CHAPTER V : RESULT AND DISCUSSION
When a metal ion combines with an electron donor, the resulting substance is said to be a complex or coordination compound. Coordination compounds are conventionally formulated as consisting of a central atom or ion surrounded by a set (usually 2 to 9) of other atoms, ions or small molecules, the latter being called ligands. The resulting conglomerate is often called a complex or coordination compound. While writing the formula of a complex compound, central metal ion and ligands are enclosed in a square bracket. Whole things inside the bracket act as an ion in each case while every thing present outside the bracket is also ionic in nature. The portion so enclosed inside the square bracket is called coordination sphere.

In the present investigation, twelve complexes of two metals namely Fe(III) and Co(II) with different ligands have been prepared and studied. The compounds have been characterised on the basis of elemental analysis, conductance, magnetic and spectral data.

The complexes are of different colours. Their individual colours have been reported in Chapter IV. All
complexes are insoluble in common solvents and soluble in DMF.

Stereochernistry of the Complexes

Magnetic measurements:

The magnetic susceptibility measurements have been helpful in deciding the stereochernistry and configuration of the complexes. Magnetic moments were measured at room temperature using CuSO₄·5H₂O as calibrant by Gouy's method.²,³ Susceptibility value of a substance is best expressed by using a quantity called magnetic moment \( \mu \).

\[
\mu_{\text{eff}} = \sqrt{3R/N}N^2D^2 \sqrt{X'_M T} = 2.83 \sqrt{X'_M T}
\]

\( X_M \) is the measured susceptibility per mole

\( X'_M = X_M + D \)

\( X'_M \) is the susceptibility corrected for diamagnetism, with the help of quantum theory it can be shown that magnetic moment due to 'n' unpaired electrons on the atom or ion is given by

\[
\mu = 2\sqrt{s(s+1)}
\]

where 's' equals the sum of all the unpaired electrons.
that is nx $\frac{1}{2}$. The unit for atomic magnetic moment is the 'Bohr Magneton' (BM). Thus when number of unpaired electrons i.e. $n = 1$, $s = \frac{1}{2}$

$$\mu_{\text{eff}} = 2\sqrt{\frac{1}{2}} (\frac{1}{2} + 1)$$

$$= 1.73 \text{ BM}$$

Thus any atom, ion or molecule having one unpaired electron should have a magnetic moment of 1.73 from the electron spin alone. This may be diminished by an orbital contribution.

Fe(III) Complexes:

The electronic configuration of Fe(III) may be represented as:

$$\text{Fe(III)} = 1s^2, 2s^22p^6, 3s^23p^63d^5$$

Fe(III) is isoelectronic with Mn(II). Fe(III) possesses the d$^5$ configuration. Only hexaco-ordinated Fe(III) complexes have been isolated and worked out. In the high spin complexes, the magnetic moments are always very close to the spin only value of 5.9 BM because the ground state has no orbital angular momentum and there is no effective mechanism for introducing any coupling with excited states.
The moments are intrinsically temperature dependent, and at liquid nitrogen temperature (77°C) they decrease. In the present work the magnetic moment value of the complexes indicate that the isolated complexes are spin-free with octahedral structure. It has been shown that in certain complexes, the ligand field strength is such that the $^6A$ and $^2T_2$ states are of nearly equal stability. The dependence of magnetic susceptibility and the electronic spectra therefore, exhibit quite complicated behaviour as a function of temperature.

Co(II) Complexes:

The electronic configuration of Co(II) possess three unpaired electrons and may be represented as:

$$\text{Co(II)} = 1s^2, 2s^22p^6, 3s^23p^63d^7$$

The three unpaired '3d' electrons correspond to the observed magnetic moment value 5.1BM (almost thrice of the spin only value). The magnetic moment for four coordinated Co(II) complexes lies in the range 4.2-4.8 BM which agrees with the theoretical value of magnetic moments for octahedral complexes. All square planar complexes should be of low spin type having one unpaired electron along with the associated very large orbital contribution to magnetic moment.
such type of complexes possess the $\mu_{\text{eff}}$ in the range 2.4-2.8 BM. During investigation no Co(II) complex has been found to possess $\mu_{\text{eff}}$ value near the calculated value of magnetic moment for square planar complexes. The possibility of the existence of Co(II) high spin complexes is very rare due to structural limitations.

It has been noted that high spin octahedral cobalt(II) complexes have magnetic moment in the range 4.7-5.2 BM. Such complexes are associated with very high orbital contribution since the spin only value for the three unpaired electron is only 3.89 BM. This is supposed to be due to high orbital contribution to three fold orbital degeneracy of $^4T_{1g}$ ground state of Co(II). Its quantitative interpretation can be done on the ground of ligand field theory. The observed magnetic momentum of Co(II) spin free octahedral and tetragonally distorted octahedral complexes is found to be greater than the corresponding spin only value by an amount 0.9 to 1.3 BM. This is due to unquenched orbital contribution in $t_{2g}^5e_g^2$ and $t_{2g}^4e_g^3$ states. But $t_{2g}^6e_g^1$ state is free from orbital contribution. Therefore its magnetic moments for spin-paired octahedral complexes is very close to the calculated value.

All isolated complexes of Co(II) show octahedral symmetry and magnetic moment value in the range of 4.8-5.3 BM.
In such complexes Co(II) can be assigned \( t_{2g}^5 e_g^2 \) state.

All square and strongly tetragonal complexes of Co(II) are low spin type having only one unpaired electron but associated with a large orbital contribution to the magnetic moment so that the effective moment are in the range 2.4 - 2.8 BM. During the present investigation such values have not been observed for any isolated complex. Therefore the possibility of such a stereochemistry is ruled out.

Thus on the basis of observed magnetic moments of complexes and their comparision with available magnetic data for different configuration,\(^9,10\) it may be concluded that all isolated Co(II) complexes are high spin octahedral complexes.

**Electronic Spectra:**

**Fe(III) Complexes:**

The energy level diagrams of Fe(III) and Mn(II) are identical except for exact energies of the states of the free ions and for somewhat larger \( \Delta \) values to be expected for the trivalent ion, much less is known of the details of Fe(III) spectra. The most striking features of electronic spectra of Fe(III) in octahedral environments are:

a. the weakness of the bands,
b. the larger number of bands, and

c. the great variation in the widths of the bands.

All these main features of the spectrum are easily understood in terms of ligand field theory.

The ground state of the $d^5$ system in a weak octahedral field has one electron in each 'd' orbital and their spins are parallel, making it a spin sextuplet. This corresponds to the $^6S$ ground state of the free ion, which is not split by the ligand field. This, however, is the only sextuplet state possible, for every conceivable alteration of the electron distribution $t_{2g}^3 e_g^2$, with all spins parallel, results in the pairing of two or four spins thus making quartet or doublet states. Hence all excited states of $d^5$ system have different spin multiplicity from the ground state and the transition to them are spin forbidden. Because of weak spin orbit interaction, such transitions are not totally absent but they give rise only to very weak absorption bands.

In octahedral Fe(III) complexes the observed peaks can be assigned to the following transitions for weak field. $^{11-16}$

$$^6A_{1g} \rightarrow ^4T_{1g}(G) \quad 18,800 \text{ cm}^{-1}$$
$^6_{A_{1g}} \rightarrow ^4_{T_{2g}}(G) \quad 23,000 \text{ cm}^{-1}$

$^6_{A_{1g}} \rightarrow ^4_{E_g}(G) \quad 24,900 \text{ cm}^{-1}$

$^6_{A_{1g}} \rightarrow ^4_{A_{1g}}(G) \quad 25,150 \text{ cm}^{-1}$

In present investigation the complexes exhibit bands at 33,333 - 23,809 cm$^{-1}$, 33,333 - 24,390 cm$^{-1}$, 33,333 - 25,000 cm$^{-1}$ and 33,333 - 26,315 cm$^{-1}$ attributable to $^6_{A_{1g}} \rightarrow ^4_{T_{2g}}(G)$, $^6_{A_{1g}} \rightarrow ^4_{E_g}(G)$, $^6_{A_{1g}} \rightarrow ^4_{A_{1g}}(G)$ and $^6_{A_{1g}} \rightarrow ^4_{A_{1g}}(G)$ transition respectively.

Thus it may concluded that isolated six coordinated Fe(III) complexes have been found to possess octahedral configuration.

Co(II) Complexes:

Electronic spectra of octahedral Co(II) complexes have been studied by many workers for the structural problems. Following transitions have been noted:

$t_{2g}^5 e_g^2 \rightarrow t_{2g}^4 e_g^3 \quad 8000 \text{ cm}^{-1}$

$t_{2g}^5 e_g^2 \rightarrow t_{2g}^6 e_g^1 \quad 11000 \text{ cm}^{-1}$

$t_{2g}^5 e_g^2 \rightarrow t_{2g}^3 e_g^4 \quad 17000 \text{ cm}^{-1}$
All the Co(II) complexes isolated in the present case are low field (high-spin) complexes with $t_{2g}^5 e_g^2$ configuration. It may be noted that in $d^7$ ions the energy states do not vary linearly with $\Delta$. Thus the ground state for Co$^{2+}$ ion in octahedral complexes do not have exactly the $t_{2g}^5 e_g^2$ configuration as it is sometimes supposed. However, for ligand fields as large as for those found in octahedral Co$^{2+}$ complexes the deviation from strong field configurations can, for qualitative purpose, safely be neglected.$^{18}$

Urbainia and Shibata$^{19}$ pointed out that two absorption maxima are observed. One in the visible region and the other in the near ultraviolet region respectively. Cotton and Goodgame$^{20}$ have reported extinction coefficients of octahedral Co(II) complex in solution. The change in colour on dissolving the solid complex indicates the structural change. In the present investigation no such complexes have been isolated indicating that these complexes retain the same structure in the solid state as well as solution.

In octahedral field of high value $^2E$ state originating in $^2G$ state of free ion will become the ground state. The ligand field strength of about $\Delta \gg 15,000$ cm$^{-1}$ is required and therefore, the low spin octahedral Co(II) complexes are obtained only with ligands which occupy a place very far
from the strong field of spectrochemical series. Since \( t_{2g}^6 e_g^1 \) configuration gives rise to considerably large John Teller distortion, a truly octahedral complex can not exist and this situation is up till now not clearly understood.

Octahedrally co-ordinated Co(II) allows three d-d transition i.e. from ground state:

\[
\begin{align*}
4_{T_1g}(F) & \rightarrow 4_{T_2g} & \text{8000 - 9000 cm}^{-1} \\
4_{T_1g}(F) & \rightarrow 4_{A_2g} & \text{16000 - 18000 cm}^{-1} \\
4_{T_1g}(F) & \rightarrow 4_{T_1g}(P) & \text{20000 - 21000 cm}^{-1}
\end{align*}
\]

The absorption band due to \( 4_{T_1g}(F) \rightarrow 4_{T_1g}(P) \) transition near high frequency side is caused due to spin orbit coupling in \( 4_{T_1g}(P) \) state. The \( 4_{T_1g}(F) \rightarrow 4_{T_2g} \) transition band occurs at 8350 cm\(^{-1}\). It is noted that the \( 4_{T_1g}(F) \rightarrow 4_{A_2g} \) transition band occurs at slightly lower energy than the \( 4_{T_1g}(F) \rightarrow 4_{T_1g}(P) \) band (560 nm).

Visible spectra of Co(II) complexes is generally associated with bands at 674 nm (14,850 cm\(^{-1}\)) and 546 nm (18,280 cm\(^{-1}\)) respectively. The first band at 674 nm
corresponds to the $^4T_{1g}(F) ightarrow ^4A_{2g}(F)$ transition and appears in 16000-1800 cm$^{-1}$ range. The second band at 546 nm corresponds to $^4T_{1g} ightarrow ^4T_{1g}(P)$ which is generally observed in 20,000 $\rightarrow$ 21,000 cm$^{-1}$ region. 21-23

In some complexes the transition observed in the region 19,000 cm$^{-1}$ is two electron transition $^4T_{1g}(F) ightarrow ^4A_{2g}(F)$ and takes place due to the promotion of two electrons from t$_{2g}$ level to e$_g$ level.

Thus it may be concluded that isolated six coordinated complexes have octahedral stereochemistry.

**Molar Conductance**

By measuring the molar conductance of the complex in very dilute solution the total number of ions present inside and outside the coordination sphere, can be determined. When the number of coordinated anion is sufficient to balance exactly the oxidation number of the central metal, a non-electrolyte results. Hence the electrolytic nature of the complexes can be elucidated on the basis of available data. 24-35

In the present investigation molar conductance of the complexes was measured using 10$^{-3}$ M DMF solution. The
measurement of molar conductance gave value less than 15 Ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in case of Co(II) complexes. But Fe(III) complexes shows a value of molar conductance between 60-72 Ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) suggesting uni-univalent electrolyte. Some of the Fe(III) complexes shows a very low value of \(\Lambda_m\) that is less than 15 Ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) namely sodium valproate complex, Cefadroxil complex and Norfloxacain complex, suggesting non-electrolytic nature.

Infra-red spectra of complexes have been discussed in the respective texts. Assignments of the infra-red bands for drugs undertaken in the present work have been reported earlier. The assignment of the bands of the complexes in the present investigation is carried out by comparative study. Infra-red spectroscopy provides a valuable information about sites of attachment of the ligand, nature of the coordinate bond and also stereochemistry of the complexes. Notable change in the intensity and position of the IR band indicates the donation of electron pair from ligand to metal ion. As a result of coordination, the shift of the bands to higher or lower wave number side takes place depending upon increase or decrease in bond order. Metal-oxygen and metal-nitrogen bands appear in the spectra of complexes in far infra-red region.

All IR and UV spectras of the drug and the complexes are enclosed in Chapter IV.
Sodium Valproate Complexes

Sodium valproate is a sodium salt of valproic acid. Its chemical name is Pentenoic acid, 2-propyl sodium salt. It is also known as sodium 2-propyl pentanoate and sodium 2-propyl valerate. It is an antiepileptic drug.

Analytical data suggests 1:2 metal : ligand stoichiometry for the complexation with Fe(III) and Co(II) ions.

**Fe(III) Complex with Sodium Valproate**

The general formula of the complex is $\left[\text{Fe(SV)}_2(H_2O)(Cl)\right]$ where SV denotes the molecule of sodium valproate. The molecular formula of the complex is insoluble in common organic solvent like alcohol, benzene, ether and chloroform but soluble in Dimethyl Formamide. The colour of the complex is Buff. The molar conductance of the complex is measured in $10^{-3}\text{M DMF}$ solution at 30°C, which has been found to be very low. This shows non-electrolytic nature. The magnetic moment of the Fe(III) complex is 5.8 BM suggesting the formation of spin free complex with octahedral structure. The electronic spectra of complex shows a broad symmetric band between 300-380 nm centered at 340 nm (Fig. 4.1) which is due to the combination of three transition assignable
to the $^6A_{1g} \rightarrow ^4A_{1g}(G)$, $^6A_{1g} \rightarrow ^4T_{1g}(P)$ and $ \rightarrow e_g$ in octahedral symmetry.\textsuperscript{36-41}

Interpretation of the IR bands in the complex (Fig. 4.14) have been carried out by the comparison with the spectrum of sodium valproate (Fig. 4.13). A broad band from 3600 cm$^{-1}$ to 3200 cm$^{-1}$ indicated the coordinated water molecule, which is absent in the spectra of the ligand. This peak is due to VO-H stretching vibrations in coordinated water molecule, which has been frequently discussed.\textsuperscript{42-49} One medium strong band at 2960 cm$^{-1}$ and one weak band at 2880 cm$^{-1}$ appear due to C-H stretching vibration in CH$_3$ group, which is present in the ligand as well as in the complex. Three peaks appear in the spectra of the ligand and in the complex, due to C-H stretching and C-H deformation in the CH$_2$ group. First peak at 2920 cm$^{-1}$ and second at 2870 cm$^{-1}$ are due to the C-H stretching vibrations in the CH$_2$ group. But the third peak at 1480 cm$^{-1}$ is due to C-H deformation frequency in the CH$_2$ group. A medium band at 1455 cm$^{-1}$, arises due to C-H deformation frequencies in C-CH$_3$ group.\textsuperscript{50} The C=O stretching vibration in the ligand appear at 1720 cm$^{-1}$ in the form of sharp peak but in the complex if shifts towards lower frequencies and appear at 1675 cm$^{-1}$. Which indicates the participation of carbonyl group in coordination.\textsuperscript{51-54} One medium peak at 1560 cm$^{-1}$
due to C=O stretching vibration present in the ligand spectra, vanishes, in the spectra of the complex, which shows the contribution of C=O- group in coordination with metal atom. A weak peak at 1375 cm\(^{-1}\) in the ligand and at 1370 cm\(^{-1}\) in the complex spectra is due to C-H bending vibration. C=O stretching vibration arises at 590 cm\(^{-1}\) in the ligand but in the complex the spectra is shifted towards lower frequencies and appear at 585, suggesting the contribution of electrons in coordination with metal atom. The two bands at 375 cm\(^{-1}\) and 355 cm\(^{-1}\) shows M-Cl bonding. The conclusive evidence of bonding is ascertained by the occurrence of the band at 530 cm\(^{-1}\), which is due to M-O bonding. The frequencies of M-O and M-Cl are in good agreement with earlier work. The band near 860 cm\(^{-1}\) in the spectra of complex may be due to the coordinated water molecule. This is further confirmed by analytical data. The structure of the complex is shown in Figure 5.1.
Table 5.1. Principal IR Frequencies (cm\(^{-1}\)) and their Assignment for Sodium Valproate and its Complexes.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Fe(III) complex</th>
<th>Co(II) complex</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3600 br</td>
<td>3600 br</td>
<td>VOH (coordinated H(_2)O molecule)</td>
</tr>
<tr>
<td></td>
<td>3200</td>
<td>3200</td>
<td></td>
</tr>
<tr>
<td>2960 m</td>
<td>2960 m</td>
<td>2960 m</td>
<td>VC-H of CH(_3)</td>
</tr>
<tr>
<td>2920 m</td>
<td>2920 m</td>
<td>2920 m</td>
<td>VC-H of CH(_2)</td>
</tr>
<tr>
<td>2880 w</td>
<td>2880 w</td>
<td>2880 w</td>
<td>VC-H of CH(_3)</td>
</tr>
<tr>
<td>2870 w</td>
<td>2870 w</td>
<td>2870 w</td>
<td>VC-H of CH(_2)</td>
</tr>
<tr>
<td>1720 s</td>
<td>1675 s</td>
<td>1680 s</td>
<td>VC=O of COOH</td>
</tr>
<tr>
<td>1560 m</td>
<td>-</td>
<td>-</td>
<td>VC=O of COO(^-)</td>
</tr>
<tr>
<td>1485 w</td>
<td>1480 w</td>
<td>1480 w</td>
<td>C-H deformation of CH(_2)</td>
</tr>
<tr>
<td>1460 m</td>
<td>1455 m</td>
<td>1465 m</td>
<td>C-H deformation of C-CH(_3)</td>
</tr>
<tr>
<td>1375 w</td>
<td>1370 w 860</td>
<td>1370 w 860</td>
<td>C-H bending of CH(_3)</td>
</tr>
<tr>
<td>590 w</td>
<td>585 w</td>
<td>580 w</td>
<td>C=O stretching of COOH</td>
</tr>
<tr>
<td>-</td>
<td>530 w</td>
<td>530 w</td>
<td>M-O bending</td>
</tr>
<tr>
<td>-</td>
<td>470 w</td>
<td>475 w</td>
<td>M-O stretching</td>
</tr>
<tr>
<td>355-375 s</td>
<td>-</td>
<td>-</td>
<td>M-Cl stretching</td>
</tr>
</tbody>
</table>

s = sharp, m = medium, w = weak, br = broad.
860 = coordinated water molecule.
Co(II) Complex with Sodium Valproate

The general formula of the complex is $[\text{Co(SV)}_2 \text{H}_2 \text{O}_2^2]$ where SV is the molecule of sodium valproate. Sodium valproate forms 1:2 Metal:Ligand complex with Co(II). The analytical data proves the molecular formula of the complex and is represented as $[\text{Co(C}_8\text{H}_{15}\text{O}_2)(\text{H}_2\text{O})_2]$. The complex is insoluble in common organic solvents like alcohol, benzene, ether etc. but freely soluble in dimethyl formamide. The colour of the complex is violet. Molar conductance of the complex has been measured in $10^{-3}$ M DMF solution at 30°C, which has been found to be very low. This shows non-electrolytic nature of the complex. Magnetic moment of the complex is 4.4 BM at room temperature, shows three unpaired electrons and also the octahedral geometry of the complex.\textsuperscript{64-69} Octahedral geometry of the complex is also proved by electronic spectra. The electronic spectra of the complex shows a broad symmetric band between 310 nm to 610 nm (Fig. 4.2) which is actually due to the combination of the three transitions assignable to the $4T_{1g}(F) \rightarrow 4T_{1g}(P)$, $4T_{1g}(F) \rightarrow 4A_{2g}$ and charge transfer in octahedral symmetry.\textsuperscript{70-76}

The interpretation of the infrared spectra of the complex (Fig. 4.15) has been carried out with the help of the
spectra of parent drug that is sodium valproate. A broad band in the complex spectra from 3600 cm\(^{-1}\) to 3200 cm\(^{-1}\), which is absent in the spectra of the ligand, is due to the coordinated water molecules. This broad band is due to the VO-H vibrations in water molecule.\(^{77}\) Two medium and strong bands appear at 2920 cm\(^{-1}\) and 2880 cm\(^{-1}\) due to the C-H stretching vibration in CH\(_3\) group, in the spectra of ligand as well as in the complex.\(^{78}\) The bands at 2920 cm\(^{-1}\) and 2880 cm\(^{-1}\) may be assigned to the C-H stretching vibrations in the CH\(_2\) group. These bands are present in both spectra. Two medium strong bands at 1480 cm\(^{-1}\) and 1465 cm\(^{-1}\) are due to C-H deformation frequencies in the CH\(_2\) group and C-CH\(_3\) group respectively.\(^{79}\) These are similar to the complex spectra. In the ligand spectra C=O stretching vibration appear at 1720 cm\(^{-1}\) in the form of a sharp peak but in the complex it shifts towards lower frequencies and arises at 1680 cm\(^{-1}\), suggesting the participation of carbonyl group in the coordination bonding.\(^{80}\) One peak, having medium intensity, at 1560 cm\(^{-1}\) in the spectra of the ligand is due to C=O- stretching vibration and vanishes in the spectra of the complex. Which shows the co-ordination of C=O group with metal ion. C-H bending vibration produces one weak band at 1375 cm\(^{-1}\) in the ligand and at 1370 cm\(^{-1}\) in the complex spectra. In the ligand a weak band at 590 cm\(^{-1}\) arises due to C=O stretching vibration. But in the
Fig. 5.1. Fe(III) complex with sodium valproate.

Fig. 5.2. Co(II) complex with sodium valproate.
case of the complex it shifts towards lower frequencies and arises at 580 cm\(^{-1}\). This suggests the coordination of C=O group with the metal atom. The conclusive evidence of bonding is ascertained by the occurrence of the bands at 530 cm\(^{-1}\) and 470 cm\(^{-1}\) which is due to M-O bonding.\(^8\) The broad band near 3600 cm\(^{-1}\) indicates coordinated water molecules. It is further proved by analytical data.

**Conclusion**

On the basis of molar conductance, magnetic moment, elemental analysis, electronic spectra and infra-red spectra it can be inferred that the Fe(III) complex is 6-coordinated with octahedral structure. The structure can be assigned by the bridging with chlorine. Co(II) complex is also 6-coordinated having octahedral geometry with two molecules of coordinated water. It is proved by analytical data. The drug binds through oxygen of carbonyl group.

Ionization of sodium valproate takes place in aqueous solution. This ionization is favoured by the presence of dilute \(\text{NH}_3\) and metal salt. Interaction of metal ion with anion thus produced results in the formation of metal chelate. The structure of the complexes may be represented as Figure 5.2.
Piroxicam Complexes

Piroxicam is a non-steroidal anti-inflammatory drug belonging to the oxicam group. Its chemical name is 4-hydroxy-2-methyl-N-(2-pyridyl)-2H-1, 2-benzothiazine-3-carboxamide-1,1-dioxide.

Analytical data suggests 1:2, metal: ligand stoichiometry for the complexation with Fe(III) and Co(II) ions.

Fe(III) Complex with Piroxicam

The general formula of the isolated Fe(III) complex with this drug is $\left[\text{Fe(PC)}_2\right]\text{Cl}$. The analytical data proves the molecular formula of complex and is represented as $\left[\text{Fe}\left(\text{C}_{17}\text{H}_{14}\text{N}_{3}\text{O}_{4}\text{S}\right)_2\right]\text{Cl}$. The complex is of black colour and is insoluble in common organic solvent but freely soluble in dimethyl formamide. The molar conductance of the complex was measured in $10^{-3}$ DMF solution at 30°C and was found to be of very low value i.e. 60.85 Ohm$^{-1}$ cm$^2$ mol$^{-1}$, suggesting formation of a uni-univalent complex. The magnetic moment of the complex is 5.1 BM at room temperature, suggesting the formation of spin free complex with octahedral geometry. The electronic spectra of the complex (Fig. 4.3) shows a broad symmetric band between 300 nm - 400 nm centered at 360 nm, which is due to the combination of three
transitions assignable to the $^{6}A_{1g} \rightarrow ^{4}A_{1g}$, $^{6}A_{1g} \rightarrow ^{4}T_{1g}(P)$ and $t_{2g} \rightarrow \pi^*$ in octahedral symmetry.\textsuperscript{82-84}

Infrared bands of the complex (Fig. 4.17) were assigned with the help of IR bands of the ligand (Fig. 4.16). In the spectra of the ligand and the complex a broad band around 3700 cm\(^{-1}\) to 3200 cm\(^{-1}\) was found to be common and did not shift from its position. This band is due to =C--H stretching in benzene ring, OH stretching vibration, ortho disubstituted benzene ring and N--H stretching vibration.\textsuperscript{85,86}

A broad shoulder band in the ligand is obtained in the region 1715-1690 cm\(^{-1}\) which is due to the C=O stretching vibration. But in the complex this shoulder band shifts towards lower frequencies and appear at 1690-1630 cm\(^{-1}\), suggesting participation of C=O group in coordination.\textsuperscript{87,88}

In the ligand spectra one shoulder band at 1610 cm\(^{-1}\) is due to the benzene ring breathing vibration but in the spectra of the complex it is at 1600 cm\(^{-1}\).\textsuperscript{89} N--H stretching vibration appear at 1590 cm\(^{-1}\) and 1575 cm\(^{-1}\) in the ligand and in the complex as a weak band respectively.\textsuperscript{90} In the spectra of the ligand a shoulder band from 1540 cm\(^{-1}\) to 1510 cm\(^{-1}\) is due to the benzene ring stretching vibration, it is an overlap of four bands. But in the spectra of the complex it appears between 1570 cm\(^{-1}\) and 1535 cm\(^{-1}\). Bands due to C--H bending and deformation frequencies appear in
the form of a weak broad band at 1460-1435 cm\(^{-1}\) and 1450 cm\(^{-1}\) to 1420 cm\(^{-1}\), in the spectra of the ligand and in the complex respectively.\(^{92}\) C-SO\(_2\)-C stretching vibration is present at 1400 cm\(^{-1}\) in the ligand in the form of a weak band but in the complex it is present at 1380 cm\(^{-1}\) as a medium band\(^{93}\). In the ligand spectra absorption due to C-N stretching in pyridine ring, is present at 1350 cm\(^{-1}\) and at 1325 cm\(^{-1}\) in the spectra of the complex as a medium band. Shifting of this band towards lower frequency shows the participation of this nitrogen atom in coordination.\(^{94,95}\) In the spectra of the complex, the band at 1250 cm\(^{-1}\) is due to orthodisubstituted benzene ring, the band at 1220 cm\(^{-1}\) is due to the OH bending, the band at 1180 cm\(^{-1}\) is due to the C-N stretching in normal aliphatic chain and the band at 1140 cm\(^{-1}\) is due to the S=O stretching vibration. But in the ligand these are represented as a broad band from 1270 cm\(^{-1}\) to 1050 cm\(^{-1}\). Absorption due to four adjacent free hydrogen atoms in benzene ring appears at the region near 770 cm\(^{-1}\) ± 10 cm\(^{-1}\).\(^{196}\) The two bands at 580 cm\(^{-1}\) and 455 cm\(^{-1}\) show M-O banding. The two bands at 530 cm\(^{-1}\) and 470 cm\(^{-1}\) show M-N bonding in the complex. The weak band at 375 cm\(^{-1}\) in the complex may be assigned to coordinated N atom of pyridine ring.\(^{101,102}\) Figure 5.3 represents the structure of the complex.
Fig. 5.3. Fe(III) complex with piroxicam or Felden
Table 5.2. Principal IR Frequencies (cm$^{-1}$) and their Assignment for Piroxicam and its Complexes.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Fe(III) complex</th>
<th>Co(II) complex</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3700 br</td>
<td>3600 br</td>
<td>3600 br</td>
<td>V=C-H in aromatic ring</td>
</tr>
<tr>
<td>3200</td>
<td>3100</td>
<td>3000</td>
<td>VO-H</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>VN-H</td>
</tr>
<tr>
<td>1715 br</td>
<td>1690 br</td>
<td>1630 br</td>
<td>VC=O</td>
</tr>
<tr>
<td>1690</td>
<td>1630</td>
<td>1615</td>
<td>VC=N</td>
</tr>
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<td>1610 sh</td>
<td>1600 sh</td>
<td>1600 sh</td>
<td>Benzene ring breathing vibration</td>
</tr>
<tr>
<td>1590 w</td>
<td>1575 w</td>
<td>1580 w</td>
<td>N-H bending</td>
</tr>
<tr>
<td>1540 br</td>
<td>1570 br</td>
<td>1560 brsh</td>
<td>Skelatel stretching vibration of benzene ring</td>
</tr>
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<td>1535</td>
<td>1520</td>
<td></td>
</tr>
<tr>
<td>1460 wbr</td>
<td>1450 wbr</td>
<td>1450 wbr</td>
<td>C-H bending and deformation in CH$_3$</td>
</tr>
<tr>
<td>1435</td>
<td>1420</td>
<td>1435</td>
<td></td>
</tr>
<tr>
<td>1400 w</td>
<td>1380 w</td>
<td>1380 w</td>
<td>C-SO$_2$-C stretching</td>
</tr>
<tr>
<td>1350 m</td>
<td>1325 m</td>
<td>1325 m</td>
<td>VC-N in pyridine ring.</td>
</tr>
<tr>
<td>1270 br</td>
<td>1250 m</td>
<td>1235 m</td>
<td>Orthodisubstituted benzene ring</td>
</tr>
<tr>
<td>1050</td>
<td>1220 m</td>
<td>1190 m</td>
<td>O-H bending</td>
</tr>
<tr>
<td></td>
<td>1180 w</td>
<td>1150 m</td>
<td>VC-N in normal aliphatic chain</td>
</tr>
<tr>
<td></td>
<td>1140 w</td>
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<td>Four adjacent free H atoms</td>
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<td>M-O bending</td>
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<td>M-O bending</td>
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<td>470 w</td>
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<td>M-N bending</td>
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<td>450 w</td>
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</tr>
<tr>
<td></td>
<td>375 m</td>
<td></td>
<td>M-Cl stretching</td>
</tr>
</tbody>
</table>
Co(II) Complex with Piroxicam

The general formula of the complex is \([\text{Co(PC)}_2]\) where PC indicates the molecule of Piroxicam. Thus Co(II) forms 1:2, metal : ligand complex with the drug. The analytical data proves the molecular formula of complex and is represented as \([\text{Co(C}_{17}\text{H}_{14}\text{N}_3\text{O}_4\text{S})_2]\). The colour of the complex is yellowish green and is insoluble in common organic solvent but soluble in dimethyl formamide. The molar conductance was measured in 10\(^{-3}\) M DMF solution at 30°C and was found to be of very low value i.e. 12.2 Ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\). This shows non-electrolytic nature of the complex.\(^{103-105}\) Magnetic moment of the complex was measured by Gouy's method, and was found to be 4.3 BM at room temperature, which suggests the octahedral geometry of the complex.\(^{106}\) Magnetic moment shows three unpaired electrons in complex.\(^{107,108}\) Octahedral geometry of the complex is also proved by electronic spectra. The electronic spectra of the complex (Fig. 4.4) shows one band at 510 nm and a broad band from 440 nm to 300 nm, which is actually due to the transition \(4\text{T}_{1g}(F) \rightarrow 4\text{T}_{1g}(P)\)\(^{109}\) in octahedral symmetry.

Interpretation of infrared spectra of the complex (Fig. 4.8) has been made with the help of IR spectra of the drug piroxicam (Fig. 4.15). A broad band in the region 3700-3200 cm\(^{-1}\) has been obtained in the ligand as well as
in the complex, which is due to =C-H stretching in benzene ring, orthodisubstituted benzene ring and N-H stretching vibration. And in the ligand also due to O-H stretching vibration. A broad shoulder band in the ligand spectra is obtained in the region 1715-1690 cm\(^{-1}\), which is due to \(\geq\)C=N and C=O stretching vibration. But in the Co(II) complex it shifts towards lower frequencies and appears at 1630-1615 cm\(^{-1}\), suggesting the participation of carbonyl group in coordination. The absorptions due to benzene ring breathing vibrations appear in the ligand spectra at 1610 cm\(^{-1}\) in the form of a shoulder band and in the form of a broad band at 1540-1510 cm\(^{-1}\). But in the complex these are present at 1600 cm\(^{-1}\), 1550 cm\(^{-1}\), 1535 cm\(^{-1}\) and 1520 cm\(^{-1}\) in the form of a broad shoulder band. The band due to the N-H bending vibration appears in the same position in the ligand and in the complex i.e. at 1580 cm\(^{-1}\) in the form of a weak peak, which shows that there is no bonding with metal atom through this nitrogen atom. In the spectra of the complex one broad band at 1470 to 1420 cm\(^{-1}\) appears due to the C-H bending and deformation frequencies. C-SO\(_2\)-C stretching vibration appears at 1380 cm\(^{-1}\) in the spectra of the complex and at 1400 cm\(^{-1}\) in the spectra of the ligand. The absorption due to C-N stretching in pyridine ring appears at 1350 cm\(^{-1}\) in the spectra of the ligand but in the case of Co(II) complex, it shifted and appears at 1325 cm\(^{-1}\) which shows participation of nitrogen
Fig. 5.4. Co(II) complex with Piroxicam or Felden.
atom of pyridine ring in coordination. The band at 1235 cm\(^{-1}\) is due to orthodisubstituted benzene ring in the ligand as well as in the complex. A broad band from 1150 cm\(^{-1}\) to 1030 cm\(^{-1}\) is due to S=O and N-H stretching vibration in both spectra. In the spectra of the ligand a medium peak at 765 cm\(^{-1}\) is due to four adjacent free hydrogen atoms, and it is similar to the spectra of the complex. The two bands at 580 cm\(^{-1}\) and 450 cm\(^{-1}\) shows M-O bonding in the complex. And the two bands at 580 cm\(^{-1}\) and 470 cm\(^{-1}\) are due to M-N banding in the complex. The structure is represented as in Figure 5.4.

**Conclusion**

On the basis of magnetic moment, electronic spectra IR spectra and other investigations it can be proved that the Fe(III) complex is 6-coordinated complex with octahedral structure. Co(II) complex is also 6-coordinated having octahedral geometry. The structure is further proved by analytical data. The drug binds with oxygen of C=O group and with nitrogen of pyridine ring. The structure of the complexes are shown in Figure 5.3 and 5.4 respectively.
**Flurazepam hydrogen Chloride Complexes**

Flurazepam hydrogen chloride is Benzodiazepin derivative with hypnotic properties similar to those of nitrazepam. Its chemical name is 7-chloro-1- \( [2-(\text{diethylamino})\text{ ethyl}] \)-5-(2-fluorophenyl)-1,3-dihydro-,dihydro chlorides or 7-chloro-1- \( [2-(\text{diethylamino})\text{ ethyl}] \)-5-(o-flurophenyl)-1,3-dihydro-2H-1,4-benzodiazepin-2-one dihydrochloride.

Present investigation indicates formation of 1:2 Metal : Ligand complex with Fe(III) and Co(II) ions.

**Fe(III) Complex with Flurazepam Hydrogen Chloride**

The investigated formula of the complex is
\[ [\text{Fe(FA)}_2(\text{Cl})_2] \text{Cl} \]
where FA represents the molecule of flurazepam hydrogen chloride. And the chemical formula is
\[ [\text{Fe(C}_{21}\text{H}_{23}\text{ClN}_{3}\text{OF})_2(\text{Cl})_2] \text{Cl} \]
which is proved by analytical data. The complex is of chocolate brown in colour. The complex is insoluble in common organic solvent but soluble in dimethyl formamide. The molar conductance of the complex in DMF at \( 10^{-3}\text{M} \) concentration has been found to be \( 72.2 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \). The molar conductance suggests a uni-univalent complex formation.\(^{122-124}\) The magnetic moment of the complex is 5.84 BM at room temperature, suggesting the formation of
spin free complex with octahedral geometry and 5 unpaired electrons. The electronic spectra of the complex (Fig. 4.5) shows a symmetric broad band between 410-300 nm, which is due to $^6A_{1g} \rightarrow ^4A_{1g}$ transition in octahedral symmetry.

Interpretation of the IR spectra of the complex (Fig. 4.20) has been made with the help of IR spectra of the drug (Fig. 4.19). The infrared spectrum of Flurozepam hydrogen chloride is not reported but the assignment of bands in the present work has been carried out with the help of the IR spectra of relevant compounds, and the metallic complexes reported. A broad band appears in the region 3600-3100 cm$^{-1}$ which is due to $\equiv$C-H stretching vibration, unsymmetrically trisubstituted benzene ring stretching vibration and C=N-H stretching vibration in the spectra of the ligand as well as in the complex. A weak band at 2900 cm$^{-1}$ appears due to C-H stretching in CH$_2$ group in the ligand and in the complex both. In the spectra of the ligand two bands appear in the form of shoulder band at 2675 cm$^{-1}$ and 2355 cm$^{-1}$ which are absent in the spectra of the complex and are due to N-H$^+$ stretching and C=NH$^+$ stretching vibration. The absence of these bands shows the participation of this nitrogen atom in the coordination. A broad shoulder band
is obtained in the ligand and in the complex at region 1670-1640 cm\(^{-1}\), which is due to unsymmetrical trisubstituted benzene ring, ortho disubstituted benzene ring and C=O stretching vibration. A medium band observed at 1610 cm\(^{-1}\) in the spectra of the ligand as well as in complex is due to the \(\geq C=\overset{\text{N}}{C}\) stretching vibration.\(^{141-143}\) C-N stretching vibration (N in tertiary position) appears at 1450 cm\(^{-1}\) in the ligand and it shifts towards 1400 cm\(^{-1}\) in the complex. This shifting shows the participation of N atom in coordination.\(^{144}\) C-F stretching vibration appears near 1320 cm\(^{-1}\) in the ligand and in the complex, which shows no any contribution in coordination.\(^{145}\) 4 bands due to unsymmetrically trisubstituted benzene ring appear at 1260 cm\(^{-1}\), 940 cm\(^{-1}\), 920 cm\(^{-1}\) and 900 cm\(^{-1}\) in the form of medium peak in both spectra. The C-N stretching vibration appears in the form of a weak band at 1220 cm\(^{-1}\) in the spectra of the ligand as well as in the complex.\(^{146}\) C-N stretching frequency due to aromatic N and aliphatic carbon has been found in the same region in the ligand spectra and in the complex spectra. This shows that there is not any coordinate banding with metal atom.\(^{147,148}\) One broad band from 780 cm\(^{-1}\) to 750 cm\(^{-1}\) is due to C-Cl stretching vibration, C-H out of plane deformation of four adjacent free hydrogen atom,\(^{149}\) in the spectra of the ligand and in the complex. In the spectra of the complex the band at 480 cm\(^{-1}\) is due
to M-N stretching vibration $^{150-152}$ band at 390 cm$^{-1}$ is due to coordinated nitrogen atom $^{153-156}$ and band at 290 cm$^{-1}$ is due to M-Cl stretching vibration. These are absent in the spectra of the ligand. Figure 5.5 represents the structure of the complex molecule.
Fig. 5.5. Fe(III) complex with Flurazepam hydrogen chloride.
Table 5.3. Principal IR Frequencies (cm$^{-1}$) and their Assignment for Flurazepam hydrogen chloride and its Complex.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Fe(III) complex</th>
<th>Co(II) complex</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600</td>
<td>3600 br</td>
<td>3600 br</td>
<td>V=C-H in aromatic ring, unsymmetrically trisubstituted benzene ring</td>
</tr>
<tr>
<td></td>
<td>3100 br</td>
<td>3100 br</td>
<td>VC=N-H</td>
</tr>
<tr>
<td>2900 w</td>
<td>2900 w</td>
<td>2900 w</td>
<td>VC-H in CH$_2$</td>
</tr>
<tr>
<td>2675 sh</td>
<td>-</td>
<td>-</td>
<td>VN-H$^+$ vibration</td>
</tr>
<tr>
<td>2355 sh</td>
<td>-</td>
<td>-</td>
<td>VC=NH$^+$ vibration</td>
</tr>
<tr>
<td>1670 sh</td>
<td>1670 sh</td>
<td>1665 sh</td>
<td>unsymmetrically trisubstituted benzene ring stretching, ortho disubstituted benzene ring stretching</td>
</tr>
<tr>
<td>1640</td>
<td>1640</td>
<td>1640</td>
<td>VC=O vibration</td>
</tr>
<tr>
<td>1600 m</td>
<td>1610 m</td>
<td>1610 m</td>
<td>C=N-C stretching</td>
</tr>
<tr>
<td>1450 m</td>
<td>1400 m</td>
<td>1400 m</td>
<td>C-N in tertiary position</td>
</tr>
<tr>
<td>1320 m</td>
<td>1320 m</td>
<td>1320 m</td>
<td>VC-F vibration</td>
</tr>
<tr>
<td>1260 w</td>
<td>1255 w</td>
<td>1260 w</td>
<td>Trisubstituted benzene ring stretching</td>
</tr>
<tr>
<td>1220 sh</td>
<td>1200 w</td>
<td>1220 sh</td>
<td>VC-N in tertiary position</td>
</tr>
<tr>
<td>940 m</td>
<td>940 m</td>
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<td>Unsymmetrically trisubstituted benzene ring stretching vibration</td>
</tr>
<tr>
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<td>920 m</td>
<td>920 m</td>
<td></td>
</tr>
<tr>
<td>900 m</td>
<td>900 m</td>
<td>900 m</td>
<td></td>
</tr>
<tr>
<td>780 br</td>
<td>780 br</td>
<td>780 br</td>
<td>C-H out of plane deformation</td>
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<td>750</td>
<td></td>
</tr>
<tr>
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<td>480 m</td>
<td>480 m</td>
<td>M-N stretching vibration</td>
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<tr>
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<td>380 m</td>
<td>390 m</td>
<td>Coordinated N atom</td>
</tr>
<tr>
<td>290 m</td>
<td>290 m</td>
<td>290 m</td>
<td>VM-Cl vibration</td>
</tr>
</tbody>
</table>

Br=broad, w=weak, sh=shoulder, m=medium, s=sharp.
Co(II) Complex with Flurazepam Hydrogen Chloride

The general formula of the complex, which is proved by different investigations, is \([\text{Co(FA)}_2(\text{Cl})_2]\). Where FA denotes the molecule of Flurazepam and the chemical formula is \([\text{Co(C}_{21}\text{H}_{23}\text{ClN}_{3}\text{OF})_2(\text{Cl})_2]\). The colour of the complex is malechite green and is insoluble in common organic solvents but freely soluble in dimethyl formamide. The complex has low conductance value in \(10^{-3}\) M DMF solution which indicates non-electrolytic nature of the complex.\(^{157,158}\) The magnetic moment of the complex is found to be 4.3 BM, which indicates three unpaired electrons and six coordinated octahedral complex. In such a complex Co(II) can be assigned \(t_{2g}^5e_g^2\) state.\(^{159-161}\) The electronic spectra of the complex (Fig. 4.6) shows a broad band between 420-300 nm which is due to \(4T_{1g}(F)\rightarrow 4T_{1g}(P)\) transition in octahedral symmetry.\(^{162-164}\)

The assignment of IR bands in the complex (Fig. 4.21) has been carried out by comparison with the spectrum of the free ligand (Fig. 4.19) relevant compounds and metallic complexes.\(^{165-170}\) In the spectra of the ligand and in the complex, a broad band in the region 3600-3100 cm\(^{-1}\) is due to =C-H stretching of pyridine and benzene rings and C=N-H stretching vibration. A weak band at 2900 cm\(^{-1}\)
is due to C–H stretching vibration in CH$_2$ group, in the spectra of the ligand as well as in the complex. The two bands, due to NH$^+$ and C=NH$^+$ stretching, are obtained at 2675 cm$^{-1}$ and 2355 cm$^{-1}$ respectively in the spectra of the ligand. But these are absent in the spectra of the complex, suggesting involvement of this nitrogen atom in coordination.$^{171}$ In the spectra of the complex a broad band is obtained in the region 1665-1640 cm$^{-1}$ which is identical with the spectra of the ligand and is due to unsymmetrically trisubstituted benzene ring stretching vibration, C=O stretching vibration and ortho disubstituted benzene ring stretching vibrations.$^{172}$ A medium band observed at 1610 cm$^{-1}$ in the spectra of the ligand as well as in the complex is due to the C=N–C stretching vibration. C–N stretching vibration (N in tertiary position) appear at 1450 cm$^{-1}$ in the ligand and it shifts towards 1400 cm$^{-1}$ in the complex. This shifting shows the involvement of N atom in coordination.$^{173,174}$ C–F stretching vibration appears near 1320 cm$^{-1}$ in the complex and in the ligand also. Four medium bands due to unsymmetrically trisubstituted benzene ring appear at 1260 cm$^{-1}$, 940 cm$^{-1}$, 920 cm$^{-1}$ and 900 cm$^{-1}$ in the form of a medium peak in both the spectra. The C–N stretching vibration appears in the form of a weak band at 1220 cm$^{-1}$ in the spectra of the ligand as well as in the
Table 5.6. Co(II) complex with Flurazepam hydrogen chloride.
complex. This C-N stretching is due to aromatic nitrogen and aliphatic carbon, and is found to be the same in the spectra of ligand and the complex. This shows that there is not any coordination bonding with metal atom. One broad band, in the spectra of the ligand, is obtained in the region 780-750 cm$^{-1}$, which is due to C-Cl stretching vibration, C-H out of plane deformation of four adjacent free hydrogen atom and is similar to the spectra of the complex. In the spectra of the complex the band at 480 cm$^{-1}$ is due to M-N stretching vibration. The band at 380 cm$^{-1}$ is due to coordinated nitrogen atom. The band at 290 cm$^{-1}$ is due to M-Cl stretching vibration. These are absent in the spectra of the ligand. Figure 5.5 shows the structure of the complex.

**Conclusion**

Flurazepam is found to be a bidentate ligand. It is coordinated by the nitrogen atom, present in the ring and tertiary nitrogen atom of diethyl moiety. This structure of the complex is proved by different investigations. The structure of the complexes with Fe(III) and Co(II) is shown in Figure 5.5 and 5.6 respectively.
Diclofenac Sodium Complex

Diclofenac sodium is a phenyl acetic acid derivative which has Analgesic/Antipyretic/Antiinflammatory actions. Its chemical name is sodium\([2-(2,6\text{-dichloroanilino})\text{ phenyl}]\) acetate.

Different investigations suggest formation of 1:2, Metal : Ligand complexes with Fe(III) and Co(II) ions.

Fe(III) Complex with Diclofenac Sodium

The investigated general formula of the complex is \([\text{Fe(DF)\textsubscript{2}}] \text{Cl}\), where DF is the molecule of diclofenac sodium and the chemical formula of the complex is \([\text{Fe(C\textsubscript{14}H\textsubscript{10}Cl\textsubscript{2}NO\textsubscript{2}}\textsubscript{2}] \text{Cl}\). The complex is yellowish brown in colour and is soluble only in dimethyl formamide. Molar conductance of the complex has been measured in DMF, which shows a low value of 65.8 Ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\). This low value suggests a uni-univalent electrolytic nature of the complex.\(^{179,180}\) The magnetic moment of the complex is 5.5 BM indicating the presence of five unpaired electrons i.e. paramagnetic in nature. This value is well within the range of octahedral complex.\(^{181}\) The electronic spectra of the complex (Fig. 4.7) shows a symmetric band between 300-380 nm. Which is a combination
of three transitions assignable to the \( {6^A_{1g}} \rightarrow {4^T_{1g}} \) (P), 
\( {t_{2g}} \rightarrow J^* \) and \( \sigma \rightarrow \pi^* \) in the octahedral geometry.\textsuperscript{182,183}

Interpretation has been carried out with the help of IR spectra of the ligand (Fig. 4.22). In the spectra of the ligand and the complex (Fig. 4.23) the bands around 3600-3000 cm\(^{-1}\) were found to be common and did not shift from their position. They have been assigned to \( \equiv C-H \) stretching vibration, \( O-Na \) stretching vibration and \( N-H \) stretching vibrations.\textsuperscript{184} \( C=O \) absorption appears at 1720 cm\(^{-1}\) in the ligand but it shifted towards lower frequencies and appears at 1650 cm\(^{-1}\) showing the participation of \( C=O \) group in coordination.\textsuperscript{185} Four characteristic bands due to skeletal carbon-carbon stretching vibrations appear at 1600 cm\(^{-1}\) to 1535 cm\(^{-1}\) in the ligand as well as in the complex.\textsuperscript{186} A weak peak appears at 1480 cm\(^{-1}\) due to trisubstituted benzene ring stretching vibration in the ligand and also in the complex. A weak peak due to 1:2 disubstituted benzene ring stretching appears at 1200 cm\(^{-1}\) in the ligand and in the complex also. The band due to \( C=O \) group appears at 1450 cm\(^{-1}\) in the ligand but it shifts towards lower frequencies and appears at 1400 cm\(^{-1}\) in the form of sharp peak. This shifting is due to the involvement of \( COO^- \) group in the
coordination.\textsuperscript{187,188} C-O stretching band of C-ON\textsubscript{a} is observed in the region 1180 cm\textsuperscript{-1} in the spectra of the ligand. But in the spectra of the complex, shifting of this band is observed and is obtained at 1160 cm\textsuperscript{-1} with less intensity. It is due to displacement of N\textsubscript{a} atom from the ligand by metal ion through adjoining oxygen atom. An absorption due to C-Cl stretching appears at 770 cm\textsuperscript{-1} in the ligand and in the complex also.\textsuperscript{189} The bands in the region 400-475 cm\textsuperscript{-1} and bands in the region 750 cm\textsuperscript{-1} may be assigned to M-N and M-O stretching respectively.\textsuperscript{190,191} A medium band in the region 300-200 cm\textsuperscript{-1} is due to M-Cl stretching. The structure of the complex assigned by this spectra is shown in Figure 5.7.
Fig. 5.7. Fe(III) complex with Diclofenac sodium.
Table 5.4. Principal IR Frequencies (cm$^{-1}$) and their Assignment for Diclofenac sodium and its Complexes.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Fe(III) complex</th>
<th>Co(II) complex</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600 br</td>
<td>3600 br</td>
<td>3600 br</td>
<td>V=C-H in aromatic ring.</td>
</tr>
<tr>
<td>3000 br</td>
<td>3000 br</td>
<td>3000 br</td>
<td>VO-Na vibration</td>
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<tr>
<td>3000 br</td>
<td>3000 br</td>
<td>3000 br</td>
<td>VN-H vibration</td>
</tr>
<tr>
<td>1720 s</td>
<td>1650 s</td>
<td>1645 s</td>
<td>VC=O vibration</td>
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<tr>
<td>1565 m</td>
<td>1575 m</td>
<td>1575 m</td>
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<td>1550 m</td>
<td>1555 m</td>
<td>1555 m</td>
<td>Stretching vibration</td>
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<tr>
<td>1535 m</td>
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</tr>
<tr>
<td>1480 w</td>
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<td>Trisubstituted benzene ring stretching.</td>
</tr>
<tr>
<td>1450 s</td>
<td>1400 s</td>
<td>1400 s</td>
<td>VC=O in COO$^-$ group.</td>
</tr>
<tr>
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<td>1200 w</td>
<td>1200 w</td>
<td>Disubstituted benzene ring stretching</td>
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<td>1160 w</td>
<td>1160 w</td>
<td>VC-ONa vibration</td>
</tr>
<tr>
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<td>VC-Cl vibration</td>
</tr>
<tr>
<td>-</td>
<td>750 w</td>
<td>750 w</td>
<td>VM-O vibration</td>
</tr>
<tr>
<td>-</td>
<td>425 w</td>
<td>400 w</td>
<td>VM-N vibration</td>
</tr>
<tr>
<td>-</td>
<td>245 s</td>
<td>-</td>
<td>VM-Cl vibration</td>
</tr>
</tbody>
</table>

s = sharp, m = medium, w = weak, br broad.
Co(II) Complex with Diclofenac Sodium

The general formula of the complex, proved by different investigations, is \([\text{Co(DF)}_2]\) where DF is the molecule of Diclofenac sodium. Therefore the chemical formula of the complex is \([\text{Co(Cl}_{14}\text{H}_{10}\text{Cl}_{2}\text{NO}_2}_2]\). The complex is brown in colour, insoluble in other organic solvents but soluble in DMF. Molar conductance of the complex is measured in a dilute solution of DMF, which shows a low value indicating non-electrolytic nature of the complex.\(^{192,193}\) The magnetic moment of the complex indicates the presence of three unpaired electrons and its paramagnetic nature by a value i.e. 4.8 BM. This value is well within the range of octahedral complex.\(^{194,195}\)

The electronic spectra of the complex (Fig. 4.8) shows a band at 320 nm, which is due to drug metal charge transfer origin in octahedral geometry.\(^{196,197}\)

Infrared bands of the complex (Fig. 4.24) were assigned with the help of IR spectra of the ligand (Fig. 4.22). A broad band in the region 3600-3000 cm\(^{-1}\) is similar to the ligand. It is due to =C–H stretching vibration, O–Na stretching vibration and N–H stretching vibration.\(^{198}\) VC=O absorption appears at 1720 cm\(^{-1}\) in the ligand but in the complex it is found at 1645 cm\(^{-1}\) indicating
involvement of C=O group in coordination with metal atom. Four characteristic bands due to skeletal carbon-carbon stretching vibrations appear in a region 1600-1540 cm\(^{-1}\) in the spectra of the ligand as well as in the complex. A weak peak appears in the spectra of the complex, at 1480 cm\(^{-1}\) due to trisubstituted benzene ring stretching vibration, it is similar to the ligand spectra. Another weak band appears in the spectra of the complex at 1200 cm\(^{-1}\) due to 1:2 disubstituted benzene ring stretching vibration, it is also similar to the ligand spectra. The band due to COO\(^{-}\) group appears at 1450 cm\(^{-1}\) in the form of a sharp peak in the ligand spectra but shifts towards lower frequencies and appears at 1400 cm\(^{-1}\) as a sharp peak in the spectra of the complex. This shifting shows the participation of the group COO\(^{-}\) in coordination. \(^{201}\) C-O stretching band of C-ONA is observed in the region 1180 cm\(^{-1}\) in the spectra of the ligand. Shifting of this band towards lower frequency and also of weak intensity has been observed in the spectra of the complex at 1160 cm\(^{-1}\). It is due to displacement of Na atom from the ligand by Co(II) ion through adjoining oxygen atom. An absorption due to C-Cl stretching appears at 770 cm\(^{-1}\) in the ligand and in the complex also. \(^{202}\) The bands in the region 400-475 cm\(^{-1}\) and band in the region 750 cm\(^{-1}\) may be assigned to M-N and M-O stretching respectively. These are in good agreement with
Fig. 5.8. Co(II) complex with Diclofenac sodium.
the literature.\textsuperscript{203-214} The structure of the complex is shown in the Figure 5.8.

\textbf{Conclusion}

On the basis of above discussion it may be inferred that Diclofenac sodium forms 1:2, metal : ligand complexes with Fe(III) and Co(II) ions. In Fe(III) complex one Cl ion is present and the complex shows uni-univalent electrolytic nature, while Co(II) complex is non-electrolytic in nature. Analytical data proves the structure of the complexes and are represented as in the figure 5.7 and 5.8 respectively.
Cefadroxil Complexes

Cefadroxil is a Cephalosporin antibiotic. Its chemical name is \((6R,7R)-7-[(R)-2-Amino-2-(p-hydroxyphenyl)acetamido]-3-methyl-8-oxo-5-thia-1-azabicyclo octa-2-ene-2-carboxylic acid.\)

Analytical investigation proves 1:2 Metal : Ligand stoichiometry for the complexation with Fe(III) and Co(II) ions.

Fe(III) Complex with Cefadroxil

According to analytical investigations the general formula of complex should be \([\text{Fe(CD)}_2(\text{H}_2\text{O})(\text{Cl})]\) and the chemical formula is \([\text{Fe(C}_{16}\text{H}_{16}\text{N}_3\text{O}_5}\text{S})_2(\text{H}_2\text{O})(\text{Cl})]\). The complex is black in colour and is soluble only in DMF. A slow value of molar conductance shows non-electrolytic nature of complex. The magnetic moment of the complex is 5.9 BM indicating the presence of five unpaired electrons i.e. paramagnetic in nature. This value is well within the range of octahedral complex. The electronic spectra of the complex (Fig. 4.9) shows a band at 400 nm, which is due to \(6\text{A}_{1g} \rightarrow 4\text{A}_{1g}\) transition and is proves the octahedral symmetry.
Infrared spectra of the complex (Fig. 4.26) was assigned with the help of IR bands of the ligand (Fig. 4.25). A broad band in the region 3500-3000 cm\(^{-1}\) in the spectra of the ligand as well as in the complex is due to OH stretching, =C-H stretching and N-H stretching vibrations.\(^{218}\) A weak shoulder band at 1890 cm\(^{-1}\), in the spectra of the ligand, is due to overtones of benzanoid group, but it disappears in the spectra of the complex. Which shows the participation of benzanoid group in coordination.\(^{219}\) Absorptions due to NH\(_2\) group, in the spectra of the ligand as well as in the complex, are \(\sim 3300\) cm\(^{-1}\), \(\sim 1600\) cm\(^{-1}\), \(\sim 1300\) cm\(^{-1}\), \(\sim 800\) cm\(^{-1}\). These absorptions are due to N-H stretching, asymmetric deformation, symmetric deformation and NH\(_2\) rocking mode respectively.\(^{220,221,222}\) Absorption due to C=O stretching vibration appears at two positions 1685 cm\(^{-1}\) and 1675 cm\(^{-1}\), first is due to C=O stretching vibration in open chain\(^{223}\) and the second is due to C=O stretching vibration in the four membered ketone ring.\(^{224}\) A broad shoulder band with several peaks appears in the region 1600-1500 cm\(^{-1}\) in the ligand and at 1600-1540 cm\(^{-1}\) in the complex due to benzene ring stretching vibration.\(^{225}\) In the spectra of the ligand and the complex, a medium band at 1450 cm\(^{-1}\) is due to C-H deformation mode in CH\(_3\).
group. A broad band at 1395-1370 cm$^{-1}$ and 1390-1370 cm$^{-1}$ in the ligand and the complex respectively is due to C-O stretching and OH deformation vibrations. A shoulder band at 1340 cm$^{-1}$ is due to C-N stretching vibration where N is in tertiary position, this absorption is similar to the ligand spectra. Absorption due to C-N stretching, N in secondary position, appears at 1280 cm$^{-1}$ in the form of a medium band in the ligand and in the complex. Absorption due to phenolic OH bending vibration, appears at 1200 cm$^{-1}$ in the ligand as well as in the complex. A weak band appears at 950 cm$^{-1}$ due to OH deformation mode in the spectra of the complex and in the ligand. In the spectra of the ligand N-H wagging vibration appears at 750 cm$^{-1}$, it is similar to the complex. A peak due to C-S-C linkage at 635 cm$^{-1}$ is same in the ligand and the complex. The non ligand bands in complex spectra observed in the region 480-460 cm$^{-1}$ are assigned to M-O stretching modes. The non ligand band at 360 cm$^{-1}$ indicates the linkage of Cl atom with metal atom. The structure of the complex proved by the investigation is shown in Figure 5.9.
Fig. 5.9. Fe(III) complex with Cefadroxil.
Table 5.5. Principal IR Frequencies (cm\(^{-1}\)) and their Assignment for Cefadroxil and Its Complexes.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Fe(III) complex</th>
<th>Co(II) complex</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>VO-H vibration</td>
</tr>
<tr>
<td>3500 br</td>
<td>3500 br</td>
<td>3500 br</td>
<td>V=C-H in aromatic ring</td>
</tr>
<tr>
<td>3000</td>
<td>3000 br</td>
<td>3000 br</td>
<td>VN-H in NH(_2)</td>
</tr>
<tr>
<td>1890 m</td>
<td></td>
<td></td>
<td>Overton of benzanoid group</td>
</tr>
<tr>
<td>1685 sh</td>
<td>1680 sh</td>
<td>1680 sh</td>
<td>VC=O in open chain</td>
</tr>
<tr>
<td>1675 sh</td>
<td>1650 w</td>
<td>1555 w</td>
<td>VC=O in close chain</td>
</tr>
<tr>
<td>1600</td>
<td>1600 w</td>
<td>1600 w</td>
<td>Benzene ring skeletal stretching vibration</td>
</tr>
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<td>1500 br</td>
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<td>1575 w</td>
<td></td>
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<td></td>
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<td>1555 w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1540 w</td>
<td>1540 w</td>
<td></td>
</tr>
<tr>
<td>1450 m</td>
<td>1450 m</td>
<td>1450 m</td>
<td>C-H deformation of CH(_3)</td>
</tr>
<tr>
<td>1395</td>
<td>1390 br, sh</td>
<td>1395 br, sh</td>
<td>C-H deformation of CH(_3)</td>
</tr>
<tr>
<td>1370 br, sh</td>
<td>1370 br, sh</td>
<td>C=O stretching vibration and O-H deformation vibration</td>
<td></td>
</tr>
<tr>
<td>1340 sh</td>
<td>1340 sh</td>
<td>1340 sh</td>
<td>VC-N in tertiary position</td>
</tr>
<tr>
<td>1280 m</td>
<td>1280 m</td>
<td>1280 m</td>
<td>VC-N in secondary position</td>
</tr>
<tr>
<td>1200 m</td>
<td>1200 m</td>
<td>1200 m</td>
<td>O-H bending of phenolic</td>
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<tr>
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<td>950 m</td>
<td>950 m</td>
<td>O-H deformation</td>
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<td>750 m</td>
<td>750 m</td>
<td>N-H wagging</td>
</tr>
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<td>635 w</td>
<td>635 w</td>
<td>635 w</td>
<td>VC-S-C vibration</td>
</tr>
<tr>
<td>480 s</td>
<td>480 s</td>
<td>480 s</td>
<td>VM-O vibration</td>
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<tr>
<td>460 s</td>
<td>460 s</td>
<td>460 s</td>
<td>VM-O vibration</td>
</tr>
<tr>
<td>360 s</td>
<td></td>
<td>360 s</td>
<td>VM-Cl vibration</td>
</tr>
</tbody>
</table>

s = sharp, sh=shoulder, m = medium, w = weak, br = broad.
Co(II) Complex with Cefadroxil

Analytical investigation suggests the general formula \([\text{Co(CD)}_2(\text{H}_2\text{O})_4]\) and the chemical formula \([\text{Co(C}_6\text{H}_{16}\text{N}_3\text{O}_5\text{S})_2(\text{H}_2\text{O})_4]\) of the complex. It is black in colour and is soluble in DMF. Molar conductance of the complex is too much low and shows a value 9.34 Ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in 10\(^{-3}\)M DMF solution suggesting the non-electrolytic nature of the complex. The magnetic moment of the complex suggests three unpaired electrons with octahedral symmetry, it is, 5.1 BM\(^{234}\). The electronic spectra of the complex (Fig. 410) shows a band at 320 nm, which is due to drug-metal charge transfer in octahedral symmetry around the Co(II) ions.\(^{235-237}\)

Infrared spectral data of complex (Fig. 4.27) was studied with the help of the spectra of the ligand (Fig. 4.25). A broad band in the region 3500-3000 cm\(^{-1}\) is due to \(=\text{C-H}\) stretching. OH stretching and N-H stretching vibration in both the spectra but in the complex also due to coordinated water molecule.\(^{238-240}\) Overtones due to benzanoid groups appear at 1890 cm\(^{-1}\) in the ligand and disappears in the spectra of the complex, suggesting the participation of benzanoid group in coordination. NH\(_2\) group shows absorption in the region \(\sim 3300\) cm\(^{-1}\), \(\sim 1600\) cm\(^{-1}\), \(\sim 1300\) cm\(^{-1}\).
and $\sim 800 \text{ cm}^{-1}$ in the spectra of the ligand and the complex. These absorptions are due to N-H stretching mode, asymmetric deformation, symmetric deformation and NH$_2$ rocking mode respectively.\textsuperscript{241} In the spectra of the ligand the C=O stretching vibration appears in two positions at 1685 cm$^{-1}$ and 1675 cm$^{-1}$, the former is due to C=O stretching in open chain and the latter is due to C=O stretching in four-membered ketone ring. In the complex the latter is shifted towards lower frequencies and appear at 1650 cm$^{-1}$ and shows participation of this C=O in coordination.\textsuperscript{242,243} A broad shoulder band with several peaks appears in the region 1600-1500 cm$^{-1}$ in the ligand and at 1600-1540 cm$^{-1}$ in the complex due to benzene ring stretching vibration. A medium band at 1450 cm$^{-1}$ in both, the ligand and the complex, is due to C-H deformation in CH$_3$.\textsuperscript{244} A broad band at 1395-1370 cm$^{-1}$ and 1400-1380 cm$^{-1}$ in the ligand and the complex respectively are due to C-O stretching and OH deformation vibrations.\textsuperscript{245} A shoulder band at 1340 cm$^{-1}$ is due to C-N stretching vibration, where N is in tertiary position, this absorption is similar to the ligand spectra. Absorption due to C-N stretching (N in secondary position) appears at 1280 cm$^{-1}$ in the form of a medium band in the ligand and in the complex. Absorption due to phenolic OH bending vibration appears at 1200 cm$^{-1}$ in the spectra of the ligand as well as in the complex.\textsuperscript{246} One peak at
Fig. 5.10. Co(II) complex with Cefadroxil.
950 cm\(^{-1}\) due to O-H deformation appears in both the spectra.\(^{247,248}\) A peak due to C-S-C linkage at 635 cm\(^{-1}\) is the same in the spectra of the ligand and the complex.\(^{249}\) M-O stretching vibration appears in the region 480-460 cm\(^{-1}\) in the spectra of the complex. The structure of the complex molecule is shown in the figure 5,10.

**Conclusion**

On the basis of above discussion it may be inferred that Cefadroxil forms 1:2, Metal : Ligand complexes with Fe(III) and Co(II) ions. IR spectra proves the participation of H\(_2\)O molecule in coordination in both the complexes. In Fe(III) complex one Cl ion present and the complex shows uni-univalent electrolytic nature. Analytical data support the structural formula of complexes.
**Norfloxacin Complexes**

Norfloxacin is a new 4-quinoline antibacterial agent. Its chemical name is 1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(piperazin-1-yl)quinoline-3-carboxylic acid.

Present investigation suggests a 1:2, metal : ligand stoichiometry for the complexation with Fe(III) and Co(II) ion.

**Fe(III) Complex with Norfloxacin**

Present investigations inferred the formula of complex as \([\text{Fe(C}_16\text{H}_{13}\text{FN}_3\text{O}_3)_2\text{(H}_2\text{O})(\text{Cl})]^{-}\). The colour of the complex is straw orange and is soluble only in DMF. A low value of molar conductance suggests non-electrolytic nature of the complex. The magnetic moment of the complex is 5.9 BM, suggesting five unpaired electrons, i.e. paramagnetic in nature. This value inferred the octahedral geometry around Fe(III) ion\(^{250}\). The electronic spectra of the complex (Fig. 4.11) shows a broad symmetric band at 380-320 nm, which is due to \(4\text{A}_{1g} \rightarrow 6\text{A}_{1g}\) transition with octahedral geometry.\(^{251,252}\)

Infrared spectra bands (Fig. 4.29) were assigned
with the help of IR spectra of the ligand (Fig. 4.28). In broad band around the region 3600–2900 cm\(^{-1}\) were found to be common, which is due to O–H stretching vibration and V=C–H vibration in the ligand and in the complex due to O–H stretching in coordinated water and =C–H stretching vibration.\(^{253}\) The VC=O vibration appears at 1720 cm\(^{-1}\) in ligand and shifts towards 1670 cm\(^{-1}\) indicating involvement of C=O group in coordination.\(^{254}\) In the spectra of the ligand a shoulder band at 1640 cm\(^{-1}\) to 1600 cm\(^{-1}\) indicates benzene ring skeleton stretching vibration, which is similar to the spectra of the complex.\(^{255}\) Absorption due to substituted benzene ring appears in the form of a shoulder band at 1530–1440 cm\(^{-1}\) in the spectra of the ligand as well as in the complex.

The band at 1390 cm\(^{-1}\) is due to C–F stretching vibration in both the spectra.\(^{256}\) Absorption due to the C–N stretching, where N is in tertiary position appears at 1320 cm\(^{-1}\) (± 10 cm\(^{-1}\)) in the complex and in the ligand spectra. And on other absorption due to C–N stretching (N is in secondary position) appears at 1300 cm\(^{-1}\) in both, the spectra of the ligand and the complex.\(^{257}\) C–H twisting and wagging modes appear in the form of a shoulder band at 1280–1230 cm\(^{-1}\) in the ligand and in the complex. Band at 880 cm\(^{-1}\) is due to C–H out of plane summation.\(^{258}\) Two bands appear due to C–H out of plane deformation
in benzanoid group in both the spectra are at 810 cm$^{-1}$ and 630 cm$^{-1}$. C-N-C bending vibration appears at 510 cm$^{-1}$ in both the spectra. In the spectra of the ligand, a shoulder band at 470 cm$^{-1}$ is due to 1,2,4 tri-substituted aromatic ring, which is similar to the spectra of the complex. The non-ligand bands appear at 475 cm$^{-1}$ and 540 cm$^{-1}$, which are assignable M-O stretching. The analytical data and IR spectral data suggests a structure for the complex which is shown in Figure 5.11.
Fig. 5.11. Fe(III) complex with Norfloxacine.
## Table 5.6. Principal IR Frequencies (cm\(^{-1}\)) and their Assignment for Norfloxacin and its complexes.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Fe(III) complex</th>
<th>Co(II) complex</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600 br</td>
<td>3600 br</td>
<td>3600 br</td>
<td>VO-H vibration</td>
</tr>
<tr>
<td>2900 br</td>
<td>2900 br</td>
<td>2900 br</td>
<td>V=C-H in aromatic ring</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>VO-H in coordinated water</td>
</tr>
<tr>
<td>1720 s</td>
<td>1670 s</td>
<td>1675 s</td>
<td>VC=O vibration</td>
</tr>
<tr>
<td>1640 br</td>
<td>1640 br</td>
<td>1640w</td>
<td>Benzene ring skeletal stretching vibration</td>
</tr>
<tr>
<td>1600 br</td>
<td>1600 br</td>
<td>1585w</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1535w</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1500w</td>
<td></td>
</tr>
<tr>
<td>1500 br, sh</td>
<td>1530 br, sh</td>
<td>1450 sh</td>
<td>Substituted benzene ring stretching vibration</td>
</tr>
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</tr>
<tr>
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<td>1390 w</td>
<td>1385 w</td>
<td>VC-F vibration</td>
</tr>
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<td>1320 w</td>
<td>VC-N (N in tertiary position)</td>
</tr>
<tr>
<td>1300 w</td>
<td>1300 w</td>
<td>1300 w</td>
<td>VC-N (N in secondary position)</td>
</tr>
<tr>
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<td>1280 sh</td>
<td>1280 sh</td>
<td>C-H twisting and wagging vibration</td>
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<td>1230 sh</td>
<td>1230 sh</td>
<td>1230 sh</td>
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</tr>
<tr>
<td>880 w</td>
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<td>C-H out of plane deformation</td>
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<td>in benzenoid aromatic</td>
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<td>630 w</td>
<td>630 w</td>
<td>ring</td>
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<tr>
<td>510 w</td>
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<td>510 w</td>
<td>C-N-C bending vibration</td>
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<td>575</td>
<td>580</td>
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<tr>
<td></td>
<td>540</td>
<td>450</td>
<td>M-O stretching</td>
</tr>
</tbody>
</table>

*Br = broad, s = sharp, w = weak, sh = shoulder, m = medium.*
**Co(II) Complex with Norfloxacin**

The investigated formula of the complex is \([\text{Co(C}_{16}\text{H}_{13}\text{FN}_{3}\text{O}_{3})_{2}(\text{H}_{2}\text{O})_{2}]\) and the colour of the complex is buff. The complex is only soluble in DMF. A low value (\(\lambda_{m} = 7.91 \text{ Ohm}^{-1} \text{ cm}^{2} \text{ mol}^{-1}\)) of molar conductance suggests a non-electrolytic nature of the complex. The value of magnetic moment (\(\mu_{\text{eff}} = 5.2 \text{ BM}\)) suggests three unpaired electrons and paramagnetic nature of the complex, which confirms the octahedral symmetry.\(^{263}\) The electronic spectra of the complex (Fig. 4.12) shows a broad symmetric band at 370-310 nm, which is due to \(4\text{T}_{1g}(\text{F}) \rightarrow 4\text{T}_{1g}(\text{P})\) transitions with octahedral geometry.\(^{264}\)

Infra-red spectra (Fig. 4.30) is analysed with the help of the spectra of the ligand (Fig. 4.28). A broad band in the region 3600-3300 cm\(^{-1}\) were found to be common in the spectra of the ligand and the complex. It is due to O-H stretching vibration and V=C-H vibration in the ligand and in the complex also due to coordinated water molecule.\(^{265}\) Vibration due to C=O stretching appears at 1720 cm\(^{-1}\) in ligand but it shifts towards lower frequencies in the complex and appears at 1675 cm\(^{-1}\) indicating the involvement of C=O group in coordination.\(^{266}\)
Four weak bands appear due to benzene ring skeletal stretching at 1600 cm\(^{-1}\), 1585 cm\(^{-1}\), 1535 cm\(^{-1}\) and at 1500 cm\(^{-1}\) in the complex but in the ligand these bands appear in the form of a shoulder band. Absorption due to substituted benzene ring appears in the form of a shoulder band at 1450-1420 cm\(^{-1}\) in the complex. The band due to C-F stretching obtained at 1385-cm\(^{-1}\) in the spectra of the complex.\(^{267}\) Two absorption bands appear at 1320 cm\(^{-1}\) and at 1300 cm\(^{-1}\), the former is due to C-N stretching (N is in tertiary position) and the latter is due to C-N stretching (nitrogen in secondary position) in both the spectra. C-H twisting mode appears at 1240 cm\(^{-1}\) in the spectra of the complex. Absorptions due to C-H out of plane appear at 865 cm\(^{-1}\), 810 cm\(^{-1}\), 680 cm\(^{-1}\) and 630 cm\(^{-1}\), which is similar to the spectra of the ligand. C-N-C bending vibration appears at 560 cm\(^{-1}\). The non-ligand bands appear at 580 cm\(^{-1}\) and at 450 cm\(^{-1}\) which are due to M-O stretching.\(^{268}\) The structural formula is shown in Figure 5.12 and is proved by present investigations i.e. IR electronic spectra and other experimental results.

**Conclusion**

On the basis of the above discussion it may be inferred that Norfloxacin forms 1:2, Metal:Ligand complex with both the ions. IR spectra proves the involvement of H\(_2\)O molecule in coordination and analytical data suggests the presence of one H\(_2\)O molecule in Fe(III) complex and two H\(_2\)O molecules in Co(II) complex.
Fig. 5.12. Co(II) complex with Norfloxacine.
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