CHAPTER V

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RESULTS AND DISCUSSION

5.1) INTRODUCTION:

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 frequency 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 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 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 IR region.

5.2) **INFRARED SPECTRAL STUDIES OF LIGAND:**

(Results and discussion)

Schiff bases used for synthesis of complexes in the present study are derived from dehydroacetic acid and different aromatic amines. The IR spectral data of ligands are tabulated in Table 5.1 and their spectra are presented in fig. 5.1 to 5.8. The data presented in the Table 5.1 is discussed by assigning various bands in the spectra with respect to vibration caused by different functional groups of 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=, lactone carbonyl C=O and enolic C-O / C=O groups of ligands that are involved in the complex formation are discussed.

5.2.1) **Enolic O-H frequency (inter molecular H bonded):**

In all Schiff bases, the-O-H stretching frequencies were observed as broad weak bands at 3362 to 3371 cm\(^{-1}\). The normal free-O-H stretching frequency ranges from 3600-3500 cm\(^{-1}\) to above value is accepted due to strong intermolecular hydrogen bonding between enolic-OH and the nitrogen of the azomethine group. (O-H……N).

Venkateshwar Rao. et.al.\(^1\) 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.\(^2\) 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.\(^3\) 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.\(^4\) 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 3362 to 3371 cm\(^{-1}\) in the present study were assigned to hydrogen bonded enolic –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.

5.2.2) Azomethine (C=N) stretching frequency:-

The Schiff bases exhibit azomethine (C=N) stretching vibrational bands at 1689-1471 cm\(^{-1}\) region.\(^5\) Rao et al.\(^6,7\) 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.\(^8\) assigned IR spectral bands at 1647-1625 cm\(^{-1}\) to C=N stretching vibration of schiff bases derived from hydrazine 5-methyl carbodithioate, thiosemicarbazide and dehydroacetic acid.

Kotwale et al.\(^9\) 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.\(^10\) 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 substituent on it, mostly causing resonance interaction and hydrogen bonding.\(^11\)

In the present work, the bands observed at 1646 to 1663 cm\(^{-1}\) are assigned to azomethine C=N stretching vibrations.

5.2.3) Lactone carbonyl (C=O) stretching frequency:-

The bands appeared at 1695 to 1715 cm\(^{-1}\) in the IR spectra of all ligands were assigned to C=O stretching vibrations of lactone carbonyl and the fact is supported by literature data. The carbonyl (C=O) stretching frequency of tri and tetradebate Schiff
bases derived from diamines, amino acids, amino phenols/alkohols and dehydroacetic acid were observed at 1740-1685 cm$^{-1}$ by Tan et.al.\textsuperscript{12} and other workers\textsuperscript{6,7}.

5.2.4) 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\textsuperscript{5}. Tan et.al.\textsuperscript{12} 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. In the present investigation the bands at 1571 to 1580 cm$^{-1}$ are assigned to (C=C) aromatic ring stretching vibrations.

5.2.5) Aryl azomethine C-N stretching frequency:-

The IR bands at 1428 to 1455 cm$^{-1}$ are due to aryl C-N vibrations. Percy and Thorton\textsuperscript{13} 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.\textsuperscript{14} 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.\textsuperscript{15}.

5.2.6) Enolic C-O / C=O stretching Frequency:-

The ligands in the present work are in tautomeric form. The carbonyl group may be in keto form or in enol form\textsuperscript{16}. The C=O stretching frequency can be reported in lower value than lactones C=O. The bands appeared at 1622 to 1634 cm$^{-1}$ in the present investigation of all ligands were assigned to enolic C=O stretching vibration mode.

The IR spectral bands due to enolic C-O stretching vibrational modes are expected to appear around\textsuperscript{17,18} 1200 cm$^{-1}$. Rao et.al.\textsuperscript{6,7} 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.\textsuperscript{19} 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.

In the present work weak strong bands observed at 1220 to 1247 cm\(^{-1}\) in the IR spectra of all ligands were assigned to enolic C-O stretching vibration mode.

**5.3) INFRARED SPECTRAL STUDIES OF METAL COMPLEXES:**

**Results and Discussion:**

Infrared spectral study is useful in the identification of functional and the effect of their surrounding groups and their bonding with metal in the complexes. The assignment for frequencies of different groups in metal complexes corresponding to those considered for ligands have been proposed on the basis of literature data of similar metal complexes.

The IR spectra of metal complexes are presented in the Fig. 5.9 to 5.48 and their spectral data along with their characteristic parameters are tabulated in Tables 5.2 to 5.6

**5.3.1) Cu(II) Complexes:**

The IR spectra of Cu(II) complexes are presented in fig.5.9 to 5.16 and their group absorption frequencies are tabulated in Table 5.2.

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

In the spectra of Cu(II) complexes, the medium to strong bands appeared in the region 1610-1651 cm\(^{-1}\) were assigned to C=N stretching vibrational mode. In the corresponding ligands, frequencies for same group are observed from 1646 to 1663 cm\(^{-1}\). A downward shift of the band by 12 to 36 cm\(^{-1}\) in complexes indicate that the C=N group of the ligands is coordinated to the metal ion via its azomethine nitrogen\(^{20}\).

Rao et.al.\(^{6}\) observed similar bathochromic shift of the C=N band for Cu(II) complex derived from DHA-gly. anil. Symal et.al.\(^{21}\) reported the lowering of C=N stretching frequency in dioxo Uranium (VI) complexes by 10-25 cm\(^{-1}\) in comparison of
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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 1560-1573 cm\(^{-1}\) in the IR spectrum of Cu(II) complexes were assigned to aromatic C=C stretching vibration\(^{22}\). These bands in the corresponding free ligands appeared almost in the same region 1571-1580 cm\(^{-1}\). 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\(^{23}\).

ii) Aryl C-N stretching frequency:-

The IR bands in the region 1428-1460 cm\(^{-1}\) attributed to aromatic C-N stretching vibrations in the free ligands spectra were appeared at higher frequency side in the region 1459 to 1463 cm\(^{-1}\) in the spectra of its Cu(II) complexes. The observed increase in magnitude of vibrational frequency of this group by about 3 to 27 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\(^{23}\). Similar observations were made by earlier workers for the Cu(II) complexes of Schiff bases derived from dehydroacetic acid and aromatic amines.

iii) Enolic C=O Frequency :-

The medium to strong bands observed at 1600 to 1626 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 1622 to 1634 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 lower frequency side by were observed by earlier worker\(^{16}\).

iv) New bands and other changes observed:-

All the ligands exhibited a broad weak band at 3362-3371 cm\(^{-1}\) assigned to O-H......N stretching vibration. The absence of these bands in the spectra of complexes
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further confirms the subsequent coordination of enolic oxygen with metal forming M-O bond.

The new bands observed in the region 639 to 565 cm\(^{-1}\) and 509 to 541 cm\(^{-1}\), in the IR spectra if complexes may be assigned to the stretching of M-O and M-N bonds respectively \(^6,7,12\).

5.3.2) Co(II) Complexes :-

The group absorption frequencies of Co(II) complex are summarized in Table 5.3 and the original spectra of these complexes are presented in fig. 5.17 to 5.24.

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

In the IR spectra of Co(II) complexes the strong bands appeared in the region 1638-1650 cm\(^{-1}\) were assigned to C=N stretching frequency. It is shifted towards lower frequency than corresponding ligands 1646 to 1663. The lowering in frequency indicate the coordination through nitrogen of azomethine C=N group \(^5,26\).

The bands due to aromatic C=C stretching frequency was observed in the same region 1562-1577 cm\(^{-1}\) as compared to its free ligand band similar to Cu(II) complexes.

ii) Aryl azomethine C-N frequency :-

The bands in Co(II) complexes at 1460-1462 cm\(^{-1}\) are due to aryl azomethine. The increase in frequency than corresponding free ligands 1428 to 1460 cm\(^{-1}\) attributed to the region similar to Cu(II) complexes \(^10,14,15,24\).

iii) Enolic C=O frequency :-

The bands observed at 1610-1628 cm\(^{-1}\) in the Co(II) complexes are assigned to enolic C=O. The frequency of this band is decreased to lower side than the corresponding free ligand 1622 to 1637 cm\(^{-1}\). This decrease in the frequency indicate the formation of bond between oxygen of C=O and metal ion.

iv) New bands and other changes observed :-
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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 $^{23,27,28}$ in Co(II) complexes.

The new bands in the region 580-619 cm$^{-1}$ and 513-538 cm$^{-1}$ in the spectra of Co(II) complex indicate the vibration of M-O and M-N bonds respectively $^{12,15,22}$.

5.3.3) Ni(II) complexes :-

The group absorption frequencies of Ni(II) complex and its corresponding ligands are tabulated in Table 5.4 and IR spectra are presented in Fig. 5.24 to 5.32.

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

In the IR spectra of Ni(II) complexes, the bands appeared at 1631 to 1653 cm$^{-1}$ are assigned due to C=N stretching vibration. The bands in the corresponding free ligands are found at 1646-1663 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 $^{29}$.

The bands due to aromatic C=C stretching frequency was observed in the same region 1581-1582 as compared to its free ligands, similar to Cu(II) complexes.

ii) Aryl azomethine C-N frequency :-

The bands observed in IR spectra of Ni(II) complexes at 1445-1475 cm$^{-1}$ are attributed to aryl azomethine C-N stretching. The same bands in free corresponding ligands are observed at 1428 to 1460 cm$^{-1}$. The observed increase in the position may be attributed to the region similar to Cu(II) complex $^{10,14,15,24}$.

iii) Enolic C-O frequency :-

The upward shift of C-O frequency in Ni(II) complex (1243-1325 cm$^{-1}$) than the corresponding free ligand (1220-1247 cm$^{-1}$) suggest the bonding of enolic oxygen with Ni(II) during complexation $^{7,10,15,19,30}$.

The higher frequency in the metal complexes may be described to delocalization of 6-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.

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iv) New bonds and other changes observed :-

The IR bands observed of ligands around 3370 cm\(^{-1}\) due to O-H…..N vibration are absent in the corresponding complex indicate the deprotonation of enolic –OH and subsequent bonding of its oxygen with Ni during complex formation.

The additional bands at 596-668 cm\(^{-1}\) and 511 to 520 cm\(^{-1}\) were assigned to Ni-O and Ni-N bonds respectively.\(^7,12,15\)

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

The group absorption frequencies of Mn(II) and Fe(III) complexes are summarized in Table 5.5, 5.6 and the original spectra of these complexes are presented in fig.5.33 to 5.40 and 5.41 to 5.48 respectively.

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

In the IR spectra of Mn(II) and Fe(III) complexes, the strong bands appeared in the region 1578-1650 cm\(^{-1}\) were assigned to C=N stretching frequency. It is shifted towards lower frequency than corresponding free ligands 1646-1663 cm\(^{-1}\). The lowering in frequency indicate the coordination through nitrogen of azomethine C=N group.\(^5,24\)

The bands due to aromatic C=C stretching frequency was observed in the same region 1546-1582 cm\(^{-1}\) as compared to its free ligands, similar to Cu(II) complexes

ii) Aryl azomethine C-N frequency :-

The bands in Mn(II) and Fe(III) complexes at 1443-1477 cm\(^{-1}\) are due to aryl azomethine. The increase in frequency than corresponding free ligands 1428 to 1460 cm\(^{-1}\) attributed to the region similar to Mn(II) and Fe(III) complexes.\(^10,14,15,23\)

iii) Enolic C=O frequency :-

The bands observed at 1585-1635 cm\(^{-1}\) in the Mn(II) and Fe(III) complexes are assigned to enolic C=O. The frequency of this band is shifted to lower side than the corresponding free ligand 1622 to 1637 cm\(^{-1}\). The decrease in the frequency indicate the formation of bond between oxygen of C=O and metal ion. The absence of C=O frequency in some complexes may be due to merges with C=N frequency.

iv) New bands and other changes observed :-
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The absence of ligand bands in the region 3362 cm\(^{-1}\) due to hydrogen bonded enolic O-H....N stretching frequency in Mn(II) and Fe(III) complexes, confirms the enolic carbonyl oxygen coordinates with metal\(^{22,25,26}\).

The new bands in the region 585-632 cm\(^{-1}\) and 490-540 cm\(^{-1}\) in the spectra of Mn(II) and Fe(III) complexes indicate the vibration of M-O and M-N bonds respectively\(^{12,15,21}\).
### Table 5.1 Salient features of IR spectral data of ligands.

<table>
<thead>
<tr>
<th>Bond vibrational mode stretching (v)</th>
<th>Ligand band position (wave number cm(^{-1}))</th>
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<tbody>
<tr>
<td></td>
<td>L1</td>
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<tr>
<td>O-H---N (bonded)</td>
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<tr>
<td>C=O lactone carbonyl</td>
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<td>C=N Azomethine group</td>
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<td>C=C Aromatic ring</td>
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<td>C-N Aryl azomethine</td>
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<td>C-O-C pyrane ring</td>
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<tr>
<td>C=O Enolic</td>
<td>1634</td>
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### Table 5.2 Salient features of IR spectral data of Cu(II) complexes.

<table>
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<tr>
<th>Bond vibrational mode stretching (v)</th>
<th>band position of Cu(II) complexes (wave number cm(^{-1}))</th>
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<td>C=O (lactone carbonyl)</td>
<td>1703</td>
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<td>1631</td>
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<td>C=C Aromatic ring</td>
<td>1573</td>
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<td>C=O (Enolic)</td>
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<tr>
<td>New bands</td>
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<tr>
<td></td>
<td>M-N</td>
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</table>
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Table 5.3  Salient features of IR spectral data of Co(II) complexes.

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<tr>
<th>Bond vibrational mode Stretching (ν)</th>
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<td>C=N(Azomethine group)</td>
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New bands

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Table 5.4  Salient features of IR spectral data of Ni(II) complexes.

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<td>C=O (lactone carbonyl)</td>
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</tr>
<tr>
<td>C=N(Azomethine group)</td>
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New bands

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<td>M-N</td>
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### Table 5.5: Salient features of IR spectral data of Mn(II) complexes.

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<th>band position of Mn(II) complexes (wave number cm$^{-1}$)</th>
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<td>-</td>
</tr>
<tr>
<td>C=O (lactone carbonyl)</td>
<td></td>
<td>1720</td>
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<td>C=C Aromatic ring</td>
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<td>C-N(Aryl azomethine)</td>
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<td>M-N</td>
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### Table 5.6: Salient features of IR spectral data of Fe(III) complexes.

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<th>Bond vibrational mode</th>
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<th>band position of Fe(III) complexes (wave number cm$^{-1}$)</th>
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<td>L1</td>
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<td>O-H---N (bonded)</td>
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<tr>
<td>C=O (lactone carbonyl)</td>
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<td>1708</td>
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<td>C=N(Azomethine group)</td>
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<td>C=C Aromatic ring</td>
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<td>1576</td>
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<td>C-N(Aryl azomethine)</td>
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<tr>
<td>C=O (Enolic)</td>
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Fig. 5.1 IR spectra of Ligand L1 (DHA+ m-Chloro Aniline).

Fig. 5.2 IR spectra of Ligand L2 (DHA+ m-Amino Phenol).
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Fig. 5.3 IR spectra of Ligand L3 (DHA+ m-Anisidine).

Fig. 5.4 IR spectra of Ligand L4 (DHA+ m-Toludine).
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Fig. 5.5 IR spectra of Ligand L5 (DHA+ m-Bromo Aniline).

Fig. 5.6 IR spectra of Ligand L6 (DHA+ m-Amino Benzoic Acid).
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Fig. 5.7 IR spectra of Ligand L7 (DHA+ o-Phenidine).

Fig. 5.8 IR spectra of Ligand L8 (DHA+ 3,4-dichloro Aniline).
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Fig. 5.9 IR spectra of Cu(II) complex with Ligand L1.
Peaks: 3396.08-63.39, 2924.42-1.55, 2854.36-9.57, 1703.83-70.17, 1631.92-64.54, 1611.34-68.87, 1573.87-60.27, 1461.19-38.16, 1377.50-50.22, 1352.78-63.70, 1280.23-75.34, 1032.69-70.57, 1005.22-68.96, 976.61-73.99, 936.95-77.82, 851.63-75.64, 776.98-75.27, 722.23-73.95, 611.28-77.85, 512.69-75.06.

Fig. 5.10 IR spectra of Cu(II) complex with Ligand L2.
Peaks: 3356.35-64.45, 2924.69-2.13, 2854.45-12.18, 1714.70-66.28, 1650.81-60.20, 1621.24-69.13, 1561.24-55.28, 1460.77-38.76, 1377.82-50.54, 1343.42-64.97, 1221.45-72.53, 1065.76-72.08, 1032.19-71.40, 1005.18-66.59, 975.71-72.19, 842.49-76.93, 777.39-75.34, 722.02-75.39, 640.32-77.51, 618.62-78.94, 541.62-74.32.

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**Fig. 5.11** IR spectra of Cu(II) complex with Ligand L3.
Peaks: 2923.28-0.14, 2726.01-54.39, 1713.35-48.45, 1651.64-46.19, 1625.24-58.41, 1567.49-35.85, 1460.93-7.0, 1377.36-12.23, 1352.48-34.21, 1270.84-55.77, 1232.17-59.23, 1168.83-59.55, 1065.36-64.48, 1032.52-62.93, 1004.72-51.67, 976.06-56.97, 936.95-62.47, 851.17-58.44, 776.82-60.20, 722.22-53.38, 639.59-75.91, 618.86-75.57, 541.60-66.88.

**Fig. 5.12** IR spectra of Cu(II) complex with Ligand L4.
IR RESULTS AND DISCUSSION

Fig. 5.13 IR spectra of Cu(II) complex with Ligand L5.
Peaks: 3355.38-61.06, 2923.79-0.88, 2853.48-1.74, 2725.80-54.83, 1713.78-57.01, 1649.61-54.98, 1622.13-61.32, 1562.87-49.91, 1462.85-6.64, 1377.31-14.16, 1231.91-59.22, 1167.30-57.81, 1065.42-62.11, 1031.44-61.68, 1005.10-55.49, 974.43-59.19, 840.93-65.51, 777.23-66.70, 765.04-65.72, 721.94-51.95, 639.85-73.68, 617.95-74.96, 509.99-69.24.

Fig. 5.14 IR spectra of Cu(II) complex with Ligand L6.
Peaks: 3304.99-37.51, 3216.58-35.51, 3117.59-38.71, 2923.15-9.53, 2853.51-12.11, 1681.84-34.09, 1610.62-52.70, 1600.28-41.35, 1591.84-38.90, 1567.91-35.35, 1463.05-18.10, 1377.52-26.19, 1327.84-41.66, 1291.25-36.22, 1223.54-46.11, 1170.57-55.50, 1149.64-52.99, 1115.73-51.67, 1094.96-41.45, 913.45-48.06, 825.64-55.31, 769.60-58.05, 755.91-44.6, 722.30-57.66, 682.95-52.50, 663.18-67.03, 565.53-65.02, 533.98-70.57.
RESULTS AND DISCUSSION

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**Fig. 5.15 IR spectra of Cu(II) complex with Ligand L7.**
Peaks: 2923.35-1.54, 2725.83-53.62, 1712.84-50.84, 1651.08-49.87, 1624.57-58.36, 1567.08-41.40, 1462.81-5.83, 1377.34-12.43, 1352.56-36.34, 1232.03-58.63, 1168.72-57.80, 1065.35-63.23, 1032.31-61.59, 1004.69-52.62, 975.98-57.45, 936.79-61.71, 851.01-59.68, 776.67-61.08, 722.18-51.65, 639.96-75.76, 618.51-74.03, 541.52-67.53.

**Fig. 5.16 IR spectra of Cu(II) complex with Ligand L8.**
RESULTS AND DISCUSSION

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Fig. 5.17 IR spectra of Co(II) complex with Ligand L1.
Peaks: 2954.16-25.92, 2924.42-10.57, 2854.35-27.06, 1705.15-75.10, 1648.62-72.17, 1610.12-64.25, 1562.22-67.71, 1461.48-54.84, 1377.80-63.51, 1005.74-75.28, 722.06-80.72, 617.41-81.42, 513.36-82.42.

Fig. 5.18 IR spectra of Co(II) complex with Ligand L2.
Peaks: 3438.43-71.81, 2924.39-1.49, 2854.36-7.72, 1713.84-75.41, 1648.25-72.40, 1610.21-72.38, 1575.99-64.90, 1460.07-34.85, 1377.39-49.48, 1240.18-74.22, 1005.65-73.77, 722.10-74.37, 612.47-75.12, 540.23-75.35.
RESULTS AND DISCUSSION

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Fig. 5.19 IR spectra of Co(II) complex with Ligand L3.
Peaks: 2954.18-30.27, 2924.47-13.98, 2854.37-31.44, 1714.52-76.23, 1648.51-73.50, 1628.34-73.11, 1575.75-70.44, 1461.87-58.28, 1377.74-66.43, 1260.45-66.54, 1026.04-76.34, 722.29-79.72, 617.44-78.43, 538.13-79.28.

Fig. 5.20 IR spectra of Co(II) complex with Ligand L4.
Peaks: 2924.53-2.69, 2854.35-12.48, 1693.55-70.71, 1640.85-68.79, 1603.25-70.88, 1577.70-65.01, 1460.22-39.22, 1377.46-55.01, 1228.55-68.32, 1005.41-71.53, 832.73-79.41, 771.53-78.82, 722.01-76.97, 617.23-76.14, 518.18-77.14.
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Fig. 5.21 IR spectra of Co(II) complex with Ligand L5.
Peaks: 2954.16-22.06, 2924.37-8.28, 2854.35-23.28, 1714.45-72.34, 1649.09-71.34, 1625.73-73.08, 1577.08-67.79, 1462.38-50.30, 1377.64-61.86, 1242.66-71.22, 1005.77-74.44, 722.03-79.37, 619.13-75.44, 538.47-76.10.

Fig. 5.22 IR spectra of Co(II) complex with Ligand L6.
RESULTS AND DISCUSSION

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Fig. 5.23 IR spectra of Co(II) complex with Ligand L7.

Fig. 5.24 IR spectra of Co(II) complex with Ligand L8.
Fig. 5.25 IR spectra of Ni(II) complex with Ligand L1.
Peaks: 2968.95-30.18, 2882.35-49.87, 1703.22-25.62, 1633.09-68.67, 1582.55-63.21, 1445.41-49.56, 1375.37-56.74, 1246.39-25.55, 1161.85-47.33, 1110.17-60.86, 1010.34-42.46, 856.04-51.61, 793.38-72.43, 762.41-61.34, 615.32-69.54, 518.41-63.71.

Fig. 5.26 IR spectra of Ni(II) complex with Ligand L2.
Peaks: 3334.59-49.08, 2967.09-16.03, 2880.19-37.01, 1723.52-22.65, 1654.35-58.35, 1638.21-58.73, 1582.17-50.97, 1475.03-45.63, 1444.49-38.00, 1370.19-47.13, 1325.39-50.65, 1244.98-22.35, 1169.42-42.47, 1111.48-55.99, 1066.96-69.92, 1008.40-33.71, 942.86-63.93, 856.01-44.80, 832.45-55.53, 792.67-61.35, 763.74-41.64, 668.03-71.33, 617.24-43.36, 515.46-61.23.
RESULTS AND DISCUSSION

Fig. 5.27 IR spectra of Ni(II) complex with Ligand L3.
Peaks: 2967.14-19.75, 2880.32-45.33, 1743.16-23.35, 1712.24-48.46, 1654.98-62.43, 1582.83-53.83, 1475.01-49.57, 1444.88-42.08, 1370.46-51.20, 1325.84-55.35, 1245.54-23.40, 1169.75-45.57, 1111.40-58.88, 1067.58-74.91, 1008.90-35.95, 943.54-71.23, 856.00-46.82, 832.70-62.09, 792.96-67.69, 763.63-48.60, 668.06-76.78, 514.64-64.53.

Fig. 5.28 IR spectra of Ni(II) complex with Ligand L4.
Peaks: 2902.22-62.63, 2792.92-75.29, 2709.78-65.40, 1631.96-71.71, 1582.12-66.62, 1483.52-68.23, 1452.80-65.82, 1369.47-76.65, 1324.96-68.88, 1243.09-81.32, 1205.07-81.11, 1169.74-82.30, 1066.93-83.34, 1033.45-82.51, 1007.30-74.32, 983.69-81.75, 960.77-84.42, 942.68-77.94, 832.59-76.00, 792.69-80.27, 763.72-60.51, 606.39-87.65, 512.75-89.11.
RESULTS AND DISCUSSION

Fig. 5.29 IR spectra of Ni(II) complex with Ligand L5.
Peaks: 2960.02-28.55, 1739.94-33.17, 1645.18-44.36, 1581.72-64.39, 1453.35-47.60, 
1384.32-55.73, 1245.68-31.15, 1161.49-50.43, 1010.51-51.34, 852.90-62.03, 763.01- 
66.65, 600.01-66.60, 512.48-68.55.

Fig. 5.30 IR spectra of Ni(II) complex with Ligand L6.
Peaks: 3346.75-85.60, 3334.16-85.75, 2902.17-42.26, 2563.22-88.94, 1724.21-71.69, 
1708.96-62.19, 1631.96-68.11, 1581.38-61.76, 1483.16-63.83, 1452.05-59.16, 1418.29- 
64.35, 1368.89-71.55, 1324.45-59.93, 1246.57-77.37, 1204.58-76.05, 1169.45-77.70, 
1066.42-78.94, 1033.39-77.47, 1006.71-63.42, 983.41-73.85, 960.62-78.47, 942.25- 
67.31, 832.34-62.74, 792.40-69.07, 760.03-60.73, 716.22-80.48, 682.85-40.96, 596.47- 
81.34, 520.44-82.41.
RESULTS AND DISCUSSION

Fig. 5.31 IR spectra of Ni(II) complex with Ligand L7.

Fig. 5.32 IR spectra of Ni(II) complex with Ligand L8.
Peaks: 2969.85-32.15, 2880.33-52.24, 1743.21-20.12, 1634.09-73.84, 1582.55-68.11, 1500.12-54.67, 1445.54-64.37, 1375.37-56.74, 1256.39-25.55, 1161.85-47.33, 1110.17-46.29, 1010.34-42.46, 856.04-51.61, 793.38-72.43, 762.41-61.34, 620.32-79.84, 522.41-73.61.
RESULTS AND DISCUSSION

Fig. 5.33 IR spectra of Mn(II) complex with Ligand L1.

Fig. 5.34 IR spectra of Mn(II) complex with Ligand L2.
RESULTS AND DISCUSSION

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**Fig. 5.35 IR spectra of Mn(II) complex with Ligand L3.**
Peaks: 2923.19-0.68, 2725.02-13.69, 2032.03-25.92, 1711.57-21.54, 1640.31-23.14, 1610.61-23.44, 1580.49-24.54, 1463.63-1.58, 1377.28-2.07, 1148.52-18.62, 1076.82-19.66, 722.03-13.69, 595.08-20.37, 505.20-24.35.

**Fig. 5.36 IR spectra of Mn(II) complex with Ligand L4.**
Peaks: 2924.42-0.03, 1702.64-36.41, 1636.54, 36.18, 1600.54-37.84, 1578.13-35.62, 1461.01-1.15, 1377.28-6.01, 1262.34-35.74, 1152.87-42.24, 721.68-35.76, 610.87-24.09, 500.75-24.25.
**IR RESULTS AND DISCUSSION**

**Fig. 5.37** IR spectra of Mn(II) complex with Ligand L5.
Peaks: 2942.81-0.02, 1718.45-50.45, 1650.58-49.67, 1632.37-49.51, 1579.24-49.69, 1455.95-8.79, 1372.47-22.70, 1155.93-47.43, 623.25-33.32, 509.46-40.16.

**Fig. 5.38** IR spectra of Mn(II) complex with Ligand L6.
Peaks: 3356.34-50.06, 2988.12-54.67, 2877.86-64.42, 2819.61-64.91, 1713.71-23.08, 1578.35-65.39, 1546.59-64.63, 1472.87-61.73, 1443.25-53.63, 1390.31-47.71, 1246.65-23.18, 1158.06-45.15, 1111.41-56.58, 1011.08-41.15, 922.85-68.73, 911.43-69.96, 898.46-68.28, 855.93-44.63, 784.91-60.36, 774.24-46.88, 585.32-67.79, 490.46-68.66.
RESULTS AND DISCUSSION

Fig. 5.39 IR spectra of Mn(II) complex with Ligand L7.
Peaks: 3331.19-63.96, 2962.89-44.90, 1714.15-37.41, 1642.42-71.28, 1620.54-70.84,
1575.61-73.90, 1477.78-61.97, 1384.11-61.27, 1245.88-32.92, 1160.80-52.48, 1010.74-55.74,
855.51-64.24, 625.19-65.39, 534.68-67.34.

Fig. 5.40 IR spectra of Mn(II) complex with Ligand L8.
Peaks: 2942.81-1.02, 1738.45-30.45, 1670.58-31.67, 1621.37-29.51, 1579.24-27.69,
**RESULTS AND DISCUSSION**

**Fig. 5.41** IR spectra of Fe(III) complex with Ligand L1.

Peaks: 2924.32-1.52, 2854.34-5.87, 1708.84-75.41, 1648.50-68.12, 1576.92-69.59, 1461.19-29.27, 1377.36-44.60, 1005.71-73.33, 722.06-71.70, 620.81-77.79, 520.69-78.54.

**Fig. 5.42** IR spectra of Fe(III) complex with Ligand L2.

Peaks: 2924.94-0.06, 2854.43-1.04, 1714.58-64.29, 1646.72-59.78, 1574.99-55.05, 1462.75-17.79, 1377.42-32.03, 1168.06-68.77, 1004.62-64.90, 721.86-61.70, 616.84-67.49, 512.37-68.28.

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Fig. 5.43 IR spectra of Fe(III) complex with Ligand L3.
Peaks: 3438.97-69.24, 2954.16-19.90, 2924.59-6.93, 2854.35-21.02, 1714.28-73.22, 1648.39-71.98, 1611.41-71.21, 1576.67-69.25, 1460.81-50.05, 1377.53-60.91, 1268.59-75.49, 1028.42-74.86, 722.11-77.66, 601.54-78.32, 518.34-78.14.

Fig. 5.44 IR spectra of Fe(III) complex with Ligand L4.
Peaks: 2954.18-16.29, 2924.46-5.45, 2854.36-17.25, 1700.42-74.89, 1628.37-71.63, 1600.27-71.14, 1576.78-68.93, 1461.84-45.72, 1377.50-57.41, 1027.08-73.58, 722.09-75.37, 630.46-76.29, 532.61-77.26.
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Fig. 5.45 IR spectra of Fe(III) complex with Ligand L5.

Peaks: 2923.87-4.81, 1711.64-55.34, 1649.03-51.25, 1613.24-44.32, 1577.38-45.31, 1462.87-11.70, 1377.35-18.59, 1281.54-53.49, 1168.57-59.83, 1004.50-58.32, 721.98-48.04, 618.57-57.69, 512.67-56.21.

Fig. 5.46 IR spectra of Fe(III) complex with Ligand L6.

RESULTS AND DISCUSSION

Fig. 5.47 IR spectra of Fe(III) complex with Ligand L7.
Peaks: 3788.31-56.12, 2924.61-0.79, 1712.25-38.50, 1643.55-29.79, 1567.95-22.80, 1463.82-2.82, 1377.51-7.98, 1351.13-27.75, 1168.06-52.02, 1069.69-55.18, 1029.06-52.94, 1004.34-44.25, 973.77-47.74, 842.98-54.63, 721.81-39.27, 580.52-54.76, 531.91-52.39

Fig. 5.48 IR spectra of Fe(III) complex with Ligand L8.
5.4) CONCLUSION:-

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

The absence of bands in the region more than 3300 cm$^{-1}$ indicates the absence of coordination and lattice water in the present metal complexes.

The disappearance of ligand bands around 3364-3371 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 further confirms the participation of phenolic oxygen of the ligands in the bond formation with Nickel(II) ion, where as with other metal ions enolic carbonyl C=O forms bond.

The lowering of C=N frequency in the complexes than the corresponding ligands indicates that the coordination of ligand to the metal ion 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 580-638 cm$^{-1}$ and 500-541 cm$^{-1}$ in the IR spectra of complexes supports the formation of M-O and M-N bonds respectively in the complexes.

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 Cu(II), Co(II), Mn(II) and Fe(II) have distorted octahedral structure and the complexes of Ni(II) have square planer structure.
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**Fig. 5.49** Expected structure of Ni(II) complex.

R= substituted aromatic ring.

Where, M= Cu(II), Co(II), Mn(II).

**Fig. 5.50** Expected structure of Metal complexes.

R= substituted aromatic ring.

**Fig. 5.51** Expected structure of Iron complex.
5.6 REFERENCES:


