



## Synthesis, Spectral and Biological Studies of Complexes with Bidentate Azodye Ligand Derived from Resorcinol and 1-amino-2-naphthol-4-sulphonic Acid

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### ABSTRACT

A new series of transition metal complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Fe(III) with the azo dye, 3-hydroxy-4-(2,4-dihydroxyphenylazo)naphthalene-1-sulphonic acid (LH) have been synthesized and characterized. The structural features have been arrived from their microanalysis, magnetic susceptibility, molar conductance measurements, mass, fluorescence, IR, UV-Vis, <sup>1</sup>HNMR and ESR spectral studies. Mössbauer spectra of two iron complexes have been done. In the light of these results, it is suggested that ligand coordinates to metal ions via hydroxyl oxygen and nitrogen of azo group. The fluorescence spectral property of ligand and complexes studied where complexes shows enhanced emission. The redox property of the Co(II) complex is studied by cyclic voltammetry. The ligand and its Mn(II) complex was investigated for non linear optical property. The *in vitro* biological activity of the ligand and complexes were tested against *Escherichia coli*, *Staphylococcus aureus*, *Aspergillus niger* and *Candida albicans*. The results indicate that the complexes have enhanced biological activity than the ligand. Antioxidant activity of the ligand and complexes was studied by free radical scavenging method. The nuclease activity of ligand and complexes show that they cleave DNA through redox chemistry.


**Keywords:** Azo dye, Mössbauer spectra, NLO property, DNA cleavage, Antioxidant activity.

### INTRODUCTION

In the last few years, a lot of interest have been taken by chemists in the synthesis and physicochemical studies of first row transition metal complexes with a number of azo dye ligands<sup>1</sup>. Azo dyes readily form stable complexes with most

of the transition metals that plays an important role in the development of coordination chemistry<sup>2</sup>. Azo dyes have massive applications in various fields of science and technology they serve as a class of widely used colouring materials<sup>3</sup>. They play a major role in textile, printing, leather, paper making, drugs<sup>4</sup> and in food industries<sup>5</sup>. The



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increasing use of these dyes in electronic industry such as colorimetric sensors, non linear optical (NLO) devices and liquid crystalline displays. They are also used as potential sensitizers for photodynamic therapy<sup>6</sup>. In bioinorganic chemistry, interest in azo dye complexes has centered on the role that complexes play in providing synthetic models for the metal containing sites in metallo-proteins and enzymes<sup>7,8</sup>. Metal ions involved in biological processes of life has been a subject of interest<sup>9,10</sup>. The modes of action of metal ions are often complex but are believed to involve bonding with the hetero atoms of the heterocyclic residues of biological molecules.

In the present paper, the synthesis and characterization of a new azo dye and its complexes have been reported. The aim of the study is to understand the spectrochemical and biological activities of this new dye and its complexes.

## EXPERIMENTAL

All reagents and solvents for synthesis and analysis were Merck products and used as supplied. FTIR spectra were recorded using KBr discs on a Perkin-Elmer Spectrum 65 spectrometer. Elemental analyses performed on a Vario EL-III CHN analyser. Conductivity measurements were made using Systronics direct reading conductivity meter. The magnetic susceptibilities were measured on a magnetic susceptibility balance Sherwood Scientific. Electronic absorption spectral measurements of the ligand and the complexes in methanol were conducted using Perkin-Elmer Lambda 25 UV-Vis spectrophotometer. <sup>1</sup>H NMR spectra was recorded on a Bruker Avance III, 400MHz FTNMR instrument using TMS as reference. The fluorescence spectral measurements of ligand and complexes in methanol were recorded on a JASCO-750 fluorescence spectrometer. The Mössbauer spectra of iron complexes recorded using Mossbauer Spectrometer Nucleonix Systems, constant acceleration mode at room temperature. The source employed was Co-57 in Rh matrix of strength 50 mCi. The velocity scale calibration was done using an enriched  $\alpha^{57}$  Fe metal foil of line width 0.23 mm/s using a Win-Normos fit program. The voltammetric measurements were carried on a BAS CV-50W voltammetric analyzer. The second harmonic generation (SHG) conversion efficiency of ligand determined by modified version of powder technique.

## Preparation of 3-hydroxyl-4-(2,4dihydroxy phenylazo)naphthalene-1-sulphonic acid [LH]

A solution of 1-amino-2-naphthol-4-sulphonic acid (0.01 mol) was prepared in least amount of HCl and cooled to 0 °C. A cold solution of NaNO<sub>2</sub> below 5 °C was added to the amine solution drop wise with continuous stirring. This cold diazonium salt solution was added to resorcinol solution (0.01 mol in NaOH) kept at 0 °C drop wise with stirring<sup>11</sup>. The dye separated was filtered off and dried in vacuo over anhydrous CaCl<sub>2</sub>. The purity of azo dye was confirmed by TLC.

## Preparation of the complexes

The complexes of LH were prepared by mixing ethanolic solutions of respective metal salt and LH in molar ratio 1:2. The solution obtained was heated under reflux for 4 h for completion of the reaction. The solid compound deposited filtered and washed three times with ethanol and dried over silica gel in a desiccator.

## RESULTS AND DISCUSSION

The metal and chloride content of the reported complexes were estimated following standard procedure<sup>12</sup>. Analytical data of complexes and the ligand are presented in Table.1. The elemental analyses shows that complexes has general stoichiometry of type [ML<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] where M = Mn(II), Co(II), Ni(II), Fe(II), Cu(II), [ZnL<sub>2</sub>] and [FeL<sub>2</sub>Cl(H<sub>2</sub>O)].

The ligand and its metal complexes are air stable, soluble in DMSO and DMF.

The <sup>1</sup>H-NMR spectra of LH and its Zn(II) complex were recorded in d<sub>6</sub>-DMSO solution on a 400 MHz FTNMR spectrometer using TMS as the reference material. The <sup>1</sup>H-NMR of LH shows a multiplet between  $\delta$  6.1 - 7.7 ppm (8H,m) due to aryl protons. The peaks respectively at  $\delta$  8.7 ppm (1H,s),  $\delta$  11.1(1H,s) and  $\delta$  9.3(1H,s) are assignable to OH of resorcinol and naphthol group. The singlet observed at  $\delta$  11.1 ppm due to one - group in LH is absent in the Zn(II) complex indicating deprotonation of one hydroxyl group before coordination to metal ion. The two other - protons were shifted to lower field. This indicates that among three phenolic - group one gets deprotonated and coordinated to Zn(II) and others remain as such. The values of aryl protons were also shifted to lower field indicating chelation of ligand. The singlet at  $\delta$  2.51 ppm corresponds to proton of sulfonic acid group in the LH shifted to lower field of  $\delta$  2.72 ppm<sup>13</sup>.

The <sup>1</sup>H-NMR spectrum of LH and [ZnL<sub>2</sub>] is given in Figure. 1 and Figure.2.

at m/z 784 and (M+Na) peak at m/z 806 confirms its stoichiometry. Mass spectrum of [ZnL<sub>2</sub>] is shown in Figure. 4.

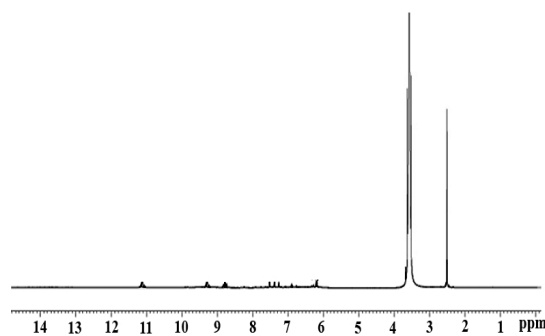
The ESI mass spectra of the LH shows a molecular ion peak at m/z =361 shown in Fig. 3. The mass spectrum of [ZnL<sub>2</sub>] shows a (M + 1) peak

The molar conductance of the complexes measured in methanol, DMF and in nitrobenzene supports the non electrolytic nature.

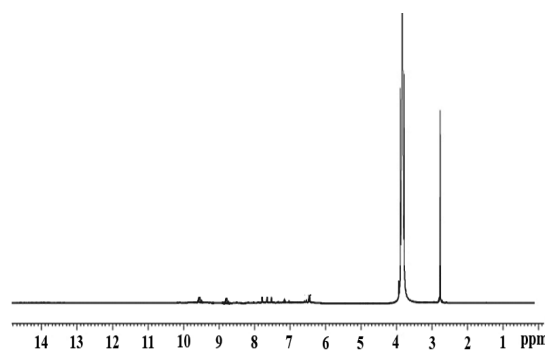
**Table. 1: Analytical data for ligand and complexes**

Compound	Mol. Wt	colour	%M	%Cl	%C	%H	%N	%S	μ <sub>eff</sub> (BM)
[LH]	360	Black	-	-	53.30(53.31)	3.32(3.33)	7.71(7.70)	8.88(8.87)	-
[MnL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	811	Black	6.77(6.76)	-	47.35(47.36)	2.72(2.70)	6.91(6.90)	7.89(7.90)	5.84
[Fe <sub>2</sub> Cl(H <sub>2</sub> O)]	829.35	Brown	6.71(6.70)	4.20(4.21)	46.43(46.30)	2.66(2.68)	6.76(6.75)	7.71(7.70)	5.71
[Fe <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	811.85	Green	6.87(6.88)	-	47.40(47.39)	2.72(2.75)	6.91(6.90)	7.88(7.87)	5.52
[Co <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	814.90	Yellow	7.23(7.22)	-	47.23(47.21)	2.72(2.71)	6.89(6.88)	7.88(7.87)	4.36
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	814.69	Black	7.20(7.19)	-	47.23(47.20)	2.71(2.73)	6.89(6.86)	7.86(7.85)	2.83
[CuL <sub>2</sub> ]	783.54	Reddish brown	8.11(8.10)	-	46.94(49.90)	2.69(2.67)	6.84(6.83)	7.82(7.83)	1.38
[ZnL <sub>2</sub> ]	785.34	Grey	8.32(8.30)	-	49.14(49.18)	2.83(2.85)	7.13(7.12)	8.15(8.14)	-

\*found(calculated)

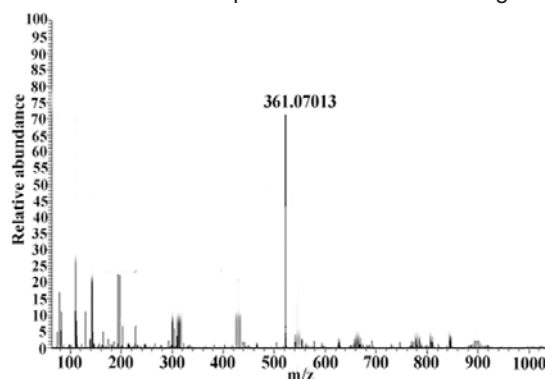


**Fig.1. <sup>1</sup>H-NMR spectra of [LH]**



**Fig 2. <sup>1</sup>H-NMR spectra of [ZnL<sub>2</sub>]**

Azo dyes are not only mere dyestuffs but also used in photodynamic therapy. There are recent reports on the photoluminescence properties of azo dyes, which are potential systems for photodynamic therapy<sup>14</sup>. LH, [MnL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] and [NiL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] exhibit fluorescence in the range 350-700 nm in methanol solution at room temperature. These are assigned



**Fig 3. Mass spectra of [LH]**

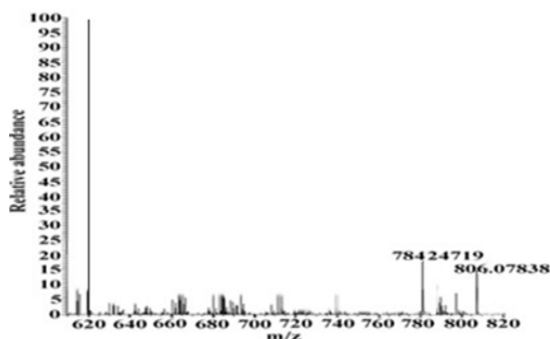


Fig 4. Mass spectra of [ZnL<sub>2</sub>]

as intraligand ( $\pi \rightarrow \pi^*$ ) fluorescence. It is interesting that Mn(II) and Ni(II) complexes show enhanced emission than that of free ligand. Metal ions can enhance the fluorescence emission of azo dye. The fluorescence spectra of LH, [MnL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] and [NiL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] are given in Fig 5. LH shows two emission bands at 470 and 594 nm when excited at 320 nm. [MnL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] shows emission at 407 nm and [NiL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] shows two bands at 409 and 569 nm when excited at 353 and 360 nm respectively.

The infrared spectra of LH and its metal complexes were recorded in the range 400 – 4000 cm<sup>-1</sup>. The infrared spectra of the complexes show characteristic absorptions of all functional groups of the ligand but at shifted position in the case of coordinated groups of the ligand.

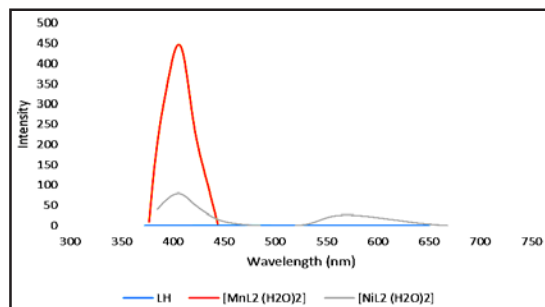


Fig. 5. Photoluminescence spectra of [LH]

The -N=N- stretching vibration of LH at 1459 cm<sup>-1</sup> shifted to 1431-1438 cm<sup>-1</sup> in its complexes indicating the azo group participation in coordination. All the complexes show additional band around 416 - 432 cm<sup>-1</sup> due to M-N coordination. The Stretching in LH complexes appears respectively at 3429 cm<sup>-1</sup>, 3436 cm<sup>-1</sup> and 3420 cm<sup>-1</sup> as broad band is due to hydrogen bonded hydroxyl groups. In the IR spectra of the complexes the disappearance of the band at 3420 cm<sup>-1</sup> indicates deprotonation of one OH group. This infers that one OH gets coordinated after deprotonation and others remain as such. The appearance of a new broad band around 3443 cm<sup>-1</sup> in complexes indicates the presence of water molecule. The presence of coordinated water molecule is again confirmed by the presence of two other bands within the ranges 1630-1600 and 970-950 cm<sup>-1</sup> due to HOH deformation and rocking. A band observed in range 1201 -1216 cm<sup>-1</sup> is due to the symmetric stretching vibration of -SO<sub>3</sub>H group. The appearance of new bands in the region 510-523 cm<sup>-1</sup> and 415-435 cm<sup>-1</sup> due to  $\nu_{M-O}$  and  $\nu_{M-N}$  supports the coordination of OH group and -N=N- group to metal ions<sup>15</sup>. The IR spectral evidences discussed so far indicate that the ligand is coordinated to the metal ion in uninegative bidentate manner. IR spectral data of LH and complexes are given in Table. 2.

The electronic spectra of ligand shows two absorption maxima at 320nm and 340 nm corresponding to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions and undergoes bathochromic shift upon coordination.

The spectrum of Cu(II) complex shows a shoulder in 462 nm due to  ${}^2A_{1g} \rightarrow {}^2B_{1g}$  d-d transition. The observed magnetic moment of this complex is 1.38 BM. This subnormal effective magnetic moment value indicates that the copper centres are ferromagnetically coupled<sup>16</sup>. The Ni(II) complex exhibits weak bands at 520 nm and 588 nm corresponds to  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}$

Table 2. Selected FT-IR data for ligand and its complexes (cm<sup>-1</sup>)

[LH]	[MnL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	[FeL <sub>2</sub> Cl(H <sub>2</sub> O)]	[FeL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	[ZnL <sub>2</sub> ]	Band assignments
3420	-	-	-	-	-	-	-	$\nu_{OH}$
-	3447	3446	3447	3445	3444	3434	-	$\nu_{H_2O}$
1459	1435	1431	1438	1438	1435	1432	1433	$\nu_{N=N}$
-	515	510	523	517	518	520	518	$\nu_{M-O}$
-	417	416	432	418	420	422	418	$\nu_{M-N}$

(F) transitions. The magnetic moment of this complex is 2.83 BM suggesting an octahedrally coordinate Ni(II) complex. The Co(II) complex exhibit peaks at 477 nm and 675 nm for  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  and  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  transitions. The magnetic moment value of 4.36 BM also indicates an octahedral geometry for the complex. The Fe(III) complex exhibits band at 660 nm and 680 nm assigned to  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  and  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  transitions. The magnetic moment value of 5.71 BM agrees to the octahedral high spin geometry of complex. The Fe(II) complex exhibit bands at 510 nm and 660 nm due to  ${}^5T_{2g} \rightarrow {}^5E_g$  transitions. This complex has an octahedral high spin state with a magnetic moment value of 5.52 BM. The Mn(II) exhibits a band at 474 nm due to d-d transition. The magnetic moment is 4.84 BM suggesting a distorted octahedral geometry<sup>18</sup>.

The X-band ESR spectrum of copper complex was recorded at 77 K is shown in Fig. 6. The frozen solution shows a well resolved four line hyperfine splitting in parallel region corresponds to the electron spin –nuclear spin interaction. The absence of half field signal at 1600G, corresponding to  $\Delta M_s = \pm 2$  transition, rules out any Cu-Cu interaction in ESR spectra. The frozen solution shows a well resolved four line hyperfine splitting in parallel region corresponding to the electron spin –nuclear spin interaction. The Cu complex exhibits two different g values, indicating the magnetic anisotropy in the complex. It exhibits two different g values, indicating the magnetic anisotropy in the complex. The spin Hamiltonian parameters, calculated for the complex are given in Table. 3. The g tensor values of the Cu(II) complex can be used to derive the ground state.

The  $g_{||}$  (2.41) >  $g_{\perp}$  (2.06) >  $g_e$  (2.0027) indicates that the complex has an axially elongated octahedral geometry. Further it is supported from the fact that the unpaired electron lies predominantly in  $d_{x^2-y^2}$  orbital as was evident from the value of exchange interaction term, G. The perpendicular component shows no hyperfine splitting  $A_{\perp} \approx \text{“} = \text{”} 0$ . The covalency factor  $\alpha^2$  calculated for the complex is 0.86, less than one indicates that the complex has some covalent character in ligand environment.

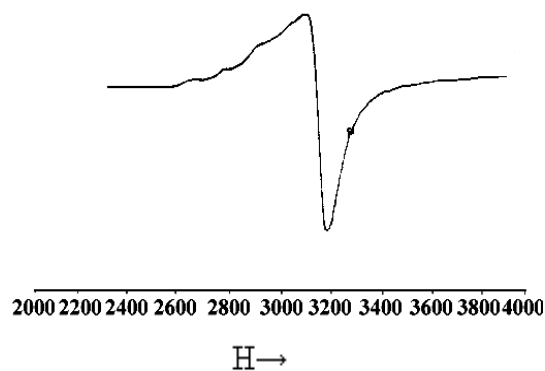
If  $G > 4$ , local tetragonal axes are aligned parallel or only slightly misaligned. The observed value for exchange interaction parameter for the Cu complex ( $G = 7.11$ ) suggests that the local tetragonal axes are aligned parallel or slightly

misaligned. The g values are taken to calculate the exchange interaction, if  $G > 4$ , the exchange coupling is negligible<sup>19</sup>.

**Table. 3: Electron Spin Resonance parameters of copper complex**

Complex	$g_{  }$	$g_{\perp}$	$g_{avg}$	$A_{  }$	G	$\alpha^2$
[CuL <sub>2</sub> ]	2.41	2.06	2.17	140	7.11	0.86

The cyclic voltammogram of the Co complex in MeCN in potential range 1.5 to -1.5 V shows a well defined redox process corresponding to the formation of Co(II)/Co(I) couple. A reduction peak at  $E_{pa} = -0.39$  V and at  $E_{pc} = -0.656$  V. This couple is found to be reversible with  $\Delta E_p = 0.266$  V. The ratio of anodic to cathodic peak currents ( $I_{pa}/I_{pc} = 1$ ) corresponding to one electron process. The



**Fig. 6. ESR spectra of [CuL<sub>2</sub>]**

complex shows another quasi reversible peak in the anodic region, characteristics of Co (II) / Co(III) couple at  $E_{pc} = 0.219$  V and at  $E_{pa} = 0.196$  V for Co(II) /Co(III) oxidation with  $\Delta E_p = 0.023$  V. The voltammetric studies proved that these complexes are relatively more stable. The peak separation of this couple is 0.023 V. The ratio of anodic to cathodic peak currents<sup>H</sup>1 corresponding to one electron process. The tapering of peak both in cathodic and anodic side may be due to ligand oxidation<sup>21</sup>. The cyclic voltammogram of [CoL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] is shown in Figure. 7.

The Mössbauer spectra of iron complexes were recorded at room temperature and given in Fig. 8 and 9 and Mössbauer parameters in Table. 4

The [FeL<sub>2</sub>Cl(H<sub>2</sub>O)] gives a signal with an isomer shift  $\delta = 0.35$  mm/s. The observed isomer shift value suggests that Fe(III) nucleus is in high spin state. A single signal indicates presence of some symmetry around Fe(III) ion in complex<sup>22</sup>.

[FeL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] shows four types of doublet with isomer shift value of 1.48, 1.26, 0.23 and 0.40 mm/s and quadruple splitting of 2.74, 3.29, 1.07 and 1.15 mm/s respectively indicating that there are four different species present in complex. The above parameters are characteristic of octahedrally coordinated high spin Fe(II) complex. The isomer shift does not indicate a similar electron density

around the iron atom. The values are consistent of iron (II) high spin configuration and are in agreement with magnetic moment value 4.52 BM<sup>23,24, 25,26,27,28</sup>.

The LH (L3), [MnL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (M3), [NiL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (N3) and [ZnL<sub>2</sub>] (Z3) complexes were tested for their inhibitory activity on antimicrobial growth by a modified disc diffusion method against

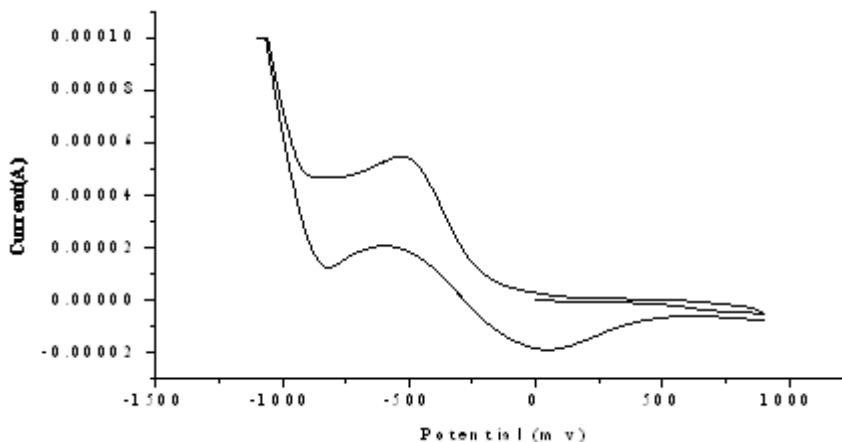


Fig. 7. CV of [CoL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]

*Escherichia coli*, *Staphylococcus aureus*, *Aspergillus niger* and *Candida albicans*. The standard drugs clotrimazole and gentamycin were taken as the standard. From the results it is clear that the inhibition zone of the complex is higher than that of the ligand. The higher activity of complexes can be explained by chelation<sup>29</sup>. The results are given in Figure.10.

The antioxidant activities of these compounds are expressed as 50% inhibitory

concentration (IC<sub>50</sub> in µg/ml) shown in Fig.11. IC<sub>50</sub> values of LH, [MnL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (M3) and [NiL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (N3) are 187±0.25, 166±0.13, and 185±0.12 µg/ml respectively. Mn complex shows better inhibitory action than ligand<sup>30</sup>.

The DNA gel electrophoresis experiment was conducted at room temperature using ligand and complexes in presence of H<sub>2</sub>O<sub>2</sub> as oxidant (Fig.12). Both ligand (L3) and its Ni(II) (N3) and Mn(II)

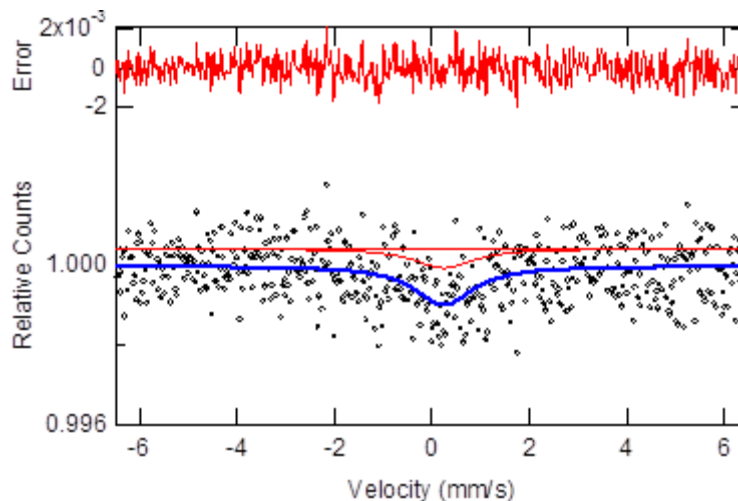


Fig. 8. Mössbauer spectra of [FeL<sub>2</sub>Cl(H<sub>2</sub>O)]

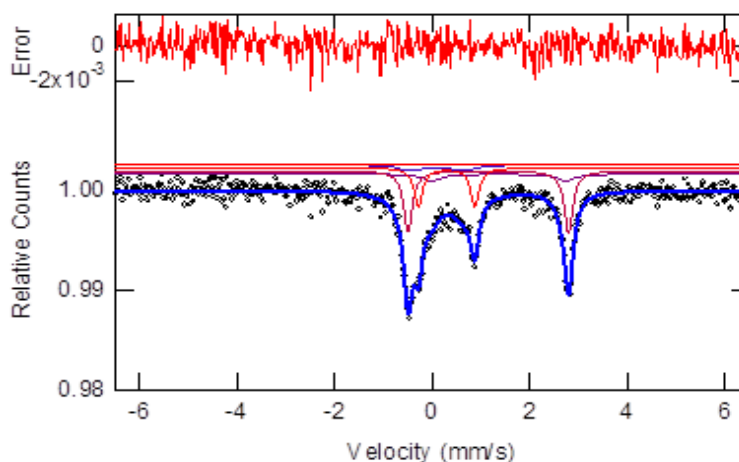


Fig. 9. Mössbauer spectra of  $[\text{FeL}_2(\text{H}_2\text{O})_2]$

Table. 4: Mössbauer parameters of compounds  $[\text{FeL}_2\text{Cl}(\text{H}_2\text{O})]$  and  $[\text{FeL}_2(\text{H}_2\text{O})_2]$

Compound	Spectral I; km component	IS, <sup>a</sup> (mm/s)	QS, <sup>b</sup> (mm/s)	Fe oxidation state	FWHM <sup>c</sup> (mm/s)	S <sub>r</sub> <sup>d</sup> ,(%)
$[\text{FeL}_2\text{Cl}(\text{H}_2\text{O})]$	Signal	+0.356	-	III(HS)	1.49±0.402	100.0
$[\text{FeL}_2(\text{H}_2\text{O})_2]$	Doublet I	+1.480	2.740	II(HS)	0.44±0.094	16.00
	Doublet II	+1.26	3.29	II(HS)	0.21±0.017	36.13
	Doublet III	+0.203	1.072	II(LS)	0.55±0.118	25.69
	Doublet IV	+0.40	1.151	II(LS)	0.22±0.040	22.12

Comp.: Compound, <sup>a</sup>Isomer Shift (IS) (relative to  $\alpha\text{-Fe}$ ), <sup>b</sup>Quadruple splitting (QS), <sup>c</sup>Full line width at half maximum (FWHM), <sup>d</sup>Partial resonant absorption areas ( $R_A$ ) of spectral components which represent relative contents of the corresponding form assuming a common recoilless fraction for all forms. HS: High spin, LS: Low spin.

M3 complexes exhibit nuclease activity due to their efficient DNA binding ability. The ligand and complexes were able to convert supercoiled DNA into open circular DNA. The reaction is modulated by metallocomplex bound hydroxyl radical<sup>31</sup>.

Control does not show any cleavage. This may be due to formation of redox couple of metal ions and its behavior. Further the presence of smear in the gel diagram indicates the presence of radical cleavage<sup>32</sup>.

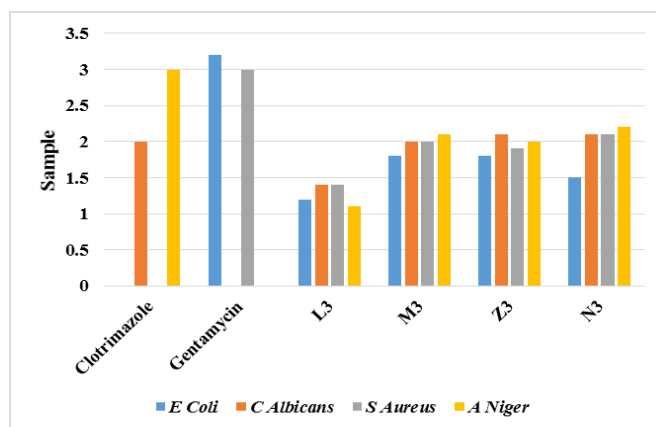


Fig.10. Antimicrobial activity of LH and its complexes

The Co(II) complex has been tested for cytotoxic activity against two human cancer cell line SiHa and SkBr<sub>3</sub>. The cells revived with RPMI medium containing 20% FBS. Procedure done in laminar air flow. For sub culturing, cells are given a media change a day after they are revived. Then onwards RPMI containing 10% FBS is used. Then cells are seeded by transferring them onto 96 well plates for Hoechst staining. The drugs were added after cells attain around 60% confluency in the culture plate and apoptosis was induced in them and observed under fluorescent microscope and is given in Fig. 13. It is interesting to observe that 100% chromatin condensation has occurred with SkBr<sub>3</sub> and an average of 95.5% condensation happened in SiHa compared to that of control<sup>32, 33,34</sup>.

The SHG efficiency of ligand and complex done by modified version of powder technique by Kurtz and Perry<sup>35</sup>. The second harmonic generation efficiency of LH and its [MnL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex were determined. The efficiency of sample was compared with microcrystalline powder of KDP. LH shows 5.1 SHG/mV, [MnL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] shows 5.3 SHG/mV compared to 11 SHG/mV for KDP. The percentage efficiency of LH is 46.36% and for [MnL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] it is 48.18% with respect to KDP. Mn(II) complex shows enhanced activity compared to LH. The experimental data infers that ligand and complex are less active. Though the present investigated azodye and its complex possesses a pathway of conjugated electrons the NLO activity is low and this may be due to absence of electron pushing and pulling substituents on aromatic rings<sup>36</sup>.

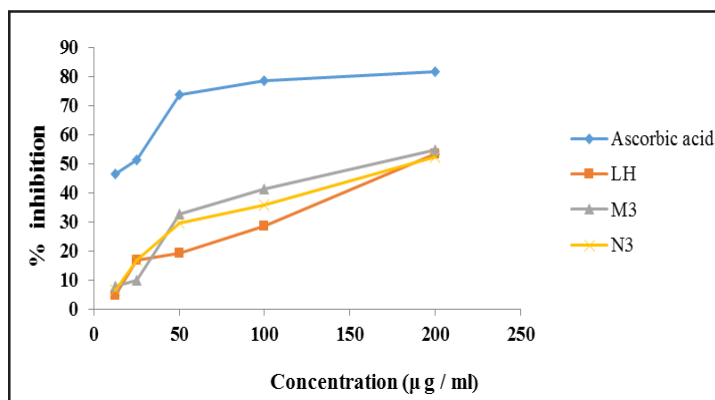


Fig. 11. Antioxidant activity

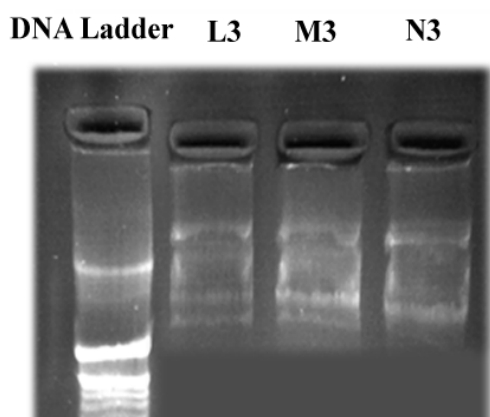


Fig. 12. DNA cleavage

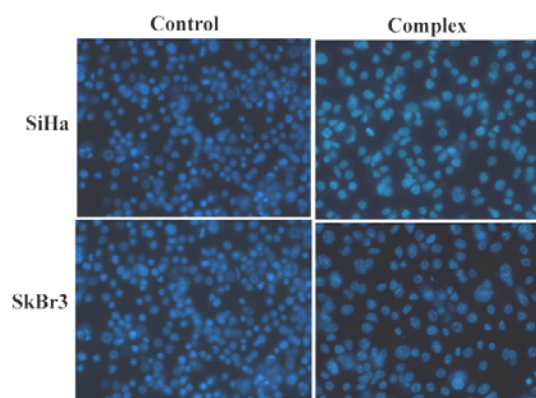


Fig. 13. Cytotoxic activity

### CONCLUSION

The coordination chemistry of ligand 3-hydroxy-4-(2,4-dihydroxyphenylazo)naphthalene-1-sulphonic acid has been investigated Analytical

data shows that in all complexes the metal ligand ratio are 1:2. The conductance value suggest that all complexes are non-electrolyte in nature. The hydroxyl proton of LH appeared at 11.10 ppm is absent in Zn(II) complex, which supports the



deprotonation of one OH group. The other NMR signals are shifted to lower field indicating the ligand chelation. The mass spectrum of LH and Zn(II) complex agrees well with the analytical data obtained. The infrared spectra of complexes indicates that LH acts as univalent bidentate ligand. Infrared spectral data also support the presence of coordinated water molecule in all complexes except for Zn(II). The mass spectrum supports this observation. The coordination centers are azo nitrogen and phenolic oxygen after deprotonation. All complexes exhibit octahedral geometry except for Zn(II) complex which is tetrahedral. This is further evidenced by electronic spectra and magnetic moment values. IR spectral data suggest univalent bidentate chelation of ligand and coordination sites are azo nitrogen and phenolic OH after deprotonation. The Mn(II) and Ni(II) complexes

show enhanced fluorescence. The NLO activity of Mn(II) complex is comparatively higher compared to the ligand. The metal complexes have enhanced antimicrobial activity than ligand. Antioxidant property of the ligand and complexes also studied. The interaction of ligand and complexes with DNA was investigated by gel electrophoresis. It is observed that ligand and complexes cleave DNA as compared to control in the presence of H<sub>2</sub>O<sub>2</sub>. This report has also highlighted the importance of Co(II) complex for anticancer activity.

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