CHAPTER -V

➤ Results and Discussion

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

➤ References.
CHAPTER V

RESULTS AND DISCUSSION: INFRARED SPECTROSCOPY

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. It is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids and solids. Infrared spectroscopy is one of the important techniques in the study of metal complexes carried out within the range 4000-400 cm\(^{-1}\). 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 co-ordinated in a known way. The characterizations of metal chelates by their vibrational spectra are usually carried out by taking into account following considerations with respect to their free ligand spectra.

1) Change in the position of bands.
2) Appearances of new bands.
3) Splitting of bands into multipletes.
4) Change in relative intensities of bands.

The change in the position of a band is observed due to change in stretching vibrational mode of bond involving co-ordinated 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 co-ordinating 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 Ligands:**

Unsymmetrical tetradentate Schiff bases used for synthesis of metal complexes in the present study are derived from aromatic diamines, dehydroacetic acid and different aldehydes. The IR spectral data of ligands are tabulated in Table 5.1 and their spectra are presented in Fig. 5.1 to 5.6. The data presented in the Table is prepared by assigning various bands in the spectra with respect to prominent bond stretching vibrational 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 –O-H, aromatic >C=C<, azomethine >C=N-, Aryl azomethine C-N and enolic C-O of ligands that are involved in the complex formation are discussed.
**Hydrogen Bonded O-H frequency:**

All unsymmetrical tetradentate Schiff bases used in the present investigation has two O-H groups. Accordingly the O-H stretching frequencies were observed as broad weak bands at 3273 to 3332 cm\(^{-1}\). The lowering of normal free O-H stretching frequency from 3600-3500 cm\(^{-1}\) to above values is expected to be due to strong intermolecular hydrogen bonding between -OH and the nitrogen of the azomethine group.

Munde et.al.\(^1\) reported a band at 3100-3400 cm\(^{-1}\) due to intermolecular hydrogen bonded OH of Schiff bases derived from dehydroacetic acid, 4-methyl-o-phenylenediamine and salicylic aldehyde.

Jadhav et.al.\(^2\) was assigned the IR bands at 3059-3300 cm\(^{-1}\) due to O-H---N intermolecular hydrogen bonding. These Schiff bases were derived from O-phenylene diamine, dehydroacetic acid (DHA) and p-chloro benzaldehyde.

Osowole et.al.\(^3\) have assigned a band at 3300 cm\(^{-1}\) to -OH vibrational of Schiff bases derived from 1-phenyl-1,3-butanedione, ethylenediamine and 2-hydroxy-4-methoxy benzophenone.

Khanmohammadi and Darvishpour et.al.\(^4\), Dicaple et.al.\(^5\), Eissa et.al.\(^6\) have assigned a band at 3414.00-3479.58 cm\(^{-1}\) to -OH vibrations of Schiff bases derived from 3-formyl-4-hydroxy phenylnazobenzene and dihydrazide of isophthalic acid. A band at 3414.00- 3471.87 cm\(^{-1}\) to -OH vibrations of Schiff...
bases derived from 3-formyl-4-hydroxy phenylazobenzene and pyridine-2,6-dicarbohydrazide. A band at 3419.00 cm$^{-1}$ to -OH vibrations of Schiff bases derived from 3-formyl-4-hydroxy phenylazobenzene and 6-methyl-1,3,5-triazine-2,4-diamine.

Nagajothi et.al.\textsuperscript{7} have assigned a band at 3200-3500 cm$^{-1}$ to -OH vibrations of Schiff bases derived from Isatin, o-phenylenediamine and salicylaldehyde ($L_1$), Acetyl acetone, o-Phenylenediamine and salicylaldehyde ($L_2$) and 2-hydroxynaphthaldehyde, phenylenediamine and salicylaldehyde($L_3$).

Thus the band at 3273 to 3332 cm$^{-1}$ in the present study may be assigned to hydrogen bonded–O-H···N stretching frequency. These bands disappeared in the spectra of their respective metal chelates owing to the deprotonation of –O-H and subsequent co-ordination of oxygen with metal ion.

**Azomethine (C=N) stretching frequency:**

The absence of vibrational peaks related to NH$_2$ and C=O groups of amine and aldehyde in the FTIR spectrum of ligand and apperance of new strong peak at 1690-1471 cm$^{-1}$. have suggested formation of new imine (C=N) functionality\textsuperscript{15} of the ligand.

Khalaji et.al.\textsuperscript{8,9} observed C=N frequencies in the Schiff bases derived from substituted 5-bromosalicylaldehyde and 1,3-phenylenediamine at 1617 cm$^{-1}$. 
Lashanizadegan et al.\textsuperscript{10} assigned 1615 cm\(^{-1}\) frequencies in the spectra of Schiff bases of 2-hydroxy acetophenone, 2-hydroxy-1-naphthaldehyde and 1,2-phenylenediamine to C=N stretching vibrations.

Chondhekar et al.\textsuperscript{11} reported C=N stretching band at 1640-1660 cm\(^{-1}\) in the IR spectra of dehydroacetic acid, 2-hydroxy-1-naphthaldehyde and o-phenylenediamine (H\(_2\)L\(_1\)), 4-methyl-o-phenylenediamine (H\(_2\)L\(_2\)) respectively.

Vibhute et al.\textsuperscript{12} assigned IR spectral bands at 1565 cm\(^{-1}\), 1570 cm\(^{-1}\), 1560 cm\(^{-1}\), 1570 cm\(^{-1}\), 1560 cm\(^{-1}\), 1570 cm\(^{-1}\), 1565 cm\(^{-1}\), 1570 cm\(^{-1}\), 1560 cm\(^{-1}\), 1565 cm\(^{-1}\), 1568 cm\(^{-1}\) to C=N stretching vibrational of Schiff bases derived from o-phenylenediamine and 2-hydroxy-3,5-di-iodo-acetophenone, 2-hydroxy-3,5-di-bromo-acetophenone, 2-hydroxy-5-chloro acetophenone, 3-bromo-4-hydroxy-5-methoxy acetophenone, 4-hydroxy-3-Iodo-5-methoxy acetophenone, 3-chloro-4-hydroxy-5-methoxy acetophenone, \(\alpha\)-methyl-2-hydroxy-3',5'-di-iodoacetophenone, \(\alpha\)-methyl-4'-hydroxy-3',5'-di-iodoacetophenone, \(\alpha\)-methyl-5'-chloro-2-hydroxy-3'-iodoacetophenone, \(\alpha\)-methyl-5'-chloro-2'-hydroxy-5'-methyl acetophenone, \(\alpha\)-methyl-3'-bromo-2'-hydroxy-5'-methyl acetophenone, \(\alpha\)-methyl-3'-bromo-5'-chloro-2-hydroxy aceto phenone.

Abraham et al.\textsuperscript{13} observed C=N frequencies in the heterocyclic Schiff bases derived from substituted chlorobenzaldehyde and 6-phenyl-1,3,5-triazine-2,4-diamine at 1616-1605 cm\(^{-1}\). The various vibrations are observed for azomethine group of conjugated system. In many Schiff bases C=N stretching frequency is
dependent on the substituent on it mostly causing resonance interaction and hydrogen bonding. \(^{14}\)

A medium to strong intensity bands observed at 1633 to 1663 cm\(^{-1}\) in infrared spectra of ligands in the present work are assigned to azomethine C=N stretching vibrations.

**Aromatic ring C=C stretching frequency:-**

The IR bands due to aromatic ring C=C stretching vibrations are often seen around 1600-1585 cm\(^{-1}\) and 1500-1400 cm\(^{-1}\) region\(^{15}\).

Montazerozohori et.al.\(^{16}\) reported the appearance of IR bands at 1600-1507 cm\(^{-1}\) for the complexes of Schiff bases derived from 4-methyl-1,2-phenyldiamine and trans cinnamaldehyde.

Tan et.al.\(^{17}\) reported the appearance of IR bands at 1590-1545 cm\(^{-1}\) for the complexes of Schiff bases derived from anilines diamines amino acids amino phenols amino alcohols and dehydroacetic acid and assigned to C=C aromatic ring. The strong/medium intensity bands appeared at 1540 - 1553 cm\(^{-1}\) and 1455-1488 cm\(^{-1}\) in the IR spectra of ligands in the present investigation are assigned to (C=C) aromatic ring stretching vibrations.

**Aryl azomethine C-N stretching frequency:-**

For the study of C-N vibrational mode, there is no systematic and reliable information on aromatic C-N frequency of vibrational in the literature.. The
bands at 1360–1350 cm\(^{-1}\) appeared in the IR spectra of transition metal complexes of Schiff bases derived from 4-amino phenol, 4-amino benzoic acid and dehydroacetic acid were assigned to stretching frequency of aryl azomethine C-N group by Shirodkar et.al.\(^\text{18}\).

Joohari et.al.\(^\text{19}\) studied Schiff bases of N,N-bis(4-chloro benzylidene) propane-1,2-diamine(L\(^1\))N,N-bis(3-nitrobenzylidene) propane-1,2-diamine(L\(^2\))and N,N-bis(4-nitrobenzylidene) propane-1,2-diamine(L\(^3\)) are suggested that the appearance of IR bands in the region is 1369 cm\(^{-1}\)(L\(^1\)),1346 cm\(^{-1}\)(L\(^2\))and 1342cm\(^{-1}\)(L\(^3\)) attributable to aromatic azomethine C-N stretching vibrations.

All the Schiff bases studied in the present work have aryl substituent at azomethine nitrogen. Due to bulky nature of aryl group the formation of chelate may alter the plane of aromatic ring and possibly the force constant of C-N bond. The bands observed at 1270-1395 cm\(^{-1}\)in the spectra of all ligands may be tentatively assigned to aryl azomethine C-N stretching vibrational frequency.

**Enolic C-O stretching Frequency:-**
The IR spectral bands due to enolic C-O stretching vibrational modes are expected to appear around\(^\text{20}\) 1200 cm\(^{-1}\).

Anitha et.al.\(^\text{21}\) has reported the enolic C-O stretching frequency at 1282 cm\(^{-1}\) for the Schiff bases derived from 5-((4-chlorophenyl)diazenyl)-2-hydroxybenzaldehyde and diaminomaleonitrile.
Kumar et.al.\textsuperscript{22} assigned the band at 1540 cm\textsuperscript{-1} (L\textsubscript{1}), between 1225 cm\textsuperscript{-1} and 1260 cm\textsuperscript{-1} (L\textsubscript{2}) for phenolic C-O stretching vibrations appeared in the IR spectra of Schiff bases derived by condensation of 3-formylsalicylic acid with 2-benzoylacetonilide and ethylene diamine(L\textsubscript{1})\textsuperscript{23} and PS-Cl, Schiff base (L\textsubscript{4}), ethyl acetate, triethylamine(L\textsubscript{2}).\textsuperscript{24}

A weak to strong intensity bands observed at 1123 to 1232 cm\textsuperscript{-1} in the IR spectra of ligands in the present study may be assigned to enolic C-O stretching vibrational mode.

Table 5.1

Silent features of IR spectral data of ligands.

(Assignment of band frequencies to bond vibrational modes)

<table>
<thead>
<tr>
<th>Bond vibrational modes</th>
<th>Ligand band positions (wave number cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H…N (bonded) Stretching($\nu$)</td>
<td>L\textsubscript{1}  L\textsubscript{2}  L\textsubscript{3}  L\textsubscript{4}  L\textsubscript{5}  L\textsubscript{6}</td>
</tr>
<tr>
<td>3277</td>
<td>3283</td>
</tr>
<tr>
<td>C= N Azomethine Stretching($\nu$)</td>
<td>1663</td>
</tr>
<tr>
<td>C=C Aromatic ring stretching ($\nu$)</td>
<td>1551</td>
</tr>
<tr>
<td>1463</td>
<td>1463</td>
</tr>
<tr>
<td>C-N Aryl azomethine stretch ($\nu$)</td>
<td>1395</td>
</tr>
<tr>
<td>C - O Enolic stretching ($\nu$)</td>
<td>1177</td>
</tr>
</tbody>
</table>
Fig. 5.1 Infrared Spectra of Ligand L₁

Fig. 5.2 Infrared Spectra of Ligand L₂
Fig. 5.3 Infrared Spectra of Ligand L₃

Fig. 5.4 Infrared Spectra of Ligand L₄
Fig. 5.5 Infrared Spectra of Ligand L₅

Fig. 5.6 Infrared Spectra of Ligand L₆
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.

Cr(III) Complexes:

The IR spectra of Cr(III) complexes of representative ligands are presented in Fig. 5.7 to 5.8 and their group absorption frequencies are tabulated in Table 5.2.

Azomethine (C=N) and Aromatic C=C Frequency:

In the spectra of Cr(III) complexes the medium to strong bands appeared in the region 1631 to 1635 cm\(^{-1}\) were assigned to C=N stretching vibrational mode. In the corresponding ligands frequencies for same group are observed from 1635 to 1663 cm\(^{-1}\). A downward shift of the band by 4 to 33 cm\(^{-1}\) in complexes indicate that the C=N group of the ligands is co-ordinated to the metal ion via its azomethine nitrogen\(^{25}\).

The frequency of free ligands for same groups is observed 1591 cm\(^{-1}\). The shifting of this band to lower frequency region in metal ligand complexes happens because in the metal ligand complexes the C=N group becomes conjugated with other ligand groups conjugations along with the metal-ligand π-
bonding are responsible for the shift peak frequency between the independent ligand and metal complexes.\textsuperscript{26,27}

Abdul wajid et.al.\textsuperscript{28} observed strong band in the region 1612-1651 cm\textsuperscript{-1} assigned to the C=N (azomethine). In this region C=N band may not be pure and it may be associated with aromatic C=C stretching band. Shifting of this band to a lower value by 20-40 cm\textsuperscript{-1} in the metal complexes in comparison to the free ligands indicates the co-ordination of azomethine nitrogen to the metal.\textsuperscript{29}

The medium to strong band in the region 1413-1542 cm\textsuperscript{-1} in the IR spectrum of Cr(III) complexes were assigned to aromatic C=C stretching vibration.\textsuperscript{30} These bands in the corresponding free ligands appeared almost in the same region. However the bands due to C=C aromatic ring vibrations may shift their position as a result of change in the distribution of electrons and molecular environment due to introduction of metal ion \textsuperscript{31}

**Aryl Azomethine C-N stretching frequency:**

The IR bands in the region 1270 to 1395 cm\textsuperscript{-1} attributed to aromatic C-N stretching vibrations in the free ligands spectra were appeared at lower frequency side of 1062 to 1339 cm\textsuperscript{-1} region in the spectra of its Cr(III) complexes. The observed increase in the magnitude of vibrational frequency of this group on complexation may be attributed to increase in double bond character of aryl
azomethine C-N bond presumably due to $\pi$ electron delocalization from the metal to the nitrogen atom and resonance interaction with the benzene ring\textsuperscript{31}.

**Enolic C--O Frequency :-**

The medium to strong bands observed at 976 to 1057 cm\textsuperscript{-1} in the spectra of Cr(III) complexes were assigned to enolic C-O stretching vibrations. These bands in the corresponding free ligands are at 1177 to 1180 cm\textsuperscript{-1}. The observed downward shift of this band on chelation indicates the participation of enolic carbonyl oxygen of DHA moiety of ligands in the complex formation.

Wankhede et.al. \textsuperscript{32} observed band is assigned to the C-O. Shifting of this band to a lower value by 11 cm\textsuperscript{-1} in transition metal complexes in comparison to the free ligand indicating the presence of oxime moiety in the complexes co-ordinating through its nitrogen and oxygen atoms.

**New bands and other changes observed:-**

All the ligands exhibited a broad band at 3273 to 3332 cm\textsuperscript{-1} assigned to O-H······N stretching vibrational. The absence of these bands in the spectra of complexes further confirms the deprotonation of O-H and subsequent coordination of enolic oxygen with metal forming M-O bond. The new bands observed in the region 609 to 825 cm\textsuperscript{-1} and 489 to 491 cm\textsuperscript{-1} in the IR spectra of Cr(III) complexes may be assigned to the stretching of M-O and M-N bonds respectively.
Table 5.2

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

(Assignment of band frequencies to bond vibrational modes)

<table>
<thead>
<tr>
<th>Complex/Ligand</th>
<th>Bond vibrational modes (stretching-(\nu)). Band Positions (cm(^{-1}))</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Azomethine (C=N)</td>
<td>Aromatic (C=C)</td>
</tr>
<tr>
<td>(L_1)</td>
<td>1663</td>
<td>1551 1463</td>
</tr>
<tr>
<td>(Cr-L_1)</td>
<td>1631</td>
<td>1542</td>
</tr>
<tr>
<td>(L_5)</td>
<td>1635</td>
<td>1540 1455</td>
</tr>
<tr>
<td>(Cr-L_5)</td>
<td>1633</td>
<td>1413</td>
</tr>
</tbody>
</table>

Fig. 5.7 Infrared Spectra of Cr(III) Complex of Ligand \(L_1\)
Fig. 5.8 Infrared Spectra of Cr(III) Complex of Ligand L₅

Co(II) Complexes :-
The IR spectra of Co(II) complexes of representative ligands are presented in Fig.5.9 to 5.10 and their group absorption frequencies are tabulated in Table 5.4

Azomethine C=N and Aromatic C=C frequency :-

In the IR spectra of Co(II) complexes the medium to strong bands appeared in the region 1640-1641 cm⁻¹ are assigned to C=N stretching vibrational mods. In the corresponding free ligand frequencies for same groups are observed at 1661-1663 cm⁻¹. Downward shift of the band by 20-22 cm⁻¹ in complexes indicates that the C=N group of the ligands is co-ordinated to the metal ion via its azomethine nitrogen. ²⁵
Nagajothi et.al.\textsuperscript{7} reported the lowering of C=N stretching frequency in transation metal complexes by 7-10 cm\textsuperscript{-1} in comparsion of the free ligands. This lowering indiated that the ligand coordinated to the metal ion via the azomethine nitrogen.

Boghari et.al.\textsuperscript{33} absorbed values of the C=N vibration for CoL are lowered by about 9-15 cm\textsuperscript{-1} than those for the free ligand which indicates the coordination of azomethine nitrogen atom to metal ions in the complexes.

The bands due to aromatic C=C stretching frequency was observed in the same region 1544-1414 cm\textsuperscript{-1} as that of their free ligand.

**Aryl azomethine C-N frequency :-**

The weak to strong intensity bands in the region 1393-1395 cm\textsuperscript{-1} attributed to aromatic C-N stretching vibrations in the free ligand were observed at lower frequency side at 1355-1414 cm\textsuperscript{-1} in the spectrum of their Co(II) complexes. The positive shift of this band infers that the nitrogen of azomethine is coordinated to the metal ion and is attributed to the reasons cited for Cr(III) complexes\textsuperscript{31}.

**Enolic C-O frequency :-**

The bands observed at 1067 cm\textsuperscript{-1} in the Co(II) complexes are assigned to enolic C-O. The frequency of this band is shifted to lower frequency side than the corresponding free ligand 1124-1177 cm\textsuperscript{-1}. This decrease in the frequency indicates the formation of bond between oxygen of C-O and metal ion.
Wankhede et.al.\textsuperscript{32} observed C-O frequencies in the Co(II) complex derived from salicylaldehyde, ethylenediamine and 8-Hydroxyquinoline. Band at 1120 cm\textsuperscript{-1} in the free azo Schiff base has been assigned to phenolic C-O stretching upon complexation, this band displaces to lower frequency 1108 cm\textsuperscript{-1} indicating coordination through phenolic oxygen.

Nagajothi et.al.\textsuperscript{34} observed lower C-O frequencies in the Co(II) complexes at 1243.16-1254.74 cm\textsuperscript{-1} as compared to C-O frequencies in the Schiff bases derived from o-phenylenediamine, salicylaldehyde and isatin / naphthaldehyde / acetylacetone at 1275.95-1279.81 cm\textsuperscript{-1} indicating co-ordinating through phenolic oxygen.

**New bands and other changes observed :-**

The absence of band in the region 3273 to 3332 cm\textsuperscript{-1} due to hydrogen bonded enolic O-H$\cdots$N stretching frequency confirms the participation of enolic oxygen in co-ordination with metal in Co(II) complexes. The new bands in the region 612-689 cm\textsuperscript{-1} and 455-615 cm\textsuperscript{-1} in the spectra of Co(II) complex indicate the vibrational of M-O and M-N bonds respectively.\textsuperscript{17,18,30}
Table 5.3
Infrared Absorption Frequencies (cm\(^{-1}\)) of Co(II) Complexes

(Assignment of band frequencies to bond vibrational modes)

<table>
<thead>
<tr>
<th>Complex/ Ligand</th>
<th>Bond vibrational modes (stretching-(\nu)). Band Positions (cm(^{-1}))</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Azomethine (C=N)</td>
<td>Aromatic (C=C)</td>
</tr>
<tr>
<td>L(_1)</td>
<td>1663</td>
<td>1551</td>
</tr>
<tr>
<td></td>
<td>1463</td>
<td></td>
</tr>
<tr>
<td>Co-L(_1)</td>
<td>1640</td>
<td>1414</td>
</tr>
<tr>
<td>L(_2)</td>
<td>1661</td>
<td>1549</td>
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<td></td>
<td>1463</td>
<td></td>
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<tr>
<td>Co-L(_2)</td>
<td>1641</td>
<td>1544</td>
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</table>

Fig. 5.9 Infrared Spectra of Co(II) Complex of Ligand L\(_1\)
Fig. 5.10 Infrared Spectra of Co(II) Complex of Ligand L₂

Ni(II) complexes:-
The IR spectra of Ni(II) complexes of representative ligands are presented in Fig. 5.11 to 5.14 and their group absorption frequencies are tabulated in Table 5.4

Azomethine C=N and Aromatic C=C frequency :-
In the IR spectra of Ni(II) complexes the bands appeared at 1624 to 1657 cm⁻¹ are assigned to C=N stretching vibrational. The bands in the corresponding free ligands are found at 1661 to 1663 cm⁻¹. The shift of this band to lower frequency on chelation indicates the participation of azomethine nitrogen in bonding with the central Ni atom. The bands at 1635 cm⁻¹, 1654 cm⁻¹, 1653 cm⁻¹ appeared in
IR spectra of Ni(II) complex of Schiff bases derived from  
3,4-diaminobenzophenone, salicylaldehyde and 5-methoxy salicylaldehyde(L₁),  
5-bromo salicylaldehyde(L₂), 5-chloro salicylaldehyde (L₃), 5- Nitro salicylaldehyde(L₄) respectively were assigned to stretching frequency of arylazomethine C=N group by Asadi et.al.³⁵

Mane et.al.³⁶ reported shift of this band to lower frequency by 20 cm⁻¹ for the Ni(II) complex derived from 3-acetyl-6-methyl-(2H)-pyran-2,4(3H)-dione (Dehydroacetic acid) and o-chloroaniline.

The bands due to aromatic C=C stretching frequency for the metal complexes was observed in the same region 1537 to 1551 cm⁻¹ as that of their free ligands.

**Aryl azomethine C-N frequency :-**

The bands observed in IR spectra of Ni(II) complexes at 1254-1263 cm⁻¹ are attributed to aryl azomethine C-N stretching. The same bands in corresponding free ligands are observed at 1391 to 1395 cm⁻¹. The observed decreased in magnitude of vibrational frequency of this group by about 32-37 cm⁻¹ on complexation may be attributed to the decreased in double bond character of aryl azomethine C-N bond presumably due to π electron delocalization from the metal to nitrogen atom and resonance interaction with the benzene ring. Sadeek et.al.³⁷ assigned the band at 1222 cm⁻¹ in the IR spectra of Ni(II) complex with
Schiff base (N,N’-o-phenylene(bis 1-cyclopropyl-6-fluoro-4-oxo-7-(piperazine-1-yl)-quinoline-3-carboxylic acid).

**Enolic C-O frequency** :-

The downward shift of C-O frequency in Ni(II) complex (1054-1067 cm\(^{-1}\)) than the corresponding free ligand (1123-1232 cm\(^{-1}\)) suggest the bonding of enolic oxygen with Ni(II) during complexation.

Reddy et.al.\(^{38}\) has reported the enolic C-O stretching frequency for the Schiff base derived from acetylacetone and salicylaldehyde and diamine. On co-ordination shifting of these bands downwards indicating that oxygen is involved in bonding.

The lower frequency in the metal complexes may be described to delocalization of \(\pi\)-electron density from the oxygen atom to the metal ion resulting in an decreased in electronegativity of oxygen atom. This will lead to lesser ionic character of the C-O bond and a consequent decrease in the C-O vibrational frequency on metal complexation.

**New bonds and other changes observed** :-

The bands observed in IR spectra of ligands at around 3273 to 3332 cm\(^{-1}\) assigned due to O-H \(\cdots\) N vibrational were not observed in the spectra corresponding Ni(II) complexes. This indicates the deprotonation of enolic –OH and subsequent bonding of its oxygen with Ni during complex formation.
The additional bands at 605-613 cm$^{-1}$ and 449-541 cm$^{-1}$ were assigned to Ni-O and Ni-N bonds respectively. \cite{17,18}

**Table 5.4**  
Infrared Absorption Frequencies (cm$^{-1}$) of Ni(II) Complexes

<table>
<thead>
<tr>
<th>Complex/ Ligand</th>
<th>Bond vibrational modes (stretching-ν), Band Positions (cm$^{-1}$)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>L$_1$</td>
<td>Azomethine (C=N) 1663</td>
<td>Aromatic (C=C) 1551 1463</td>
</tr>
<tr>
<td>Ni-L$_1$</td>
<td>1626 1551 1254 1066</td>
<td>613 449</td>
</tr>
<tr>
<td>L$_2$</td>
<td>1661 1549 1393 1124</td>
<td>---- ----</td>
</tr>
<tr>
<td>Ni-L$_2$</td>
<td>1646 1545 1261 1054</td>
<td>605 486</td>
</tr>
<tr>
<td>L$_3$</td>
<td>1663 1547 1393 1123</td>
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<td>Ni-L$_3$</td>
<td>1657 1538 1263 1062</td>
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<tr>
<td>L$_4$</td>
<td>1662 1553 1391 1232</td>
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<tr>
<td>Ni-L$_4$</td>
<td>1624 1537 1260 1067</td>
<td>612 541</td>
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</table>
Fig. 5.11 Infrared Spectra of Ni(II) Complex of Ligand L₁

Fig. 5.12 Infrared Spectra of Ni(II) Complex of Ligand L₂
Fig. 5.13 Infrared Spectra of Ni(II) Complex of Ligand L₃

Fig. 5.14 Infrared Spectra of Ni(II) Complex of Ligand L₄
Cu (II) complexes:-

The group absorption frequencies of Cu(II) complexes are summarized in Table 5.5 and the original spectra of these complexes are presented in Fig.5.15 to 5.18.

Azomethine (C=N) and Aromatic C=C Frequency:-

In the spectra of Cu(II) complexes the medium to strong bands appeared in the region 1627-1645 cm$^{-1}$ were assigned to C=N stretching vibrational mode. In the corresponding ligands, frequencies for same group are observed 1635-1663 cm$^{-1}$. Chondhekar et.al.$^{11}$ reported C=N bands at 1640-1660 cm$^{-1}$ in IR spectra of the Schiff bases derived from dehydroacetic acid and o-phenylenediamine and 2-hydroxy-1-naphthaldehyde. On complexation, the C=N band is shifted to lower wave number with respect to free ligand denoting that nitrogen of azomethic group is coordinated to metal ion.

A downward shift of the band by 10 to 54 cm$^{-1}$ in complexes indicate that the C=N group of the ligands is coordinated to the metal ion via its azomethine nitrogen.$^{25}$ Rao et.al.$^{39}$ observed similar bathochromic shift of the C=N band for Cu(II) complex derived from DHA-gly. anil.

The medium to strong band in the region 1407-1540 cm$^{-1}$ in the IR spectrum of Cu(II) complexes were assigned to aromatic C=C stretching vibration$^{30}$. These bands in the corresponding free ligands appeared almost in the same region. However the bands due to C=C aromatic ring vibrations may shift their position
as a result of change in the distribution of electrons and molecular environment due to introduction of metal ion 31.

**Aryl Azomethine C-N stretching frequency:-**

The IR bands in the region 1270-1395cm\(^{-1}\) attributed to aromatic C-N stretching vibrations in the free ligands spectra were appeared at lower frequency side in the region 1265-1269cm\(^{-1}\) in the spectra of its Cu(II) complexes. The observed decrease in magnitude of vibrational frequency of this group on complexation may be attributed to increase in double bond character of aryl azomethine C-N bond presumably due to \(\pi\) electron delocalization from the metal to the nitrogen atom and resonance interaction with the benzene ring 31. Similar observations were made by earlier workers for the Cu(II) complexes of Schiff bases derived from dehydroacetic acid and aromatic amines. Sadeek et.al. 37 assigned the band at 1184cm\(^{-1}\) in the IR spectra of Cu(II) complex with Schiff base(N,N'-o-phenylene(bis 1-cyclopropyl-6-fluoro-4-oxo-7-(piperazine-1-yl)-quinoline-3-carboxylic acid.

**Enolic C-O Frequency :-**

The medium to strong bands observed at 1071-1085 cm\(^{-1}\) appeared in the spectra of copper complexes was assigned to enolic C-O stretching vibrations. These bands in the corresponding free ligands are at 1123-1232 cm\(^{-1}\). The observed upward shift of this band on chelation indicates the participation of enolic carbonyl nitrogen of DHA moiety of ligands in the complex formation.
Wankhede et.al.\textsuperscript{32} observed C-O frequencies in the Cu(II) complex derived from salicylaldehyde, ethylenediamine and 8-Hydroxyquinoline. Band at 1120 cm\textsuperscript{-1} in the free azo Schiff base has been assigned to phenolic C-O stretching upon complexation, this band displaces to lower frequency 1112 cm\textsuperscript{-1} indicating coordination through phenolic oxygen.

Reddy et.al.\textsuperscript{38} has reported the enolic C-O stretching frequency at 1248-1260 cm\textsuperscript{-1} for the Schiff base derived from acetylacetone and salicylaldehyde and diamine. On co-ordination shifting of these bands downwards indicating that oxygen is involved in bonding. The lower C-O frequency in metal complexes may be ascribed to delocalization of $\sigma$– electron density from the Nitrogen atom to metal ion resulting in an decrease in electronegativity of Nitrogen atom. This will lead to lesser ionic character of bond and consequent decrease in C-O vibrational frequency on metal complexation.

**New bands and other changes observed:-**

All the ligands exhibited a broad band at 3273 to 3332 cm\textsuperscript{-1}. assigned to O-H……N stretching vibrational. The absence of these bands in the spectra of complexes further confirms the deprotonation of O–H and subsequent coordination of enolic oxygen with metal forming M-O bond. The new bands observed in the region 507-510 cm\textsuperscript{-1} and 467-469 cm\textsuperscript{-1} in the IR spectra of Cu(II) complexes may be assigned to the stretching of M-O and M-N bonds respectively.\textsuperscript{17}
### Table 5.5

**Infrared Absorption Frequencies (cm\(^{-1}\)) of Cu(II) Complexes**

(Assignment of band frequencies to bond vibrational modes)

<table>
<thead>
<tr>
<th>Complex/Ligand</th>
<th>Bond vibrational modes (stretching-(\nu)). Band Positions (cm(^{-1}))</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Azomethine (C=N)</td>
<td>Aromatic (C=C)</td>
</tr>
<tr>
<td>(L_1)</td>
<td>1663</td>
<td>1551</td>
</tr>
<tr>
<td>(Cu-L_1)</td>
<td>1627</td>
<td>1410</td>
</tr>
<tr>
<td>(L_2)</td>
<td>1661</td>
<td>1549</td>
</tr>
<tr>
<td>(Cu-L_2)</td>
<td>1627</td>
<td>1410</td>
</tr>
<tr>
<td>(L_3)</td>
<td>1663</td>
<td>1547</td>
</tr>
<tr>
<td>(Cu-L_3)</td>
<td>1632</td>
<td>1407</td>
</tr>
<tr>
<td>(L_4)</td>
<td>1662</td>
<td>1553</td>
</tr>
<tr>
<td>(Cu-L_4)</td>
<td>1645</td>
<td>1540</td>
</tr>
<tr>
<td>(L_5)</td>
<td>1635</td>
<td>1540</td>
</tr>
<tr>
<td>(Cu-L_5)</td>
<td>1632</td>
<td>1538</td>
</tr>
</tbody>
</table>
Fig. 5.15 Infrared Spectra of Cu(II) Complex of Ligand L₁

Fig. 5.16 Infrared Spectra of Cu(II) Complex of Ligand L₂
Fig. 5.17 Infrared Spectra of Cu(II) Complex of Ligand L₃

Fig. 5.18 Infrared Spectra of Cu(II) Complex of Ligand L₄
Zn(II) complexes:-

The group absorption frequencies of Zn(II) complex and its corresponding ligands are tabulated in Table 5.6 and IR spectra are presented in Fig. 5.19 to 5.20.

Azomethine C=N and Aromatic C=C frequency :-

In the IR spectra of Zn(II) complexes, the bands appeared at 1616 to 1640 cm\(^{-1}\) are assigned to C=N stretching vibration. The bands in the corresponding free ligands are found at 1661-1663 cm\(^{-1}\). The shift of this band to lower frequency on chelation indicates the participation of azomethine nitrogen in bonding with the central Zn(II) atom.
The IR spectrum for the ligand shows a broad and intense band at 1615 cm\(^{-1}\), it is assignable to the stretching vibrational of the C=N band. The absorption values of the C=N vibrational at 1603 cm\(^{-1}\) for ZnL are lower by about 9-15 cm\(^{-1}\) than those for the free ligand which indicates the coordination of azomethine nitrogen atom to metal ions in the complexes.\(^{39}\)

Sadeek et.al.\(^{37}\) assigned the band at 1578 cm\(^{-1}\) in the IR spectra of Cu(II) complex with Schiff base (N,N'-o-phenylene(bis 1-cyclopropyl-6-fluoro-4-oxo-7-(piperazine-1-yl)-quinoline-3-carboxylic acid).

Wankhede et.al.\(^{32}\) observed C=N frequencies in the Zn(II) complex derived from salicylaldehyde, ethylenediamine and 8-Hydroxyquinoline. Band at 1580 cm\(^{-1}\) in the free azo Schiff base has been assigned to phenolic C=N stretching upon complexation, this band displaces to lower frequency 1499 cm\(^{-1}\) indicating coordination through azomethine nitrogen.

The bands due to aromatic C=C stretching frequency was observed in the same region 1430-1537 cm\(^{-1}\) as compared to its free ligands similar to Cr(III) complexes.

**Aryl azomethine C-N frequency :-**

The bands observed in IR spectra of Zn(II) complexes at 1303-1352 cm\(^{-1}\) are attributed to aryl azomethine C-N stretching. The same bands in free corresponding ligands are observed at 1393-1395 cm\(^{-1}\). The observed decrease
in the position C-N band may be attributed to the region similar to Cr(III) complex\textsuperscript{31}.

**Enolic C-O frequency** :-

The downward shift of C-O frequency in Zn(II) complex (1119-1248 cm\textsuperscript{-1}) than the corresponding free ligand (1124-1117 cm\textsuperscript{-1}) suggest the bonding of enolic oxygen with Zn(II) during complexation.

The lower frequency in the metal complexes may be ascribed to delocalization of $\pi$-electron density from the oxygen atom to the metal ion resulting in an decreased in electronegativity of oxygen atom. This will lead to lesser ionic character of the C-O bond and a consequent decrease in the C-O vibrational frequency on metal complexation.

**New bonds and other changes observed** :-

The bands observed in IR the spectra of ligands at around 3273 to 3332 cm\textsuperscript{-1} assigned due to O-H$\cdots$N vibrational were not observed in the spectra corresponding Zn(II) complexes. This indicates the deprotonation of enolic –OH and subsequent bonding of its oxygen with Zn(II) during complex formation. The additional bands at 510-511 cm\textsuperscript{-1} and 445-451 cm\textsuperscript{-1} were assigned to Zn-O and Zn-N bonds respectively.
### Table 5.6

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

(Assignment of band frequencies to bond vibrational modes)

<table>
<thead>
<tr>
<th>Complex/Ligand</th>
<th>Bond vibrational modes (stretching-(\nu))</th>
<th>Band Positions (cm(^{-1}))</th>
<th>New Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Azomethine (C=N)</td>
<td>Aromatic (C=C)</td>
<td>Aryl Azomethine (C=N)</td>
</tr>
<tr>
<td>L(_1)</td>
<td>1663</td>
<td>1551</td>
<td>1395</td>
</tr>
<tr>
<td>Zn-L(_1)</td>
<td>1640</td>
<td>1537</td>
<td>1352</td>
</tr>
<tr>
<td>L(_2)</td>
<td>1661</td>
<td>1549</td>
<td>1393</td>
</tr>
<tr>
<td>Zn-L(_2)</td>
<td>1616</td>
<td>1430</td>
<td>1303</td>
</tr>
</tbody>
</table>

Fig. 5.20 Infrared Spectra of Zn(II) Complex of Ligand L\(_1\)
Fig. 5.21 Infrared Spectra of Zn(II) Complex of Ligand L$_2$
Reference:


