FINAL REPORT

OF

MINOR RESEARCH PROJECT

(Ref. No. (WRO) 47-240/12 (WRO) 18/02/2013

ON

"Synthesis and Characterization of Biologically Active Ligand and their Metal complexes"

IN

CHEMISTRY

SUBMITTED TO THE UGC (WRO) PUNE

BY

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ACKNOWLEDGEMENT

I take it as an honor, to express my deep sense of gratitude to Dr. Shivraj Birajdar, Principal, S.B.E.S. College of Science, Aurangabad for his continuous encouragement and inspiration throughout the research work.

I express my sincere gratitude to Head of Department, Dr. C. D. Thakur for her guidance, inspiration and valuable suggestion of my research work.

I am thankful to my collegues and friends Dr. Deolankar D.S., Dr. A.M. Dodkey , Dr. Kayande D.D., Mr. Kamble D.P., Dr. Davne P.M., Dr. Khobragade K.S., Dr. Dhakane P.M, Dr. Vishal Deshpande, Dr. Madhekar R.D., Dr. Pardeshi , Dr. Shastri, Dr. Joshi for their inspiration during course of work.

I have special thanks to my research students and friends Mr. S.B. Ingole, Mrs. V.D. Bhale, Dr. V.L. Borde, Mr. G.S. Sanap and Mr. D.T. Sakhare for his kind co-operation and constant encouragement of my research work.

I express my sincere appreciation and thanks to my brothers, beloved wife and my son Mr. Aniket for constant encouragement during the progress of my work.

I am specially thankful to U.G.C. (WRO) Pune for sanction me the minor research project.

I would like to thank many individuals who helped me directly and indirectly to completion of my research work.

Dr. Shankarwar Anil Govin

DECLARATION

I hereby declare that, the present work completed in the form of Minor Research Project, "**Synthesis and Characterization of Biologically Active Ligands and their Metal complexes",** is an original work and has not been submitted or published in any form for the fulfillment of any other degree or any other university.

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Date: /   /2015

CHAPTER I

- General Introduction to Co-ordination Chemistry.

- Schiff Bases and their metal complexes.

- Applicational Importance of Schiff Bases and their Metal Complexes.

- Literature Survey on Previous Related Study.

- Aim of the Present Investigation.

CHAPTER I

Introduction:-

Coordination compounds have been a challenge to the inorganic chemist's right from the time these were identified, in the nineteenth century. In the early days these compounds seemed unusual because they appeared to defy the usual rules of valence. Today these comprise a large body of current inorganic research. Although the usual bonding theories can be extended to accommodate these compounds, they still present stimulating theoretical problems and in the laboratory continue to provide synthetic challenges. One such class involving metal carbon bonds is the focus of an entire sub discipline known as organometalic chemistry. The field of bioinorganic chemistry also is centered on coordination compounds present in the living systems.

Complexes are playing increasingly important role in industry, ranging from anticorrosion and soil treatment agents to medicinal agents, which certainly testify for their significance in contemporary life. The biologically important complexes such as chlorophyll, hemoglobin, and vitamin B12- all with varying complex structures suggest a need to undertake the study of the chemistry of metals involved in biological problems.

Even though much progress has been made in this field, no work could be compared to that of Alfred Werner's in the 1890's. Our present Understanding of co-ordination chemistry is due to his ingenious insight. His theory had been a guiding principle in inorganic chemistry. It led to a better understanding of the structures of hundreds of complex compounds, their stereochemistry and isomerism.

It however, had an inherent weakness in that it postulated two different kinds of valencies, primary and secondary, for metal ions in coordination compounds.

Despite of these shortcomings, Werner's theory was used by many of the contemporaries, which include Feiffer, Tschugaeff and Ley. The subsequent

development of electronic theory of valency by Lewis, Kossel, Langmuir, Sidgwick, Fajans and others, however reasonably explained the ideas regarding primary and secondary valencies in complexes.

Sidgwick and Lowry gave an electronic interpretation of Werner's theory, according to which the linkage of coordination groups to metal ion arises due to the donation of electron pairs to the central metal ion. The central metal ion thus acquires effective atomic number of the next inert gas. Bonds of this type were termed as coordinate bonds.

In 1931, Linus Pauling introduced a new theory based on the idea of hybridization. He considered the formation of complex between metal ion and the ligand. The valence bond theory could interpret many magnetic and stereo chemical properties of the coordination compounds.

H. Bethe introduced the crystal field theory and suggested that ligands could be considered as negative point charges, placed around metal ion producing negatively charged electric field which develops repulsive interaction with the electrons in d or f orbital of the metal ion and splits them.

The attraction between the central metal ion and ligands in a complex is regarded as purely electrostatic and the interaction between the electrons of the cation and those of the ligands being purely a repulsive one.

The crystal field theory, however does not take cognizance of the covalent nature of the metal-ligand bond and therefore is inadequate to account for many of the properties of metal complexes.

For this purpose it was adjusted to include the covalent character in metal-ligand bond and is known as the ligand field theory or adjusted crystal field theory. The extent of covalent character in M-L bond is to be generally low as compared to that of the ionic one. There are many experimental evidences for mixing of the ligand and metal ion orbital.

The molecular orbital theory includes all situations from no overlap to maximum overlap and assumes this to take place between metal ion and ligand orbital, matching each other symmetrically.

The molecular orbital theory could satisfactorily account for the spectral and magnetic properties of metal complexes including those of the pi type, like metal carbonyls and metal olefins.

Though the metal-ligand bond, in a coordination compound has been described in many ways, a very simple definition of coordination compound itself has been given by Rossotti and Rossotti. They defined coordination compound as a species formed by the association of two or more simpler species, each capable of independent existence, where one of the species is a metal ion and the other is a ligand.

The term ligand is applied to a molecules or a particular atom in the molecules, by means of which it is bonded to the central metal ion. As a whole ligand is an electron donor group.

Coordination compound was played a prominent role in the extraordinary development of inorganic chemistry. Alfred Werner, Lewis, Bethe, Vanvlck, Jannik, Bjerrum,Martel, Rossotti, are the noteworthy worker's who gave the present status to inorganic chemistry.

Somewhere, it has been said that, coordination chemistry is a meeting place of all branches of chemistry.

Origin of the research problem:-

Coordination chemistry of biologically active ligands has been a fascinating area of current research in inorganic chemistry all over the world due to its wider applications and the unusual binding abilities. The award of 1987 Noble Prize in chemistry to Pedersen, Lehn and Cram is a testimony to the importance of this field. The biologically active ligands and their metal complexes find paramount applications in the field of food and dye industries, agriculture, analytical chemistry, catalysis, polymer science, biological science as antimicrobial agents, medical science as anticancer, antiseptic, antidiarrhoeal, anti ulcer agents, metal corrosion inhibition etc. Various studies have shown that the azomethine group (>C=N) in the ligand has

considerable biological significance and found to be responsible for biological functions such as fungicidal and insecticidal activity.

A survey of research reveals that very less work has been done on the synthesis of metal complexes of biologically active ligands and their characterization by various physicochemical techniques. Therefore in view of these considerations it is decided to study the synthesis of biologically active ligands and its coordination behaviors with transition metals ions.

Metal complexes are very important because of their variety of applications. Approach of chemists, during the last ten to fifteen years is to go in for novel compounds of biological importance. The biologically active ligands and their metal complexes find paramount applications in the field of food and dye industries, agriculture, analytical chemistry, catalysis, polymer science, biological science as antimicrobial agents, medical science as anticancer, antiseptic, antidiarrhoeal, anti ulcer agents, metal corrosion inhibition etc. The ligands are modified molecules especially the drug molecules. These are simulated through computers and a specific metal ion is fixed in the cavity. Drug designing, biologically active compounds are the new branches which are of tremendous pharmacological importance.

Importance of Schiff bases and Their Metal Complexes:

The Schiff bases and their metal complexes have more importance recently because of their application as biological, biochemical, analytical, antimicrobial, anticancer, antibacterial, antifungal and anti tumor activity. They have been studied as a class of ligands and are known to coordinate with metal ions through the azomethine nitrogen atom. The synthesis of transition metal complexes with Schiff base ligands are studied due to sensitivity, selectivity and synthetic flexibility towards metal atoms. They used as catalyst, in medicine like antibiotics and anti-inflammatory agents and in the industry as anticorrosion.

Literature Survey of Previous Related Studies:

Literature survey reveals that several organic molecules act as chelating ligands. These organic molecules include hydrazones, semicarbazones, thiosemicarbazones, Schiff bases, amines, carboxylic acids, β-diketones and many more. The chemical properties of their metal complexes were studied with great interest. A wide variety of structural configuration was observed during the investigation of metal complexes of different ligands. However, there is always curiosity for the synthesis of new ligands with specific design which can influence the structural configuration of metal complexes. The design and geometrical consideration of the ligands also influence the stability of metal chelates. Hence, the structural investigation of new coordination compounds has become a challenge for researchers and scientists.

Aim of the Present Investigation:

With this aim in view, the present study deals with the synthesis of solid complexes of Co(II) and Fe(III) metal ions with the newly synthesized unsymmetrical tetradentate Schiff bases derived from the following primary aromatic amines and aldehydes.

1. 2 -amino 4, 6- dihydroxypyrimidine.

2. benzaldehyde.

3. P-methoxy benzaldehyde.

The characterization of Schiff bases and their transition metal complexes was carried out by various physicochemical and spectroanalytical methods. The fungicidal and bactericidal activity of these Schiff bases and their metal complexes were also screened.

CHAPTER II

SYNTHESIS AND CHARACTERISATION OF

SCHIFF BASES AND THEIR METAL

COMPLEXES

- Basic Requirements.

- Synthesis of Schiff Base Ligands.

- Characterization of Ligands.

- Synthesis of Metal Complexes.

SYNTHESIS AND CHARACTERISATION OF SCHIFF BASES AND THEIR METAL COMPLEXES

Basic requirements

Apparatus: -

The experimental work was carried out using borosilicate glass apparatus. They were calibrated before use by standard analytical method. All the glasswares used for experimental work were cleaned by means of chromic acid as cleaning agent followed by tap water and portions of deionised water. The chemicals used were weighed on one pan analytical balance with 0.01mg sensitivity.

Chemicals: - All the chemicals used for experimental work were of AR-grade.

a. Solvents:

I. Water: - Throughout experimental work, the glass-distilled water was used. The glass distill water was obtained by distillation of metal distilled water in presence of crystals of potassium permanganate in alkaline condition.

II. Super dry ethanol: - For the synthesis of Schiff bases and their metal complexes, ethanol was used as solvents. The commercial alcohol was distilled over calcium oxide to obtain absolute ethanol. Distilled ethanol was directly stored in polyethylene vessel and protected from atmospheric moisture. All other solvents used during the experimental work were of AR grade.

b. Reactants and Reagents

The reactants such as aldehyde, amines, metal salts and other chemicals used for the synthesis of Schiff bases and their metal complexes were of ARgrade. The A.R.grade chemicals and standard reagents were used for the determination of metal ions in metal chelates.

Synthesis of Schiff Bases

The procedure used for the preparation of Schiff bases involves one step. The first is one that is suggested by Osowole. Schiff base was synthesized by the condensation of 1:1 ratio of benzaldehyde with hetrocyclicamine i.e. benzaldehyde, P-methoxybenzaldehyde, with 2-amino-4, 6- dihydroxypyrimidine dissolved in ethanol. The resulting reaction mixture was refluxed for 3 hour and then allowed to cool overnight. The coloured solid precipitate of Schiff base obtained was filtered, washed with cold ethanol and finally recrystallized from ethanol and dried in air at room temperature. The purity of synthesized compounds was checked by TLC (yield: 70%)

Characterisation of Ligands:

All ligands are found to be stable to air and moisture, soluble in ethanol, dimethyl formamide and dimethylsulphoxide and are insoluble in water. The structural features of the ligands are elucidated with the help of element analysis, electronic, infrared absorption and nuclear magnetic resonance techniques.

Elemental analysis, colour and melting point of Ligands:-

The elemental analysis of ligands was carried out by micro combustion method using CHNS. The sample weighted between 0.02 to 1gm was used for analysis. The colour, melting point, molecular weight and percentage of carbon, hydrogen and nitrogen found and calculated theoretically are given in Table. 1

Reaction:

Where,

R= -OH,

R'=

Mechnism:-

I

II

III

IV

V

-H₂O
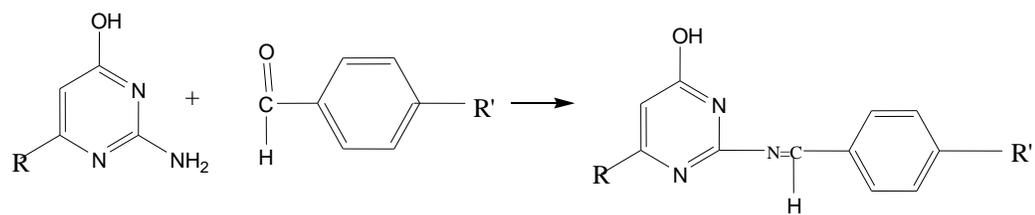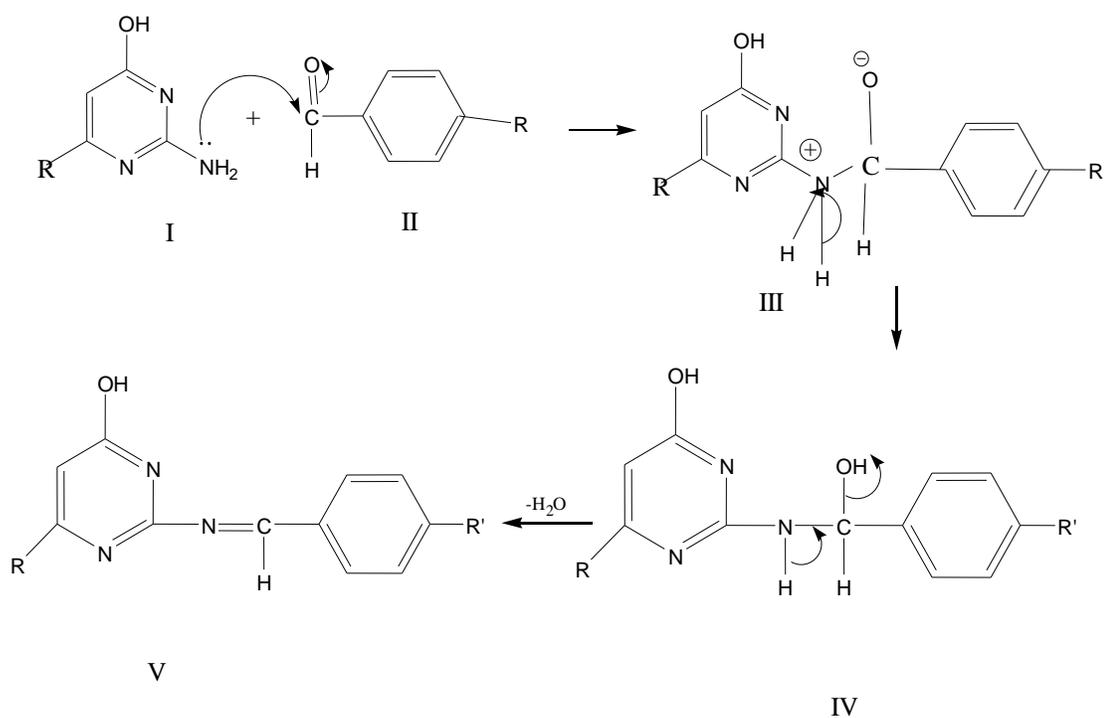
Table 1

Analytical data, molecular weight and melting point of ligands

Ligand	Symbol	Colour	Mol. Wt.	M.P. °C	Found (Calculated)		
					C	H	N
$C_{11}H_8N_3O_2$	L_1	Yellow	214	80	52.2 (43.2	3.64 (3.95	16.75 (16.93
$C_{12}H_{11}N_3O_3$	L_2	Yellow	245	118	54.78 (49.29	3.45 (3.67)	20.13 (17.55

Spectral study of Ligands:

Among the spectroscopic methods used for structure determination of ligands, the ultra violet visible (UV-VISIBLE), infrared (IR), are the main techniques useful for the structural determination of organic ligands.

a. Electronic absorption spectral study of ligands

(uv-visible spectra):

Molecular absorption in the ultraviolet and visible region of the electromagnetic spectrum depends on the electronic structure of molecule. In practice the ultraviolet spectroscopy is primarily used to measure the multiple bonds and aromatic conjugation within a molecule.

The amount of ultraviolet radiation absorbed changes the electronic energy of molecule, resulting in the transitions of valence electrons. These transitions consist of the excitation of an electron from an occupied molecular orbital usually a non-bonding η or bonding σ and π-orbital to the next higher energy unoccupied molecular orbital, that is an antibonding π* or σ * orbital. The possible transitions are from σ → σ *, η

→ σ *, η→π * and π→π*. But among these transitions, significant transitions are π→π* and η→π *. The energy required for different transitions is in the order η→π* < π→π* < η→ σ * < σ → σ *. These electronic transitions are designated by the letters assigned by Buraway as R, K, B and E bands.

Letters assigned for designation of band (Type of band)	Electronic transition	ε max
R K B E	η→π* π→π* π→π* π→π*	< 100 > 10,000 - 1000 to 5000 2000 to 14000

The solutions of known concentration (1×10^{-4} M) of Schiff base ligands were prepared in chloroform (A.R.) and their UV/VIS (electronic absorption) spectra were recorded on UV/VIS spectrophotometer model UV-1601, SHIMADZU, Japan in the range 190-400 nm. The instrument was calibrated using solution of 0.04 gm. potassium chromate in 0.05M potassium hydroxide solutions. The ligand solution spectra were recorded by filling reference cell with pure solvent.

The electronic absorption spectra of ligands are represented in fig. 1 to 2. The electronic absorption peak positions were used to assign the observed λ_{max} values to prominent chromophores, such as >C = N, -OH group present in the ligands.

The observed λ_{max} values for >C=N of bidentate Schiff bases are found to be nearly same 340-370 nm. (Table-2.2). the >C = N azomethine π→π* transitions are expected in the range 220 to 230 nm. The present Schiff bases show a weak absorption band in the higher wavelength region. The red shift may be attributed to the larger polarization of

azomethine group present in unsymmetrical ligands. The ligands L_1 to L_2 shows absorption bands at 350 nm to 400 nm respectively, which may be due to the presence of hydroxyl group in the ligands.

Table 2
Electronic Absorption Spectral Data of Ligands.

Sr. no.	Ligand	Symbol	λ_{max} for > C=N in nm.	Other
1	2-(4-benzylideneamino) pyrimidine-4, 6-diol.	L_1	340	370
2	2-(4-methoxybenzylideneamino) pyrimidine-4, 6-diol	L_2	350	368
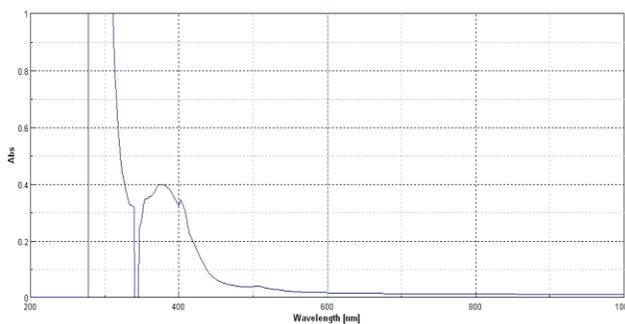
Fig. 2.1 Electronic Absorption Spectra of Ligand L_1
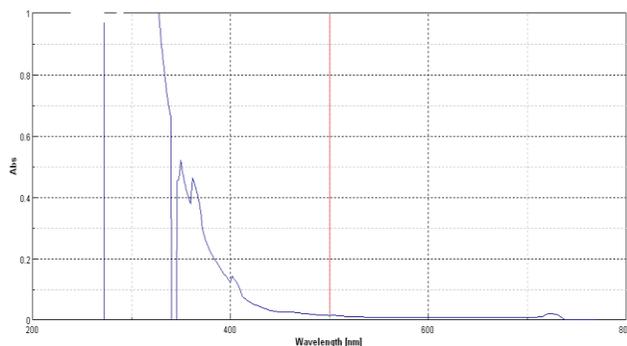
Fig. 2.2 Electronic Absorption Spectra of Ligand L2

Table No. 3 Nomenclature, Molecular and Structural Formula of Schiff Base Ligands

Sr. No.	Nomenclature and Molecular Formula	Symbol (MolWt)	Molecular Structure (Predicted)	Donor Atoms
1	2-(benzylideneamino) pyrimidine-4, 6-diol. **MF: $C_{11}H_8N_3O_2$**	**L_1** **214**		**N_2O_2**
2	2-(4-methoxybenzylideneamino) pyrimidine-4, 6-diol. **MF: $C_{12}H_{11}N_3O_3$**	**L_2** **245**		**N_2O_2**

Synthesis of Metal Complexes:

The metal complexes are synthesised by various methods. In the present work, the transition metal complexes of Schiff bases are synthesized by refluxing the ethanolic solutions of ligand and metal chloride in 2:1 molar ratio. The complexes were precipitated by the addition of 10% alcoholic ammonia solution.

Procedure:

0.01 mole of ligand in slight excess was taken in round bottomed flask containing 30 ml of ethanol and refluxed for few minutes so as to

dissolve ligand completely. A solution of 0.01 mole of metal chloride in 20 ml. of ethanol was then added drop-wise to the solution of the ligand. The contents were refluxed for three hours and then cooled to observe the occurrence of precipitation which rarely found in the cold reaction mixture, a ten percent ethanolic solution of ammonia was added drop wise to increase the P^H till the metal complex precipitates out completely. The precipitate was digested for one hour. The solid metal complex separated out was then filtered in hot condition. It was washed with portions of hot ethanol and dried in vacuum desiccator over anhydrous granular calcium chloride. The P^H range of precipitation, colours and melting points for all the synthesised metal complexes are presented in Tables 4 to 5.

Table 4
P^H range of precipitation of Cobalt (II) Complexes.

Sr.No.	Cobalt (II) complexes of	P^H range of precipitation	Colour	Melting point/ Decomposition temp. ^0C
1	L_1	7.8 – 8.5	Dark Brown	>300
2	L_2	7.8 – 8.5	Dark Brown	>300

Table 5

P^H range of precipitation of Iron (III) Complexes.

Sr.No.	Iron (III) complexes of	P^H range of precipitation	Colour	Melting point/ Decomposition temp. ^0C
1	L_1	8.2 – 9.0	Brown	>300
2	L_2	8.2 – 9.0	Brown	>300

Characterisation of Metal Complexes:

All the metal chelates prepared are stable to air and moisture. These are insoluble in water and in different polar and non polar organic solvents at room temperature. Some complexes are easily soluble and some are sparingly soluble in dimethyl sulfoxide.

The synthesized metal complexes are characterized by elemental analysis, solution conductivity, and electronic and infrared absorption spectroscopy.

Colour and melting point/decomposition temperatures of complexes:

The melting point / decomposition temperatures of the complexes were determined by melting apparatus. The observed values of melting point / decomposition temperatures and colour of complexes are tabulated in Tables 4 to 5.

Elemental Analysis of Metal Complexes

Analysis of Carbon, Hydrogen and Nitrogen:

The C, H and N content of metal complexes were performed using Elemental Analyzer Elementar model vario EL-III. The percentage of C, H and N found in metal complexes and those calculated theoretically are tabulated in Table 6 to 7. The molecular stoichiometry of each compound is established on the basis of elemental analysis.

Analysis of Metal ions:

The metal ions were estimated by means of complexometric titrations using ethylene diamine tetra acetic acid (EDTA) under optimum conditions of P^H using suitable metal ion indicators. The metal content data is used to decide the stoichiometric ratio of metal to ligand in the complexes.

i) Preparation and standardization of EDTA solution: -

The dry, pure A.R. grade disodium salt of EDTA was weighed accurately (3.7224 gm) and dissolved in deionised glass distilled water and diluted to 1 liter to obtain 0.01 M. solution. It is standardized with Zn^{+2} solution prepared from A.R. zinc pellets, using buffer of 10 P^H and erichrome black-T indicator. The exact molarity of EDTA was determined.

ii) Preparation of metal solution of complexes: -

The sample of each metal complex weighed between 20-30 mg taken in beaker, was decomposed by repeated heat treatment with small amount of concentrated hydrochloric acid. It was evaporated carefully to dryness at least twice. Then it was treated with few drops of perchloric acid and evaporated carefully to dryness. It was then extracted with small volume of deionised glass distilled water. The contents were transferred to 100 ml standard flask and diluted to mark.

Estimation of Cobalt (II):

To the solution of Co (II) contained in conical flask, 4-5 drops of freshly prepared indicator solution of xylenol orange was added. Then granules of powdered hexamine were added with continuous stirring until the yellow colour of the solution changed to deep red (P^H = 6), followed by 0.5 ml addition of 0.001 M solution of 1,10- phenanthroline to improve the correct estimation of the end point. The contents were then titrated against 0.01 M EDTA solutions, until the colour changes from red to yellow orange. A mean of three readings was taken and the amount of metal can be estimated by the conversion factor,

1ml of 0.01M EDTA = 0.5893 mg of Co (II).

Estimation of Iron (III):

From the diluted solution the 25 ml solution of Fe(III) in conical flask was made acidic with 10-15 ml concentrated hydrochloric acid and heated the liquid to boiling. To the hot solution, an acidic solution of $SnCl_2$ was added drop by drop with constant shaking until the yellow colour just disappears. Then 1 or 2 drops of $SnCl_2$ were added in excess so that Fe(III) is completely reduced to Fe(II). The contents were cooled under tap water and 5 ml of 10% aqueous mercuric chloride ($HgCl_2$) was added to remove the excess of $SnCl_2$, resulting in the formation of silky white precipitate. The 10 ml phosphoric-sulfuric acid mixture and 5 drops of 0.2% aqueous solution of sodium diphenylamine sulphate were added.

The Fe(III) obtained was slowly titrated against 0.01N $K_2Cr_2O_7$ solution until a grey blue tint colour appear near the end point. The titration was continued until the addition of one drop gives violet blue coloration even vigorous shaking. The mean of three such burette readings was used to calculate the percentage of Fe (III) in the complex by conversion factor.

1 ml 0.01M $K_2Cr_2O_7$ = 0.5585 mg of Fe(III).

Table 6
Analytical data of Co (II) complexes.

Complex	Molecular formula	Mol.Wt	% Found (Calculated)			
			C	H	N	M
L$_1$	[C$_{22}$H$_{16}$N$_6$O$_4$Co(H$_2$O)$_2$]	522	44.46 (44.35)	3.39 (3.29)	14.14 (14.15)	9.92 (9.88)
L$_2$	[C$_{24}$H$_{22}$N$_6$O$_6$Co(H$_2$O)$_2$]	558	47.85 (47.37)	3.80 (3.50)	16.10 (15.76)	9.58 (9.45)

Table 7
Analytical data of Fe (III) complexes.

Complex	Molecular formula	Mol.Wt	% Found (Calculated)			
			C	H	N	M
L_1	$[C_{22}H_{16}N_6O_4Fe(H_2O)_2]$	519	44.69 (44.55	3.40 (3.35	14.21 (14.10	9.44 (9.30
L_2	$[C_{24}H_{22}N_6O_6Fe(H_2O)_2]$	582	48.05 (47.59	3.69 (3.55	15.80 (15.60	9.12 (9.00

CHAPTER III

EXPERIMENTAL TECHNIQUES

- Solution Conductivity.

- Electronic Absorption Spectroscopy.

- Infra-Red Spectroscopy.

- Biological studies of Metal Complexes

CHAPTER- III

EXPERIMENTAL TECHNIQUES

The different techniques are used to study structural features, bonding and properties of the metal complexes. All such physiochemical techniques help to ascertain the exact structure of metal chelates.

2. SOLUTION CONDUCTIVITY:

It is one of the recent methods for studying the complexes. The solution conductivity depends on the concentration of solute and the number of charges on ions, which are formed on dissociation in an ionic material. The solution of an electrolyte conducts electric current by migration of ions under the influence of electric field. Hence the ability of any ion to transport charge depends on mobility of ions. Therefore by measuring the solution conductivity one can decide the electrolytic or non-electrolytic nature of the metal complexes, which helps in ascertaining its ionic and covalent nature.

The molar conductivity μ_v of a solution of solute is a measure of the number and rate of migration of anions and cations in one mole of the solute. By comparison of molar conductivities of complexes with that of known simple ionic materials, the total number of charges on the species formed, when the complex dissolve can be deduced, this decides the composition of complexes by cryoscopy measurement together.

Measurement of Solution Conductivity:

The solution conductivities of 10^{-4}M solution of all metal complexes in DMSO were measured on "ELICO" digital conductivity meter CM-180 with range $20\mu\Omega$ to 20 mΩ at 298 K temperature. As the conductivity of solution rises by about 2 percent per degree, the temperature must be controlled. A simple conductivity meter with dip type cell electrodes with cell constant 1.001 was used for this purpose.

The instrument and conductivity cell were calibrated using 0.005M KCL, solution at room temperature.

In practice the observed conductance (x) of solution was measured and specific conductivity K_v was calculated by multiplying the cell constant with observed conductance. Finally from specific conductivity and molarity (M) of solution, the molar conductivity µv was calculated by equation[8].

$$\mu_v = \frac{K_v \times 1000}{M}$$

Where,   M- is molarity of a solution.

The molar conductivity has the unit $S\ cm^2\ mol^{-1}$ or $ohm^{-1}\ cm^2\ mol^{-1}$. The molar conductance values were interpreted with the help of literature data.

3. ELECTRONIC ABSORPTION SPECTRA:

When continuous radiation passes through a transparent material, a portion of radiation may be absorbed and when residual radiation is passed through a prism, it gives a spectrum, called absorption spectrum. The absorption of ultraviolet (UV) or visible light results in a change in the energy of electrons of the absorbing molecule. The electronic spectrum consists of bands containing several absorption lines. Each band corresponds to a definite change in the electronic energy and individual lines within the band are due to definite transitions.

The structure of metal complexes can be predicted from interpretation of their electronic absorption spectra and comparing them with the electronic absorption spectra of corresponding ligands. The complexes can be identified by their characteristic absorption, which is based on the position of maxima and minima in the absorption spectra along with the molar extinction coefficient value. In the spectra of transition metal ions, basically bands are of three types,

I) Bands due to d-d transitions.

II) Charge transfer bands.

III) Bands due to electron transfer within the ligand.

In the transition metal complexes, visible spectra arises when an electron is excited between t_{2g} and e_g orbital with different energy levels. Charge transfer bands may arise from the transition of an electron from an orbital of ligand to the central metal atom. The molar extinction coefficient of a charge transfer band is about hundred times than that of d-d transition bands.

By recording absorption spectra of known molecule, the wavelength of radiation absorbed is correlated with the characteristic structural feature. This information is then used in determining the structure of unknown molecules from their spectra. In more stable complexes, the change in the spectrum of the ligand will depend on the degree of covalency of the metal ligand bond. The magnitude of the shift depends on the coordination number of the central atom and its ionic radius. In complexes, stability increases back coordination and charge transfer bands also appear besides the bands of the ligands. The UV/Vis spectroscopy is, therefore a powerful tool, for structure elucidation.

The correct interpretation of the absorption bands gives an insight into the energy of orbital, mode of bonding in the complexes and their geometries. By this means, it is possible to distinguish tetrahedral, octahedral and square planar complexes and whether the shape is distorted or regular. Both the intensity and wavelength of absorption band is associated with resonance states of molecule. The intensity of absorption band is associated with energy difference between the ground and excited state of molecule. In general there is an increase in intensity as the length of conjugation chain increases.

Most organic molecules absorb in the near UV region (200-400 nm) in which the atmosphere is transparent where as transition metal

complexes absorb in the visible region (400-800 nm) because of coloured solutions.

Scanning of UV/Vis. Spectra:

All Co(II), and Fe(III) complexes of unsymmetrical Schiff bases in the present study were soluble in DMSO. Therefore absorption spectra of solution were recorded on Jasco V-530 UV /Vis spectrophotometer in the region 200-1000 nm using quartz optic tubes of 2 cm path length.

4. INFRARED SPECTROSCOPY:

The absorption of Infra-red radiations causes an excitation of molecule from a lower to higher vibrational level. Every type of bond has a different natural frequency of vibration and since same type of bond in two different compounds is in two different environments, no two molecules of different structure have exactly the same infrared absorption pattern or infrared spectrum. Thus, the infrared spectrum can be used for molecules as a fingerprint, used for humans. Infrared radiation refers to that part of electromagnetic spectrum, which is in between visible and microwave region. An infrared radiation occurs when the frequency of alternating field associated with the incident radiations matches a possible change in the vibration or rotational frequency of the absorbing molecule. It is suggested that when metal ion combines with the ligands to form complex, its vibrational spectrum is expected to change. The change in the vibration can be related to molecular symmetry or with the change in the individual frequency. A molecule can undergo two types of vibrations, stretching (υ) and bending (δ-deform). Stretching vibrations have higher frequencies than deformation.

Some of the important applications of IR spectroscopy are the identification of major types of bonds, various functional groups, hydrogen bonding in metal complexes and cis-trans isomers. One of the best features of IR spectroscopy in qualitative analysis is that, the

absorption or lack of absorption in the specific frequency region can be corrected with specific stretching and bending modes and in some cases, with the relationship of these groups to rest of the molecule.

IR absorption occurs not only with organic molecules but also with covalently bonded metal complexes, which are generally active in the longer wavelength IR region. The inorganic complexes derived from organic chelating groups have a tendency to absorb in the IR region 400-660 cm^{-1} which is of greatest practical value in the study of metal complexes.IR studies thus provide much useful information about metal complexes.

Scanning of IR Spectra:

The infrared spectra of ligands and metal complexes were recorded on a SHIMADZU Model No.8400 over the range 4000 cm^{-1} to 400 cm^{-1} using KBr pellet technique.

Biological studies of Metal Complexes

Now days the study of biological activity of ligands and their metal complexes has received very much importance in coordination chemistry. It is found that the activity of ligands enhances by the introduction of metal ions in their structure. Number of Transition complexes is reported to have significant biological activities. Therefore we have also studied the biological activities of the present ligands and their metal complexes.

CHAPTER IV

RESULTS AND DISCUSSION

- Solution Conductivity.

- Electronic Absorption Spectral Studies of Metal Complexes.

- Infrared Spectral Studies of Schiff Bases and Their Metal Complexes.

- Biological studies of Metal Complexes.

CHAPTER-IV

RESULTS AND DISCUSSION

Elemental Analysis, Solution Conductivity, and Electronic Absorption Spectral Studies, **Biological studies of Metal Complexes.**

COBALT (II) COMPLEXES:

The Co(II) ion having d^7 configuration, forms number of complexes in various stereochemical types. Most of them were found to have either octahedral or tetrahedral geometry. However quite a good number of complexes of Co(II) with low spin square planar and five coordinated geometries were reported. Co(II) complexes with three unpaired electrons may be either octahedral or tetrahedral.

Co(II) forms tetrahedral complexes more than any other transition metal ion particularly with large ligands. This is in accordance with respect to d^7 configuration, which favours tetrahedral configuration relative to octahedral one. Due to the small stability difference between octahedral and tetrahedral Co(II) complexes, the complexes of both types with same ligand may be in equilibrium. The d^7 Co(II) is less satisfactory to Jahn-Teller distortion unless there is a sufficient strong field to induce spins pairing. In octahedral configuration, the ground state for Co(II) is t_{2g}^5, e_g^2 or t_{2g}^6, e_g^1 out of these, the latter one is rare because the high ligand field energy is required owing to Jahn-Teller distortion.

In octahedral Co(II) complexes $^4T_{2g}$ and ^2E_g are the spin-free and spin-paired ground states arising from t_{2g}^5, e_g^2 (high-spin) and t_{2g}^6, e_g^1(low-spin) configurations respectively. A band near 8000-10000 cm^{-1} may be assigned to the $^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$ (υ_1) to the lowest transition and a multiple band observed around 20000 cm^{-1} to the $^4T_{1g}$ (F) $\rightarrow$ T_{1g} (P) (υ_3) to the highest transition. The asymmetric visible band is typical of octahedral Co(II) complexes. The existence of distortion from a regular octahedral symmetry is indicated by an appreciable

enhancement of intensity of electronic absorption spectra. For low-spin octahedral Co(II) complexes, with ^2E ground state arises from t_{2g}^6, e_g^1 configuration, Jahn-Teller distortion would be expected.

Elemental Analysis and Solution Conductivity:

In the present investigation, all the Co(II) complexes are brown coloured, stable to air and moisture. Decomposes at high temperature rather than showing sharp melting points. They are insoluble in water and soluble in DMSO. The low conductivity values in DMSO solution (1×10^{-4} M) are given in Table 1 indicates non-electrolyte nature.

Elemental analysis data reveals that the observed percentages of C, H, N and metal ion are in good agreement with values predicted and calculated for Co(II) complexes with 1:2 metal to ligand ratio.

Electronic Absorption Spectral Studies of Co(II) Complexes:

The electronic spectra of Co(II) complexes showed three bands at 13446-19895 cm^{-1}, 20395-24820 cm^{-1} and 25610-29014 cm^{-1} which are assignable to $^4T_{1g} \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and charge transfer transitions respectively and are summarized in Table 1. The ligand field parameters for these complexes have been calculated. The calculated values of ligand field splitting energy (10Dq), Racha inter electronic repulsion parameter (B), covalent factor (β), ratio υ_2/υ_1 and ligand field stabilization energy (LFSE) support the octahedral geometry for Co(II) complexes. The nephelauxetic ratios (υ_2/υ_1) are found to be less than 2 indicating partial covalent character in the metal ligand bond. These values are falling in the range of octahedral Co(II) complexes.

Table 1: Solution Conductivity, Electronic Absorption Spectral Data of Co(II) Complexes.

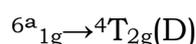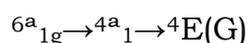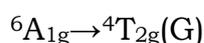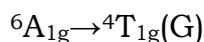| Co(II) complex of	Molar Conductance Ohm^{-1}cm^2 mol^{-1}	Absorption Maxima cm^{-1} (nm)		
		$^4T_{1g} \rightarrow T_{2g}(F)$	$^4T_{1g} \rightarrow {}^4A_{2g}(F)$	Charge transfer
L$_1$	23.35	13446(739) 13802(720)	20395(485)	25610(385) 28730 (345)
L$_2$	21.45	13446(739) 19895(500)	24820(395)	27621(360) 29015 (334)

On the basis of elemental analysis, conductivity and electronic absorption spectral measurement, the Co(II) complexes in present work may be suggested as dimeric structures with octahedral geometry.

IRON (III) COMPLEXES-

Iron (III) with d^5 configuration forms a large number of complexes, mostly octahedral. Depending on the ligand field, three types of Fe(III) complexes generally be expected. The high spin (S=5/2), low spin (S=1/2) and intermediate spin (S=3/2), crossover complexes are very well known. The crossover of ferric has ligand field strength near the crossover point of low spin and high spin. These are very well known for six coordinated iron (III) complexes. Literature survey reveals the formation of few tetrahedral and square planar Fe(III) complexes. The high spin octahedral Fe(III) complexes with d^5 configuration give rise to ground term $^6A_{1g}$ and low spin complexes with ground term ^2T_g. The electronic absorption spectra of octahedral Fe(III) complexes show multiple and very weak bands due to spin and multiplicity forbidden transitions. In octahedral Fe(III) complexes $^6A_{1g}$

and $^2T_{2g}$ are the high spin and low-spin ground terms derived from t_{2g}^3, e_g^2 (spin free) and $t_{2g}^5 e_g^0$ (spin paired) configurations respectively.

Following transitions are expected to occur in Fe(III) octahedral complexes.

$$^6A_{1g} \rightarrow {}^4T_{1g}(G)$$

$$^6A_{1g} \rightarrow {}^4T_{2g}(G)$$

$$^{6a}_{1g} \rightarrow {}^{4a}_1 \rightarrow {}^4E(G)$$

$$^{6a}_{1g} \rightarrow {}^4T_{2g}(D)$$

$$^6A_{1g} \rightarrow {}^4E(D).$$
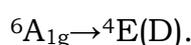
These assignments are not certain due to charge transfer bands in the visible region and near ultraviolet region in Fe(III) complexes and which almost completely mask the very weak d-d bands.

Elemental Analysis, Solution Conductivity:

In the present investigation, all the Fe(III) complexes synthesized are dark brown in colour and are stable to air and moisture at room temperature. They decompose at high temperature without melting. All of them are insoluble in water but soluble in DMSO.

The low solution conductivity values (Table 2) in $10^{-4}M$ solution indicate their non-electrolyte nature. Elemental analysis reveals that the Fe(III) complexes have 1:2 metal to ligand ratio in dimeric structure. The data is represented in and respectively.

Electronic Absorption Spectra:

The spectrum shows three bands at 13471-19895, 20580-24900 and 29123-29211 cm^{-1}, which may be, assigned to high spin octahedral complexes, for transitions $^6A_{1g} \rightarrow {}^4T_1(D)$, $^6A_{1g} \rightarrow {}^4T_1$ and $^6A_{1g} \rightarrow {}^4T_{2g}$ respectively corresponds to octahedral geometry.

The last d-d band assigned to transition $^6A_{1g}{\rightarrow}^4T_{2g}$ in the present case may be associated with the charge transfer band traveling into visible region of spectra.

Fe(III) complexes of bidentate Schiff base ligands of dehydroacetic acid with some aromatic amines were characteriz and characterized by Shirodhkar, the results of physicochemical analysis, shows 1:2 metal to ligand stoichiometric ratio. The electronic spectra showed bands in the region 16666-17000, 22985-25000 and 26660-27777cm^{-1} assigned to $^6A_{1g}{\rightarrow}^4T_2(D)$, $^6A_{1g}{\rightarrow}^4T_{1g}$ and $^6A_{1g}{\rightarrow}^4T_{2g}$ respectively. He suggested monomeric structure with high spin octahedral geometry for Fe(III) complexes.

Table 2. Solution Conductivity, ElectronicAbsorption Spectral Data of Fe(III) Complexes.

Fe(III) complex of	Molar Conductance Ohm^{-1}cm^{2}mol^{-1}	Absorption Maxima cm^{-1} (nm)		
		$^6A_{1g}{\rightarrow}^4T_{2g}$ (^4D)	$^6A_{1g}{\rightarrow}^4T_1$	Charge transfer
L$_1$	79.23	13471(738) 13803(721)	20580(469)	----- 29213 (338)
L$_2$	40.72	13803(721) 19895(500)	24900(405)	27614(355) 29210 (340)

On the basis of inferences drawn from the literature and interpretation of data on the conductivity, elemental and metal analysis, magnetic and electronic absorption spectral measurements of complexes, a monomeric structure with octahedral geometry may be proposed to Fe(III) complexes in the present study

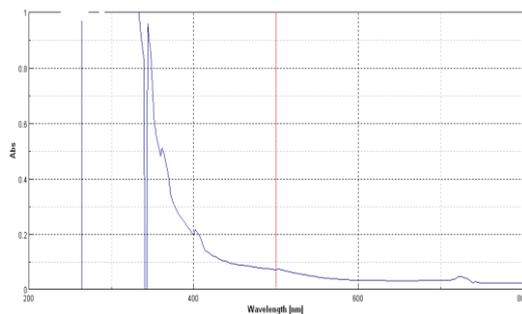**Fig. 1. Electronic Absorption Spectra of Co(II) Complex of Ligand L₁**

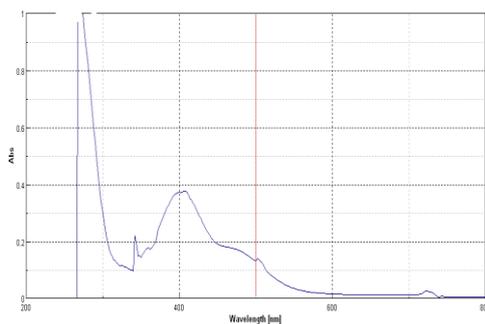**Fig. 2 Electronic Absorption Spectra of Co(II) Complex of Ligand L2**

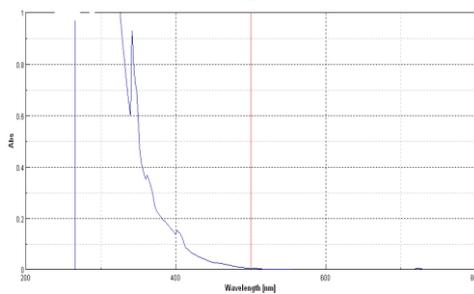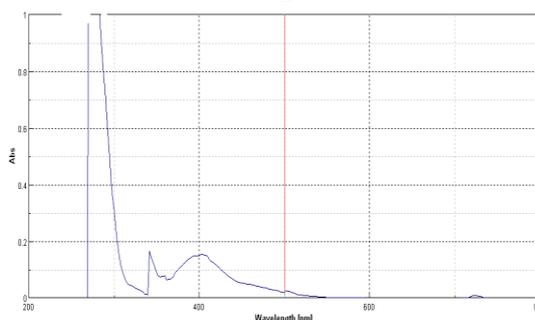**Fig. 3 Electronic Absorption Spectra of Fe(III) Complex of Ligand L₁**

Fig. 4 Electronic Absorption Spectra of Fe(III) Complex of Ligand L$_2$

INFRARED SPECTROSCOPY

Almost any compound whether organic or inorganic absorbs various frequencies of electromagnetic radiation in the infrared region of the electromagnetic spectrum. Infrared absorption of molecule is due to changes of vibration states when subjected to infrared irradiation. This technique is more useful as compared to other methods because it gives more useful information regarding the structure of molecule quickly. Infrared spectroscopy is one of the important techniques in the study of metal complexes. This offers the possibility of chemical identification and provides useful information about the structure of molecule. The vibrational frequencies of the bonds and functional groups of ligands are influenced by the neighboring bonded groups. The interaction of functional group with its surrounding can be identified by this technique. Infrared spectrum is useful to study the organic groups / bonds in the ligands and their bonding with metals in the complexes.

The infrared spectra of metal complexes are different than the corresponding free ligands to certain extent. The change in vibrational frequency can be related to change in molecular symmetry or group frequency or both. By correlating the spectra of ligands with that of their metal complexes the bonding character in the metal complexes can be deduced.

The usual method of study of infrared spectrum of metal chelates is to compare the ligand spectrum with that of the complex in which the ligand is coordinated in a known way. The characterizations of metal chelates by their vibrational spectra are usually carried out by taking into account following consideration with respect to their free ligand spectra.

a) Change in the position of bands.
b) Appearances of new bands.
c) Splitting of bands into multipletes.
d) Change in relative intensities of bands.

The change in the position of a band is observed due to change in stretching vibration mode of bond involving coordinated atom. Introduction of additional bonds on chelation favours appearance of new peaks. Replacement of a bond by newer one causes replacement of earlier peak by a new peak. Coordination of ligands with metal ion affects the symmetry of ligands resulting into splitting of band into closely spaced multipletes.

The infrared spectra of metal complexes studied in the present investigation were scanned with an objective of procuring information about the coordinating atoms in ligands which would help in deciding the stereochemistry of complexes. The different types of bonding in metal complexes were also investigated from vibrational spectra. The assignment of various stretching and bending vibrations for a molecule can be made by the selection rules given in the literature the interaction of the functional group along with the surrounding ions is important and can be identified by absorption spectra of metal complexes in the infrared region.

Infrared Spectral Studies of Ligand:

Unsymmetrical tetradentate Schiff bases used for synthesis of metal complexes in the present study are derived from aromatic amines and aldehydes. The IR spectral data of ligands are tabulated in

Table 3 and their spectra are presented in fig. 5 to 6. The data presented in the table is prepared by assigning various bands in the spectra with respect to prominent bond stretching vibration modes in ligands. The absorption pattern in infrared spectra exhibits complex nature due to various vibrational modes. However with limited objective only important band frequencies related to enolic –OH aromatic >C=C< azomethine >C=N- and enolic C-O groups of ligands that are involved in the complex formation.

A weak to strong intensity bands observed at 1197 to 1288 cm^{-1}in the IR spectra of ligands in the present study may be assigned to enolic C-O stretching vibrational mode.

Table 3 Salient features of IR spectral data of ligands.
(Assignment of band frequencies to bond vibration modes)

Bond vibrational modes	Ligand band positions (wave number cm^{-1})	
	L_1	L_2
O-H Free Stretching(ν)	3324	3319
C = N Azomethine Stretching(ν)	1635	1666
C = C Aromatic ring stretching(ν)	1480	1511
C -- N Aryl azomethine stretch (ν)	1199	1340
C -- O Enolic stretching (ν)	1087	1191
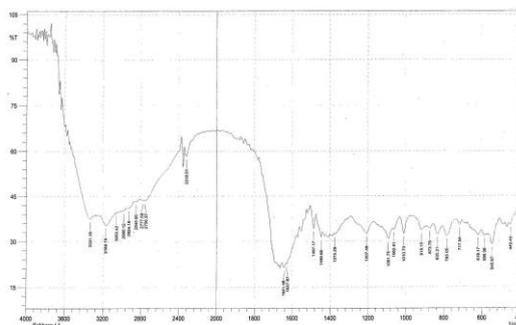
Fig. 5 Infrared Spectra of Ligand L₁
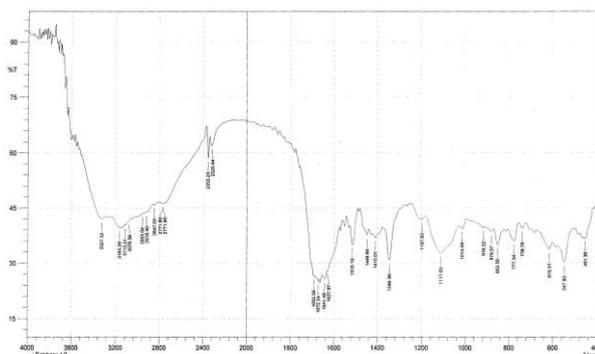
Fig. 6 Infrared Spectra of Ligand L₂

Infrared Spectral Studies of Metal Complexes

The assignments of band frequencies for different groups in metal chelates corresponding to those considered for ligand spectra have been proposed on the basis of data available in the literature on metal complexes of similar ligands and taking into account the sensitivities of characteristic group frequencies to metal complexation.

Co(II) Complexes :

The group absorption frequencies of Co(II) complex are summarized in Table 4 and the original spectra of these complexes are presented in fig. 7 to 8.

Table 4

Infrared Absorption Frequencies (cm^{-1}) of Co(II) Complexes

(Assignment of band frequencies to bond vibration modes)

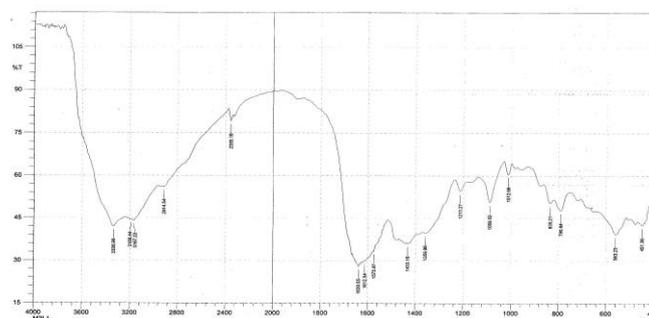| Complex/ Ligand	Bond vibrational modes (stretching-ν). Band Positions (cm^{-1})					
					New Peaks	
	Azometh-ine(C=N)	Aromatic (C=C)	Aryl Azom-ethine(C-N)	Enolic (C-O)	M-O	M-N
L$_1$	1639	1483	1201	1089	---	---
Co-L$_1$	1636.50	1430.11	1353.36	1209.21	499.08	446.16
L$_2$	1669	1512	1342.05	1191	---	---
Co-L$_2$	1648.67	1491.05	1351.20	1256.27	519.25	429.26

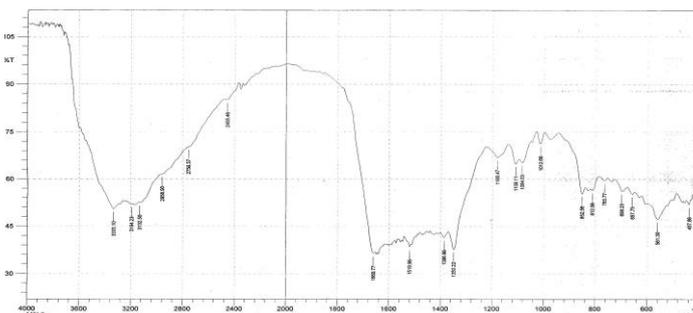**Fig. 7 Infrared Spectra of Co(II) Complex of Ligand L$_1$**

Fig. 8 Infrared Spectra of Co(II) Complex of Ligand L$_2$

Fe(III) complexes:

The group absorption frequencies of Fe(III) complexes are summarized in Table 5 and the original spectra of these complexes are presented in fig.9 to 10.

Table 5

Infrared Absorption Frequencies (cm^{-1}) of Fe(III) Complexes

(Assignment of band frequencies to bond vibration modes)

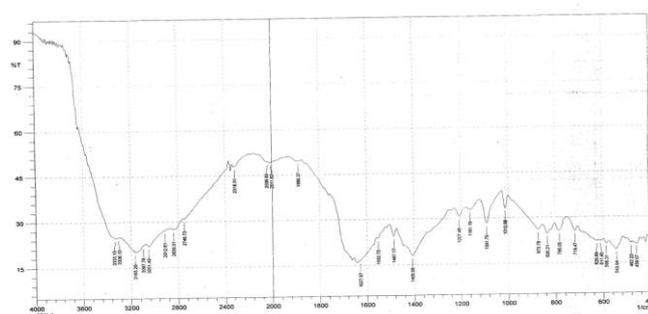| Complex / Ligand	Bond vibrational modes (stretching-ν). Band Positions (cm^{-1})					
					New Peaks	
	Azometh-ine(C=N)	Aromatic (C=C)	Aryl Azom-ethine(C-N)	Enolic (C-O)	M-O	M-N
L$_1$	1636	1479	1201	1089	---	---
Fe-L$_1$	1619.67	1401.03	1216.41	1151.13	542.34	456.02
L$_2$	1665	1508	1336	1184	---	---
Fe-L$_2$	1611.07	1451.13	1318.25	1204.10	541.02	424.08

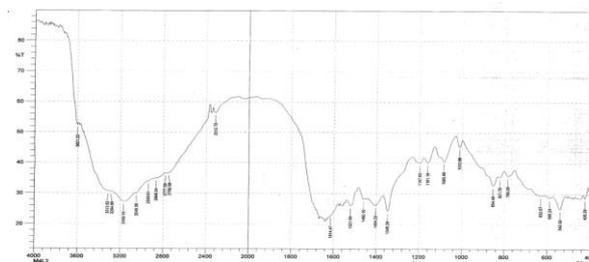**Fig. 9 Infrared Spectra of Fe(III) Complex of Ligand L$_1$**

Fig. 10 Infrared Spectra of Fe(III) Complex of Ligand L₂

From the above IR spectral data of ligands and their metal chelates the following conclusion may be drawn.

The disappearance of ligand bands around 3327-3481 cm^{-1} due to hydrogen bonded enolic O-H stretching frequency in the spectra of their respective metal chelates indicates the deprotonation of enolic O-H and subsequent coordination of enolic oxygen with metal ion forming M-O bond. A significant shift of the ligand bands due to enolic C-O stretching vibration to higher frequency side on complexation further confirms the participation of phenolic oxygen of the ligands in the bond formation with metal ion.

The considerable shift in the position of the band attributed to C=N group of ligands on complexation to lower frequency side infers that coordination of the ligand to the metal ion also takes place through azomethine nitrogen. This observation is further supported by significant upward shift of the band due to aromatic C-N stretching vibration on chelation.

The appearance of new band in the region 501-561 cm^{-1} and 410-497 cm^{-1} in the IR spectra of complexes supports the formation of M-O and M-N bonds respectively in the complexes.

In the IR spectra of Co (II) and Fe (III) complexes a broad band is observed in the region 3150 – 3500 cm^{-1} corresponding to the stretching frequency of vOH this indicates the presence of coordinated water. The presence of coordinated water is further confirmed by the appearance of non-ligand band in the region 810 – 850 cm^{-1} assignable to rocking mode of water.

On the basis of results of elemental analysis, solution conductivity measurement, IR, electronic spectral data it may be concluded that the complexes of Co(II) and Fe(III) contains coordinated water molecules and have octahedral structure.

Experimental: Antifungal Activity

The fungi toxicity of Schiff bases and metal complexes in liquid medium was studied by the method followed R.J.Cruickshank, P.Duguid, R.R.Swain, in vitro against *Aspergillus niger, Penicillium chrysogenum, Fusarium moneliforme, Aspergillus flavus at* 1% and 2% separately. The species were collected from department of Microbiology N.S.B.College Nanded. The same method is used in the present investigation

Table 6 Antifungal activity of ligands and their metal complexes

Test Compound	Antifungal growth			
	Aspergillusniger		*Penicillium chrysogenum*	
	1%	2%	1%	2%
L₁	-ve	-ve	-ve	-ve
L₁ – Co	-ve	-ve	-ve	-ve
L₁ – Fe	-ve	+ve	-ve	-ve
L₂	₊ve	RG	RG	-ve
L₂ – Co	-ve	-ve	-ve	-ve
L₂ – Fe	-ve	+ve	RG	RG
+ve control	+ve	+ve	+ve	+ve
-ve control (Griseofulvin)	-ve	-ve	-ve	-ve

Experimental: Antibacterial Activity:

The antibacterial activity of ligand and their metal complexes was studied by the method followed R.J.Cruickshank, P.Duguid, R.R.Swain, were screened in vitro against *Escherichia coli, Salmonella typhi , Staphylococcus aureus* and *Bacillus subtilis* using Penicillin as standard at 1% and 2% separately. The species were collected from department of Microbiology N.S.B.College Nanded.

Table 7 Antibacterial activity of ligands and their metal complexes

Test Compound	Diameter of inhibition zone (mm)			
	E. Coli		*Bacillus subtlis*	
	1%	2%	1%	2%
L₁	-ve	11mm	-ve	13mm
L₁ – Co	11mm	13mm	12mm	12mm
L₁ – Fe	-ve	-ve	14mm	16mm
L₂	-ve	14mm	-ve	17mm
L₂ – Co	11mm	13mm	09mm	12mm
L₂ – Fe	10mm	11mm	12mm	15mm
DMSO	-ve	-ve	-ve	-ve
Pennicillin	13mm	13mm	17mm	17mm

The percentage of inhibition of growth of both fungi due to ligand found to be in the order $L_1 > L_2$ and that due to their metal complexes was found to be in the order Co(II) > Fe(III).

Conclusion:

- The Schiff bases used in the present study were synthesized by condensation of heterocyclic amine and aldehydes.

- All these ligands are soluble in DMSO.

- All these metal complexes co-ordinate with tetrdentate ligands with 1:1 metal- ligand stoichiometry.

- All these metal complexes are insoluble in common organic solvents but soluble in DMSO.

- All metal complexes are stable at room temperature, since they do not decompose even at 300^0C.

- All metal complexes show low value of molar conductivity which indicate that these metal complexes are non electrolytic in nature.

- IR spectra of metal complexes shows that the complexation occur through azomethine nitrogen and enolic –OH. This is confirmed by shifting the bands (C=N) towards lower frequency.

- The new bands found in the range of 430-750 cm^{-1} due to (M-N) and (M-O) confirm the complexation.

- The antifungal and antimicrobial activity of ligands and metal complexes show that the metal complexes are more biologically active than the respective ligands.

- The outcome of the project will be published in the form of research paper and due acknowledge will be made to U.G.C. (WRO) Pune for its financial support.

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