Chapter - V

Result and Discussion

Infrared Spectral Studies of Schiff Bases and their Metal Complexes

References.
INFRARED SPECTROSCOPY RESULT AND DISCUSSION

INTRODUCTION

Infrared spectroscopy is a useful technique in the study of metal complexes. This offers the possibility of chemical identification and provides the structural information about a molecule. A small range of absorption can be defined for each type of bond. Every type of bond has a different natural frequency of vibration, and two of the same types of bond in two different compounds are in two slightly different environments, no two molecules of different structure have exactly the same infrared spectrum. For 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 system. Infrared spectrum is useful to study the organic groups or bonds in the ligands and their bonding with metals in the complexes. The organic and inorganic compounds absorb various frequencies of electromagnetic radiation in the infrared region of the electromagnetic spectrum. This technique is more useful as compared to other methods because it gives more useful information regarding the structure of molecule. 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 Study of infrared spectrum of metal chelates is to compare the ligand spectrum with that of the complex in which the ligand is coordinated to in a known way. The characterizations of metal complexes 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, appearances of new bands, splitting of bands into multipletes, 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 Infrared spectroscopy region.

INFRARED SPECTRAL STUDIES OF LIGAND

In this present work Schiff bases are derived from dehydroacetic acid and different aromatic amines are used for the synthesis of complexes. The Infrared spectral data of ligands are given in Table 5.1 and their spectra are represented in fig. 5.1 to 5.8. The data given 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.

Hydrogen bonded O-H frequency:-

In the present study the-O-H stretching frequencies of all Schiff bases were observed as broad weak bands at 3441 to 3475 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).

Thakar et al.$^2$ mention that the IR bands at 3315-3434 cm$^{-1}$ due to –O-H intermolecular hydrogen bonding. The –OH of Schiff bases derived from N—phenyl-2-hydroxyacetophenonoimide and aniline. The absence of these bands in the metal chelates suggested coordination of the deprotonated dianionic ligands to the metal ions.
Munde et al. reported a band at 3100-3400 cm\(^{-1}\) to intermolecular hydrogen bonded phenolic -OH stretching of the Schiff base ligands derived from dehydroacetic acid, 4-methyl-o-phenylene diamine and salicyclaldehyde. Its disappearance in the spectra of the chelates indicated deprotonation of –OH and subsequent coordination at oxygen with metal ion. Venkateshwar Rao. et al. have assigned a band at 3400 cm\(^{-1}\) to –OH (intermolecular H-bonded) vibrations of Schiff bases derived from dehydroacetic acid and thiocarbohydrazide.

Mahapatra et al. reported the IR bond at 3475-3380 cm\(^{-1}\) due to O-H intermolecular hydrogen bonding. The absence these bond in the metal chelates suggested coordination of the deprotonated dianionic ligands to the metal ions.

Thus the broad weak bands at 3441 to 3475 cm\(^{-1}\) in the present work were assigned to hydrogen bonded enolic –O-H…N stretching frequency. These bands disappeared in the spectra of their respective metal complexes owing to the deprotonation of –O-H and subsequent coordination of oxygen with metal ion.

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

The bands observed at 1691 to 1728 cm\(^{-1}\) in the IR spectra of all ligands were assigned to C=O stretching vibrations of lactones carbonyl and which is supported by literature data. The carbonyl (C=O) stretching frequency of Schiff bases derived from diamines, amino acids, amino phenols/alcohols and dehydroacetic acid were observed at 1740-1685 cm\(^{-1}\) by Tan et al. and other workers.

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

The Schiff bases showed azomethine (C=N) stretching vibrational bands at 1689-1471 cm\(^{-1}\) region. Rao et al. 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.

Mane et al. reported that 1670-1660 cm\(^{-1}\) frequencies in the spectra of Schiff bases of dehydroacetic acid and aromatic amines to C=N stretching vibrations.
Abdulla et al.\textsuperscript{11} reported that IR spectral bands at 1647-1625 cm\textsuperscript{-1} to C=N stretching vibration of Schiff bases derived from hydrazine 5-methyl carbodithioate, thiourea, thiourea-bisnitrite and dehydroacetic acid.

Omar et al.\textsuperscript{12} found that C=N frequencies in the Schiff bases derived from 4-aminoantipyrane and 2-amino benzoic acid at 1638 cm\textsuperscript{-1}.

Angela et al.\textsuperscript{13} assigned C=N absorption at 1640 cm\textsuperscript{-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\textsuperscript{14}.

In the present work, the bands observed at 1660 to 1662 cm\textsuperscript{-1} 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\textsuperscript{-1} and 1500-1400 cm\textsuperscript{-1} region.\textsuperscript{9} Tan et al.\textsuperscript{6} reported the appearance of IR bands at 1590-1545 cm\textsuperscript{-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 1568 to 1580 cm\textsuperscript{-1} are assigned to (C=C) aromatic ring stretching vibrations.

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

For study of C-N vibration mode there is no systematic and consistent information on aromatic C-N frequency of vibration in the literature.

Maria et al.\textsuperscript{15} assigned the bond at 1330-1315cm\textsuperscript{-1} in the IR Spectra of Schiff base metal complexes derived from 4,6-diamino1,2 dihydro-2 thiopyrimidine to C-N stretching vibrational mode

Percy and Thornton\textsuperscript{16} synthesized N-aryl salicylaldehydeimines and reported that the appearance of two IR band in the region 1350-1375 cm\textsuperscript{-1} and 1470-1450 cm\textsuperscript{-1} attributable to aromatic azomethine C-N stretching vibrations. Munde\textsuperscript{17}
reported that a band at 1354 cm$^{-1}$ in the IR spectra of Schiff base metal complexes derived from Dehydroacetic acid, 4-methyl-o-phenylene diamine and salicyclaldehyde 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.$^{18}$

In the present work weak strong band observed at 1330-1357 cm$^{-1}$ in the IR spectra of all ligands were assigned to C-N vibration.

**Enolic C-O stretching Frequency:**

The IR spectral bands due to enolic C-O stretching vibrational modes are expected to appear around$^{19,20}$ 1200 cm$^{-1}$. Rao et al.$^{7,8}$ reported that 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 synthesized by condensation of dehydroacetic acid with glycine, thioethanol amine and benzoyl hydrazide/semicarbazide respectively.

Abdul-latif et al.$^{21}$ assigned the enolic C-O of free ligand is observed at 1275 cm$^{-1}$ for Schiff base derived from salicyclaldehyde and the appropriate amine which upon chelating shifted to higher wave number.

Mane et al.$^{22}$ assigned the enolic C-O stretching frequency at 1250-1230 cm$^{-1}$ for the Schiff bases prepared from p-totuidine, p-bromoaniline, p-anisidine with dehydroacetic acid when coordination shifting of these bands upwards by 20-30 cm$^{-1}$ indicated that oxygen is involved in bonding.

Ishan A. et al.$^{23}$ mention the enolic C-O stretching frequency at 1290 cm$^{-1}$ for Schiff base prepared from 3,3’-diamino benzidine and salicyclaldehyde on coordination shifted upward by 10-40 cm$^{-1}$.

In the present steady weak strong bands observed at 1230 to 1245 cm$^{-1}$ in the IR spectra of all ligands were assigned to enolic C-O stretching vibration mode.
INFRARED SPECTRAL STUDIES OF METAL COMPLEXES

The study of the Infrared spectroscopy 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 Infrared spectra of metal complexes are presented in the Fig. 5.9 to 5.48 and their spectral data with their characteristic parameters are given in Tables 5.2 to 5.6

Cu(II) Complexes :-

The Infrared spectra of Cu(II) complexes are represented in fig.5.9 to 5.16 and their group absorption frequencies are given in Table 5.2.

i) Azomethine (C=N) stretching Frequency:-

The IR spectra of Cu(II) complexes in the present study assigned the medium to strong bands appeared in the region 1640-1656 cm\(^{-1}\) to C=N stretching vibrational mode. In the corresponding ligands, frequencies for same group are observed from 1660 to 1662 cm\(^{-1}\). A downward shift of the band by 6 to 20 cm\(^{-1}\) in complexes indicate that the C=N group of the ligands is coordinated to the metal ion via its azomethine nitrogen\(^ {24,25}\).

R N Patel et al.\(^ {26}\) mention the lowering of C=N stretching frequency in Cu (II) complexes of salicylidene amino thiophenol by 35 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. Rao et al.\(^ {7}\) assigned similar bathochromic shift of the C=N band for Cu(II) complex derived from DHA-gly. anil.

ii) Aromatic(C=C) stretching Frequency:-

The medium to strong band in the region 1556-1581cm\(^{-1}\) in the IR spectrum of Cu(II) complexes were assigned to aromatic C=C stretching vibration\(^ {27}\). These
bands in the corresponding free ligands appeared almost in the same region 1568-1580 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 \(^{28}\).

iii) Aryl C-N stretching frequency:-

The IR bands in the region 1330-1357 cm\(^{-1}\) attributed to aromatic C-N stretching vibrations in the free ligands spectra were appeared at higher frequency side in the region 1350 to 1367 cm\(^{-1}\) in the spectra of its Cu(II) complexes. It is found in magnitude of vibrational frequency of this group by about 10 to 20 cm\(^{-1}\) on complexation may be attributed to increase in double bond character of aryl azomethine C-N bond most probably due to \(\pi\) electron delocalization from the metal to the nitrogen atom and resonance interaction with the benzene ring\(^{17,28}\). Similar observations were made by earlier workers for the Cu(II) complexes of Schiff bases derived from dehydroacetic acid and aromatic amines.

iv) Enolic C-O Frequency :-

The medium to strong bands observed at 1239 to 1275 cm\(^{-1}\) in the spectra of copper complexes was assigned to enolic C-O stretching vibrations. These bands in the corresponding free ligands are at 1230 to 1245 cm\(^{-1}\). It was found that upward 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 Rao et al.\(^{8}\) and Chondhekar et al.\(^{29}\) They reported shift of this band to higher frequency by 15-25 cm\(^{-1}\) for Cu (II) complex of 5-chloro-2-hydroxy acetophenone aryl anil. The shift of C-O band to higher frequency by 16 cm\(^{-1}\) for Cu(II)complex (L2 of munde) has reported by Munde.\(^{17}\)

v) New bands and other changes observed:-

All the ligands observed a broad weak band at 3441-3475 cm\(^{-1}\) assigned to O-H.N stretching vibration. The absence of these bands in the spectra of complexes further confirms the subsequent coordination of enolic oxygen with
metal forming M-O bond. In the IR spectra of Cu (II) complexes a broad band is observed in the region 3150 – 3450 cm\(^{-1}\) corresponding to the stretching frequency of vOH this indicates the presence of coordinated water.

The presence of coordinated water is further confirmed by the appearance of non-ligand band in the region 810 – 850 cm\(^{-1}\) assignable to rocking mode of water.

The new bands found in the region 538 to 550cm\(^{-1}\) and 470 to 482 cm\(^{-1}\), in the IR spectra if complexes may be assigned to the stretching of M-O and M-N bonds respectively \(^{6,7,8,25,30}\).

**Ni(II) Complexes :-**

The group absorption frequencies of Ni(II) complex and its corresponding ligands are given in Table 5.3 and IR spectra are presented in Fig. 5.17 to 5.24.

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

In the IR spectra of Ni(II) complexes, the bands appeared at 1642 to 1658cm\(^{-1}\) are assigned due to C=N stretching vibration. The bands in the corresponding free ligands are found at 1660-1662 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\(^{31,32}\).

B. H. Meheta et al.\(^{25}\) reported the Ni(II) complex of Schiff base derived from\{ N,N’-bis( 2-hydroxy benzylidine)-1,2 benzenediamin\}, shifted band from 1610-1620 cm\(^{-1}\) frequency indicating the coordination of azomethine nitrogen with Ni (II).

The bands due to aromatic C=C stretching frequency was found in the same region 1580-1585 as compared to its free ligands, it is similar to Cu(II) complexes.

ii) Aryl azomethine C-N frequency :-

The bands appeared in IR spectra of Ni(II) complexes at 1340-1369 cm\(^{-1}\) are attributed to aryl azomethine C-N stretching. The same bands in free corresponding ligands are obtained at 1330 to 1357 cm\(^{-1}\). It observed that increase
in the position may be attributed to the region similar to Cu(II) complex$^{12,06,17,16,18,26}$.

iii) Enolic C-O frequency :-

The upward shift of C-O frequency in Ni(II) complex (1242-1254 cm$^{-1}$) than the corresponding free ligand (1230-1245 cm$^{-1}$) suggest the bonding of enolic oxygen with Ni(II) during complexation$^{7,12,18,22}$.

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.

iv) New bonds and other changes observed :-

The Infrared spectral bands observed of ligands around 3441-3475 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. In the IR spectra of Ni (II)complexes a broad band is observed in the region 3150 – 3450 cm$^{-1}$ corresponding to the stretching frequency of vOH this indicates the presence of coordinated water.

The presence of coordinated water is further confirmed by the appearance of non-ligand band in the region 810 – 850 cm$^{-1}$ assignable to rocking mode of water.

The additional bands at 528-557 cm$^{-1}$ and 434 to 462 cm$^{-1}$ were assigned to Ni-O and Ni-N bonds respectively$^{7,11,14,16,18}$.

**Co(II) Complexes :-**

The group absorption frequencies of Co(II) complex are tabulated in Table 5.4 and the IR spectra of these complexes are presented in fig. 5.25 to 5.32.

i) Azomethine C=N and Aromatic C=C frequency:-
In the Infrared spectra of Co(II) complexes the strong bands developed in the region 1649-1658 cm\(^{-1}\) were assigned to C=N stretching frequency. It is shifted towards lower frequency than corresponding ligands 1660 to 1662. The lowering in frequency it is indicate that the coordination through nitrogen of azomethine C=N group\(^3,7,28\).

Kavita Rathore et al.\(^33\) mention the Co(II) complex of Schiff base, the C=N band shift from 1616-1610 cm\(^{-1}\) frequency than corresponding ligands. The lowering in frequency indicate that the coordination through N of azomethine C=N group. The bands due to aromatic C=C stretching frequency was appeared in the same region 1564-1585 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 1342-1381 cm\(^{-1}\) are due to aryl azomethine. The increase in frequency than corresponding free ligands 1330 to 1357 cm\(^{-1}\) it similar to Cu(II) complexes\(^11,06,17,16,28\).

iii) Enolic C-O frequency:-

The bands developed at 1242-1265 cm\(^{-1}\) in the Co(II) complexes are assigned to enolic C=O. The frequency of this band is increased to higher side than the corresponding free ligand 1230 to 1245 cm\(^{-1}\). This increase in the frequency indicate the formation of bond between oxygen of C-O and metal ion\(^17,25\).

iv) New bands and other changes observed:-

The absence of band in the region 3441-3475 cm\(^{-1}\) due to hydrogen bonded enolic O-H….N stretching frequency, indicate that the participation of enolic oxygen in coordination with metal\(^24,28\) in Co(II) complexes. In the IR spectra of Co(II) complexes a broad band is appeared in the region 3150 – 3450 cm\(^{-1}\) corresponding to the stretching frequency of vOH this shown 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 new bands appeared in the region 515-545 cm$^{-1}$ and 420-465 cm$^{-1}$ in the spectra of Co(II) complex indicate that vibration of M-O and M-N bonds respectively.$^{14,15,16,18,21,27}$

**Mn(II) Complexes:**

The absorption frequencies of Mn(II) complexes are given in Table 5.5 and the spectra of these complexes are presented in fig.5.33 to 5.40.

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

In the Infrared spectra of Mn(II) complexes, the strong bands developed in the region 1640-1650 cm$^{-1}$ were assigned to C=N stretching frequency. It is shifted towards lower frequency than corresponding free ligands 1660-1662 cm$^{-1}$.

The lowering in frequency indicate the coordination through nitrogen of azomethine C=N group.$^{3,7,34,35}$

Syama A.Shankar et al.$^{36}$ mention the Mn(II) complex of Schiff base prepared from bezothiazole and benzimidazole, the C=N band appeared at 1640 cm$^{-1}$ shifted to lowering in frequency suggested that the coordination through N of azomethine C=N group.

The bands due to aromatic C=C stretching frequency was appeared in the same region 1583-1587 cm$^{-1}$ as compared to its free ligands, similar to Cu(II) complexes

ii) Aryl azomethine C-N frequency :-

The bands appeared in Mn(II) complexes at 1340-1359 cm$^{-1}$ are due to aryl azomethine. The increase in frequency than corresponding free ligands 1330 to 1357 cm$^{-1}$ attributed to the region similar to Mn(II) complexes.$^{11,15,16,18,24,28}$

iii) Enolic C-O frequency :-
The Infrared bands developed at 1242-1270 cm\(^{-1}\) in the Mn(II) complexes are assigned to enolic C-O. The frequency of this band is shifted to higher side than the corresponding free ligand 1230 to 1245 cm\(^{-1}\). The increase in the frequency indicate the formation of bond between oxygen of C-O and metal ion\(^3\)

iv) New bands and other changes observed :-

The absence of ligand bands in the region 3441-3475 cm\(^{-1}\) due to hydrogen bonded enolic O-H….N stretching frequency in Mn(II) complexes, confirms the enolic carbonyl oxygen coordinates with metal \(^{21,36,26}\). In the IR spectra of Mn (II) complexes a broad band is observed in the region 3150 – 3450 cm\(^{-1}\) corresponding to the stretching frequency of \(\nu_{OH}\) 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 new bands in the region 505-528 cm\(^{-1}\) and 420-453 cm\(^{-1}\) in the spectra of Mn(II) complexes indicate the vibration of M-O and M-N bonds respectively \(^{6,14,16,18,22,26}\).

**Fe(III) Complexes:-**

The absorption frequencies of Fe(III) complexes are given in Table 5.6 and the spectra of these complexes are presented in fig. 5.41 to 5.48 respectively.

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

In the Infrared spectra of Fe(III) complexes, the strong bands developed in the region 1629-1649 cm\(^{-1}\) were assigned to C=N stretching frequency. It is shifted towards lower frequency than corresponding free ligands 1660-1662 cm\(^{-1}\). The lowering in frequency indicate that the coordination through nitrogen of azomethine C=N group\(^{3,7,26}\).

Nobil S. Youssef et al.\(^{37}\) mention the Fe (III) complex synthesized from 4,5-dimethylbenzene-1,2 diamine and 7-hydroxy-3-methoxy-2-methyl-4-oxo-chromene-6-carbaldehyde indicate that the C=N stretching frequency shifted to
downward from 1642 to 1614 cm\(^{-1}\) suggest that the coordination through nitrogen of azomethine C=N group.

The bands due to aromatic C=C stretching frequency was found in the same region 1562-1599 cm\(^{-1}\) as compared to its free ligands, similar to Cu(II) complexes

ii) Aryl azomethine C-N frequency:-

The bands in Fe(III) complexes at 1340-1383 cm\(^{-1}\) are due to aryl azomethine the increase in frequency than corresponding free ligand 1330-1357 cm\(^{-1}\) attributed to the region similar to Fe(III) complexes\(^{11,15,16,18,24,28}\).

iii) Enolic C-O frequency :-

The bands appeared at 1246-1273 cm\(^{-1}\) in the Fe(III) complexes are assigned to enolic C-O. it is shifted to higher side than the corresponding free ligand 1230 to 1245 cm\(^{-1}\). Increase in the frequency that is the formation of bond between oxygen of C-O and metal ion\(^{3}\).

iv) New bands and other changes observed:-

The absence of ligand bands in the region 3300-3475 cm\(^{-1}\) due to hydrogen bonded enolic O-H….N stretching frequency in Fe(III) complexes, confirms the enolic carbonyl oxygen coordinates with metal\(^{21,27}\).

In the IR spectra of Fe(III) complexes a broad band is observed in the region 3150 – 3450 cm\(^{-1}\) corresponding to the stretching frequency of vOH this indicates the presence of coordinated water. The presence of coordinated water is further confirmed by the appearance of non-ligand band in the region 810 – 850 cm\(^{-1}\) assignable to rocking mode of water.

The new bands appeared in the region 520-570 cm\(^{-1}\) and 420-466 cm\(^{-1}\) in the spectra of Fe(III) complexes indicate the vibration of M-O and M-N bonds respectively\(^ {14,15,17,18,22}\).

**Aromatic –NO\(_2\) Stretching Frequency**
In aromatic nitro group, the bands occur near 1550 cm\(^{-1}\). In the present work of ligand L\(_3\) and L\(_5\) showed two bands at 1533, 1555 cm\(^{-1}\) and 1355 cm\(^{-1}\) due to asymmetric and symmetric stretching frequency respectively.

The stretching frequency remains nearly same in their respective metal complex between 1533, 1560 cm\(^{-1}\) and 1355,1365 cm\(^{-1}\) Which shows non-coordination of –NO\(_2\) group. Iswar, Patel et al.\(^{38}\) reported the Schiff base ligand derived from 2-(4-{(4-chlorophenyl)(phenyl)(methyl)-1-piperazonyl}-1-(4{(3nitrophenyl) (methyledine)amino}phenyl)ethanone and reported that –NO\(_2\) stretching frequency at1344 cm\(^{-1}\).

**Aromatic–NH\(_2\) stretching frequency**

In aromatic Amine group the in N-H stretching bands occur near 3180 cm\(^{-1}\)to 3550\(^{39}\) cm\(^{-1}\). In the present work of ligand L\(_6\) showed bands at 3375 cm\(^{-1}\) and 3475 cm\(^{-1}\). The stretching frequency remains nearly same in their respective metal complex between 3380-3390 cm\(^{-1}\) which shows non-coordination of NH\(_2\) group.

**Aromatic amide stretching frequency**

In aromatic Amide group the N-H stretching bands occur near 3300\(^{40}\) cm\(^{-1}\) in the present work of ligand L\(_1\) showed bands at 3298 cm\(^{-1}\). The stretching frequency remains nearly same in their respective metal complex which shows non-coordination of amide group.
### Table 5.1 Infrared Absorption Frequencies (cm$^{-1}$) of Ligands

(Assignment of band frequencies to bond vibration modes)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Bond vibrational modes (stretching- $\nu$). Band Positions (cm$^{-1}$)</th>
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<tbody>
<tr>
<td></td>
<td>Enolic (C=O)</td>
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<tr>
<td>L$_1$</td>
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<td>L$_8$</td>
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### Table 5.2 Infrared Absorption Frequencies (cm$^{-1}$) of Cu(II) Complexes

(Assignment of band frequencies to bond vibration modes)

<table>
<thead>
<tr>
<th>Cu (II) Comp.</th>
<th>Bond vibrational modes (stretching- $\nu$). Band Positions (cm$^{-1}$)</th>
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<td></td>
<td>Lactone (C=O)</td>
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### Table 5.3 Infrared Absorption Frequencies (cm\(^{-1}\)) of Ni (II) Complexes

*(Assignment of band frequencies to bond vibration modes)*

<table>
<thead>
<tr>
<th>Ni(II) Comp.</th>
<th>Bond vibrational modes (stretching- (\nu)). Band Positions (cm(^{-1}))</th>
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<tbody>
<tr>
<td></td>
<td>Lactone (C=O)</td>
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### Table 5.4 Infrared Absorption Frequencies (cm\(^{-1}\)) of Co(II) Complexes

*(Assignment of band frequencies to bond vibration modes)*

<table>
<thead>
<tr>
<th>Co (II) Comp.</th>
<th>Bond vibrational modes (stretching- (\nu)). Band Positions (cm(^{-1}))</th>
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<td>Lactone (C=O)</td>
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<tr>
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<tr>
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<td>L(_8)</td>
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Table 5.5 Infrared Absorption Frequencies (cm\(^{-1}\)) of Mn (II) Complexes
(Assignment of band frequencies to bond vibration modes)

<table>
<thead>
<tr>
<th>Mn(II) Comp.</th>
<th>Bond vibrational modes (stretching- (\nu)). Band Positions (cm(^{-1}))</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>Nitro (NO(_2))</th>
<th>New Peaks M-O</th>
<th>New Peaks M-N</th>
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<td>1359</td>
<td>1242</td>
<td>509</td>
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<tr>
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<td>1583</td>
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Table 5.6 Infrared Absorption Frequencies (cm\(^{-1}\)) of Fe (III) Complexes
(Assignment of band frequencies to bond vibration modes)

<table>
<thead>
<tr>
<th>Fe (III) Comp.</th>
<th>Bond vibrational modes (stretching- (\nu)). Band Positions (cm(^{-1}))</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>Nitro (NO(_2))</th>
<th>New Peaks M-O</th>
<th>New Peaks M-N</th>
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<td>560</td>
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</table>
Fig. 5.1 Infrared Spectrum of Ligand L₁

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

Fig. 5.4 Infrared Spectrum of Ligand L₄
Fig. 5.5 Infrared Spectrum of Ligand $L_5$

Fig. 5.6 Infrared Spectrum of Ligand $L_6$
Fig. 5.7 Infrared Spectrum of Ligand L₇

Fig. 5.8 Infrared Spectrum of Ligand L₈
Fig. 5.9 Infrared Spectrum of Cu(II) Complex of Ligand L1

Fig. 5.10 Infrared Spectrum of Cu(II) Complex of Ligand L2
Fig. 5.11 Infrared Spectrum of Cu(II) Complex of Ligand L₃

Fig. 5.12 Infrared Spectrum of Cu(II) Complex of Ligand L₄
Fig. 5.13 Infrared Spectrum of Cu(II) Complex of Ligand L₅

Fig. 5.14 Infrared Spectrum of Cu(II) Complex of Ligand L₆
Fig. 5.15 Infrared Spectrum of Cu(II) Complex of Ligand L\textsubscript{7}

Fig. 5.16 Infrared Spectrum of Cu(II) Complex of Ligand L\textsubscript{8}
Fig. 5.17 Infrared Spectrum of Ni(II) Complex of Ligand L₁

Fig. 5.18 Infrared Spectrum of Ni(II) Complex of Ligand L₂
Fig. 5.19 Infrared Spectrum of Ni(II) Complex of Ligand L₃

Fig. 5.20 Infrared Spectrum of Ni(II) Complex of Ligand L₄
Fig. 5.21 Infrared Spectrum of Ni(II) Complex of Ligand L$_5$

Fig. 5.22 Infrared Spectrum of Ni(II) Complex of Ligand L$_6$
Fig. 5.23 Infrared Spectrum of Ni(II) Complex of Ligand L₇

Fig. 5.24 Infrared Spectrum of Ni(II) Complex of Ligand L₈
Fig. 5.25 Infrared Spectrum of Co(II) Complex of Ligand $L_1$

Fig. 5.26 Infrared Spectrum of Co (II) Complex of Ligand $L_2$
Fig. 5.27 Infrared Spectrum of Co(II) Complex of Ligand L₃

Fig. 5.28 Infrared Spectrum of Co (II) Complex of Ligand L₄
Fig. 5.29 Infrared Spectrum of Co(II) Complex of Ligand L₅

Fig. 5.30 Infrared Spectrum of Co(II) Complex of Ligand L₆
Fig. 5.31 Infrared Spectrum of Co(II) Complex of Ligand L₇

Fig. 5.32 Infrared Spectrum of Co(II) Complex of Ligand L₈
Fig. 5.33 Infrared Spectrum of Mn(II) Complex of Ligand $L_1$

Fig. 5.34 Infrared Spectrum of Mn(II) Complex of Ligand $L_2$
Fig. 5.35 Infrared Spectrum of Mn(II) Complex of Ligand L₃

Fig. 5.36 Infrared Spectrum of Mn(II) Complex of Ligand L₄
Fig. 5.37 Infrared Spectrum of Mn(II) Complex of Ligand $L_5$

Fig. 5.38 Infrared Spectrum of Mn(II) Complex of Ligand $L_6$
Fig. 5.39 Infrared Spectrum of Mn(II) Complex of Ligand L₇

Fig. 5.40 Infrared Spectrum of Mn(II) Complex of Ligand L₈
Fig. 5.41 Infrared Spectrum of Fe(III) Complex of Ligand L₁

Fig. 5.42 Infrared Spectrum of Fe(III) Complex of Ligand L₂
Fig. 5.43 Infrared Spectrum of Fe(III) Complex of Ligand L₃

Fig. 5.44 Infrared Spectrum of Fe(III) Complex of Ligand L₄
Fig. 5.45  Infrared Spectrum of Fe(III) Complex of Ligand \( L_5 \)

Fig. 5.46  Infrared Spectrum of Fe(III) Complex of Ligand \( L_6 \)
Fig. 5.47 Infrared Spectrum of Fe(III) Complex of Ligand $L_7$

Fig. 5.48 Infrared Spectrum of Fe(III) Complex of Ligand $L_8$
CONCLUSIONS

From the entire discussion on Infrared spectral data of ligands and their metal Complexes the following conclusion may be drawn.

The disappearance of ligand bands around 3441-3475 cm\(^{-1}\) due to hydrogen bonded enolic -O-H\(\cdots\)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 remarkable shift in the position of the band attributed to C=N group of ligands on chelation to lower frequency side suggest 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 Complexes.

The appearance of new band in the region 505-570 cm\(^{-1}\) and 420-482 cm\(^{-1}\) in the Infrared spectra of complexes supports the formation of M-O and M-N bonds respectively in the complexes.

In the IR spectra of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) complexes a broad band is observed in the region 3150 – 3450 cm\(^{-1}\) corresponding to the stretching frequency of vOH this indicates the presence of coordinated water. The presence of coordinated water is further confirmed by the appearance of non-ligand band in the region 810 – 850 cm\(^{-1}\) assignable to rocking mode of water. This observation is further confirmed by TGA-DTA analysis.

The stretching frequency of –NO\(_2\) group in the ligand L\(_3\) and L\(_5\) and their metal complexes remain nearly same that is confirmation of non-coordination of –NO\(_2\) group. Thus it can be concluded that the ligand behave as bidentate, coordinating through enolic oxygen and azomethaine nitrogen.
The following probable structures may be proposed to the metal Complexes of Schiff base ligands in the present study.

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), Ni(II), Co(II), Mn(II) and Fe(III) have distorted octahedral structure.

Fig.5.50 structure of Cu(II), Ni(II), Co(II), Mn(II)

Fig.5.51 structure of Fe (III) complex.
REFERENCES


