and H_2O .

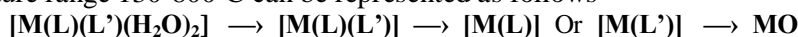


In addition to the molecular ion peak due to the mixed ligand complex MLL', peaks are also observed due to the formation of ML^+ and ML'^+ species, which are formed as a result of the loss of one or the other ligand moiety. In complex $[\text{Zn}(5\text{-NO}_2\text{sal})(2\text{-hnp})(\text{H}_2\text{O})_2]\text{-}$



A peak can be seen in the mass spectrum of complex at m/z 230 due to ML^+ species. The peak corresponding to ML'^+ , which would have resulted by the loss of 5-nitrosalicylaldehyde moiety is observed in the complex. Thus the loss of hnp moiety is less favorable and hence it may be concluded that 5-nitrosalicylaldehyde is less strongly bonded to the zinc atom than hnp ligand [21].

Thermo gravimetric analysis: The results of thermal analysis of mixed ligand complexes $[\text{Zn}(5\text{-NO}_2\text{sal})(\text{sal})(\text{H}_2\text{O})_2]$, $[\text{Zn}(5\text{-NO}_2\text{sal})(\text{acac})(\text{H}_2\text{O})_2]$ & $[\text{Zn}(5\text{-NO}_2\text{sal})(\text{bzac})(\text{H}_2\text{O})_2]$ have been shown in **Table-4**. The results showed that the complex was thermally decomposed in three successive decomposition steps within the temperature range 130-800°C can be represented as follows-



The TG curves of these complexes indicated the presences of coordinated water molecules and the final product were the metal oxides. The first decomposition step for all three complexes within the temperature range 130-230^oc which is reasonably accounted for the removal of two coordinated water molecules, which confirms the presence of two coordinated water molecules in the Zn-complex. The perusal of thermogram shows the presence of water molecules in the complexes which further corroborates the observation made on the basis of infrared spectral studies and is in the good agreement with the elemental analysis.

Table 4- Thermal data of Mixed ligand complexes [Zn(L)(L')(H₂O)₂]

S.No	Complexes	Step	Temp. range (°C)		Mass Loss %		Assignments (Mass)
			T _i	T _f	Cal.	Obs.	
1	[Zn(5-NO ₂ sal)(sal)(H ₂ O) ₂]	1	168	200	9.28	9.31	Loss of 2H ₂ O
		2	200	350	30.36	31.03	Loss of sal moiety
		3	350	800	43.36	43.19	Loss of 5-NO ₂ sal
2	[Zn(5-NO ₂ sal)(acac)(H ₂ O) ₂]	1	130	230	11.12	9.81	Loss of 2H ₂ O
		2	230	460	45.3	45.53	Loss of 5-NO ₂ sal
		3	460	868	25.5	23.0	Loss of acac moiety
3	[Zn(5-NO ₂ sal)(bzac)(H ₂ O) ₂]	1	160	200	8.4	8.39	Loss of 2H ₂ O
		2	200	512	40.3	38.92	Loss of 5-NO ₂ sal
		3	512	870	38	37.52	Loss of bzac moiety

El-Wahed *et al* [11] have also reported the loss of coordinated water molecules in the temperature range 150-300^oC in a sulfasalazine Mn(II) complex of the type [Mn(SuzH) (H₂O)₄].2H₂O. The second step is found between the temperature range 200-512^oC may be attributed to the liberation of salicylaldehyde ligand moiety in first complex while 5-nitrosalicylaldehyde ligand moiety in remaining both complexes. The decomposition of the rest of the complex molecule ended with the formation of ZnO in the third step within the temperature range 350-870 °C. Kriza *et al*[22] have been found the decomposition range 272-800^oc for the complex [Zn(INNMH)(ac)₂].2H₂O, the decomposition of the rest of the complex molecule ended with the formation of ZnO, which supports our result, as we have also found ZnO in last step.

APPLICATIONS

In vitro antibacterial screening: The ligands and the complexes [Zn(5-NO₂sal)(L')(H₂O)₂] were screened against the pathogenic bacterial strains gram - negative *E.coli* and gram- positive *Entrococci*, *S.aureus* and *Straptococcus pneumoniae*. The solvent DMSO was used as a negative control whereas **Ciprofloxacin**, a standard antibiotic, was used as a positive control. The antibacterial screening data have shown (**Table-5**).

The results showed that ligands like salicylaldehyde and substituted salicylaldehyde exhibit moderate activity against all tested bacteria but β -diketones showed least effect or no effect.

Table 5-: Zone of inhibition of mixed ligand complexes $[Zn(L)(L')(H_2O)_2]$ in mm

S.No	Complexes	<i>E.coli</i>	<i>Entrococii</i>	<i>Staphylococii</i>	<i>Straptococii</i>
1	$[Zn(5-NO_2sal)(sal)(H_2O)_2]$	8	12	8	8
2	$[Zn(5-NO_2sal)(5-Brsal)(H_2O)_2]$	8	9	-	-
3	$[Zn(5-NO_2sal)(2-hnp)(H_2O)_2]$	11	7	10	8
4	$[Zn(5-NO_2sal)(2-hap)(H_2O)_2]$	10	9	11	8
5	$[Zn(5-NO_2sal)(2-hpp)(H_2O)_2]$	11	9	10	7
6.	$[Zn(5-NO_2sal)(acac)(H_2O)_2]$	8	8	6	6
7.	$[Zn(5-NO_2sal)(bzac)(H_2O)_2]$	6	10	-	7
8	$[Zn(5-NO_2sal)(dbzm)(H_2O)_2]$	15	8	13	7
9	Ciprofloxacin	24	22	20	20
10	DMSO	0	0	0	0

It is important to note that the metal chelates exhibit more inhibitory effects towards bacterial strain than the parent ligands. Increased activity of the metal chelates as compared to ligands can be explained on the basis of chelation theory [23,24]. According to chelation theory, 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 lipophilic character of the metal chelate and favors its permeation through the lipid 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 some other factors like solubility, conductivity and bond length between the metal and the ligand, which also increase the activity. Moreover, Tweedy's overtone concept of cell permeability [25-28] 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 complexes are much potent bactericides than the standard control ciprofloxacin against *S. aureus* and *E. coli*.

CONCLUSIONS

In the light of the above discussion, an octahedral geometry for Zn (II) complexes is proposed. All the complexes are non-electrolyte and diamagnetic in nature. In the IR spectra of the complexes, shifting of $\nu(C=O)$ to lower wave number side supports the chelation of the ligand to the metal atom and also 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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