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Der Pharmacia Lettre, 2016, 8 (21): 55-74
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Metal Complexes of Multidentate Azo Dye Ligand Derived From 4-Aminoantipyrine and 2, 4 -Dihydroxy Acetophenone; Synthesis, Characterisation, Computational and Biological Study

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ABSTRACT

A series of Co(II), Ni(II), Cu(II) and Zn(II) metal complexes have been synthesized with the new azo dye ligand 4-(2',4'-dihydroxy-5'-ethanoylphenylazo)antipyrine derived from 4-aminoantipyrine and 2,4-dihydroxyacetophenone. The ligand and its metal complexes have been characterized by various physico-chemical techniques such as analytical, molar conductance measurement, magnetic susceptibility measurement, IR, NMR, ESR, electronic spectral study, thermal and XRD study. Since their analytical and spectral characteristics, octahedral geometry for Co(II), Ni(II), Cu(II) and distorted tetrahedral for Zn(II) are suggested. The XRD (powder pattern) study of the Cu(II) complex indicated tetragonal crystal system. The fluorescence study of the Zn(II) complex revealed its photo conducting properties and thermo gravimetric properties of the complex indicated its thermal stability. Computational study provided global reactive descriptors and geometrical parameters of the ligand and its metal complexes. The biological study of the newly synthesized compounds indicated their antibacterial properties and DNA binding ability.

Keywords: 4-amino antipyrine, gel electrophoresis, SEM image, non-linear optical properties

INTRODUCTION

Azo compounds are known for widespread applications in various fields and have been attracting the attention of synthetic and theoretical chemists. They are the subject of large research work due to their applications as textile dyes [1], pharmaceuticals [2], indicators[3]. Azo dyes are the important class of dyes accounting for about 50% of all commercial dyes. With the report of Gratzel's group, scientific community have been attracting towards the dye sensitized solar cells as the promising photovoltaic devices. Azo dyes derived from heterocyclic amines containing nitrogen in the aromatic rings and their metal complexes have been receiving the attention of research groups due to their biological activities as antitumor [4], antibacterial [5], antifungal [6]. These compounds are now in good demands as optical and conducting organic materials [7]. Azo dyes derived from Triazolyl moiety is used as a chromogenic agent for the micro determination of metal ions [8] and its metal complexes acted as antibacterial, antifungal, cytotoxic agents[9]. Metal complexes with azo Schiff base derived from heterocyclic amines are showing cytotoxic and antibacterial properties [10,11]. These observations encouraged us to synthesize a new azodye ligand

from 4-aminoantipyrine and 5-2,4-dihydroxyacetophenone, their Co(II), Ni(II), Cu(II), Zn(II) complexes for evaluation of their biological activities.

MATERIALS AND METHODS

All the solvents, the metal salts and other chemicals used are either analytical grade or high purity supplied by Merck and BDH. Doubly distilled water is used in all experiments.

Equipment's

Elemental analysis of the ligand and complexes is carried out by Perkin –Elmer elemental analyzer, cobalt, nickel, copper and Zn(II) contents is determined by Perkin –Elmer2380 atomic absorption spectroscopy and chloride contents are estimated by standard procedure, Systronic conductivity bridge 30 is used to measure molar conductance of the complexes, Magnetic susceptibility of the complexes is measured by Guoy's balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant at room temperature and diamagnetic correction have been made by pascal's constants, IR spectra of the ligand and metal complexes are recorded on using KBr pellets by perkin elmer FT- IR spectrometer within the range $4000\text{--}450\text{ cm}^{-1}$, UV-Visible spectra of the complexes are collected using a THERMO SPECTRONIC 6 HEXIOS α and fluorescence spectra are recorded in a Fluorescence spectrometer, ^1H NMR spectra of the ligand and the Zn(II) complex are obtained from Bruker AV III 500 MHZ FT NMR spectrometer using TMS as reference, ESR spectrum of the Cu(II) complex is recorded on JES-FA 200 ESR spectrometer, mass spectra of the ligand and its complexes are recorded through JEOL GC Mate GC-MS Mass Spectrometer, thermal study of the metal complex is done by NETZSCH STA 449 F3 JUPITOR, SEM image of the complexes are taken in JES FA 200, the XRD powder pattern of the Cu(II) complex is collected using a Philips X'Pert Pro diffractometer.

Computational study

Molecular modeling is now considered as a important tool for calculating certain physic-chemical and geometrical parameters of the chemical compounds. In order to get the better picture about reactivity and geometrical parameters, computational study of the ligand and the metal complexes are performed by Gaussian 03 software package[12]. The molecular geometry of the ligand and its complexes are fully optimized using B3LYP level of theory along with 6-331G(d,p) basis set. The B3LYP provides better results than the Hartree-Fock method and reproduce better geometrical parameters comparable to the experimental values.

Biological Activity

The DNA binding study of the azo compounds is made by Gel electrophores method[13]. 10 μL of the metal complexes are taken along with 15 μL of CT DNA solution dissolved in Tris-EDTA in centrifuge tubes. The tubes are incubated at 37°C for 1 hour. After incubation, the tubes containing solution are kept in a refrigerator at 0°C for few minutes, 5 μL gel loading buffer with tracking dye (0.25% bromo phenol) is taken in the tubes for electrophoresis. The electrophoresis is continued under constant voltage (50 V) and photographed under UV illumination.

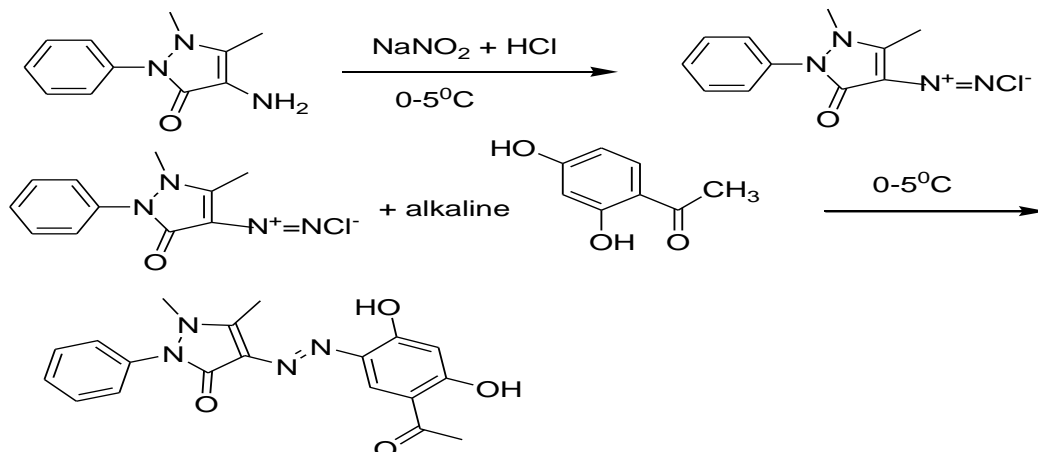
Hydrodynamic volume change[14] is observed by Ostwald Viscometer immersed in a thermostatic bath maintained at 37°C . A digital stopwatch is used to measure the flow time, mixing of complexes under investigation with CT-DNA is carried out by bubbling nitrogen. Data are presented by plotting a graph indicating $(\eta/\eta_0)^{1/3}$ verses $[\text{complex}]/[\text{DNA}]$ where η is the viscosity of DNA in presence of complexes and η_0 represents the viscosity of DNA alone. Viscosity values are collected by following the equation $\eta = t - t_0$ where t is the flow time of the DNA containing solutions and t_0 is the flow time of DNA alone.

The antibacterial activity of the ligand and its metal complexes is studied in vitro by the cup-plate method[15] against the *Escherichia coli* (MTCC-40) and *Staphylococcus aureus* (MTCC-87) using agar nutrient as the medium by the cup plate method[15]. The investigated ligand and its complexes are dissolved in DMF. The sterilized agar

plates are swabbed with the bacteria culture and filled with test solutions, then incubated at 37 °C for 24 hours. The activity is evaluated by measuring the zone of inhibition with respect to the standard drug Tetracycline

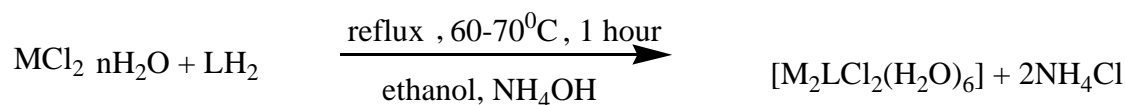
Synthesis of ligand

The ligand 4-(2',4'-dihydroxy-5'-ethanoylphenylazo)antipyrine is synthesized by the coupling reaction between the diazonium chloride produced from 4-aminoantipyrine and alkaline solution 2,4-dihydroxyacetophenone. This can be achieved by diazotization of 4-aminoantipyrine by dissolving 0.01M, 2.03 gram of it in hydrochloric acid, cooling it to 0-5°C and adding equivalent amount of ice cooled sodium nitrite solution with stirring. The cooled diazonium chloride is then made to react with the alkaline solution of 2,4-dihydroxyacetophenone(0.01M,1.52 gram). The colored azo dye ligand is formed which is recrystallized from ethanol.

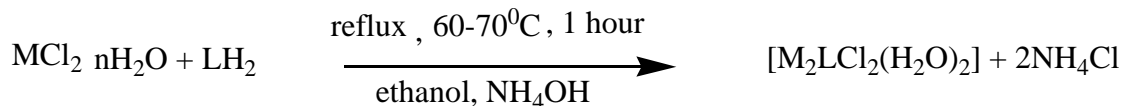


Synthesis of Metal complexes

The Metal (Co(II), Ni(II), Cu(II) and Zn(II)) chlorides(0.01 mol) in ethanolic solution are added to the DMF solution of the ligand(0.01 mol) separately. The reaction mixtures are refluxed for about one hour and the refluxed solutions are allowed to cool and concentrated Ammonia solution was added drop by drop till the formation of precipitates of Co(II), Ni(II), Cu(II) and Zn(II). The precipitates of azo metal complexes as given in Figure-1, Figure-2 are collected by filtration, washed with ethanol and dried in vacuum. This is represented in reaction Scheme-2



M=Co(II), Ni(II), Cu(II)



M= Zn(II)

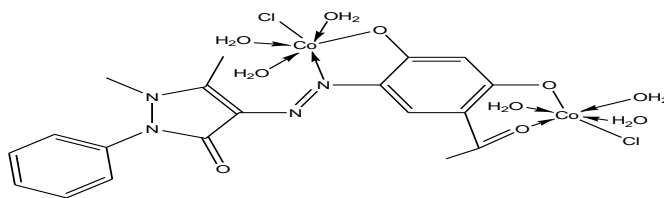


Figure-1: Co(II) complex of the ligand

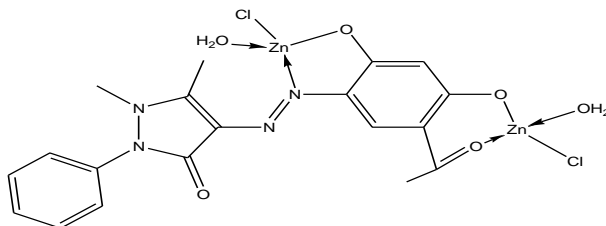


Figure-2: Zn(II) complex of the ligand

RESULTS AND DISCUSSION

The ligand and all its metal complexes are coloured and stable to air. The complex compounds are soluble in solvents like DMF and DMSO but remain insoluble in ethanol, chloroform, acetone. The high melting point of all complexes from the melting point of ligand indicates more thermal stability of the complexes than the ligand.

Table: 1. Analytical data

comp	Colour	Yield (%)	M.P (°C)	% Found(calcd)				
				M	C	H	N	Cl
1	Red	61	65	-	62.09 (62.29)	4.81 (4.95)	15.05 (15.09)	-
2	Bright red	53	>300	17.61 (17.83)	34.42 (34.51)	4.11 (4.27)	8.26 (8.47)	10.55 (10.72)
3	Coffee red	58	>300	17.49 (17.77)	34.38 (34.54)	4.13 (4.27)	8.23 (8.48)	10.49 (10.72)
4	Brown	60	>300	18.61 (18.96)	33.98 (34.04)	4.05 (4.21)	8.25 (8.36)	10.38 (10.58)
5	Brickred	53	>300	21.43 (21.72)	37.49 (37.90)	3.15 (3.35)	9.08 (9.31)	11.54 (11.78)

Note: 1.LH₂, 2. [Co₂LCl₂(H₂O)₆], 3. [Ni₂LCl₂(H₂O)₆], 4. [Cu₂LCl₂(H₂O)₆], 5. [Zn₂LCl₂(H₂O)₂]

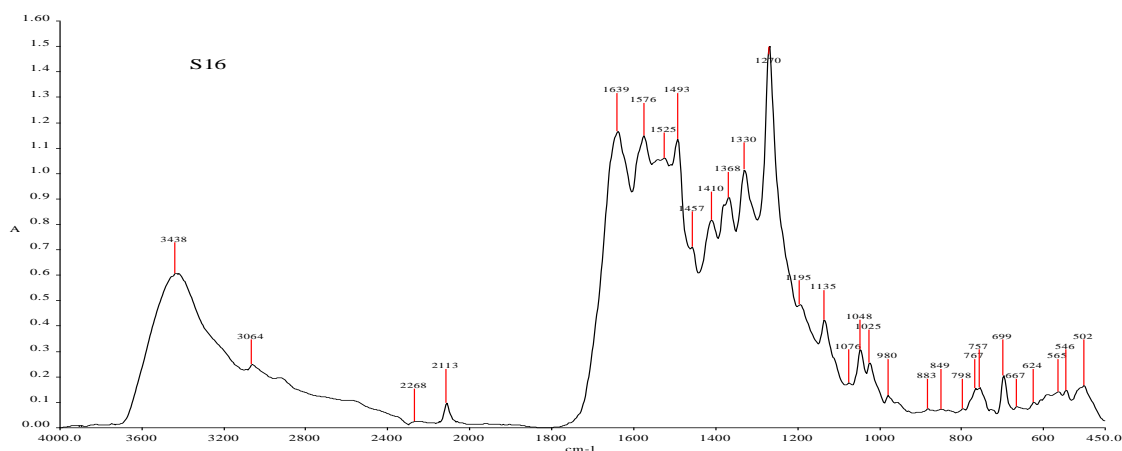
Conductance measurements

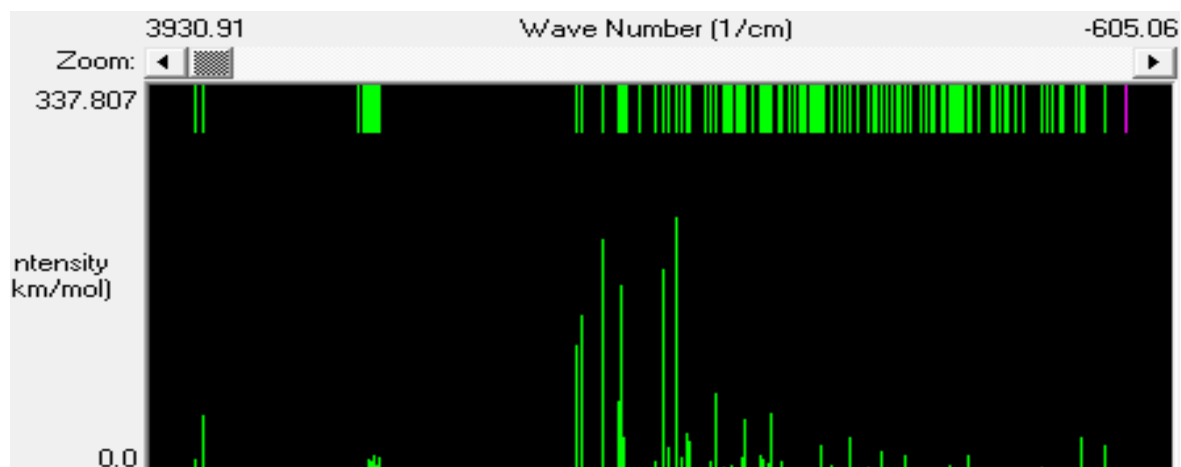
The Conductance measurements of the solutions of the metal complexes(10^{-3} M in DMF) show the value in the range of 2-20 $\text{Ohm} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. These values suggest that all metal complexes are non-electrolyte in nature [16].

Spectral study

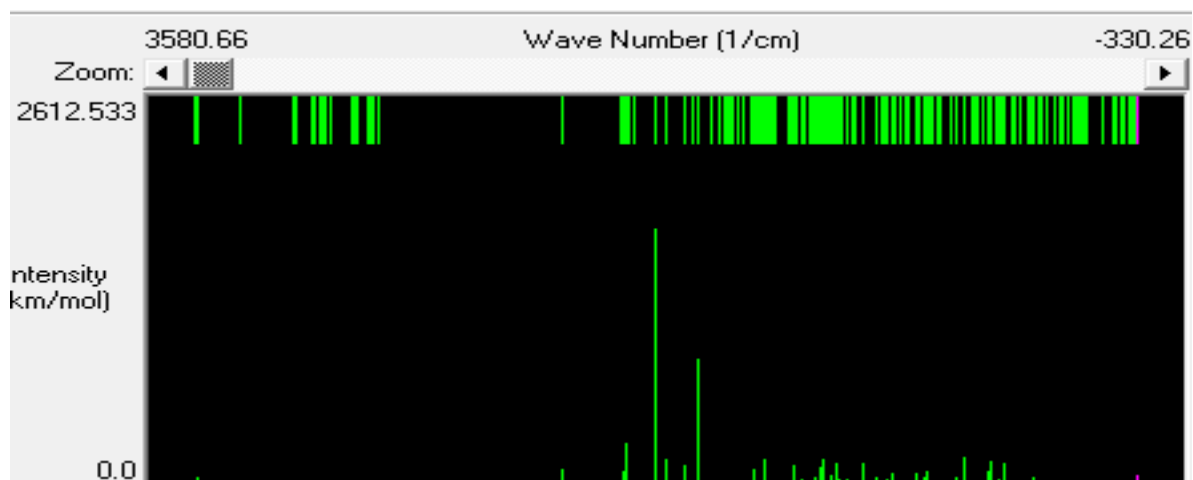
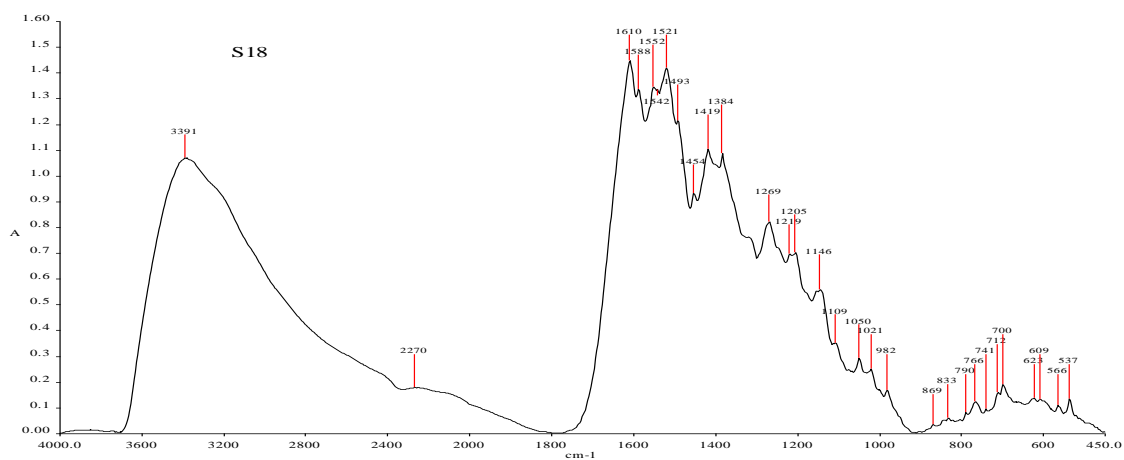
IR Spectra and mode of bonding

The IR spectrum of the ligand(Graph-1) is compared with the spectra of metal complexes(Graph-2) in order to examine the mode of bonding between ligand and complexes(Table-2). The IR spectrum of the ligand shows a broad band at 3438 cm^{-1} which is missing from the spectra of the metal complexes that indicates deprotonation of phenolic(-OH) and bonding of metal atoms with oxygen atom of the -OH group. The C-O frequency vibration band observed at 1270 cm^{-1} in ligand is shifted to $\sim 1219 \text{ cm}^{-1}$ in complexes confirming bonding of metal atoms with oxygen atom of -OH group[17].The peak at 1639 cm^{-1} due to $\nu(\text{C}=\text{O})$ in the spectrum of the ligand is shifted to $\sim 1610 \text{ cm}^{-1}$ In the spectra of metal complexes indicating the coordination of carbonyl oxygen with the metal ion[18]. A band appears at 1493 cm^{-1} corresponds to -N=N- group in the ligand is shifted to $\sim 1454 \text{ cm}^{-1}$ in metal complexes that suggests bonding of azo nitrogen with the metal ions[19]. The spectra of complexes reveal the presence of band at $\sim 3391 \text{ cm}^{-1}$ due to the vibration frequency of O-H of coordinated/ lattice held water. The presence of coordinated water is further confirmed by the rocking band at $\sim 869 \text{ cm}^{-1}$ and twisting band at $\sim 741 \text{ cm}^{-1}$ [20].The vibration frequencies of M-O and M-N bonds which appear at $\sim 566 \text{ cm}^{-1}$ and $\sim 537 \text{ cm}^{-1}$ respectively confirm the bonding between metal ions with the ligand through phenolic oxygen and azo nitrogen atoms[21]. The IR spectra of the ligand and its Co(II) complex are computationally generated and compared with the experimental IR spectra. The computationally generated data closely match with the experimental data.





Graph-1: IR spectrum of the ligand



Graph-2: IR spectrum of the Co(II) complex

Table: 2. IR data of the investigating compounds

compound	$\nu(\text{C-O})$ cm^{-1}	$\nu(\text{N=N})$ cm^{-1}	$\nu(\text{C=O})$ cm^{-1}	$\nu(\text{M-O})$ cm^{-1}	$\nu(\text{M-N})$ cm^{-1}
1	1270	1493	1639	566	537
2	1219	1454	1610	565	536
3	1218	1452	1609	566	537
4	1217	1453	1610	564	536
5	1218	1454	1610	566	536

1-LH₂, 2- Co(II) complex, 3-Ni(II)complex, 4- Cu(II) complex and 5- Zn(II) complex

Electronic spectra and magnetic moment

The electronic spectra and magnetic measurements are taken in to account to establish the geometric structures of the complexes since I failed to synthesize single crystal of all the complexes. The electronic spectrum of Co(II) complex displays weak absorption bands at 12987 cm^{-1} , 16393 cm^{-1} and 22727 cm^{-1} characteristic of octahedral geometry corresponding to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})(\nu_1)$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})(\nu_2)$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})(\nu_3)$ transitions respectively[22]. The Co(II) complex also shows magnetic moment of value 3.51 B.M. which supports octahedral geometry for the complex. The Ni(II) complex also exhibits three weak absorption bands at 13157 cm^{-1} , 16528 cm^{-1} and 23255 cm^{-1} assignable to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ which are characteristic of octahedral geometry[23]. The magnetic moment of the Ni(II) complex which is found to be 2.71 B.M. also supports octahedral geometry for the complex. The Cu(II) complex depicts a broad band in the region 13560 cm^{-1} to 17760 cm^{-1} with maximum at 15650 cm^{-1} in its spectrum, the broadness of the band may be due to tetragonal distortion[24].

The other electronic parameters for the Co(II) complex are calculated by using the following equations and summarized in the table-3.

$$Dq = \nu_2 - \nu_1/10$$

$$B = \nu_2 + \nu_3 - 3 \nu_1/15$$

$$\beta_{35} = B/971$$

$$\beta_{35}\% = (1 - \beta_{35}) \times 100$$

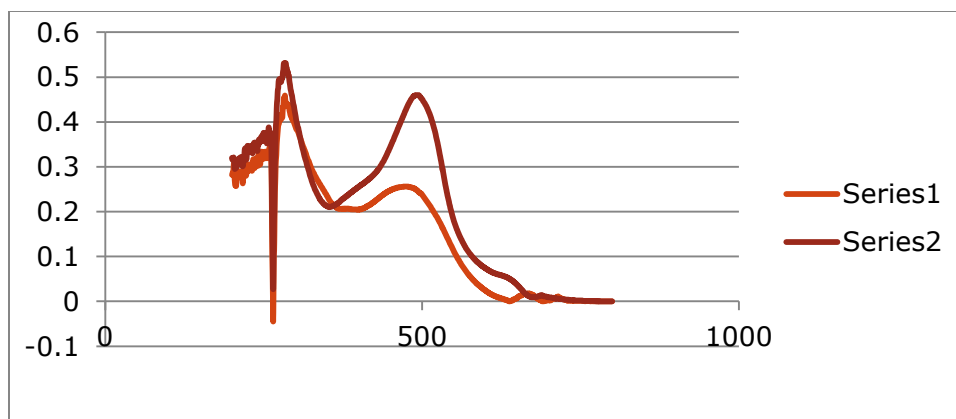
Similarly, electronic parameters for the Ni(II) complex are also calculated by using the following equations and summarized in the same table.

$$Dq = \nu_1/10$$

$$B = \nu_2 + \nu_3 - 3 \nu_1/15$$

$$\beta_{35} = B/1041$$

$$\beta_{35}\% = (1 - \beta_{35}) \times 100$$



Graph-3: Electronic spectra Series-1-Co(II) complex, Series-2- Ni(II) complex

Table-3 Electronic data of the metal complexes

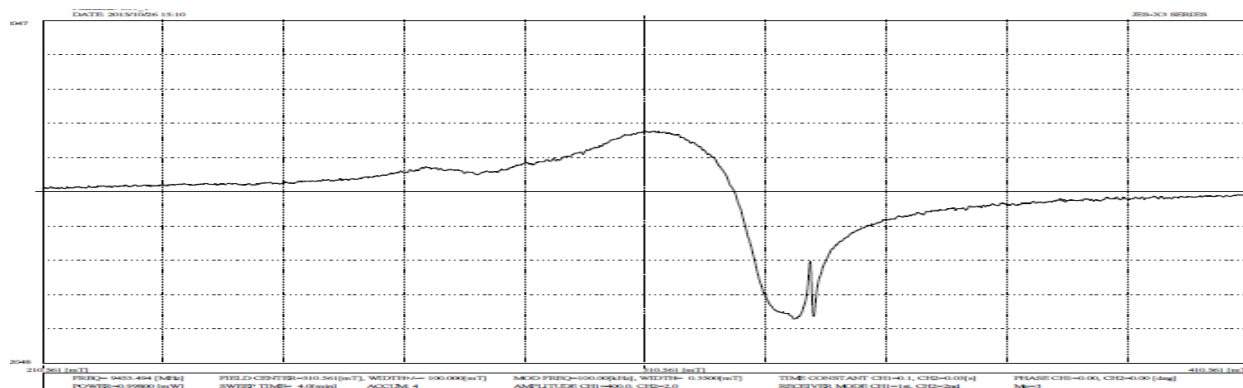
Com	λ_{\max} (cm^{-1})	Transitions	B	β_{35}	% of β_{35}	ν_2/ν_1	Geometry	μ_{eff} B.M.
1	12987	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$	23.93	0.024	97.6	1.26	octahedral	3.51
	16393	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$						
	22727	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$						
	36363	CT						
2	13157	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$	20.8	0.019	98.1	1.25	octahedral	2.71
	16528	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$						
	23255	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$						
	36231	CT						
3	15650	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$	-	-		-	Distorted octahedral	1.64

Note: 1-Co(II) complex, 2-Ni(II)complex, 3- Cu(II) complex

ESR spectral study

The esr spectrum of the Cu(II) complex is recorded at X-band at room temperature. The room temperature solid state of the Cu(II) spectrum(Graph-4) exhibits an axially symmetric g-tensor having g_{\parallel} value 2.11 and g_{\perp} value 2.02. As $g_{\parallel} > g_{\perp} > 2.0023$, the unpaired electron is localised in $d_{x^2-y^2}$ orbital of the Cu(II) ion and axial symmetry tetragonal geometry of the complex is implied[25]. This is confirmed by the electronic spectrum and XRD study of the complex. The G is related to g_{\parallel} , g_{\perp} by the expression $G = g_{\parallel} - 2/g_{\perp} - 2$ and it is found to be 5.5 that indicates negligible exchange interaction between the Cu^{2+} centers in the solid state[26]. The g_{av} value of the complex is calculated as 2.05 by using the relation $g_{\text{av}} = 1/3(g_{\parallel} + 2g_{\perp})$. The spin-orbit coupling constant is also calculated by using the equation $g_{\text{av}} = 2(1 - 2\lambda/10dq)$ and it is found to be -391.25 cm^{-1} . This value is found to be less than the free ion value (-830 cm^{-1}) that indicates overlapping of metal-ligand orbitals[27]. The covalent bonding between metal ion and orbitals of the ligand is also confirmed from the g_{\parallel} value. According to Kivelson and Neiman covalent bonding can be predicted for a Cu(II) complex with g_{\parallel} value less than 2.3[28]. Hence,

distorted octahedral geometry may be proposed for the Cu(II) complex, electronic study of the complex also supports this.

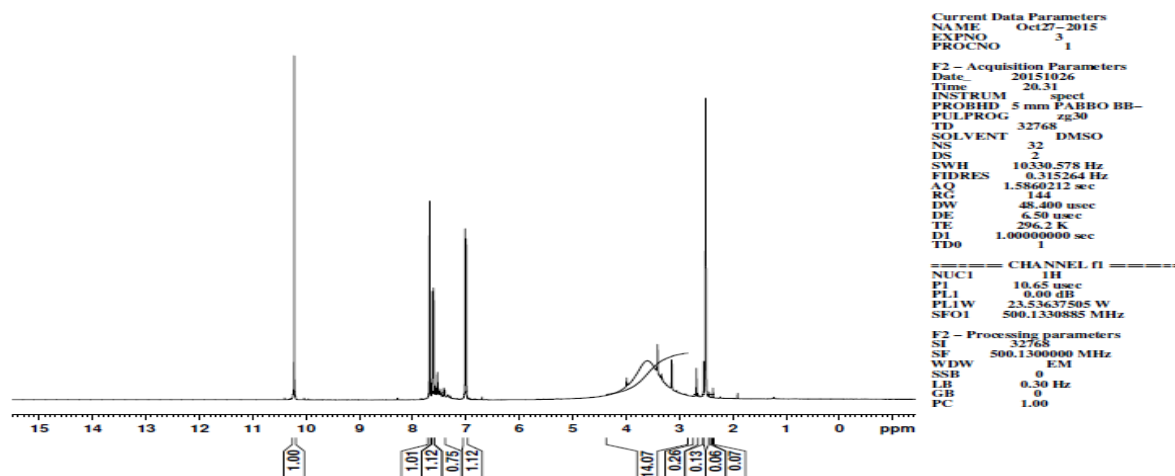


Graph-8: ESR spectra of the Cu(II) complex

¹H NMR spectra

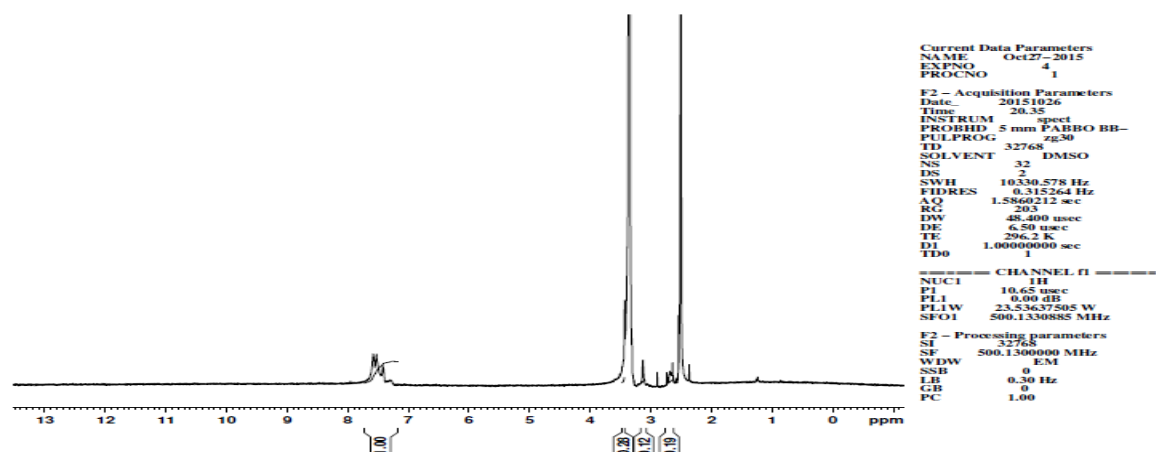
The spectra of the ligand (Graph-5) and Zn(II) complex (Graph-6) is recorded in DMSO-d₆ solvent. The ¹H NMR spectrum of the ligand shows multiplet at δ 5.63-8.13 ppm which may be assigned to aromatic protons. The peaks observed at δ 10.22 ppm correspond to phenolic (-OH). The peak observed at δ 3.14 ppm confirms the presence of -CH₃ group [29].

S-21....Sathyanarayan



Graph-4: ¹H spectrum of the ligand

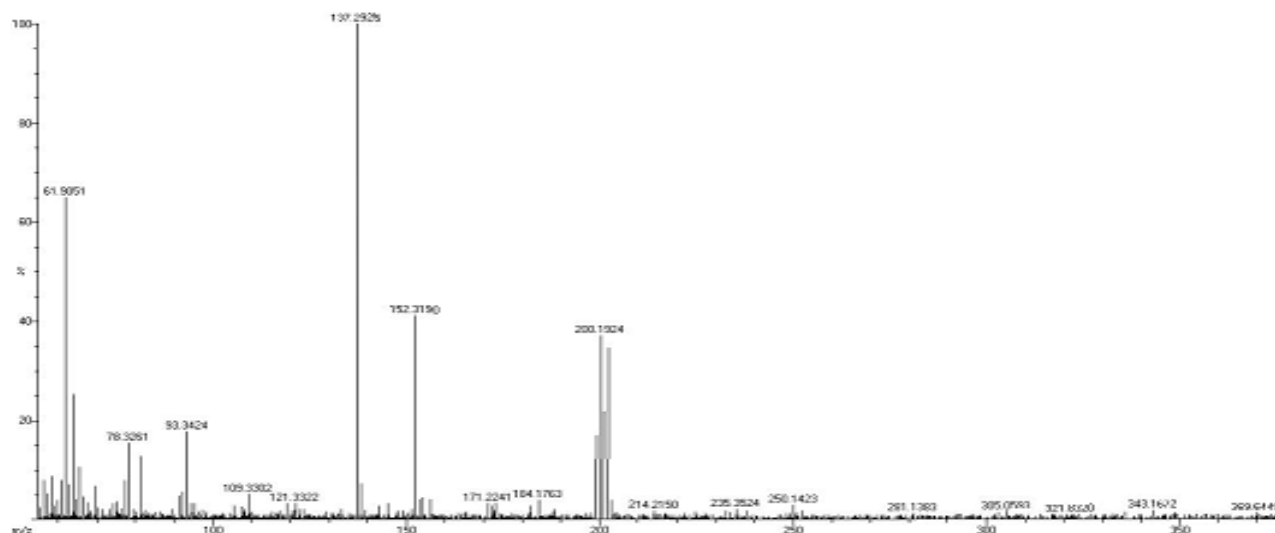
S-25....Sathyanarayan

Graph-5: ^1H spectrum of the Zn(II) complex

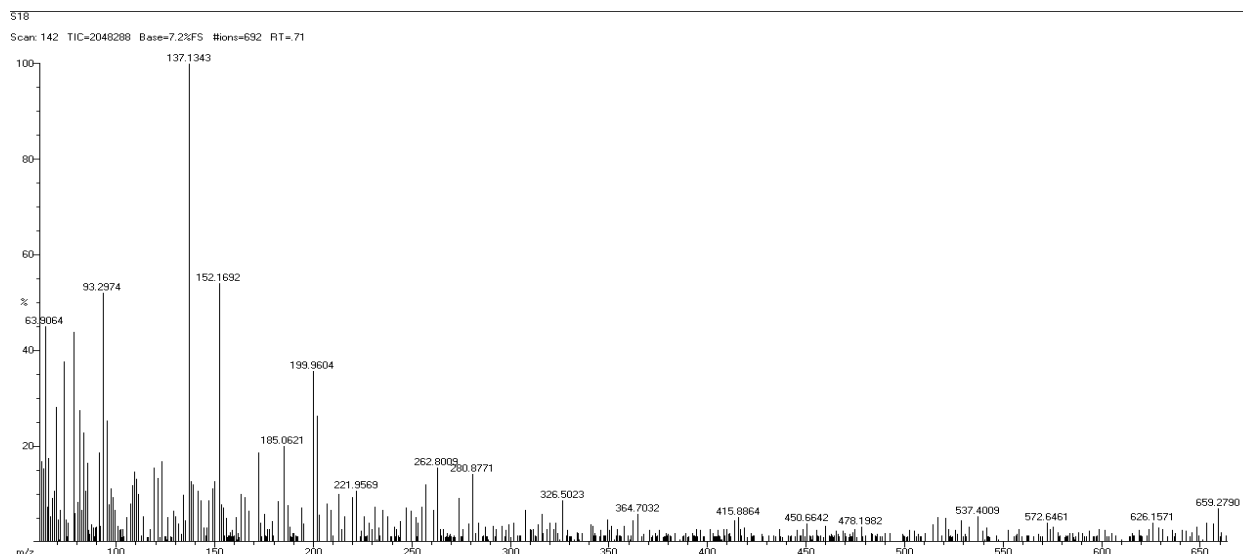
The spectrum of Zn(II) complex is compared with the azo dye ligand and it is observed that the peaks due to $-\text{OH}$ found in the the ligand was found missing in the complex. This indicates deprotonation of $-\text{OH}$ group and formation of metal-O bond [30] in accordance with the data by revealed IR.

Mass Spectra

The mass spectra of the ligand(Graph-7) and its Co(II)(Graph-8) complexes are recorded to confirm their molecular mass since mass spectra of the compounds provides vital information for their structural elucidations. The spectrum of the ligand shows the molecular ion peak at 369.499 m/z corresponding to the molecular mass of $[\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_4]^+$. The spectrum of the Co(II) complex of the ligand gives molecular ion peak at m/z 659.2790 which confirms its proposed molecular formula as $[\text{Co}_2\text{LCl}_2(\text{H}_2\text{O})_6]$.



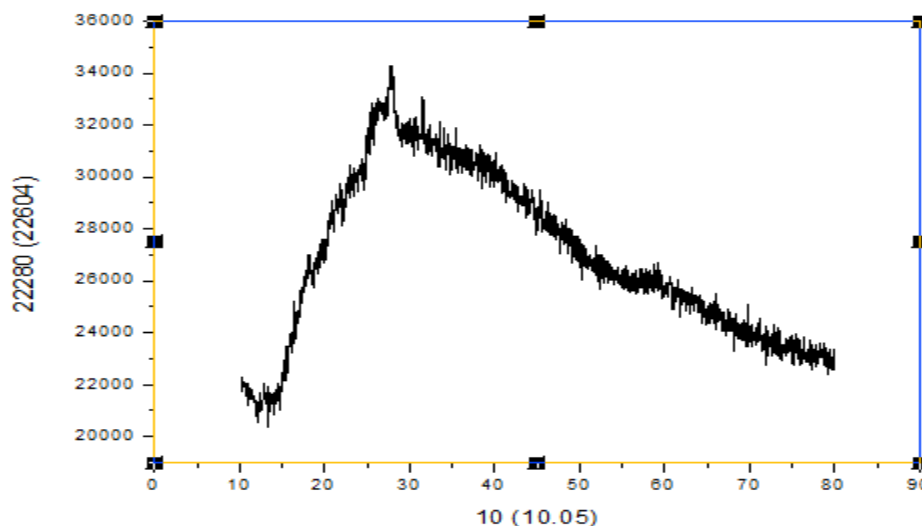
Graph-6: Mass spectrum of the ligand



Graph-7: Mass spectrum of the Co(II) complex

XRD study

The XRD study of the Co(II) complex is made to determine its lattice parameters and crystal system. The X-ray powder diffraction diagram is collected from the X'Pert diffractometer and the recording conditions are 40 kv and 40 mA for CuK α with $\lambda = 1.542\text{\AA}$ between 20° to 80° with a step size of 0.0089° .

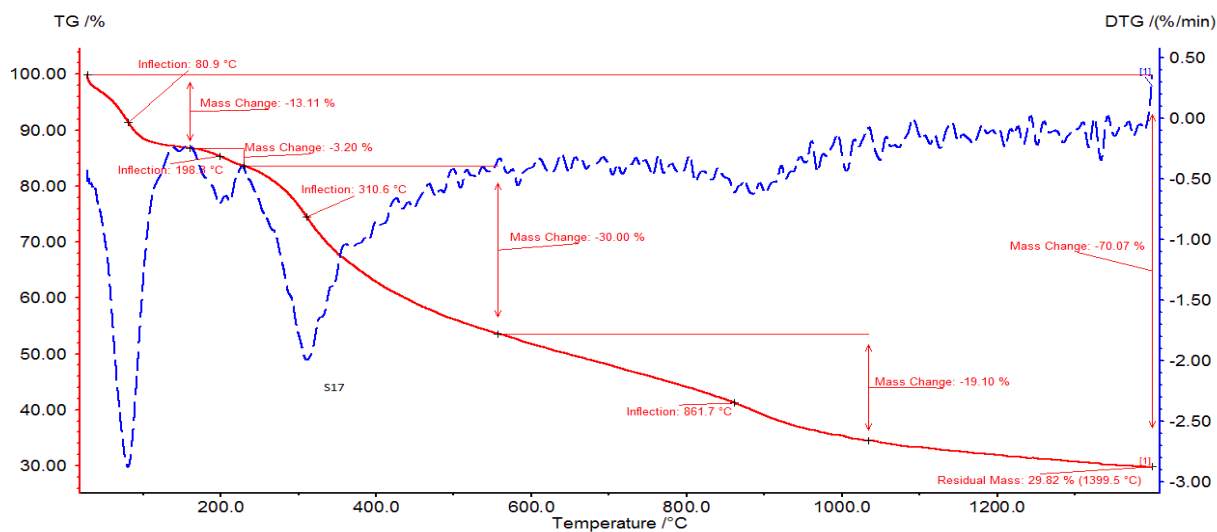
Graph-9: Diffractogram indicating intensity versus 2θ of Cu(II) complex

The XRD powder pattern is processed in X'pert high score software package. The search matching procedure is adopted for the PXRD pattern for the Cu(II) complex and revealed a match with a copper compound corresponding JCPDS powder diffraction file with PDF No 712047. The pattern can be indexed to be a tetragonal crystal system with $a = b = 10.19$, $c = 5.468$, $\alpha = \beta = \gamma = 90^\circ$, lattice = body centred and space group is $14/mmm(139)$.

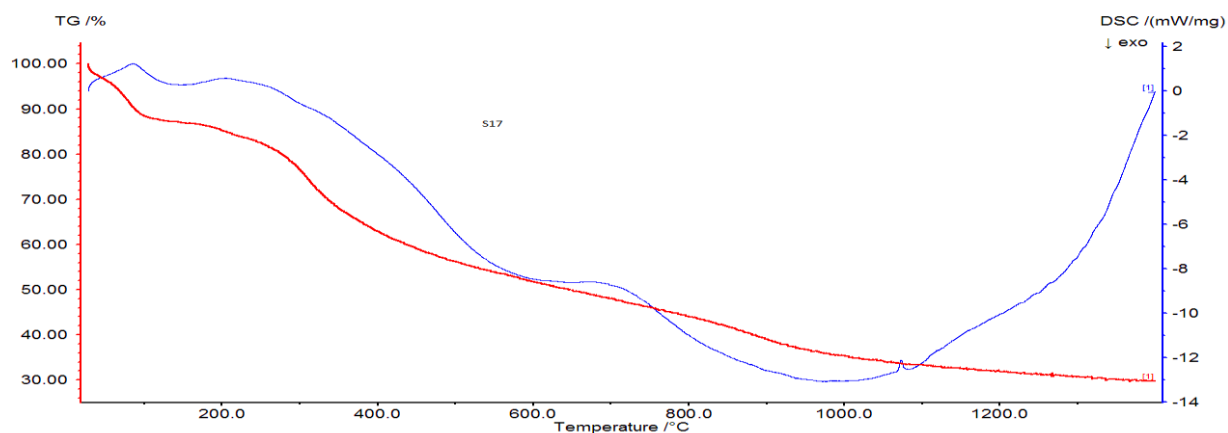
Thermo gravimetric analysis

The Co(II) complex is subjected to thermogravimetric study as a representative example to examine the thermal stability. The thermo gravimetric study of the Ni(II)(Graph-11,12) complex as a representative member of the

investigating complexes is carried out by the simultaneous TG,DTG and DSC techniques in the atmosphere of nitrogen at a rate of 10 °C per minute from the ambient temperature to 1400 °C. The TG /DTG curves show that the complex suffers mass loss in a number of stages. The compound suffers a mass loss of 13.11% at about 80.9 °C, this loss may be due lattice held water. Again, the compound loses mass 30 % between 200 °C and 600°C due loss of coordinated water and part of ligand moiety. Between 600°C – 800 °C, the compound suffers a loss of 19.10% due to loss of both chlorine atoms and part of ligand moiety supported by an exothermic peak at 702.4°C. At 1399. 6°C there exists a residual mass of 29.82% with the formation of NiO as the residue. This study indicates thermal stability of the metal complexes.



Graph-10: TG/DTA curve of Ni(II) complex

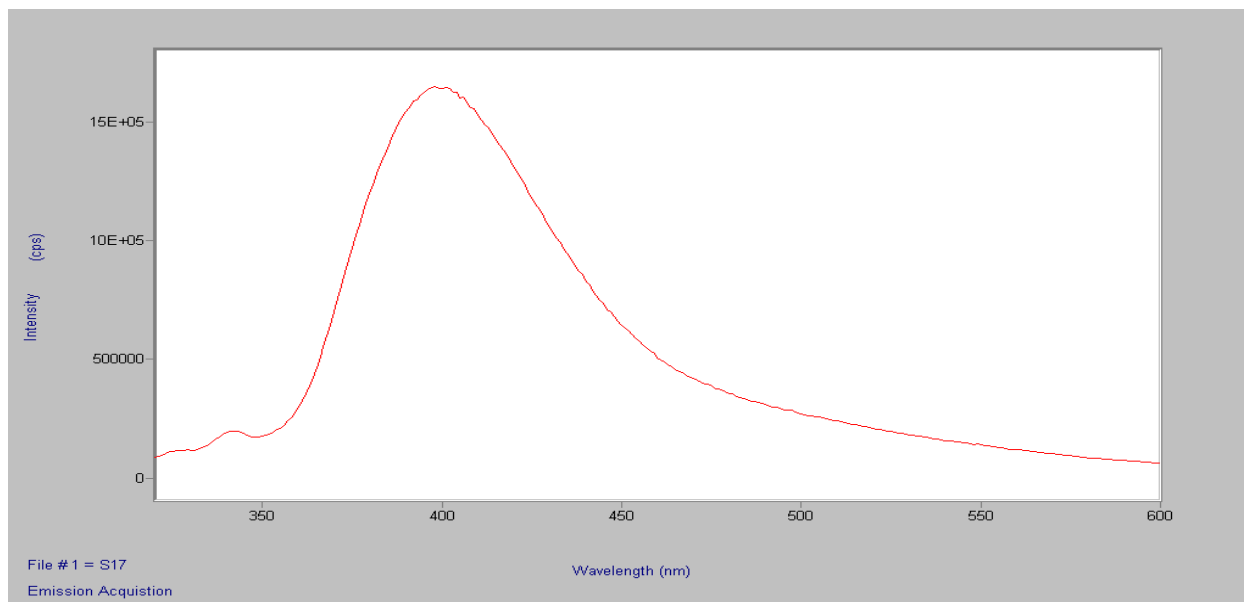


Graph-11: DSC curve of Ni(II) complex

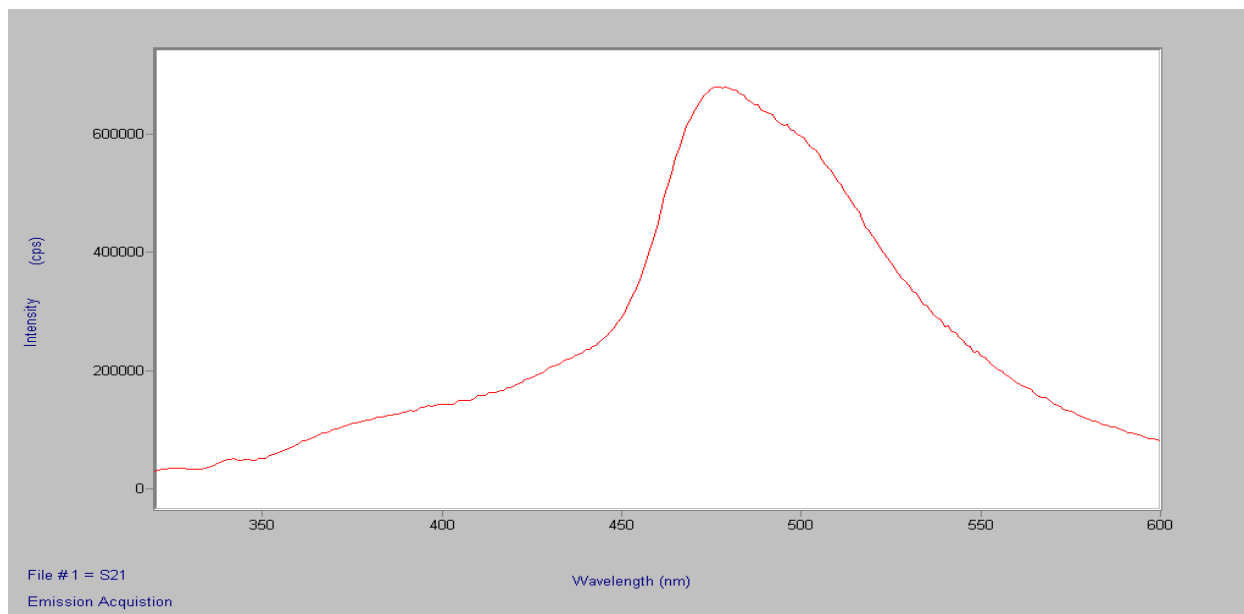
Fluorescence study

The fluorescence study of the ligand and its Ni(II) complex is undertaken to ascertain the fluorescent nature of the investigating compounds in solid state at 298K. The ligand exhibits an emission maximum at 400 nm which is shifted to 475 nm upon binding to the metal ions. The red shift of the λ_{max} value of the complex compared to the ligand may be due to deprotonation of the phenolic (OH) group[31]. The fluorescence emission intensity of the

ligand increases due to complexation as it enhances conformational rigidity and non-radiative energy loss. This study indicates that the ligand and its metal complexes have fluorescent properties[32].



Graph-12; Emission graph of the ligand



Graph-12: Emission graph of the Ni(II) complex

Scanning electron micrography

The Scanning electron micrography study of the Zn(II) complex is undertaken to study surface morphology of the complex. The SEM image of the complex shows the presence of micro rods, the diameter of which is 5 μm at lower and higher resolutions.

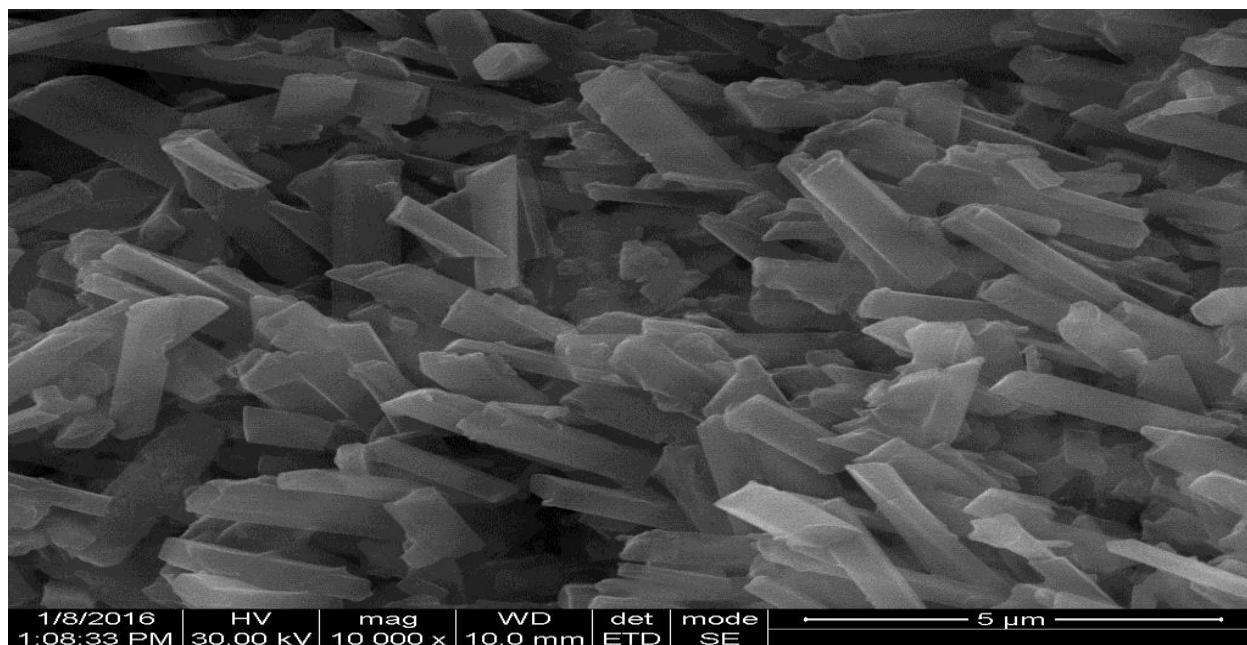


Figure-1: SEM Studies

Computational study

A computational study of the investigating compounds is made to examine their reactivities and to evaluate geometrical parameters. Gauss view 4.1[33] is used to draw the structures. The structures of the ligand and its all metal complexes are optimized at B3LYP[34] level of theory using 6-311++G(d,p) basis set. 6-311++G(d,p) is a large basis set which include diffused and polarized wave functions to take in to account the characteristics associated with ionic species having heavy atoms like N. Chemcraft software[35] is used to visualize the optimized geometry of the investigating compounds. The harmonic frequency calculation is also carried out at the same level of theory to ensure that the structures are true minima. Optimization was performed without any symmetry constraint using the default convergence criteria provided in the software. The molecular calculations in this work are done using the Gaussian 03 routine. This computational strategy is used successfully on coordination compounds and organic molecules.

Conceptual DFT defines chemical potential μ as the first derivative of energy with respect to number of electrons

$$\mu = \left(\frac{\partial E}{\partial N} \right) \vartheta(r) \text{ where } E = \text{energy, } N = \text{number of electrons of the system at constant external pressure } \vartheta(r).$$

and chemical hardness n as the half of the second derivative of energy with respect to number of electrons, so chemical hardness will be the first derivative of energy with respect to number of electrons

$$n = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right) \vartheta(r)$$

But chemical potential(μ) and chemical hardness(n) are also calculated in most cases in terms ionisation potential(IP) and electron affinity(EA) and therefore

$$\mu = - \left(\frac{IP+EA}{2} \right) \text{ and } n = \left(\frac{IP-EA}{2} \right)$$

According Koopman's theorem, IP and EA are related to energies of the Highest occupied molecular orbital (E_{HOMO}) and Lowest occupied molecular orbital (E_{LUMO}) in this way $-IP = -E_{\text{HOMO}}$ and $EA = -E_{\text{LUMO}}$

$\mu = \left(\frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \right)$ and $n = \left(\frac{E_{\text{LUMO}} + E_{\text{HOMO}}}{2} \right)$ and Parr and co-workers proposed electrophilicity [36] as a measure of electrophilic power of a compound the electrophilicity can be represented as

$$\omega = \frac{\mu^2}{2n}$$

The chemical potential (μ) and chemical hardness (n), electrophilicity and dipole moment of the ligand and complexes are given in the table-6. The reactivity of the ligand and its metal complexes can be predicted by considering the minimum electrophilicity principle. According to minimum electrophilicity principle, compound having minimum electrophilicity will have maximum stability. The chemical potential (μ), chemical hardness (n), electrophilicity (ω) are calculated from the HOMO and LUMO value of the ligand (Fig-1,2) and its complexes (Fig-3-10) and presented in the table-5. The metal complexes are more reactive than the ligand and the order of reactivity of the complexes is $[\text{Zn}_2\text{LCl}_2(\text{H}_2\text{O})_2] > \text{Cu}_2\text{LCl}_2(\text{H}_2\text{O})_2 > [\text{Co}_2\text{LCl}_2(\text{H}_2\text{O})_6] > [\text{Ni}_2\text{LCl}_2(\text{H}_2\text{O})_6]$.

Table:5. Global Reactive indices and dipole moment of the investigated compounds

compound	HOMO	LUMO	n(eV)	μ (eV)	ω	μ (D)
LH ₂	-0.27954	0.09337	0.186	-0.093	0.023	7.13
[Co ₂ LCl ₂ (H ₂ O) ₆]	-0.18286	0.00882	0.095	-0.087	0.039	22.18
[Ni ₂ LCl ₂ (H ₂ O) ₆]	-0.23143	-0.02274	0.104	-0.127	0.077	11.8
[Cu ₂ LCl ₂ (H ₂ O) ₆]	-0.20425	-0.02072	0.091	-0.112	0.068	23.95
[Zn ₂ LCl ₂ (H ₂ O) ₂]	-0.30454	-0.10663	0.094	-0.205	0.212	6.21

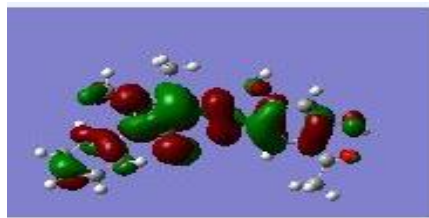


Figure-3: HOMO of the ligand

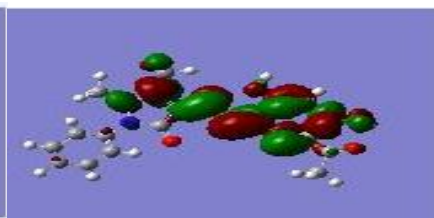


Figure-4: LUMO of the ligand

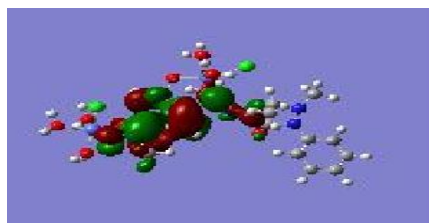


Figure-5: HOMO of the Co(II) complex

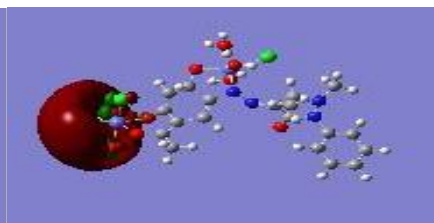


Figure-6: LUMO of the Co(II) complex

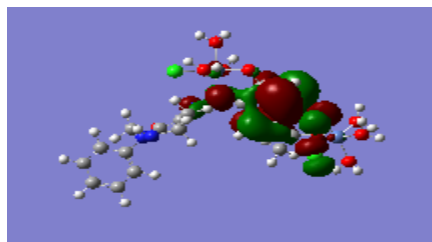


Figure-7: HOMO of the Ni(II) complex

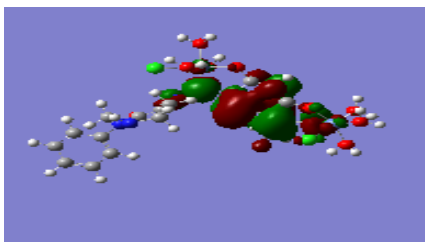


Figure-8: LUMO of the Ni(II) complex

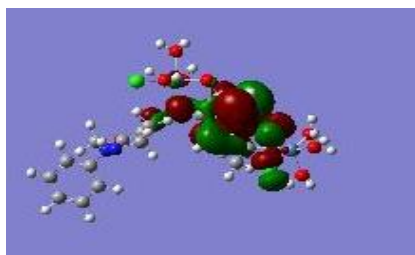


Figure-9: HOMO of the Cu(II) complex

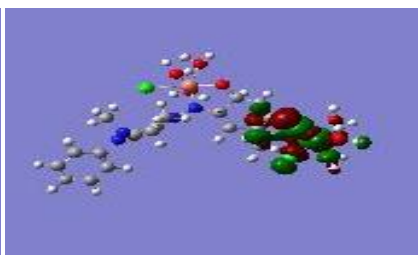


Figure-10: LUMO of the Cu(II) complex

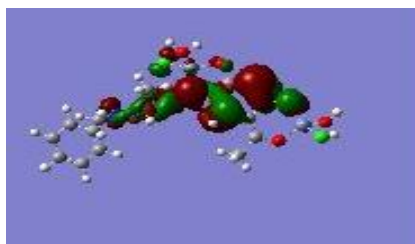


Figure-11: HOMO of the Zn(II) complex

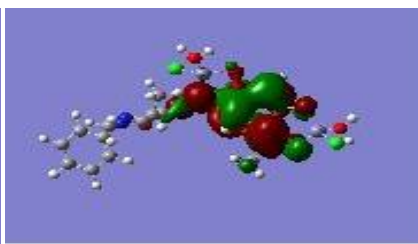


Figure-12: LUMO of the Zn(II) complex

The geometrical parameters of the investigating compounds are also collected from their optimised geometry and presented in the table no-6. It is seen from the table that the bond angles around the metal ion in case of Co(II), Ni(II) and Cu(II) complexes are close to 90° and in case of Zn(II) it is close to 109° . Therefore, distorted octahedral geometry for Co(II), Ni(II) and Cu(II) complexes and distorted tetrahedral geometry may be suggested for the Zn(II) complex.

Table: 6. Selected bond length and bond angle

comp	Bond length(Å)				Bond angle($^\circ$)		
	N(16)-N(15)	N(16)-C(17)	O(26)-C(20)	C(18)-O(27)	N(16)-M(28)-O(32)	N(16)-M(28)-O(27)	O(32)-M(28)-O(27)
1	1.235	1.442	1.364	1.360	-	-	-
2	1.352	1.446	1.410	1.410	80.90	91.47	99.9
3	1.393	1.446	1.260	1.435	88.568	90.166	89.430
4	1.388	1.511	1.461	1.433	94.830	82.521	114.3
5	1.243	1.447	1.387	1.323	113.411	86.733	97.802

Note:1-LH₂, 2- Co(II) complex, 3-Ni(II)complex, 4- Cu(II) complex and 5- Zn(II) complex

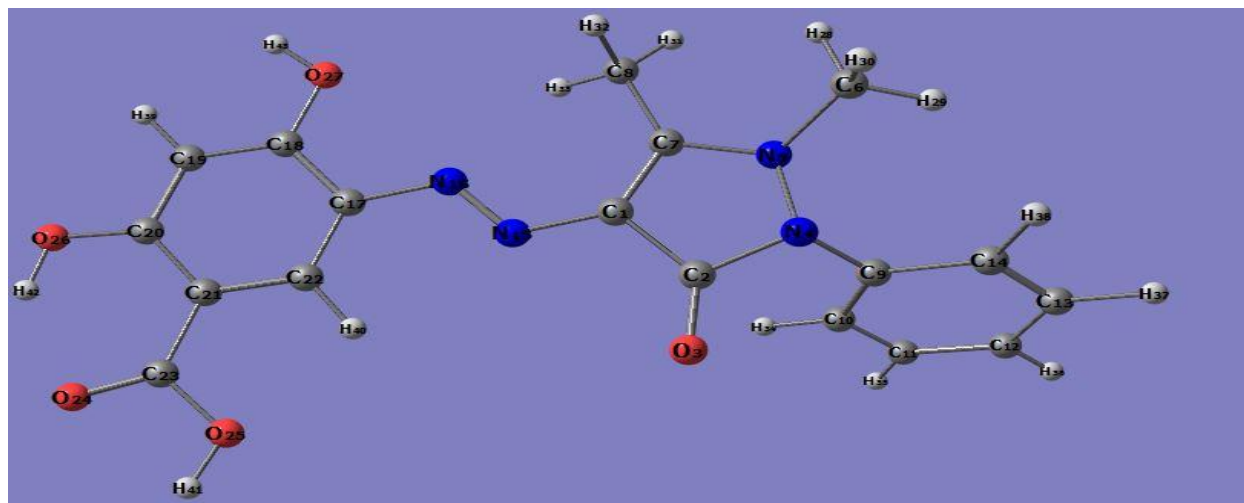


Figure-13: Optimized geometry of the ligand

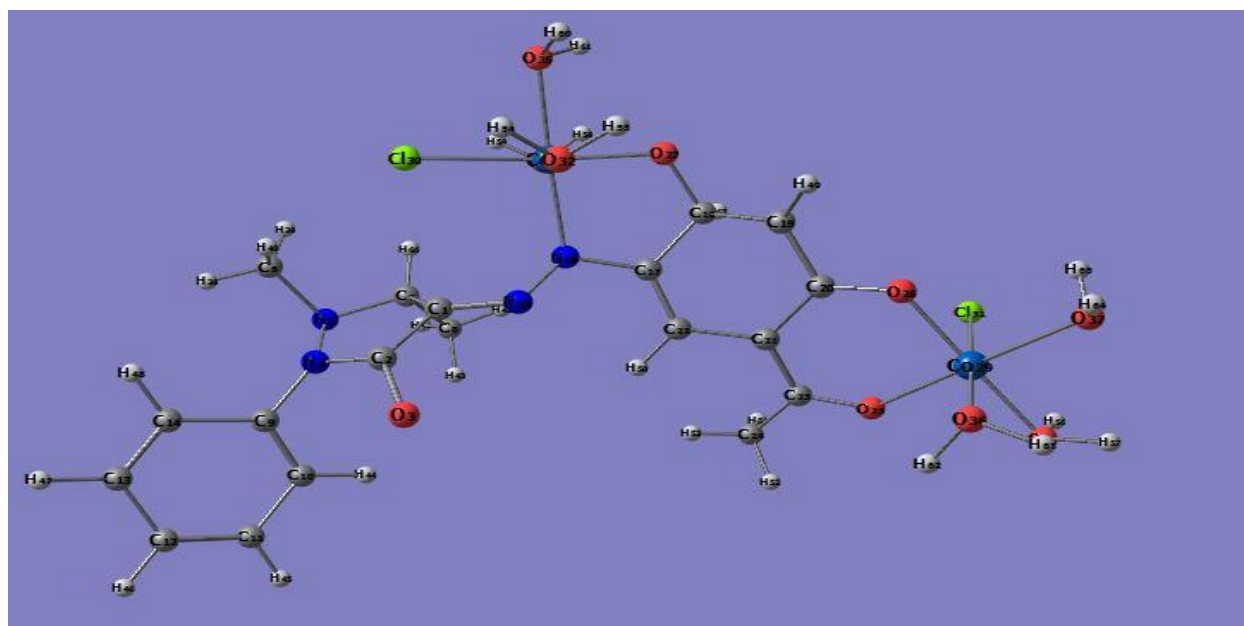


Figure-14: Optimized geometry of the Co(II) complex

Non-linear optical properties

The electronic properties of a compound depend upon its non-linear optical properties and basic requirement for a good non-linear optical material is the easy electron transition between the molecular orbitals. The table indicates that all the metal complexes have small energy gap between the HOMO and LUMO in all complexes as compared to the ligand. This indicates metal complexes have better non-linear optical properties[37] and the order can be represented by $[\text{Cu}_2\text{LCl}_2(\text{H}_2\text{O})_6] > [\text{Zn}_2\text{LCl}_2(\text{H}_2\text{O})_2] > [\text{Co}_2\text{LCl}_2(\text{H}_2\text{O})_6]$.

Biological study

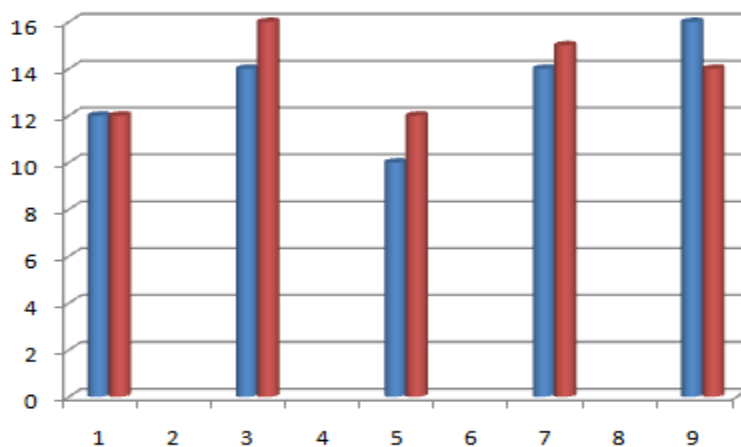
Antibacterial study

The ligand and its metal complexes are screened against gram positive *S. aureus* and *E. coli*. The study indicates that all investigating compounds have antibacterial properties. However, metal complexes have greater power than

the ligand and the order of activity of complexes follows the order $[\text{Zn}_2\text{LCl}_2(\text{H}_2\text{O})_2] > [\text{Cu}_2\text{LCl}_2(\text{H}_2\text{O})_6] > [\text{Co}_2\text{LCl}_2(\text{H}_2\text{O})_6] > [\text{Ni}_2\text{LCl}_2(\text{H}_2\text{O})_6]$. The enhanced activity of the metal complexes may be due to chelation theory[38]. The charge of metal ions is reduced due to complex formation and delocalization of charge over the entire chelate therefore lipophilicity of the complex compounds increases so the compounds easily pass through the cell membrane and inhibit the growth of microorganisms.

Table: 7. Antibacterial screening of the investigating compounds

compound	concentration	<i>E. coli</i>	<i>S. aureus</i>
1.LH ₂	500 µg/ml	12	12
2.[Co ₂ LCl ₂ (H ₂ O) ₆]	500 µg/ml	14	16
3.[Ni ₂ LCl ₂ (H ₂ O) ₆]	500 µg/ml	10	12
4.[Cu ₂ LCl ₂ (H ₂ O) ₆]	500 µg/ml	14	15
5.[Zn ₂ LCl ₂ (H ₂ O) ₂]	500 µg/ml	16	14
6.Tetracycline	500 µg/ml	30	30



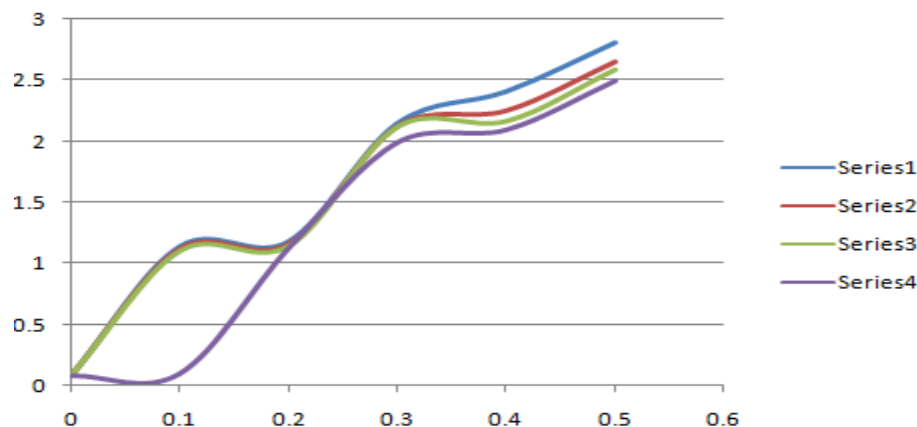
Graph-14: Antibacterial activity of the ligand and its complexes

DNA binding study

Viscosity measurement

The viscosity measurement study of the metal complexes is made in order to know the interaction between DNA and metal complexes. This study provides the information regarding the effect metal complexes on the viscosity of the DNA. The graph indicates the viscosity of the metal complexes increases with increase in their concentration because they intercalate between the DNA base pairs. so there is increase in the length of the helix causing

increasing of the viscosity of the compounds[39]. The viscosity of the complexes can be arranged as $[\text{Cu}_2\text{LCl}_2(\text{H}_2\text{O})_6] > [\text{Zn}_2\text{LCl}_2(\text{H}_2\text{O})_2] > [\text{Co}_2\text{LCl}_2(\text{H}_2\text{O})_6] > [\text{Ni}_2\text{LCl}_2(\text{H}_2\text{O})_6]$.



Graph-15: Viscosity measurement Series-1-Cu(II), 2-Zn(II), 3- Co(II), 4-Ni(II) complexes

Gel electrophoresis

The Gel electrophoresis study of the metal complexes is undertaken to study their binding ability with the CT DNA. The study indicates that intensity of the lane of the free DNA is more than the lanes of metal complexes with DNA. The intensity of DNA containing metal complexes decreases as complex compounds intercalates between the DNA base pairs and preventing intercalation of tracking dye. The intensity of the DNA containing Cu(II) complex is less than the DNA containing Ni(II) complex, therefore Cu(II) complex has greater binding ability than the Ni(II) complex



Figure-2: From left 1. DNA control 2. Cu(II) 3. Ni(II) complexes

CONCLUSION

The synthesized ligand is suggested to be a tetradentate ligand on the basis of analytical, spectral study. It is coordinated with the metal ions through the azo nitrogen, phenolic oxygen and carbonyl oxygen of the ethanoic group. The computational study of the ligand and its metal complexes indicated change in bond lengths, bond angles and dihedral angles. The global reactive descriptors study predicted Ni(II), Cu(II) and Zn(II) complexes are more reactive than the ligand. Both the ligand and its metal complexes are suggested to have non-linear optical properties. The DNA binding study revealed that metal complexes could bind with the CT DNA in a intercalative mode and the antibacterial study suggests the complex compounds have more antibacterial properties than the ligand.

ACKNOWLEDGEMENTS

UGC is gratefully acknowledged for the award of minor research project. The author is indebted to SaIF, IIT, madras for providing spectral data.

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