CHAPTER V

RESULT AND DISCUSSION: 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.

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 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 multiplets.

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 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 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 –O-H -N-H aromatic >C=C< azomethine >C=N- lactone carbonyl C=O and enolic C-O / C=O groups 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 2600 to 2800 cm\(^{-1}\) and at 3312 to 3380 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.

Chondhekar et.al\(^1\) have assigned a broad weak band at 2600-2350 cm\(^{-1}\) to -OH (intermolecular H- bonded ) stretching frequency in Schiff bases derived from 5-chloro-2 - hydroxy acetophenone and 4-substituted anilines. It is reported that
disappearance of this band in the spectra of their metal complexes is indicative of involvement of oxygen of hydroxyl group in coordination with metal ion after deprotonation.

Parihari et.al.\(^2\) reported a band at 2700 cm\(^{-1}\) due to intramolecular hydrogen bonded OH of Schiff bases derived from 2- amino thiophenol and salicylaldehyde.

Venkateshwar Rao. et.al.\(^3\) have assigned a band at 3400 cm\(^{-1}\) to –OH (intermolecular H-bonded) vibrations of Schiff bases derived from Dehydroacetic acid and thiocarbohydrazide.

More et.al.\(^4\) have assigned a broad weak band at 2900 cm\(^{-1}\) for the intermolecular hydrogen bonded –OH of Schiff bases derived from substituted 2-amino thiazoles and o-hydroxy aldehydes.

Mahapatra et.al.\(^5\) was assigned the IR bands at 3000 and 3475-3380 cm\(^{-1}\) due to –O-H···N intermolecular hydrogen bonding. The absence of these bands in the metal chelates suggested coordination of the deprotonated dianionic ligands to the metal ions.

Bahed et.al.\(^6\) assigned a band at 2935-2915 cm\(^{-1}\) to intermolecular hydrogen bonded phenolic -OH stretching of the Schiff base ligands derived from 2-hydroxy-5-methyl acetophenone and diamino propane. Its disappearance in the spectra of the chelates indicated deprotonation of –OH and subsequent coordination at oxygen with metal ion.

Thus the broad weak bands at 2600 to 2800 cm\(^{-1}\) and at 3200 to 3400 cm\(^{-1}\) in the present study were 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 coordination of oxygen with metal ion.
Infrared Spectroscopy: Result and Discussion

**Lactone carbonyl (C=O) stretching frequency:**

The C=O lactone carbonyl stretching vibration is expected to appear at 1680 to 1710 cm\(^{-1}\). The carbonyl (C=O) stretching frequency of tri and tetradentate Schiff bases derived from diamines amino acids amino phenols/alcohols and dehydroacetic acid were observed at 1740-1685 cm\(^{-1}\) by Tan et.al.\(^7\) and other workers\(^8\). Thus the bands (strong/medium) appeared at 1680 to 1707 cm\(^{-1}\) in the IR spectra of all ligands in the present study were assigned to C=O stretching vibrations of lactone carbonyl.

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

The Schiff bases exhibit azomethine (C=N) stretching vibrational bands at 1689-1471 cm\(^{-1}\) \(^{10}\). Rao et.al.\(^8\) reported C=N stretching band at 1665 cm\(^{-1}\) and 1650 cm\(^{-1}\) in the IR spectra of dehydroacetic acid-glycine anil and dehydroacetic acid-ethylene diamine anil respectively. Abdulla et.al.\(^11\) assigned IR spectral bands at 1647-1628 cm\(^{-1}\) to C=N stretching vibration of Schiff bases derived from hydrazine 5-methyl carbodithioate thiosemicarbazide and dehydroacetic acid.

Kotwale et.al.\(^12\) observed C=N frequencies in the heterocyclic Schiff bases derived from substituted salicylaldehyde 2-hydroxy-1-napthaldehyde and amino pyridines at 1621-1608 cm\(^{-1}\). Mane et.al.\(^13\) assigned 1670-1660 cm\(^{-1}\) frequencies in the spectra of Schiff bases of dehydroacetic acid and aromatic amines to C=N stretching vibrations.

The various vibrations are observed for azomethine group of conjugated system. In many Schiff bases C=N stretching frequency is dependent on the substitutent on it mostly causing resonance interaction and hydrogen bonding.\(^14\)

A medium to strong intensity bands observed at 1612 to 1662 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\(^{-1}\) \(^{10}\). Tan et.al.\(^7\) 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.
Infrared Spectroscopy: Result and Discussion

The strong/ medium intensity bands appeared at 1562 to 1576 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 vibration mode there is no systematic and reliable information on aromatic C-N frequency of vibration in the literature. Percy and Thorton\(^{15}\) studied N-aryl salicylaldehydeimines and suggested that the appearance of two IR bands in the region 1350-1375 cm\(^{-1}\) and 1470-1450 cm\(^{-1}\) attributable to aromatic azomethine C-N stretching vibrations. Maria et.al.\(^{16}\) assigned the bands at 1330-1315 cm\(^{-1}\) in the IR spectra of Schiff base metal complexes derived from 4 6 diamino 1 2 dihydro-2 thiopyrimidine to C-N stretching vibrational mode. 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.\(^{17}\).

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 1338 to 1362 cm\(^{-1}\) in the spectra of all ligands may be tentatively assigned to aryl azomethine C-N stretching vibration frequency.

**Enolic C-O stretching Frequency:**

The IR spectral bands due to enolic C-O stretching vibrational modes are expected to appear around\(^{18,19}\) 1200 cm\(^{-1}\). Rao et.al.\(^{89}\) assigned the bands at 1245 - 1212 cm\(^{-1}\) and 1260 cm\(^{-1}\) for enolic C-O stretching vibrations appeared in the IR spectra of Schiff bases derived by condensation of dehydroacetic acid with glycine thioethanol amine and benzoyl hydrazide/semicarbazide respectively. Mane et.al.\(^{20}\) has reported the enolic C-O stretching frequency at 1250-1230 cm\(^{-1}\) for the Schiff bases derived from p-totuidine p-bromoaniline p-anisidine and dehydroacetic acid. On coordination shifting of these bands upwards by 20-30 cm\(^{-1}\) indicated that oxygen is involved in bonding.
Infrared Spectroscopy: Result and Discussion

A weak to strong intensity bands observed at 1209 to 1275 cm\(^{-1}\) in the IR spectra of ligands in the present study may be assigned to enolic C-O stretching vibrational mode.

<table>
<thead>
<tr>
<th>Bond vibrational modes</th>
<th>Ligand band positions (wave number cm(^{-1}))</th>
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<tbody>
<tr>
<td></td>
<td>(L_1)</td>
</tr>
<tr>
<td>O-H…N (bonded) Stretching((\nu))</td>
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</tr>
<tr>
<td></td>
<td>2752</td>
</tr>
<tr>
<td>C = O Lactone Stretching((\nu))</td>
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<tr>
<td>C = N Azomethine Stretching((\nu))</td>
<td>1657</td>
</tr>
<tr>
<td>C = C Aromatic ring stretching((\nu))</td>
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</tr>
<tr>
<td></td>
<td>1462</td>
</tr>
<tr>
<td>C -- N Aryl azomethine stretch ((\nu))</td>
<td>1354</td>
</tr>
<tr>
<td>C -- O Enolic stretching ((\nu))</td>
<td>1209</td>
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</tbody>
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Fig. 5.1 Infrared Spectra of Ligand $L_1$

Fig. 5.2 Infrared Spectra of Ligand $L_2$
**Infrared Spectroscopy: Result and Discussion**

Fig. 5.3 Infrared Spectra of Ligand L₃

Fig. 5.4 Infrared Spectra of Ligand L₄
Infrared Spectroscopy: Result and Discussion

Fig. 5.5 Infrared Spectra of Ligand L₅

Fig. 5.6 Infrared Spectra of Ligand L₆
Infrared Spectroscopy: Result and Discussion

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.

Cu(II) Complexes:

The IR spectra of Cu(II) complexes of representative ligands are presented in fig. 5.7 to 5.10 and their group absorption frequencies are tabulated in Table 5.2.

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

In the spectra of Cu(II) complexes the medium to strong bands appeared in the region 1602-1619 cm\(^{-1}\) were assigned to C=N stretching vibrational mode. In the corresponding ligands frequencies for same group are observed from 1612 to 1663 cm\(^{-1}\). 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\(^{21}\).

Rao et.al.\(^{8}\) observed similar bathochromic shift of the C=N band for Cu(II) complex derived from DHA-gly. anil. Symal et.al.\(^{22}\) reported the lowering of C=N stretching frequency in dioxo Uranium (VI) complexes by 10-25 cm\(^{-1}\) in comparison of the free ligands. This lowering may be due to reduction in electron density in the azomethine link as the nitrogen coordinates to the metal ion.

The medium to strong band in the region 1535-1541 cm\(^{-1}\) in the IR spectrum of Cu(II) complexes were assigned to aromatic C=C stretching vibration\(^{23}\). 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\(^{24}\).

Aryl Azomethine C-N stretching frequency:-

The IR bands in the region 1338-1362 cm\(^{-1}\) attributed to aromatic C-N stretching vibrations in the free ligands spectra were appeared at higher frequency side in the
region 1365 to 1405 cm\(^{-1}\) in the spectra of its Cu(II) complexes. The observed increase in magnitude of vibrational frequency of this group by about 10 to 50 cm\(^{-1}\) on complexation may be attributed to increase in double bond character of aryl azomethine C-N bond presumably due to π electron delocalization from the metal to the nitrogen atom and resonance interaction with the benzene ring\(^{24}\). Similar observations were made by earlier workers for the Cu(II) complexes of Schiff bases derived from dehydroacetic acid and aromatic amines.

**Enolic C--O Frequency:**

The medium to strong bands observed at 1259 to 1285 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 1223 to 1275 cm\(^{-1}\). 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.

A similar shift of C--O band to higher frequency side by 15-20 cm-1 was observed by Rao et.al.\(^{79}\). Chondhekar et.al.\(^{1}\) reported shift of this band to higher frequency by 15-25 cm-1 for the Cu(II) complexes of 5- chloro-2- hydroxyl acetophenonearyl anil.

The shift of C--O band to higher frequency by 25 cm-1 for the Cu(II) complexes of 24-dihydroxy acetophenone oxime was reported by kelkar.\(^{25}\)

The higher C-O frequency in metal complexes may be ascribed to delocalization of σ – electron density from the oxygen atom to metal ion resulting in an increase in electronegativity of oxygen atom. This will lead to greater ionic character of bond and consequent increase in C-O vibration frequency on metal complexation.

**New bands and other changes observed:**

All the ligands exhibited a broad band at 3312 to 3380 cm\(^{-1}\). assigned to O-H------N stretching vibration. 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.
Infrared Spectroscopy: Result and Discussion

The new bands observed in the region 478 to 542 cm\(^{-1}\) and 386 to 460 cm\(^{-1}\) in the IR spectra of Cu(II) complexes may be assigned to the stretching of M-O and M-N bonds respectively.

Table 5.2

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

(Assignment of band frequencies to bond vibration modes)

<table>
<thead>
<tr>
<th>Complex/Ligand</th>
<th>Bond vibrational modes (stretching-ν). Band Positions (cm(^{-1}))</th>
<th>New Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lactone (C=O)</td>
<td>Azomethine (C=N)</td>
</tr>
<tr>
<td>L(_2)</td>
<td>1683.7</td>
<td>1632.0</td>
</tr>
<tr>
<td>Cu-L(_2)</td>
<td>1678.0</td>
<td>1618.2</td>
</tr>
<tr>
<td>L(_3)</td>
<td>1683.7</td>
<td>1640.0</td>
</tr>
<tr>
<td>Cu-L(_3)</td>
<td>1691.5</td>
<td>1606.6</td>
</tr>
<tr>
<td>L(_4)</td>
<td>1703.0</td>
<td>1662.5</td>
</tr>
<tr>
<td>Cu-L(_4)</td>
<td>1687.6</td>
<td>1608.5</td>
</tr>
<tr>
<td>L(_5)</td>
<td>1679.9</td>
<td>1612.4</td>
</tr>
<tr>
<td>Cu-L(_5)</td>
<td>1678.0</td>
<td>1602.7</td>
</tr>
</tbody>
</table>
Infrared Spectroscopy: Result and Discussion

Fig. 5.7 Infrared Spectra of Cu(II) Complex of Ligand L₂

Fig. 5.8 Infrared Spectra of Cu(II) Complex of Ligand L₃
Fig. 5.9 Infrared Spectra of Cu(II) Complex of Ligand L₄

Fig. 5.10 Infrared Spectra of Cu(II) Complex of Ligand L₅
Ni(II) complexes :-

The group absorption frequencies of Ni(II) complex and its corresponding ligands are tabulated in Table 5.3 and IR spectra are presented in Fig. 5.11 to 5.15.

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

In the IR spectra of Ni(II) complexes the bands appeared at 1602 to 1626 cm\(^{-1}\) are assigned due to C≡N stretching vibration. The bands in the corresponding free ligands are found at 1632-1663 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 due to aromatic C=C stretching frequency was observed in the same region 1535-1572 as compared to its free ligands similar to Cu(II) complexes.

Aryl azomethine C-N frequency :-

The bands observed in IR spectra of Ni(II) complexes at 1357-1403 cm\(^{-1}\) are attributed to aryl azomethine C-N stretching. The same bands in free corresponding ligands are observed at 1338 to 1362 cm\(^{-1}\). The observed increase in the position C-N band may be attributed to the region similar to Cu(II) complex\(^{13161726}\).

Enolic C-O frequency :-

The upward shift of C-O frequency in Ni(II) complex (1245-1387 cm\(^{-1}\)) than the corresponding free ligand (1209-1275 cm\(^{-1}\)) suggest the bonding of enolic oxygen with Ni(II) during complexation\(^{9131720}\).

The higher 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 increase in electronegativity of oxygen atom. This will lead to greater ionic character of the C-O bond and a consequent increase in the C-O vibration frequency on metal complexation.

New bonds and other changes observed :-

The bands observed in IR the spectra of ligands at around 3312-3380 cm\(^{-1}\) assigned due to O-H\(\cdots\)N vibration 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.
Infrared Spectroscopy: Result and Discussion

The additional bands at 457-553 cm\(^{-1}\) and 407 to 461 cm\(^{-1}\) were assigned to Ni-O and Ni-N bonds respectively \(^7\)\(^9\)\(^1\)\(^7\).

Table 5.3

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

(Assignment of band frequencies to bond vibration modes)

<table>
<thead>
<tr>
<th>Complex/Ligand</th>
<th>Bond vibrational modes (stretching-(\nu)). Band Positions (cm(^{-1}))</th>
<th>New Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lactone (C=O)</td>
<td>Azomethine (C=N)</td>
</tr>
<tr>
<td>L(_1)</td>
<td>1706.9</td>
<td>1656.7</td>
</tr>
<tr>
<td>Ni-L(_1)</td>
<td>1685.7</td>
<td>1602.7</td>
</tr>
<tr>
<td>L(_2)</td>
<td>1683.7</td>
<td>1632.0</td>
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<tr>
<td>Ni-L(_2)</td>
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<td>L(_3)</td>
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<td>Ni-L(_3)</td>
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<tr>
<td>L(_4)</td>
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<td>Ni-L(_4)</td>
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<td>L(_6)</td>
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<td>Ni-L(_6)</td>
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</table>
Infrared Spectroscopy: Result and Discussion

Fig. 5.11 Infrared Spectra of Ni(II) Complex of Ligand L₁

Fig. 5.12 Infrared Spectra of Ni(II) Complex of Ligand L₂
Infrared Spectroscopy: Result and Discussion

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

Fig. 5.14 Infrared Spectra of Ni(II) Complex of Ligand L₄
Fig. 5.15 Infrared Spectra of Ni(II) Complex of Ligand L₆
Infrared Spectroscopy: Result and Discussion

Co(II) Complexes :-

The group absorption frequencies of Co(II) complex are summarized in Table 5.4 and the original spectra of these complexes are presented in fig. 5.16 to 5.19.

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

In the IR spectra of Co(II) complexes the strong bands appeared in the region 1596-1610 cm\(^{-1}\) were assigned to C=N stretching frequency. The azomethine bands in the corresponding free ligand spectra were observed in the region 1632-1663 cm\(^{-1}\). Thus shift of this band to lower frequency on chelation indicates the coordination through nitrogen of azomethine C=N group\(^{10,27}\).

The bands due to aromatic C=C stretching frequency was observed in the same region as compared to its free ligand band similar to Cu(II) complexes

Aryl azomethine C-N frequency :-

The weak to strong intensity bands in the region 1353-1362 cm\(^{-1}\) attributed to aromatic C-N stretching vibrations in the free ligand were observed at higher frequency side at 1362-1406 cm\(^{-1}\) 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 Cu(II) complexes\(^{1316,1726}\).

Enolic C-O frequency :-

The bands observed at 1259-1297 cm\(^{-1}\) in the Co(II) complexes are assigned to enolic C-O. The frequency of this band is shifted to higher frequency side than the corresponding free ligand 1209 to 1248 cm\(^{-1}\). This increase in the frequency indicates the formation of bond between oxygen of C-O and metal ion.

New bands and other changes observed :-

The absence of band in the region 3362 due to hydrogen bonded enolic O-H···N stretching frequency confirms the participation of enolic oxygen in coordination with metal\(^{2428,29}\) in Co(II) complexes.

In the IR spectra of Co(II) 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 820 – 850 cm\(^{-1}\) assignable to rocking mode of water.

The new bands in the region 516-565 cm\(^{-1}\) and 437-484 cm\(^{-1}\) in the spectra of Co(II) complex indicate the vibration of M-O and M-N bonds respectively\(^{71723}\).

**Table 5.4**

*Infrared Absorption Frequencies (cm\(^{-1}\)) of Co(II) Complexes*  
(Assignment of band frequencies to bond vibration modes)

<table>
<thead>
<tr>
<th>Complex/Ligand</th>
<th>Lactone (C=O)</th>
<th>Azomethine (C=N)</th>
<th>Aromatic (C=C)</th>
<th>Aryl Azomethine (C-N)</th>
<th>Enolic (C-O)</th>
<th>New Peaks M-O</th>
<th>M-N</th>
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<td>L(_1)</td>
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<td>1353.9</td>
<td>1209.3</td>
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<tr>
<td>Co-L(_1)</td>
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<td>536</td>
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<td>L(_2)</td>
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Infrared Spectroscopy: Result and Discussion

Fig. 5.16 Infrared Spectra of Co(II) Complex of Ligand $L_1$

Fig. 5.17 Infrared Spectra of Co(II) Complex of Ligand $L_2$
Infrared Spectroscopy: Result and Discussion

Fig. 5.18 Infrared Spectra of Co(II) Complex of Ligand L₄

Fig. 5.19 Infrared Spectra of Co(II) Complex of Ligand L₆
Infrared Spectroscopy: Result and Discussion

Mn(II) and Fe(III) complexes:-

The group absorption frequencies of Mn(II) and Fe(III) complexes are summarized in Table 5.5 and the original spectra of these complexes are presented in fig.5.20 to 5.21 and 5.22 to 5.24 respectively.

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

In the IR spectra of Mn(II) complexes it can be seen that C=N stretching vibrational frequencies appear in the region 1602.7-1607.6 cm\(^{-1}\). The corresponding band frequencies in the free ligand were observed in the region 1656.7-1662.5 cm\(^{-1}\). For Fe(III) C-N vibrational frequency bands appeared in the region 1602.7-1610.0 cm\(^{-1}\) were assigned to C=N stretching frequency. It is shifted towards lower frequency side than the corresponding free ligands 1656.7-1662.5. The lowering in frequency indicate the coordination through nitrogen of azomethine C=N group\(^{1026}\).

The bands due to aromatic C=C stretching frequency was observed in the same region as compared to its free ligands similar to Cu(II) complexes

Aryl azomethine C-N frequency :-

The bands in Mn(II) and Fe(III) complexes at 1363.6-1386.7 cm\(^{-1}\) are due to aryl azomethine. The increase in frequency than corresponding free ligands 1344.3-1361.7 cm\(^{-1}\) is attributed to the reasons similar to Cu(II) and Ni(II) complexes\(^{13161724}\).

Enolic C-O frequency:-

The bands observed at 1245.9-1263.3 cm\(^{-1}\) in the Mn(II) and Fe(III) complexes are assigned to enolic C-O. The frequency of this band is shifted to higher side than the corresponding free ligand 1209.3-1223.0 cm\(^{-1}\). The increase in the frequency indicates the formation of bond between oxygen of C-O and metal ion.

New bands and other changes observed:-

The absence of ligand bands in the region 3362 cm\(^{-1}\) due to hydrogen bonded enolic O-H\(\cdots\)N stretching frequency in Mn(II) and Fe(III) complexes confirms the enolic carbonyl oxygen coordinates with metal\(^{232730}\).

In the IR spectra of Mn(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 – 830 cm$^{-1}$ assignable to rocking mode of water.

The new bands in the region 526-580 cm$^{-1}$ and 401-513 cm$^{-1}$ in the spectra of Mn(II) and Fe(III) complexes indicate the vibration of M-O and M-N bonds respectively.

Table 5.5

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

(Assignment of band frequencies to bond vibration modes)

<table>
<thead>
<tr>
<th>Complex/Ligand</th>
<th>Lactone (C=O)</th>
<th>Azomethine (C=N)</th>
<th>Aromatic (C=C)</th>
<th>Aryl Azomethine (C=N)</th>
<th>Enolic (C-O)</th>
<th>New Peaks</th>
<th>M-O</th>
<th>M-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_1$</td>
<td>1706.9</td>
<td>1656.7</td>
<td>1573.8</td>
<td>1353.9</td>
<td>1209.3</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Mn-$L_1$</td>
<td>1670.2</td>
<td>1606.6</td>
<td>1531.4</td>
<td>1384.8</td>
<td>1245.9</td>
<td>526</td>
<td>401</td>
<td></td>
</tr>
<tr>
<td>$L_4$</td>
<td>1703.0</td>
<td>1662.5</td>
<td>1575.7</td>
<td>1361.7</td>
<td>1223.0</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Mn-$L_4$</td>
<td>1670.2</td>
<td>1602.7</td>
<td>1527.5</td>
<td>1380.9</td>
<td>1263.3</td>
<td>559</td>
<td>513</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 5.20 Infrared Spectra of Mn(II) Complex of Ligand L₁

Fig. 5.21 Infrared Spectra of Mn(II) Complex of Ligand L₄
Table 5.6

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

(Assignment of band frequencies to bond vibration modes)

<table>
<thead>
<tr>
<th>Complex/Ligand</th>
<th>Bond vibrational modes (stretching-(\nu)). Band Positions (cm(^{-1}))</th>
<th>New Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lactone (C=O)</td>
<td>Azomethine (C=N)</td>
</tr>
<tr>
<td>L(_1)</td>
<td>1706.9</td>
<td>1656.7</td>
</tr>
<tr>
<td>Fe-L(_1)</td>
<td>1697.2</td>
<td>1610.0</td>
</tr>
<tr>
<td>L(_4)</td>
<td>1703.0</td>
<td>1662.5</td>
</tr>
<tr>
<td>Fe-L(_4)</td>
<td>1680</td>
<td>1606.6</td>
</tr>
<tr>
<td>L(_6)</td>
<td>1699.2</td>
<td>1660.0</td>
</tr>
<tr>
<td>Fe-L(_6)</td>
<td>1700.0</td>
<td>1602.7</td>
</tr>
</tbody>
</table>
Infrared Spectroscopy: Result and Discussion

Fig. 5.22 Infrared Spectra of Fe(III) Complex of Ligand L₁

Fig. 5.23 Infrared Spectra of Mn(II) Complex of Ligand L₄
Conclusions:-

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

The disappearance of ligand bands around 3312-3380 cm\(^{-1}\) due to hydrogen bonded enolic -O-H…N 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 457-580 cm\(^{-1}\) and 386-513 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 Mn(II) Fe(III) and Co(II) complexes a broad band is observed in the region 3150 – 3500 cm\(^{-1}\) corresponding to the stretching frequency of νOH 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. The absence of such band in the IR spectra of Cu(II) and Ni(II) suggest that these complexes are anhydrous. This observation is further confirmed by TGA-DTA analysis.

On the basis of results of elemental analysis magnetic susceptibility solution conductivity measurement thermoanalytical IR and electronic spectral data X-ray diffraction it may be concluded that the complexes of Co(II) Mn(II) and Fe(II) contains coordinated water molecules and have octahedral structure. Where as the complexes of Cu(II) and Ni(II) have square planer structure with no coordinated water.

The following probable structures may be proposed to the metal chelates of tetradeutate Schiff base ligands in the present study. (L\(_1\) as representative ligand)
Infrared Spectroscopy: Result and Discussion

Where \( M = \text{Cu(II)} & \text{Ni(II)} \)  And  \( R = \text{H/CH}_3 \)

Where \( M = \text{Mn(II)} & \text{Co(II)} \)  And  \( R = \text{H/CH}_3 \)

Where  \( R = \text{H/CH}_3 \)

\([\text{formula]}\)
Infrared Spectroscopy: Result and Discussion

Reference:
Infrared Spectroscopy: Result and Discussion


