CHAPTER V

Results
And
Discussions
In the present investigation 20 complexes of five metals namely manganese (II), Iron (III), Nickel (II), Copper (II) and Zine (II) with different drugs like nalidixic acid, norfloxacin, ciprofloxacin and cloxacillin have been prepared and studied. The compounds have been characterized on the basis of elemental analysis, molar conductance, magnetic measurements, electronic and infrared spectral data.

On the basis of elemental analysis the molecular formula of the complexes, their individual colours and decomposition temperature have been reported in the chapter IV.

STEREO CHEMISTRY OF THE COMPLEXES

General:

To deal with the subject of co-ordination compounds, it is necessary to have a clear conception of what a coordination compound is. If a simple electron acceptor molecule or cation is brought in contact with electron donor molecule or an anion and combination takes place, the product is a complex ion or complex compound depending upon whether it is charged or neutral. In a complex compound formula, central metal ion and ligands are enclosed in a square bracket. The entire material within brackets functioning as an ion in each case while everything present outside the brackets is also being ionic in nature. The portion so enclosed inside the square bracket is called coordination sphere.

The total number of ions present inside and outside the co-ordination sphere can be determined by measuring the molar conductance of the complex solution in very dilute condition. When the number of co-ordinated anions are 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.\textsuperscript{1-12} In the present investigation molar conductance of the complexes was measured using 10\textsuperscript{-3} M methanol and DME solution. The measurement of molar conductance gave value less than 50 ohm\textsuperscript{-1} cm\textsuperscript{2} mol\textsuperscript{-1} in nalidixic acid, norfloxacin, ciprofloxacin and cloxacillin complexes. The low value of molar conductance below 60 ohm\textsuperscript{-1} cm\textsuperscript{2} mol\textsuperscript{-1} indicated that complexes are non-electrolytic in nature. nalidixic acid Mn (II) complex and Cloxacillin Ni (II) complex were found insoluble in all the solvents tried. So it is not possible to measure their molar conductance.

Magnetic susceptibility measurements have been helpful in deciding the stereochemistry and configuration of the complexes. Magnetic moments were measured at room temperature by Gouy's method using CuSO\textsubscript{4}.5H\textsubscript{2}O as Calibrant.\textsuperscript{13-14}

**MANGANESE (II) COMPLEXES :**

(a) Magnetic Measurements :

Mn (II) electronic structure possess the [Ar] [3d]\textsuperscript{5} configuration. The magnetic susceptibility of manganous salts and complexes have been reviewed by Van-Vleck et al.\textsuperscript{15} and Goldenberg.\textsuperscript{16} The ground level of the 3d\textsuperscript{5} electron system of the free Mn\textsuperscript{2+} is 6s. On the basis of Russelt-Saunders coupling, Mn\textsuperscript{2+} ion should have 5.92 BM as its magnetic moment. But if the manganous ion is the central ion in the complexes considerable deviation in the magnetic moment values is expected. According to valence bond theory manganous ion should have three values for magnetic moment viz. 5.92 BM., 3.87 BM and 1.73 BM\textsuperscript{17} as shown below :
Type of Mn (II) complexes and their geometries-

<table>
<thead>
<tr>
<th>Ground State</th>
<th>No. of unpaired electrons</th>
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<tbody>
<tr>
<td>(i) Mn (II)</td>
<td>5</td>
</tr>
<tr>
<td>3d</td>
<td>4s</td>
</tr>
<tr>
<td>4p</td>
<td>4d</td>
</tr>
<tr>
<td>(ii) Spin free octahedral</td>
<td>5</td>
</tr>
<tr>
<td>3d</td>
<td>4s</td>
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<td>xx</td>
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<td>L</td>
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<tr>
<td>4p</td>
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<td>xx</td>
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<td>L</td>
<td>L</td>
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<tr>
<td>(iii) Spin paired octahedral</td>
<td>1</td>
</tr>
<tr>
<td>3d</td>
<td>4s</td>
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<td>xx</td>
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<td>4p</td>
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<td>xx</td>
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<td>L</td>
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<tr>
<td>(iv) Spin free tetrahedral</td>
<td>5</td>
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<tr>
<td>3d</td>
<td>4s</td>
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<td>xx</td>
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<td>L</td>
<td>L</td>
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<tr>
<td>(v) Spin paired square planar</td>
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<tr>
<td>3d</td>
<td>4s</td>
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<td>xx</td>
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<td>4p</td>
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<td>L</td>
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</table>

The free Mn (II) contains five unpaired electrons, in the presence of ligands around Mn (II) depending upon their number, two possibilities exist: (i) If the coordination number of Mn (II) is four only, in one condition the electron arrangement of the ion is not altered and 3d level remain as such. The next four vacant orbitals available for ligands are one 4s and three 4p and the hybridisation is $4sp^3$. In the tetrahedral structure Mn (II) complexes have a moment of 6.8 BM$^{18}$.

In other event, if the ion is approached by four comparatively strong ligand, the ligands electrons occupy one 3d, one 4s and two 4p orbitals and hybridization is $dsp^2$ and the geometry of the complex is square planer with the low magnetic moment value for three unpaired electron.

(ii) If six ligands approach Mn (II), the electronic arrangement of 3d orbitals usually do not change as six desired orbitals are already available and these are
one 4s, three 4p and two 4d and hybridization is 4sp³d² [in high spin, outer orbital complexes] and the geometry of the complex is octahedral.

There is another possibility which theoretically exists, but is very seldom found in complexes and that is the four electrons are paired and one is unpaired. For such complexes, the hybridization is d²sp³ [in low spin, inner orbital complexes]. In the formation of inner orbital complexes since pairing of d electrons, this process requires energy to be spent, the ion becomes unstable.

(b) Electronic Absorption Measurements:

On the basis of magnetic moment data, complexes of Mn (II) have five unpaired electrons it means that the system of Mn (II) complexes is d³. This system shows that the only high spin state Russell-Saunders term is 6S which in an octahedral geometry changes its ground state term ⁶A₁g. Since there is no excited state with the spin multiplicity 6, all electronic transitions in a high spin d³ complex are doubly forbidden. In fact, it is difficult to locate these double forbidden transition, some of the transitions are.²⁹⁻²⁰

\[
⁶A₁g \rightarrow ^{4}T_{1g} \quad 18,600 \text{ cm}^{-1}
\]

\[
\rightarrow ^{4}T_{2g} \quad 22,900 \text{ cm}^{-1}
\]

\[
\rightarrow ^{4}E_{g} \quad 24,900 \text{ cm}^{-1}
\]

\[
\rightarrow ^{4}A₁g \quad 25,150 \text{ cm}^{-1}
\]

The electronic spectra suggest that the metal ion can be octahedral, tetrahedral or square planar environments depending upon the complexation with ligands. ²¹⁻²⁴
IRON (III) COMPLEXES

(a) Magnetic Measurements:

Iron (III) is isoelectronic with Mn (II), Fe (III) possesses the d⁵ configuration. Only hexacoordinated 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 [derived from the 6S state of the free ion] has no orbital angular momentum and there in no effective mechanism for introducing any coupling with excited states. The low spin complexes with d⁵ configurations usually have considerable orbital contributions to their moments at around room temperature, values of ~ 2.3 BM being obtained.

The moments are, however, intrinisically temperature dependent, and at liquid nitrogen temperature (77⁰K) they decrease to ~ 1.9 BM. In the present work the magnetic moment value of the complexes indicate that the isolated complexes are spin free with octahedral structure.²⁵ It has been shown that in certain complexes, the ligand field strength is such that the ⁶A₁, and ²T₂ states are of nearly equal stability. The dependence of magnetic susceptibility and the electronic spectra therefore exhibit quite complicated behavior as a function of temperature.²⁶

<table>
<thead>
<tr>
<th></th>
<th>3d</th>
<th>4s</th>
<th>4p</th>
<th>4d</th>
<th>electron</th>
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<tbody>
<tr>
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<td>1l</td>
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<tr>
<td>Fe (III) ion</td>
<td>1111</td>
<td></td>
<td></td>
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<td>4</td>
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<tr>
<td>Ground state</td>
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<td>5</td>
</tr>
<tr>
<td>Fe (III) ion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Octahedral complex</td>
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<td></td>
</tr>
</tbody>
</table>

No. of unpaired sp³d² hybridization
(b) **Electronic Absorption Measurements**:

Although the energy level diagram 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 environment are (a) the weakness of the bands, (b) the large 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 d⁵ 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 electronic distribution $t_{2g}^3e_g^2$, with all spins parallel, results in the pairing of two or four spins thus making quartet or doublet states, hence, all excited states of the d⁵ system have different spin multiplicity from the ground state and the transition to them are spin forbidden. Because of weak spin orbit interactions, 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.

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

$$
\rightarrow {^4}T_{2g} \ (G) \ 23,000 \ \text{cm}^{-1}
$$

$$
\rightarrow {^4}E_g \ (G) \ 24,900 \ \text{cm}^{-1}
$$

$$
\rightarrow {^4}A_{1g} \ (G) \ 25,150 \ \text{cm}^{-1}
$$
NICKEL (II) COMPLEXES

(a) Magnetic Measurements:

Ni (II) complexes possess the [Ar] [3d]⁸ configuration. Two types of complexes have been isolated, one having tetra co-ordinated metal atom and the other having hexa co-ordinated metal atom. The 3d⁸ electronic configuration of Ni (II) leaves two unpaired electrons in 3d orbital, resulting in a paramagnetic nature of Ni (II) ground state with a magnetic moment of 2.88 BM (i.e. spin only value). The ligand electrons occupy the vacant orbitals resulting in octahedral, tetrahedral and square planar symmetries depending upon the nature of hybridization.

In case of octahedral Ni (II) complexes, the temperature independent magnetic moment lies in the range of 2.9 - 3.4 BM the value being higher than the corresponding spin only values. Ni (II) octahedral complexes possess 4sp³d⁵ hybridization with triplet ground state ⁴A₂g of Ni (II).

In tetra-coordinated complexes of Ni (II) two groups of magnetic moments are generally observed. One group of complexes is paramagnetic with values of magnetic moments in the range 3.3 - 4.0 BM where as the other group is diamagnetic having a value of μeff less than one.
The paramagnetic four coordinated complexes have been supposed to be tetrahedral in symmetry with 4sp³ hybridization.

Several workers 27-28 have reported the structure of yellow diamagnetic Ni (II) complexes to be square planar. Yellow complexes of Ni (II) possess magnetic moment less than 1 BM.29 If the ligand is strong enough, the two unpaired electron of the 3d levels are forced into one and they are paired.30 In general, the square planar complexes of Ni (II) have been assigned dsp² hybridization D₄h symmetry.31

In such hybridization the four pairs of co-ordinated electrons distribute themselves, one in 3d, one in 4s, and two in 4p orbitals resulting in the only possible square planar D₄h symmetry. There are two factors responsible for the formation of tetrahedral and square planar complexes. Increase of electronegativity favours the tetrahedral configuration.32 Second factor is the anion contribution perturbing effects and steric effects.33

(b) Electronic Absorption Measurements:

All the isolated Ni (II) complexes are coloured and absorb in visible region. Octahedral complexes of Ni (II) have been extensively studied. 34-36

There are transitions at:

\[
\begin{align*}
^3A_{2g} & \rightarrow \ ^3T_{2g} (F) & 8,600 \text{ cm}^{-1} (10,700) \\
& \rightarrow \ ^3T_{1g} (F) & 13,500 \text{ cm}^{-1} (17,000) \\
& \rightarrow \ ^3T_{1g} (P) & 25,300 \text{ cm}^{-1} (28,200)
\end{align*}
\]

for weak fields, other transition at 15,400, 18,500 and 25,500 cm⁻¹ have been observed.37-38 With d⁹ configuration of Ni (II) a considerable John Taller
distortion effect is observed. This distortion is responsible for the formation of yellow diamagnetic complexes of Ni (II). 39

Ballausen 40 has shown that at least 3-4 transition are expected in octahedral Ni (II). The observed peaks in Ni (II) can be assigned as follows.

\[ \begin{align*}
^3A_{2g} & \rightarrow \; ^3T_{2g} \quad 10,800 \text{ cm}^{-1} \\
& \rightarrow \; ^1E_g \quad 12,500 \text{ cm}^{-1} \\
& \rightarrow \; ^3T_{1g} (F) \quad 18,700 \text{ cm}^{-1} \\
& \rightarrow \; ^3T_{1g} (P) \quad 28,600 \text{ cm}^{-1}
\end{align*} \]

It is clear from the energy level diagram in figure [4.1] that in octahedral field such complexes have ground state \(^3A_{2g}(t_{2g})^6(e_g)^2\) and they will possess two unpaired spins. The three absorption bands corresponding to the transitions are expected having the energies.

![Energy Level Scheme for the Triplet State in Octahedrally Coordinated Ni (II) Complexes](image)

\[ \begin{align*}
^3A_{2g} (F) & \rightarrow \; ^3T_{2g} (F) : \quad \nu_1 = 10 \text{ Dq.} \\
& \rightarrow \; ^3T_{1g} (F) : \quad \nu_2 = 15 \text{ Dq} + [15/2] \text{ B-Q} \\
& \rightarrow \; ^3T_{1g} (P) : \quad \nu_3 = 15 \text{ Dq} + [15/2] \text{ B+Q}
\end{align*} \]

Where, \(Q = 1/2 [(15B-6Dq)^2+64(Dq)^2]^{1/2}\)
Observation and assignments to the two bands allow the simultaneous solution of these equation for both Dq and B. The lowering of 3P state in the complex compared to the energy of 3P state in the free gaseous ion (1030 cm⁻¹).

\[ \beta = B' \text{ Complex ion/ B free ion} \]

The electronic spectra of six co-ordinated Ni (II) complexes exhibit only two d-d bands, \( \nu_1 \) and \( \nu_2 \) in visible and near IR region. The characteristic ratio \( \frac{\nu_2}{\nu_1} \) for the octahedral complexes lies between 1.6-1.8. It is noticed that second absorption band, Corresponding to the transition \( ^3A_{2g} (F) \rightarrow ^3T_{1g} (F) \) is a double-peak in some cases. This double peak is due to the closeness of \( 1E_g \) state coming from \(^1D\) but in view of the calculation of Liehr and Ballhausen who solved the complete energy level diagram for \( 3d^8 \) with spin-orbit coupling included, this explanation does not appear very reasonable. It is observed that \(^1E_g\) (\( T_1 \)) levels never approaches very closely to any triplet \( T_3 \) level, making the assignment doubtful.

On consultation with energy level diagram in Fig (4.1) and other data the visible absorption bands for tetra co-ordinated Ni (II) complexes have been assigned the following transitions:

- \( T_1 (F) \rightarrow T_1 (P) \quad 15,000 \text{ cm}^{-1} \)
- \( T_1 (F) \rightarrow A_2 \quad 7,000 - 8,000 \text{ cm}^{-1} \)

Practically all tetrahedral Ni (II) complexes have an intense blue colour due to the presence of an absorption band in the red part of the visible region.

**COPPER (II) COMPLEXES :**

(a) **Magnetic Measurements :**

Copper has electronic structure \([Ar] (3d)^{10} (4s)^1\). The divalent copper
has the electronic configuration [Ar] (3d)\(^9\). The magnetic moments of simple Cu (II) complexes are generally in the range 1.75 - 2.2 BM regardless of stereochemistry\(^{44,45}\) because the Cu (II) complexes, whether octahedral, square planar or tetrahedral almost always contain one unpaired electron and no change is observed in the \(\mu_{\text{eff}}\) value on changing the geometry. It has been shown that in a perfectly regular tetrahedral environment Cu (II) should have an effective

<table>
<thead>
<tr>
<th>Cu atom</th>
<th>3d</th>
<th>4s</th>
<th>4p</th>
<th>4d</th>
</tr>
</thead>
</table>
| Cu (II) in Ground state | \(\begin{array}{cccc}
\text{Cu} & \text{Cu} & \text{Cu} & \text{Cu} \\
\text{Cu} & \text{Cu} & \text{Cu} & \text{Cu}
\end{array}\) | \(\begin{array}{cccc}
1 & \text{xx} & \text{xx} & \text{xx} \\
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\text{xx} & \text{xx} & \text{xx} & \text{xx} \\
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\end{array}\) |

Octahedral complex \(\text{sp}^3\text{d}^2\) hybridization

<table>
<thead>
<tr>
<th>Cu(II) in Square planar</th>
<th>3d</th>
<th>4s</th>
<th>4p</th>
<th>4d</th>
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</thead>
</table>
| \(\begin{array}{cccc}
\text{Cu} & \text{Cu} & \text{Cu} & \text{Cu} \\
\text{Cu} & \text{Cu} & \text{Cu} & \text{Cu}
\end{array}\) | \(\begin{array}{cccc}
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\end{array}\) |

moments about 2.2 BM.\(^{56}\) It is assumed that the distortion of these ions from regular tetrahedral symmetry cause quenching of some of the orbital contribution to the moment.\(^{57}\) About 1.9 BM magnetic moment would be equally consistent with planar or distorted tetrahedral configuration.\(^{58}\) Cu (II) complexes with distorted octahedral stereochemistry are also expected to have little effect on the magnetic moment of the metal ion. Since the \(\text{^2E}_g\) ground term of octahedrally co-ordinated bivalent copper is composed of two non-interacting Kramer's spin doublets, it is expected that curie law should be obeyed in the absence of magnetic exchange between copper ions. A review of the so far reported complexes Cu (II) shows that all the complexes, whether octahedral, square planar or tetrahedral almost always contain the one unpaired electron and no change is observed in the \(\mu_{\text{eff}}\) value [1.7-2.2 BM] on changing geometry. The subnormal magnetic moment value arise from strong exchange interaction in these Cu (II) complexes.\(^{59-62}\) The interaction either the dx\(^2\)- y\(^2\) orbitals of the two metal
atoms directly or transmission through the \( \pi \) orbital of the bridge group or both
and a partial quenching of the unpaired spins on the Cu (II) ions.

(b) **Electronic Absorption Measurement**:

The electronic spectra of Cu (II) complexes have been used to
established their geometries. The spectra conclusively proove the tentative
geometry assigned to the complexes on the basis of magnetic measurement. In a
comprehensive review, Mellor\(^63\) considered, the electronic configuration of
metals which will favour octahedral, planar or tetrahedral structure. The
tetra-coordinated Cu (II) complex can exist in two possible grometries, i.e.
tetrahedral and square planar. Square planar complexes are common for Cu \(^{2+}\). In
this case all the d electrons will be filled in d orbitals except \( dx^2-y^2 \). This orbital
together with the s, px and py orbitals forms a set of hybrids, \( dsp^2 \), directed
towards the vertices of a square, the distribution of electrons in the orbitals will
be in such a way that the energy of the system is a minimum. The stabilization
energy due to the crystal field will be greater for a square planar structure than
the tetrahedral structure. A four coordinated Cu (II) complex can take on a
tetrahedral configuration only when the steric repulsion among the ligands is large
enough to compensate for the diminution in CFSE. In case of weak ligand field
such a configuration will be less difficult to obtain. Moreover a perfectly
tetrahedral complex will be orbitally triply degenerate so that it becomes
unstable due to John-Teller effect and hence it must distort. These reasons
account for the rarity of the tetrahedral complexes.\(^64\)

The nine outer electrons of the \( \text{Cu}^{2+} \) ion give \( ^2D \) ground state which
spilits into several terms under the influence of the ligand field \( ^2D \rightarrow ^2A_1, ^2B_1, ^2B_2, ^2E. \) Bethe has given the proper eigfunctions for the above split terms from which
energy may be calculated.\(^65\) The energy difference between these terms and their
assignment are.\(^66\)
\[ \nu_1 = \frac{E_1}{hc} = \frac{(E_2 - E_1)}{hc} \text{ (main peak)} \]
\[ \nu_2 = \frac{E_2}{hc} = \frac{(E_2 - E_4)}{hc} \]
\[ \nu_3 = \frac{E_3}{hc} = \frac{(E_2 - E_3)}{hc} \]

The crystal field theory provides a way of determining, by simple electrostatic considerations, how the energies of the metal ion orbitals will be affected by the set of surrounding atoms or ligand to form octahedral geometry. In the octahedral environment of six negative charges, the metal ion will have two kinds of a d orbitals; three of one kind equivalent to one another and labeled \( t_{2g} \), and two of another kind equivalent to each other, labeled \( e_g \); furthermore the \( e_g \) orbitals are of higher energy than the \( t_{2g} \) orbitals. This may be expressed in an energy level diagram as shown in fig. (4.2) In the figure energy difference between \( e_g \) and the \( t_{2g} \) orbitals is designated by \( \Delta_0 \), where the subscript \( \Delta_0 \) stands for octahedral. The figure also indicates that \( e_g \) levels lie \( 3/5 \Delta_0 \) above and the \( t_{2g} \) levels lie \( 2/5 \Delta_0 \) below the energy of unsplit d orbitals.

As fig. (4.2) shows, it is in general possible for the tetragonal distortion to become so large that the \( dz^2 \) orbital eventually drops below the \( dxy \) orbital.

Fig: 4.2 ENERGY LEVEL DIAGRAM SHOWING THE SPLITTING OF A SET OF D' ORBITALS, (I) OCTAHEDRAL COMPLEX, (II) TETRAHEDRAL COMPLEX AND SQUARE PLANAR.
Semiquantitative calculation with parameters appropriate for square planar complexes of Cu (II) lead to the energy level diagram shown in fig (4.2) in which the dz² orbital has dropped so far below the dxy orbital that it is nearly as stable as the (dzy, dzx) pair.

On irradiation with light of frequency v equal to Δ₀/h, where h is planck's constant and Δ₀ is the energy difference between the t₂g and e_g orbitals, it should be possible for Cu (II) ion to capture a quantum of radiation and convert that energy into energy of excitation of the electron from the t₂g to the e_g orbitals. The absorption band that results from this process is found in the visible spectrum of Cu (II) complex and is responsible for its coloured cation.

Jorgenson⁶⁷ was the first, who recorded the spectra of some Cu (II) complexes and observed that both five and six coordinate Cu (II) complexes can exist. Now it has been fairly established that electronic transistions in the region 11-16 kk (1 kk = 1000 cm⁻¹) are the characteristic of the hexa-coordinated.⁶⁸-⁶⁹ In the visible region three transitions σ₁g → A₁g, B₁g → B₂g and B₁g → Ε₉g occurs for Cu (II) octahedral complexes. But they are very close in energy and often give rise to one broad band envelop. So many references on spectral study of octahedral Cu (II) complexes are reported, of which only a few are referred here.

The present investigation for all the Cu (II) complexes the geometries are found to be octahedral.

**ZINC (II) COMPLEXES**

Zinc has electronic structure [Ar] 3d¹⁰4s². The electronic configuration Zn and Zn (II) complexes indicate its diamagnetic nature.
INFRA - RED ABSORPTION STUDIES:

The IR spectra of the present complexes have been recorded in the region 4000-400 cm\(^{-1}\). Infra-red bands and their assignments for the 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 has been frequently used for structure determination of transition metal complexes. IR which is a main tool of investigation in the present work is quite informative. It has provided significant information about the nature of the coordinate bond, sites of attachment of ligands and stereochemistry of complexes. The donation of electron pair from ligand to metal ion is generally accompanied notable changes in the positions and intensity of IR bands. As a result of coordination the shift in the frequencies of the bands to higher and lower wave number sides takes place depending upon the increase or decrease in the bond order. The lowering of the symmetry of complex molecules causes appearance of some new bands and splitting of degenerate modes. Metal-nitrogen and metal-oxygen bands appear in the spectra of complexes in the far-infrared region. Presence of aquo ligand can be ascertained by appearance of new bands due to symmetric and asymmetric stretches, bending, rocking, wagging and twisting modes produced by coordinated water molecule. Similarly in some cases presence of hydroxo, chloro or sulphato groups were determined by the appearance of new bands. Details of these IR bands have been discussed in the respective texts.
NALIDIXIC ACID COMPLEXES:

All the complexes are crystalline, stable at room temperature, insoluble in water and most of the organic solvents, but soluble in methanol or DMF. The elemental analysis [reported in experimental data chapter IV] suggests 1 : 1 for Cu (II) and Zn (II) and 1 : 2 for Mn (II) Fe (III) and Ni (II) [metal to legand stoichiometry] complexes. The complexes have low conductance value in DMF at $10^{-3}$ M concentration [17.05, 15.07, 20.15 and 19.2 ohm$^{-1}$ cm$^2$ mol$^{-1}$ respectively for Fe (III), Ni (II), Cu (II) and Zn (II) complexes] which indicates non-electrolytic nature of the complexes. The Mn (II) complex was found insoluble in all the solvents tried. So it is not possible to measure its molar conductance and electronic spectra. The electronic spectra of all the complexes of nalidixic acid show broad band in the region ~35077 cm$^{-1}$ which is due to $\pi_2 \rightarrow \pi^*_1$ transition. The magnetic moment of the complex of Mn (II) is 5.88 BM indicating five unpaired electrons which is well within range of octahedral Mn (II) complexes.

The Fe (III) complex showed bands at 13404, 17361 and 23866 cm$^{-1}$ corresponding to $^6A_{ig}\rightarrow^4T_{ig}$, $^6A_{ig}\rightarrow^4T_{2g}$ and $^6A_{ig}\rightarrow^4E_g$ transitions respectively. The magnetic moment value 5.7 BM indicates octahedral geometry. The ligand field parameters Dq, B and $\beta$ values were found to be 613.8 cm$^{-1}$, 558 cm$^{-1}$ and 0.5497 respectively.

Ni (II) complex shows magnetic moment 3.5 BM at room temperature which suggest octahedral arrangement of the ligand molecule around the Ni (II) ion. The electronic spectral bands around 12610, 19120 and 25575 cm$^{-1}$ due to transitions $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$, $^3A_{2g} \rightarrow ^3T_{1g}$ (F), $^3A_{2g} \rightarrow ^3T_{1g}$ (P) respectively indicate that the central Ni ion is present in an octahedral field. The ligand field parameters Dq, B and $\beta$ values were found to be 1261 cm$^{-1}$, 457 cm$^{-1}$ and 0.4436 respectively.
The magnetic moment of Cu (II) complex was found to be 1.93 BM, showing paramagnetic character. Cu (II) complex shows one broad band near 12500-14285 cm\(^{-1}\) due to transition \(^{2}E_{2g} \rightarrow ^{2}T_{2g}\) suggests in a distorted octahedral geometry.\(^70\)

The co-ordination of ligand is obtained from comparision of infrared spectra of the complexes with drug [Table - 4.A]. In the IR spectra of Mn (II), Fe (III), Ni (II), Cu (II) and Zn (II) complexes broad band ~ 3600 cm\(^{-1}\) followed by appearence of sharp peaks at ~1610 and ~ 850 cm\(^{-1}\) asignable to OH stretchting, bending and rocking vibrations respectively indicating the presence of co-ordinated water molecules in the complexes. The band in the region 1620 cm\(^{-1}\) observed due to \(\nu\) C = O respectively in the ligand and in the complexes is shifted by \(\pm\) 10 wave numbers, indicating the co-ordination through these group. Presence of OH\(^-\) group has been supported by a sharp medium bands present at 1113 and 1132 cm\(^{-1}\) which indicates Cu-OH and Zn - OH bending. Presence of Cl ion in the Fe (III) complex has been confirmed on the basis of elemental analysis. All the complexes show new medium intensity band ~ 450 cm\(^{-1}\) may be due to \(\nu\) M-O.

Conclusion:

Nalidixic acid complexes were isoleted at pH 4-5.5. On the basis of molar conductance, magnetic moment, elemental analysis, electronic and infra-red spectra it can be inferred that all the complexes are six coordinated with octahedral structure. On the basis of various physico-chemical investigations it has been found that the drug nalidixic acid behaves as a monoprotic bidentate ligand coordinating through oxygen of \(>\text{C} = \text{O}\) and COO\(^-\) groups. The
stoichiometric ratio of the metal ion and the ligand has been found to be 1 : 1 for Cu (II) and Zn (II) and 1 : 2 for Mn (II), Fe (III) and Ni (II) complexes. One/two coordination position are occupied by water molecules. In case of Cu (II) and Zn (II) complexes three coordination positions are occupied by water molecules and another by OH\(^{-}\) group. Presence of coordinated water molecule, and OH\(^{-}\) groups has been confirmed by IR and elemental analysis. The presence of chloride ion in Fe (III) complex has been confirmed by elemental analysis.
<table>
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<th>Mn (II) Complex</th>
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s - strong, m - medium, w - weak, br - broad, sh - shoulder, sp - sharp
(Fig. 4.3) NALIDIXIC ACID

(Fig. 4.4) NALIDIXIC ACID - Mn (II) and Ni (II) COMPLEXES.
(Fig. 4.5) NALIDIXIC ACID - Fe (III) COMPLEX.

(Fig. 4.6) NALIDIXIC ACID = Cu (II) and Zn (II) COMPLEXES

R=OH⁻ for Cu (II) and Zn (II) COMPLEXES
NORFLOXACIN COMPLEXES:

The elemental analysis shows 1:1 for Mn (II), Fe (III), Ni (II) and Zn (II) complexes and 1:2 metal ligand ratio for Cu (II) complex. The complexes have low conductance value in DMF at 10^{-3} M concentration [12.5, 16.20, 10.50, 13.10 and 15.08 ohm^{-1} cm2 mol^{-1} respectively for Mn (II), Fe (III), Ni (II), Cu (II), and Zn (II) complexes] which indicates non-electrolytic nature of the complexes.

The electronic spectra of all the complexes of norfloxacin shows broad band in the region ~ 35587 cm^{-1} which is due to \pi_2 \rightarrow \pi_4\text{ transition. The high spin Mn (II) complex with d}^5\text{ configuration have the ground state }^{6}A_{1g}\text{ and all the d-d transition are spin and Laporte forbidden.}^{71}\text{ The Mn (II) complex exhibit a weak and a broad band at 13800 and 19200 cm}^{-1}\text{ respectively which could be attributed to }^{6}A_{1g} \rightarrow ^{4}T_{1g}\text{ (4G) transition.}^{72-76}\text{ The magnetic moment of the complex of Mn (II) is 5.80 BM indicating five unpaired electrons which is well within the range of octahedral Mn (II) complexes.}

In the electronic spectra of Fe (III) complex the band ~ 23807 cm^{-1} can be assigned to ligand-metal charge transfer origin. Broad and asymmetric bands near 13368 and 17331 cm^{-1} may be assigned to \text{ }^{6}A_{1g} \rightarrow ^{4}T_{1g}\text{ (D) transition which is characteristic of octahedral stereochemistry around metal ion.}^{77-79}\text{ The magnetic moment of the Fe (III) complex (ground state }^{6}A_{1g}\text{) is 5.8 BM indicating five unpaired electrons which is well within the range of octahedral Fe (III) complexes.}

The d^8 configuration of Ni (II) leaves two unpaired electrons in 3dorbital, resulting in a paramagnetic nature of Ni (II) ground state with a magnetic moment 2.83 BM [i.e. spin only value]. In the present case Ni (II) complex shows magnetic moment 3.20 BM which is well within the range of octahedral [range for octahedral 2.9-3.4BM] complexes possessing 4sp^2d^2 hybridization with
triplet ground state \(^3\text{A}_{2g}\).\(^{80}\) The electronic spectral bands around 12550, 19000 and 25500 cm\(^{-1}\) due to transitions \(^3\text{A}_{2g}(F) \rightarrow ^3\text{T}_{2g}(F), ^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(F), ^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(P)\) respectively indicate that the central nickel ion is present in an octahedral field. The ligand field parameters Dq, B and \(\beta\) values were found to be 1255 cm\(^{-1}\), 456 cm\(^{-1}\) and 0.4427. Cu (II) complex shows one broad assymmetric ligand field band in the region 12030 -13650 cm\(^{-1}\) assignable to \(^2\text{Eg} \rightarrow ^2\text{T}_{2g}\) transition in a distorted octahedral geometry.\(^{81}\) The magnetic moment of Cu (II) complex has been found to be 1.80 BM which indicates its paramagnetic nature with a single unpaired electron.

The infrared spectra of norfloxacin is reported. In the present investigation the assignment of bands in the complexes have been carried out with the help of the comparision of the spectra of free ligand. [Table - 4.8] In the IR spectra of Mn (II), Fe (III), Ni (II), Cu (II) and Zn (II) complexes broad band\(\sim 3890\) cm\(^{-1}\) followed by sharp peaks at\(\sim 1630, \sim 830\) cm\(^{-1}\) assigned to OH stretching bending and rocking vibration respectively indicate the presence of water molecules in the complexes. The band \([\nu\text{C} = \text{O}]\) which is present in the ligand at 1575 cm\(^{-1}\) shifted by \(\pm 15\) to 20 cm\(^{-1}\) in the complexes indicating the coordination through this group.\(^{82}\)

In Ni (II) and Zn (II) complexes additional bands at 1577, \(\sim 1492, \sim 1448, \sim 1340\) and 746 cm\(^{-1}\) can be assigend to \(\nu\) asy \([\text{COO}^-], \nu\) asym \([\text{COO}^-],\) sym \([\text{COO}^-],\) \(\delta [\text{CH}_2]\) and \(\delta [\text{COO}^-]\) respectively indicating the presence of acetate ion in the coordination sphere. Presence of Cl\(^-\) ion in the Mn (II) and Fe (III) complexes have been confirmed on the basis of elemental analysis. All the complexes show new medium intensity bands \(\sim 482\) cm\(^{-1}\) may be due to \(\nu\) M-O.\(^{83-84}\)
Conclusion:

Norfloxacine complexes were isolated at pH 5-6.5. On the basis of various physico-chemical observations it has been found that the drug norfloxacine behaves as a monoprotic bidentate ligand coordinating through oxygen of $\text{C} = \text{O}$ and $\text{COO}^-$ groups. The complexes were octahedral with the metal ion and the ligand in the molar ratio 1:1 for Mn (II), Fe (III), Ni (II) and Zn (II) and 1:2 for Cu (II) complex. Two/three coordination positions are occupied by water molecules. Presence of coordinated water molecules and $\text{CH}_3\text{COO}^-$ groups were confirmed by IR and elemental analysis. The presence of $\text{Cl}^-$ ion in Fe (III) complex has been confirmed by elemental analysis.
<table>
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<th>Drug</th>
<th>Mn (II) Complex</th>
<th>Fe (III) Complex</th>
<th>Ni (II) Complex</th>
<th>Cu (II) Complex</th>
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<td>516 w</td>
<td>505 w</td>
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$\delta$ [COO$^-$]

C-H out of plane deformation in benzanoid aromatic ring

C - N - C bending vibration
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</table>

s - strong, m - medium, w - weak, br - broad, sh - shoulder, sp - sharp
Fig (4.7) NORFLOXACIN

Fig (4.8) NORFLOXACIN = Mn (II), Ni (II) and Zn (II)

R=Cl⁻ for Mn (II) COMPLEX
R=CH₃COO⁻ for Ni (II) and Zn (II) COMPLEX
Fig (4.9) NORFLOXACIN = Fe (III) COMPLEX

Fig (4.10) NORFLOXACIN - Cu (II) COMPLEX
CIPROFLOXACIN COMPLEXES:

Complexes were insoluble in water and common organic solvents like, benzene, ether, chloroform but were soluble in methanol and DMF. The stoichiometry of the complexes were found to be 1:1 for Mn (II), Ni (II) and Zn (II) complexes and 1:2 metal - ligand stoichiometry for Fe (III) and Cu (II) complexes of ciprofloxacin. Molar conductance of the complexes, measured in $10^{-3} \text{M DMF}$ solution at 27-30° has been found very low. This shows non-electrolytic nature of the complexes.

The electronic spectra of all the complexes of ciprofloxacin shows broad band in the region ~ 35971 cm$^{-1}$ which is due to $\pi \rightarrow \pi^*$ transition. The Mn (II) complex exhibits a weak and broad band near 14044-19305 cm$^{-1}$ which could be attributed to $^6A_{1g} \rightarrow ^4T_{1g}$ (4G) transition. The magnetic moment of Mn (II) complex was found to be 5.2 BM indicating the presence of five unpaired electrons i.e., paramagnetic in nature. This value is well within the range of octahedral Mn (II) complex.

The Fe (III) complex showed bands ~ 23923 cm$^{-1}$ and a broad and asymmetric band near 17421 cm$^{-1}$ may be assigned to the $^6A_{1g} \rightarrow ^4E_g$ (G), $^6A_{1g} \rightarrow ^4T_{1g}$ (G) transitions characteristic of octahedral stereochemistry around metal ion. Magnetic moment of Fe (III) complex was found to be 5.6 BM indicating the presence of five unpaired electrons i.e. paramagnetic in nature. This value is well within the range of octahedral Fe (III) (ground state $^6A_{1g}$) complexes.$^{85}$

The Ni (II) complex gave three band at 12531, 18867 and 25445 cm$^{-1}$ due to transition $^3A_{2g}(F) \rightarrow ^3T_{2g}$ (F), $^3A_{2g} \rightarrow ^3T_{1g}$ (F), and $^3A_{2g} \rightarrow ^3T_{1g}$ (P) indicating an octahedral geometry.$^{86}$ The ligand field parameters Dq, B and $\beta$ values were found to be 1253 cm$^{-1}$, 447 cm$^{-1}$ and 0.4339 respectively. 3.20 BM magnetic moment of Ni (II) complex also indicates its octahedral geometry, because the range for
octahedral Ni (II) complexes is 2.9 - 3.4 BM, indicating the presence of two unpaired eletrons.  

The magnetic moment of Cu (II) complex was found to be 1.62 BM, showing paramagnetic character. In the electronic spectra of Cu (II) complex one broad band in the region 12150-13703 cm\(^{-1}\) has been observed which may be assigned to \(^2\)Eg \(\rightarrow\) \(^2\)T\(_{2g}\) transition in distored octahedral field.

The assignment of the infrared bands in the complexes have been carried out by comparision with the spectrum of pure drug [Table - 4.C]. In the IR spectra of Mn (II), Fe (III), Ni (II), Cu (II) and Zn (II) complexes broad bands\(-3800\)cm\(^{-1}\) followed by sharp peaks at 1625 and \(-880\)cm\(^{-1}\) assigned to OH stretchting bending and rocking vibration respectively indicate the presence of water molecules in the complexes. The band \(\nu\)C = O which is present in the ligand at 1600 \(\text{cm}^{-1}\) shifted by \(\pm \) 25 \(\text{cm}^{-1}\) in the complexes indicating the coordination through this group. Presence of \(\text{OH}^-\) group is supported by a sharp band present at 1143 \(\text{cm}^{-1}\) which indicate Fe - OH bending.

In Ni (II) and Zn (II) complexes additional bands at 1580, 1485, \(-1450, 1309\) and 754 \(\text{cm}^{-1}\) can be assigned to \(\nu\) asy (COO\(^{-}\)) \(\nu\) asym (COO\(^{-}\)), sym (COO\(^{-}\)), \(\delta\) (CH\(_3\)) and \(\delta\) (COO\(^{-}\)) respectively indicating the presence of acetate ion in the coordination sphere. Presence of Cl\(^-\) ion in the Mn (II) has been confirmed on the basis of elemental analysis. The chelates show new medium intensity bands at 450 \(\text{cm}^{-1}\) (\(\pm\) 30) may be due to \(\nu\) M-O.

Conclusion :

Ciprofloxacin complexes were isolated at pH 5-6. On the basis of various physico-chemical investigations it has been found that the drug ciprofloxacin behaves as a monoprotic bidentate ligand coordinating through
oxygen of >C = O and COO⁻ groups. The complexes were octahedral having metal to ligand stoichiometric ratio 1 : 1 for Mn (II), Ni (II) and Zn (II) and 1:2 for Fe (III) and Cu (II). Two/three coordination positions are occupied by water molecules but in the case of Fe (III) complex one coordination position is occupied by water molecule and another by OH⁻ group. Presence of coordinated water molecules, OH⁻ and CH₃COO⁻ groups has been confirmed by IR and elemental analysis. The presence of chloride ion in the Mn (II) complex has been confirmed by elemental analysis.
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<th>Mn (II) Complex</th>
<th>Fe (III) Complex</th>
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<th>Cu (II) Complex</th>
<th>Zn (II) Complex</th>
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<td>827 w</td>
<td>862 w</td>
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</tbody>
</table>

Table - 4.C

PRINCIPAL IR FREQUENCIES [cm\(^{-1}\)] AND THEIR ASSIGNMENT FOR CIPROFLOXACIN AND ITS COMPLEXES.

- \( \nu - \text{OH} \)
- \( \nu \text{ N-H} \)
- \( \nu \text{ C = O} \)
- \( \nu \text{ sym (COO}^{-}\) \)
- \( \nu \text{ C - F Vibration} \)
- \( \delta \text{ CH}_3, \nu \text{ C-N (N-in tertiary position)} \)
- \( \nu \text{ C-N [N in secondary position]} \)
- \( \nu \text{ M - OH bending} \)
- \( \nu \text{ Rocking vibration coordinated H}_2\text{O} \)
<table>
<thead>
<tr>
<th></th>
<th>775s</th>
<th>725sp</th>
<th>550w</th>
<th>754 mw</th>
<th>790 br</th>
<th>752 w</th>
<th>δ (COO)</th>
</tr>
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<tbody>
<tr>
<td>775s</td>
<td>748 w</td>
<td>785 w</td>
<td>-</td>
<td>754 mw</td>
<td>-</td>
<td>752 w</td>
<td>7 (COO)</td>
</tr>
<tr>
<td>725sp</td>
<td>-</td>
<td>725 mw</td>
<td>-</td>
<td>-</td>
<td>790 br</td>
<td>-</td>
<td>C-H out of plane deformation</td>
</tr>
<tr>
<td>550w</td>
<td>623 w</td>
<td>621 w</td>
<td>626 w</td>
<td>626 w</td>
<td>756 m</td>
<td>-</td>
<td>in benzanoid aromatic ring</td>
</tr>
<tr>
<td></td>
<td>545 br</td>
<td>545 w</td>
<td>551 w</td>
<td>513 w</td>
<td>513 w</td>
<td>513 w</td>
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</tr>
<tr>
<td>480 w</td>
<td>499 w</td>
<td>426 w</td>
<td>416 w</td>
<td>470 w</td>
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<tr>
<td>416 w</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>416 w</td>
<td></td>
</tr>
</tbody>
</table>

s - strong, m - medium, w - weak, br - broad, sh - shoulder, sp - sharp

C - N-C bending vibration
ν M - O
ν M - Cl
Fig. (4.11) CIPROFLOXACIN

Fig. (4.12) CIPROFLOXACIN = Mn (II), Ni (II) and Zn (II) COMPLEXES.
R = Cl$^-$ for Mn (II) COMPLEX.
R = CH$_3$COO$^-$ for Zn (II) & Ni (II) COMPLEXES.
(Fig. 4.13) CIPROFLOXACIN - Fe (III) COMPLEX.

(Fig. 4.14) CIPROFLOXACIN - Cu (II) COMPLEX.
CLOXACILLIN COMPLESES:

The analytical data of the complexes shown in experimental data chapter IV indicatcs 1:1 metal-ligand ratio for Mn (II), Fe (III), Ni (II), Cu (II) and Zn (II) complexes. The molar conductance of these complexes [in methanol or DMF] have been found to be low [22.10, 17.05, 14.60 and 17.10 ohm⁻¹ cm² mol⁻¹ for Mn (II), Fe (III), Cu (II) and Zn (II) respectively] which indicates that complexes are non electrolytic in nature. Cloxacillin Ni (II) complex has been found to be insoluble in all the solvents tried. So it is not possible to measure their molar conductance.

The electronic spectra of all the complexes of cloxacillin show a broad band in the region ~ 40000 cm⁻¹ which is due to \( \pi_2 \rightarrow \pi_4^* \) transition. The electronic spectra of the Mn (II) complex exhibited three bands at 17320, 23510 and 26215 cm⁻¹ assigned to the transitions \( 6A_{1g} \rightarrow 4T_{1g} \), \( 6A_{2g} \rightarrow 4T_{2g} \) and \( 6A_{1g} \rightarrow 4T_{1g} \) (P), respectively, indicating octahedral geometry. The ligand field parameters Dq, B and \( \beta \) values were found to be 793.8 cm⁻¹, 721 cm⁻¹ and 0.8391 respectively. Magnetic moment of Mn (II) complex has been found 4.90 BM which indicates its paramagnetic nature with five unpaired eletrons.

The Fe (III) complex showed bands at 13774, 17513 and 23980 cm⁻¹ corresponding to \( 6A_{1g} \rightarrow 4T_{1g} \), \( 6A_{1g} \rightarrow 4T_{2g} \) and \( 6A_{1g} \rightarrow 4E_g \) transitions respectively\(^{89}\), characteristic of octahedral stereochemistry around metal ion. The magnetic moment value 5.10 BM indicates presence of five unpaired electrons and octahedral geometry.\(^{90}\) The ligand field parameters Dq, B and \( \beta \) values were found to be 630.3 cm⁻¹, 573 cm⁻¹ and 0.5645 respectively.

The magnetic moment of Ni (II) complex is 3.10 BM which lies between the range of octahedral Ni (II) complexes. The Ni (II) complex was insoluble and hence it is not possible to measure the electronic spectra and molar
conductance of the complex.

In the electronic spectra of Cu (II) complex one broad band in the region 11764 - 13793 cm$^{-1}$ has been observed which may be assigned to $^2\text{Eg} \rightarrow ^2\text{T}_{2g}$ transition in distorted octahedral field. The magnetic moment of Cu (II) complex has been found 1.72 BM which indicates its paramagnetic nature with a single unpaired electron.

Interpretation of IR bands in the complexes has been carried out by comparison with the spectrum of cloxacillin [Table - 4.D]. IR of cloxacillin and related compounds have been well studied. A broad band around 3649 - 3444 cm$^{-1}$ in the spectra of the drug and the complexes is due to the presence of water of crystallisation and coordinated water molecule respectively. The bands present in the drug due to NH 3200 cm$^{-1}$ and amide C = O 1690 cm$^{-1}$ remained almost unchanged in the complexes indicating non-involvement of these group in chelation. A new imino group is produced due to degradation of $\beta$-lactum carbonyl group by metal ion. This group takes part in chelation. In complexes vibration due to this new group was observed $\sim$ 3200 cm$^{-1}$. The band present at 1780 cm$^{-1}$ in the drug was assigned to $\beta$-lactum carbonyl group and was found absent in complexes, because after degradation this group gets converted into-COOH group [cloxacillin $\rightarrow$ cloxacilloic acid]. Carboxylic group present in ligand displays its vibration due to asym and sym stretch at $\sim$ 1630 cm$^{-1}$ and 1410 cm$^{-1}$. Although this group takes part in chelation by deprotonation but, at the same time a new carboxylic group is produced by degradation of $\beta$-lactum C = O group. Hence in complexes, two new bands appearing at 1600 cm$^{-1}$ and 1345cm$^{-1}$ were assigned to shifted asymmetric and symmetric stretch of original carboxylic group. Similar shifting were observed by Fowles et.al.

New carboxylic group has shown its vibrations at normal frequencies
[1630 cm\(^{-1}\) and 1410 cm\(^{-1}\)]. Presence of OH\(^-\) group is supported by a sharp band present at 1127–1112 cm\(^{-1}\) which indicates Ni-OH, Cu-OH and Zn-OH bending. In the cases of Fe III complex, the SO\(_4\)^{-2} ion present in the coordination sphere is confirmed by IR bands. The sulfate ion belongs to high symmetry point group Td. Of the four fundamental \([\nu_1, \nu_2, \nu_3\text{ and } \nu_4]\) vibrations of sulfate ion, only the latter two are infrared active. In the drug, a band appearing near 1035 cm\(^{-1}\) indicates Td symmetry of the sulfate ion. In the complex, this was lowered to C\(_2\)V suggesting chelating bidentate co-ordination. Bands appearing near 989 and 483 cm\(^{-1}\) in Fe (III) complex can be assigned to \(\nu_1\) and \(\nu_2\). As a rule, \(\nu_3\) and \(\nu_4\) each splits into three bands in chelating bidentate co-ordination. Here also, three splitting bands of \(\nu_3\) appear in the region 1112, 1059 and 1035 cm\(^{-1}\) in the spectra of the complex. The band due to \(\nu_4\) splitting have been observed near 650 cm\(^{-1}\). Presence of Cl\(^-\) ion in the Mn (II) complex has been confirmed on the basis of elemental analysis. All the complexes show new medium intensity bands ~ 586 and ~ 462 cm\(^{-1}\) may be due to \(\nu\) M-N and \(\nu\) M-O.

Conclusion:

Cloxacillin complexes were isolated at pH 4.5-5.5. On the basis of various physico-chemical observations it has been found that the drug cloxacillin behaves as a monoproptic bidentate ligand. The complexes were octahedral having metal to ligand stoichiometric ratio 1 : 1 for all complexes. Two/three coordination position are occupied by water molecules. In case of Fe (III) complex the SO\(_4\)^{-2} ion present in the coordination sphere has been confirmed by IR bands and elemental analysis. In this complex Td symmetry of the SO\(_4\)^{-2} ion present in the drug was lowered to C\(_2\)V in the complex suggesting chelating bidentate coordination. Presence of coordinated water molecules and OH\(^-\) group has been confirmed by IR and elemental analysis. The presence of chloride ion in the Mn (II) complex has been confirmed by elemental analysis.
Table - 4.D

PRINCIPAL IR FREQUENCIES [cm\(^{-1}\)] AND THEIR ASSIGNMENT FOR CLOXACILLIN AND ITS COMPLEXES.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Mn (II) Complex</th>
<th>Fe (III) Complex</th>
<th>Ni (II) Complex</th>
<th>Cu (II) Complex</th>
<th>Zn (II) Complex</th>
<th>Assignment</th>
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</tr>
<tr>
<td>3200s</td>
<td>3649 w</td>
<td>3652 w</td>
<td>3510 w</td>
<td>3498 br</td>
<td>3520 w</td>
<td>(\nu) - OH (H(_2)O)</td>
</tr>
<tr>
<td></td>
<td>3564 w</td>
<td>-</td>
<td>3490 w</td>
<td>3749 br</td>
<td>3495 w</td>
<td>(\nu) N-H</td>
</tr>
<tr>
<td></td>
<td>3548 w</td>
<td>-</td>
<td>-</td>
<td>3444 br</td>
<td>-</td>
<td>(\nu) C = O ((\beta)-lactum)</td>
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<tr>
<td>1780s</td>
<td>3206 w</td>
<td>3210 mw</td>
<td>3215 w</td>
<td>3219 wbr</td>
<td>3225 br</td>
<td>(\nu) C = O (amide)</td>
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<tr>
<td></td>
<td>1775 mw</td>
<td>1782 m</td>
<td>1715 w</td>
<td>1726 w</td>
<td>1710 mw</td>
<td>(\nu) C = O (amino)</td>
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<tr>
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<td>1670 br</td>
<td>1657 w</td>
<td>1695 mw</td>
<td>1643 sh</td>
<td>1685 mw</td>
<td>(\nu) COO (asym) of newly produced - COOH gr.</td>
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<td>1655mw</td>
<td>1631 mbr</td>
<td>1604 w</td>
<td>1620 mw</td>
<td>1627 sh</td>
<td>1635 w</td>
<td>(\nu) COO (asym) of original -COOH group</td>
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<td>1423 w</td>
<td>1401 mbr</td>
<td>1402 mbr</td>
<td>1408 mw</td>
<td>1402 mw</td>
<td>(\nu) COO (sym) of newly produced - COOH gr.</td>
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<td>1345 m</td>
<td>1324 w</td>
<td>1333 w</td>
<td>1344 w</td>
<td>1350 w</td>
<td>(\nu) COO (sym) of original -COOH gr.</td>
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<td>1410m</td>
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<td>M-OH (bending)/(\nu_3) splitting of SO(_4) case of complex</td>
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<td>(\nu_3) splitting of SO(_4)</td>
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<td>(p\nu) H(_2)O/(\nu_1) of SO(_4)</td>
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<td>(\nu) M - N</td>
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<td>(\nu) M - O</td>
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<td>(\nu) M - Cl</td>
</tr>
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</table>

s - strong, m - medium, w - weak, br - broad, sh - shoulder, sp - sharp
(Fig. 4.15) CLOXACILLIN SODIUM

(Fig. 4.16) CLOXACILLIN - Mn (II), Ni (II), Cu (II) and Zn (II) COMPLEXES

R = Cl⁻ Mn (II) COMPLEX
R = OH⁻ Ni (II), Cu (II) and Zn (II) COMPLEXES
(Fig. 4.17) CLOXACILLIN - Fe (III) COMPLEX
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