CHAPTER VI

ELECTRONIC SPECTRA AND MAGNETIC MEASUREMENTS
ELECTRONIC SPECTRA:

Visible and ultraviolet spectroscopy play an important role for the structural determination of the metal complexes. In this chapter the structure of Co(II), Ni(II) and Cu(II) complexes have been elucidated making use of the electronic spectra and the magnetic properties of the complexes. Visible spectroscopy has been used to study the complexes of transitional metals, lanthanides and actinides whereas the ultraviolet spectroscopy elucidation of all the metal complexes.

In many cases a series of crystal field bands have been observed for the transition metal complexes. In many cases these bands lie in the visible region depending upon the nature of the metal ion and donor atoms. The crystal field transitions have been divided into two classes, the spin-allowed transitions and spin-forbidden transitions. The ultra-violet spectrum consists of electronic transitions within the ligand itself ($\pi - \pi^*$ and $\delta - \delta^*$) and charge transfer transition (between ligand and metal ion). The intensities of the crystal field transitions do not exceed a molar extinction coefficient above 500 whereas the transitions within the ligand possess high value of molar extinction coefficient ($\varepsilon > 7500$).

MAGNETIC PROPERTIES:

Magnetic susceptibility measurement have been useful for the determination of structure of metal complexes. The theory of magnetic properties of metal complexes have also been developed. In many transition metal complexes the magnetic ions are separated from each other.
by several omgstorm units which do not show any magnetic interaction. Those substances are referred to be magnetically dilute and exhibit normal magnetic moments. A number of excellent review works in this field have been reported\(^1,^2\). A large number of compounds in which magnetic dilution is insufficient, because either the distance between the magnetic atoms is small or the intervening atoms are capable of coupling with the magnetic ions. The magnetic properties of such systems have been found to exhibit magnetic exchange such interactions are two types, (a) ferromagnetic exchange and (b) antiferromagnetic exchange.

In case of ferromagnetic interaction, the magnetic dipoles tend to align themselves in the same direction, whereas in antiferromagnetic interaction, the magnetic dipoles tend to align antiparallel. The exchange energy between the two centres is given by \((-2J)\) \(\text{Si} \text{ Sj}\) (where \(J\) is the exchange integral for a binuclear complex) A positive value for \(J\) corresponds to ferromagnetic interaction and negative value for \(-J\) corresponds to antiferromagnetic interaction.

SECTION - B

ELECTRONIC SPECTRA AND MAGNETIC PROPERTIES OF COBALT(II) COMPLEXES.

ELECTRONIC SPECTRA:

The Cobalt(II) ion have \(3d^7\) electronic configuration. Which can form a variety of complexes having different geometry. Among the complexes the octahedral and tetrahedral structure are the most common\(^3,^4\) though it forms a fair number of square planar and five coordinated complexes. The ground state splits into three levels i.e. orbital triplets \(4T_1g\) ang \(4T_2g\) and the orbital singlet
ENERGY LEVEL DIAGRAM FOR COBALT (II) ION

(a) Free ion

(b) Octahedral field

Fig-161
octahedral ligand field. The order of energy being $^4T_1g < ^4T_2g < ^4A_2g$ as shown in Fig.- (161). But in tetrahedral complexes this order of energy is found to be reversed. The term $4P$ transforms as $^4T_1g$ under Oh symmetry. Therefore three spin-allowed transitions for octahedral cobalt(II) complexes are expected.

The visible absorption spectrum of $[\text{Co(H}_2\text{O)}_6]^2^+$ ions shows two bands at 8,350 and 20,000 cm$^{-1}$. The lower energy value is due to $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ transition and high frequency band with $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ transition. Octahedral cobalt(II) complexes show a band in the region 8,000 - 10,000 cm$^{-1}$ which has been assigned to the transition $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$. A weak band is found due to the transition $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ in the region 11,000 - 18,500 cm$^{-1}$. The band appears in the region 18,500 - 22,000 cm$^{-1}$ which arises due to the transition $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$. In most of the cases it appears as a double peak due to spin-orbit coupling of the $^4T_{1g}(P)$ state.

Tetra-coordinated cobalt(II) complexes may be either tetrahedral or planar. Both spin free and spin paired complexes are known with planar configuration for the tetrahedral structure, the transitions are observed in a lower frequency region than the octahedral case. The tetrahedral transitions are wide (band width ranging from 1500 - 2500 cm$^{-1}$) and more intense than the main absorption bands in an octahedral complex. The lower symmetry fields are responsible for the broad bands observed for tetrahedral $[\text{Co X}_4]^2^-$ ion in solution. Goodgame has also studied extensively the spectrum of cobalt(II) complexes and suggested$^5$ the possibility of a dynamic
Jahn–Teller effect in the excited states of the ion.

Cotton and Holm have studied on energy level diagram (group theoretically) for four coordinated spin free cobalt(II) ion. Also they have reported the electronic spectra of quadri-coordinated spin free square planar complexes. The quadri coordinated spin free square planar complexes show a broad band in the energy range 16,600 – 25,000 cm\(^{-1}\) and low spin square planar complexes exhibit a narrow band near 8,500 – 22,000 cm\(^{-1}\). Other square planar Co(II) complexes also exhibit a band near 20,000 cm\(^{-1}\).

Livingstone and Nolan have examined a number of Cobalt(II) complexes of the type \(MX_2(NSSN)\). The magnetic moment (4.9–5.0 BM) values of the complexes are within the range expected for octahedral Co(II). The spectra show a single peak at \(\sim 18,000\) cm\(^{-1}\) which may be assigned to the \(^4T_{1g}(F) \rightarrow ^4T_{1g}(P)\) transition. It forms a doublet in the region 6,600 → 9,300 cm\(^{-1}\) which can be assigned to the \(^4T_{1g}(F) \rightarrow ^4T_{2g}(F)\) transition for octahedral Co(II). The splitting of this band into two components is probably due to distortion from regular octahedral geometry. Similar splitting of the low frequency bands occurs with the trimethyl phosphin oxide complex Co(NO\(_3\))\(_2\) (Me\(_3\)PO\(_2\)). It has been shown by x-ray analysis to be six-coordinate with the Me\(_3\) PO groups. Tetrahedral Cobalt(II) complexes display two multiple absorptions in the region 4,600 – 9,000 cm\(^{-1}\) and 13,00 – 17,000 cm\(^{-1}\).

**MAGNETIC PROPERTIES**

A lot of works have been carried out on magnetic susceptibility measurement of Cobalt(II) complexes. On the basis of
spin-only formula Cobalt(II) ion should have a moment of 3.88 B.M., corresponding to three unpaired electrons. However, in the most of the ionic compounds of Cobalt(II) a much higher value of $1^{\text{eff.}} (4.3 - 5.6 \text{ B.M.})$ is observed showing the effect of large orbital contribution. In the low-spin complexes much smaller values 1.9 - 2.3 B.M. have been observed suggesting $\text{dsp}^2$ hybridization. In the ground state Cobalt(II) ion contains three unpaired 3d-electrons. The magnetic moments arise due to the presence$^{21}$ of higher level covalent bonds and these three unpaired electrons for Co(II) ion. The higher level covalent bonds expected may be $4s\ 4p^3$ (tetrahedral) and $4s\ 4p^2\ 4d$ (square planar) in a four coordinate complex and $4s\ 4p^3\ 4d^2$ (octahedral) in a six coordinate complex. The magnetic moment values more than that of spin-only formula is attributed$^{22}$ to incomplete quenching of orbital contribution. The lower magnetic moment values found in the low-spin complexes arises due to electron pairing in the formation of strong covalent bonds which involves the use of one or two of the 3d-orbitals of Co(II) ion. The different values of spin-free complexes vary from compound to compound.

Low-spin type complexes where the ligands are attached to the Co(II) atom by lower level covalent bonds have not been examined theoretically. The experimental data given in the table, have been examined which provide a good correlation between stereochemistry and magnetic moment. It is experimentally found that tetrahedral complexes have moments in the range of 4.2-4.7 B.M., while for those of octahedral complexes the moment lies in the range$^{23,24}$ 4.5-5.6 B.M.
Both four and six coordinate complexes of Co(II) have been reported containing three unpaired electrons. The six-coordinate compounds such as \([\text{Co(NO}_2\text{)}_6]^{-4}\) are undoubtedly octahedral$^{23,25}$ complexes. On the other hand four coordinate compounds are believed to be invariably square planar. It is observed that complexes for which $\mu_{\text{eff}}$ lies in the range 2.1 - 2.9 B.M. may be regarded as square planar. Envidence of square planar arrangement has been provided by x-ray studies on some quadridentate Co(II) schiff base complexes used as oxygen carrier. It has further supported by the fact that the Co(II) phthalocyanine contains one unpaired electron and the complex is undoubtedly square planar due to steric require­ments of the ligand.

RESULTS AND DISCUSSION :

The electronic spectral data, ligand field parameters and magnetic moment values of Co(II) complexes study in the present work are recorded in Table - 25.

All the Cobalt complexes show a band in the region 19,230 - 21,685 cm\(^{-1}\) which posses characteristic feature of the electronic spectra of known octahedral complexes. The spectral transitions can be unambiguously interpretated arising due to ligand field transitions of the octahedral component of the Cobalt (II) complex and may be assigned to $^4T_{1g} (F) \rightarrow ^4T_{1g} (F)$ (\(\not\equiv 3\)) transition in an approximate octahedral field. In addition to this the bands in the region 8400 - 9022 cm\(^{-1}\) and 16,460 - 18,460 cm\(^{-1}\) are observed in the spectra of the complexes which can be assigned to the transitions $^4T_{1g} (F) \rightarrow ^4A_{2g} (\not\equiv 2)$ respectively. The
bands that appear beyond this range may be attributed to charge
transfer bands.

The ligand field parameters like Racah parameter (B), crystal
field splitting energy (Dq), nephelauxetic ratio (β₃), transition
ergy ratio (ν₂/ν₁) and percentage covalency (δ) have been
calculated for the complexes (Table -2.5) and all these values sug­
gest an octahedral chemistry for the Cobalt(II) complexes except
complex \[ \text{Co}_2(\text{HPAN})_2\text{Cl}_2 \]. The β₃₅ value of the complexes is less
than unity indicating partial covalency in the metal ligand bond.
The electronic spectrum of the complex \[ \text{Co}_2(\text{HPAN})_2\text{Cl}_2 \] displays
three bands 11,450 (ν₂), 15,300 (ν₃) and 19,560 cm⁻¹ (ν₄) in
conformity with earlier observation for penta-coordinated square
pyramidal Co(II) complexes.²⁶,²⁷

The magnetic moments of the complexes except \[ \text{Co}_4(\text{BAHD})(\text{H}_2\text{O})_8 \],
\[ \text{Co}_4(\text{BHBFPAD})_2(\text{H}_2\text{O})_8 \] and \[ \text{Co}_4(\text{BHEF ADM})_2(\text{H}_2\text{O})_8 \] fall in
the range 5.0 - 5.10 B.M. expected for high spin octahedral cobalt(II)
complexes.²⁸ The lowering of magnetic moments in case of these above
complexes can be attributed to magnetic interaction between the
metal ions in polynuclear Cobalt(II) complexes \( \text{M}^{2+} \overset{0}{\rightleftharpoons} \text{M}^{2+} \).²⁹
These complexes have been suggested to possess octahedral geometry
basing upon their spectral band positions and values of spectral
parameters which are in agreement with those reported in the
literature.

The magnetic moment of the complex \[ \text{Co}_2(\text{HPAN})_2\text{Cl}_2 \] is
found to be 2.4 B.M. This sub-normal magnetic moment is due to metal-
metal interaction in a dimeric structure. The dimerisation is
Energy level diagram for nickel (II) for triplet states
(a) free ion (b) splitting in octahedral field
(c) splitting in tetragonal field (D_{4h} symmetry)

Fig. 162
Table - 25

Electronic spectra, Magnetic moments and ligand field parameters of Co(II) complexes.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Complexes</th>
<th>$\mu_{\text{eff}}$ B.M. at room temp.</th>
<th>Electronic spectral bands.</th>
<th>Assignments</th>
<th>$D_q$</th>
<th>$B$</th>
<th>$\gamma_2/\gamma_1$</th>
<th>$g$</th>
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<td>1</td>
<td>$\left[ \text{Co}_2(\text{HPAN})_2 \text{Cl}_2 \right] $</td>
<td>2.4</td>
<td>11450</td>
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<td>2</td>
<td>$\left[ \text{Co}_4(\text{BAH})_2(\text{H}_2\text{O})_8 \right] $</td>
<td>2.61</td>
<td>8850</td>
<td>$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$</td>
<td>895</td>
<td>804.6</td>
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<td>20820</td>
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5. \( \left[ \text{Co}_3(\text{HAN})_2(\text{H}_2\text{O})_{10} \right] \) 5.10

\( A_{2g}(F) \rightarrow 4T_{1g}(F) \):
- 8640
- 17180
- 19820
- 31150

\( A_{2g}(P) \rightarrow 4T_{1g}(P) \):
- 20170

6. \( \left[ \text{Co}_3(\text{CAH})_2(\text{H}_2\text{O})_{10} \right] \) 5.10

\( A_{2g}(F) \rightarrow 4A_{2g}(F) \):
- 9840

\( A_{2g}(P) \rightarrow 4T_{1g}(P) \):
- 20170

7. \( \left[ \text{Co}_2(\text{BDH})_2(\text{H}_2\text{O})_8 \right] \) 5.0

\( A_{2g}(F) \rightarrow 4A_{2g}(F) \):
- 8665
- 16400

\( A_{2g}(P) \rightarrow 4T_{1g}(P) \):
- 18405

8. \( \left[ \text{Co}_2(\text{BDH})_2(\text{Cl}_2(\text{H}_2\text{O})_6 \right] \) 5.1

\( A_{2g}(F) \rightarrow 4A_{2g}(F) \):
- 9022
- 18405

\( A_{2g}(P) \rightarrow 4T_{1g}(P) \):
- 21630

9. \( \left[ \text{Co}_2(\text{BDH})_2(\text{Cl}_2(\text{H}_2\text{O})_6 \right] \) 5.1

\( A_{2g}(F) \rightarrow 4A_{2g}(F) \):
- 8955
- 18170

\( A_{2g}(P) \rightarrow 4T_{1g}(P) \):
- 21685

\( \text{CT} \):
- 35450
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<td>$[\text{Co}_2(\text{BHFAD})\text{Cl}_2(\text{H}_2\text{O})_6]$</td>
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<td>$[\text{Co}_2(\text{BAAD})\text{Cl}_2(\text{H}_2\text{O})_6]$</td>
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achieved due to phenolic oxygen atoms acting as a bridge between two cobalt atoms and the lowering of magnetism is attributed to antiferromagnetism via superexchange mechanism\(^{30,31}\).

SECTION - C

ELECTRONIC SPECTRA AND MAGNETIC PROPERTIES OF NICKEL(II) COMPLEXES.

The Ni(II) ion have 3d\(^8\) electronic configuration, which gives rise to \(^3\)F ground state. In a cubic field, \(^3\)F ground state of Ni(II) ion splits into three levels, the orbital singlet \(^3\)A\(_{2g}\) and orbital triplet \(^3\)T\(_{1g}\) and \(^3\)T\(_{2g}\). In the octahedral arrangement of the ligands the order of energies is \(^3\)A\(_{2g}\) < \(^3\)T\(_{2g}\) < \(^3\)T\(_{1g}\). The first excited term for free Ni(II) is \(^3\)F which transforms as \(^3\)T\(_{1g}\) under the split into two other components. The energy level scheme for nickel(II) ion in an octahedral and tetragonal field is shown in (Fig -162).

There are three spin allowed transitions observed in an octahedral nickel(II) complexes, namely \(^3\)A\(_{2g}\) \(\rightarrow\) \(^3\)T\(_{2g}\)(\(\gamma_1\)), \(^3\)A\(_{2g}\)(\(\pi\)) \(\rightarrow\) \(^3\)T\(_{1g}\)(\(\gamma_2\)) and \(^3\)A\(_{2g}\)(\(\delta\)) \(\rightarrow\) \(^3\)T\(_{1g}\)(\(\pi_2\)). The octahedral nickel(II) complexes are by far the most common followed by square planar or tetragonal nickel(II) complexes. Indeed, very few tetrahedral complexes of nickel (II) are known 32-35.

Livingstone et.al.\(^{18}\) have prepared a number of complexes with sulphur-nitrogen donor ligands of the type MX\(_2\)(N SSN) where MSSN = 1,6-bis(2-pyridyl)-2,5-dithiahexane and \(x = \text{Cl}^-, \text{Br}^-, \text{I}^-\) and SCN\(^-\). The magnetic moments (3.1 - 3.0 B.M.) an electronic spectral bands of the complexes are characteristic of octahedral nickel(II). The band at 8,000 - 10,500 cm\(^{-1}\) is assigned to the \(^3\)A\(_{2g}\) \(\rightarrow\) \(^3\)T\(_{2g}\)(\(\pi\)) transition. Both bands are symmetrical and the absence of splitting
of the higher frequency bands suggests that there is little tetra-
gonal distortion. Controversy has been arisen on the assignment of
tetrahedral stereochemistry to four-coordinated nickel(II) complexes
on the basis of their paramagnetism. In the past years this stereo-
chemistry has been suggested by several workers on the basis of
Pauling criterion of bond type that in case of quadri-coordinated
nickel(II) complexes which states that paramagnetic complexes are
4s 4p^3 hybridised and tetrahedral whereas dimagnetic complexes are
3d 4s 4p^2 hybridised and square planar. Several dimagnetic quadri-
coordinated complexes of bis (dimethyglyoxime) Ni(II), bis (dithio-
oxalato) Ni(II)^{37}, Ni(II) phthalocyanine^{38}, bis (salicylaldoxime)
Ni(II)^{39} and bis (salicylaldimine) Ni(II)^{40} are proposed to be
square planar on the basis of x-ray analysis.

In the case a number of tetra-coordinated paramagnetic nickel
(II) complexes of 8-hydroxyquinoline, O-hydroxyacetophenone, anthra-
nilic acid, etc. which have magnetic moments in the range (3.0 - 3.3
B.M.); the stereochemistry seems to be planar. There is no convincing
evidence in favour of one of these complexes to be tetrahedral. It
has been pointed out by Ballhausen and his coworkers^{41-42} that
quadri-coordinated planar nickel(II) complex can exist under certain
condition. These workers have discussed the magnetic and spectral
properties of quadri-coordinated nickel(II) complexes in the light
of the modern ligand field theory and have pointed out that such
complexes are more correctly viewed as slightly perturbed octahedral
complexes, though their simplified treatment does not correctly
predict the absorption spectra of weakly tetragonal nickel(II)
complexes. In a perfectly square planar field (diamagnetic) of
nickel(II) complex, the well defined bands are obtained due to
\[ {1A_g \rightarrow 1B_g} \quad \text{and} \quad {1A_g \rightarrow 1A_g \rightarrow 1B_{2g}} \quad \text{at about} \quad 20,000 - 25,000 \quad \text{cm}^{-1}. \]

**MAGNETIC PROPERTIES:**

From magnetic characteristic, nickel(II) complexes have been divided into three types.

(a) Octahedral paramagnetic complexes with \( 3A_{2g} \) ground term.

(b) Square planar dimagnetic complexes with a spin single ground term.

(c) Tetrahedral paramagnetic complexes with a \( 3T_1 \) ground state.

The magnetic moment value for the octahedral complexes should be given by the term \( 2.83 (1 - 4 \eta / 10 Dq) \), since \( \eta = 315 \text{ cm}^{-1} \), the amount should be higher than 2.83 B.M. and independent of temperature. On the other hand, for tetrahedral complexes the moment should lie between 3.2 - 4.0 B.M. at room temperature and is a function of temperature and depends upon the symmetry of the ligand field. Much more information are available on the magnetic behaviour of octahedral and square planar Ni(II) complexes. Magnetic moments of octahedral complexes usually lie between 2.9 - 3.3 B.M. and only one octahedral complex \( [\text{Ni(diars)}_3 \text{(ClO}_4)_2 \) is reported to be dimagnetic.

The Ni(II) compounds with sub-normal magnetic moments at room temperature have been reported. The magnetic properties of some polynuclear nickel(II) complexes are quite important. The complex \( [\text{Ni}_3(\text{acac})_6 \) is a linear trimer with an octahedral...
distribution of oxygen atoms around each nickel atom and oxygen bridges between two pairs of nickel atoms. The metal-metal (Ni-Ni) distance is 2.8 Å. The $\mu_{\text{eff}}$ is found to be 3.2 B.M. Though the metal-metal distance is very small the exchange interaction between the nickel ions is small$^{51-52}$.

RESULTS AND DISCUSSION

The electronic spectral data, magnetic moments and ligand field parameters of Ni(II) complexes studied in the present investigation are recorded in (Table - 26).

The visible spectra of red coloured complexes $[\text{Ni}_2 (\text{BHAD}) (\text{H}_2\text{O})_4 ]$, $[\text{Ni}_2 (\text{BHAD}) \text{Cl}_2 (\text{H}_2\text{O})_2 ]$, $[\text{Ni}_2 (\text{BHFAD}) \text{Cl}_2 (\text{H}_2\text{O})_2 ]$ and $[\text{Ni}_2 (\text{BAAD}) \text{Cl}_2 (\text{H}_2\text{O})_2 ]$, display ligand field bands at 15850 cm$^{-1}$, 18120 cm$^{-1}$, 15965 cm$^{-1}$, 18325 cm$^{-1}$, 16350 cm$^{-1}$, 17430 cm$^{-1}$ and 16250 cm$^{-1}$, 17435 cm$^{-1}$, respectively assignable to a square planar configuration. It is further supported by the diamagnetic nature of the complexes.

The other Ni(II) complexes recorded here in the present investigation show three spin allowed transitions suggestive of an octahedral ligand field around the metal ions. The ligand field bands occur in the region 8950-11120 cm$^{-1}$ ($\gamma_1$), 14470-19920 cm$^{-1}$ ($\gamma_2$) and 19890-26630 cm$^{-1}$ ($\gamma_3$) corresponding to the transitions $^3A_2g(F) \rightarrow ^3T_2g(F)$ ($\gamma_1$), $^3A_2g(F) \rightarrow ^3T_1g(F)$ ($\gamma_2$) and $^3A_2g(F) \rightarrow ^3T_1g(F)$ ($\gamma_3$) respectively. In addition to it, the complexes also exhibit a bond in the range of 32350-34350 cm$^{-1}$ which may be assigned to the L-M charge transfer transition. The ligand field parameter like Racah parameter (B), crystal field splitting energy ($D_J$), nephelauxetic ratio ($\beta$), transition energy ratio ($\gamma_2/\gamma_1$) and percent covalency ($\delta'$) have been calculated by adopting octahedral model.

The value compared to that of free Ni(II) ion($10^4$) suggest the presence of an appreciable orbital overlap & partial covalent character of
the metal ligand bond. For the most of the Ni(II) complexes studied here the ratio of the second band to the first band ($\gamma_2/\gamma_1$) lies in the range 1.55 – 1.84 which is well in agreement with the reported value 53.

The complex $[\text{Ni}_2(\text{HPAN})_2\text{Cl}_2]$ exhibit band at 8215 cm$^{-1}$, 11180 cm$^{-1}$, 15450 cm$^{-1}$ and 24470 cm$^{-1}$ which can be assigned to transition $3_{B_1} \rightarrow 3_{B_2}$, $3_{B_1} \rightarrow 3_{E_a}$, $3_{B_1} \rightarrow 3_{A_2}$ and $3_{B_1} \rightarrow 3_{E_b}$ respectively is in conformity with earlier observations for penta-coordinated square pyramidal structure.

All these Ni(II) complexes except $[\text{Ni}_2(\text{EHAND}) (\text{H}_2\text{O})_4]$, $[\text{Ni}_2(\text{BDHAD})\text{Cl}_2 (\text{H}_2\text{O})_2]$ $[\text{Ni}_2(\text{BHفاد})\text{Cl}_2 (\text{H}_2\text{O})_2]$ and $[\text{Ni}_2(\text{BAAD})\text{Cl}_2 (\text{H}_2\text{O})_2]$ show magnetic moment values in the range 3.1 – 3.2 B.M. which is expected value for octahedral Ni(II) complexes and also the same complexes are found to be paramagnetic. The above complexes exhibit subnormal magnetic moments and it can be attributed to magnetic interactions between the metal ions present in a dinuclear structure.

The magnetic moment of the complex $[\text{Ni}_2(\text{HPANO})_2\text{Cl}_2]$ is found to be 2.1 B.M. This sub-normal magnetic moment is due to metal-metal interaction in a dimeric structure. The dimerisation is achieved due to phenolic oxygen atoms acting as a bridge ($\text{Ni}_0\text{O}_0\text{Ni}$) between two nickel atoms and the lowering of magnetism is attributed to antiferromagnetism via - superexchange mechanism.
LIGAND FIELD SPLITTING OF THE $d$ SYSTEM IN OCTAHEDRAL AND SQUARE PLANNAR ENVIRONMENT.

Fig-163
| Sl. No. | Complexes | $|\mu|_{\text{eff}}$ B.M. at spectral room temp. | Electronic spectral bands. | Assignments | $D_q$ | $B$ | $\beta$ | $\gamma_2/\gamma_1$ | $\delta$ |
|--------|-----------|-----------------------------------------------|-----------------------------|--------------|------|-----|-------|----------------|------|
| 1.     | $[\text{Ni}_2(\text{HPAN})_2\text{Cl}_2]$ | 2.10 | 8215 | $^3B_1 \rightarrow ^3B_2$ | - | - | - | - | - |
|        |                                                     | 11180 | $^3E_a$ |
|        |                                                     | 15450 | $^3A_2$ |
|        |                                                     | 24470 | $^3E_b$ |
| 2.     | $[\text{Ni}_4(\text{BAFD})_2(\text{H}_2\text{O})_8]$ | 2.22 | 8950 | $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ | 895 | 749.3 | 0.719 | 1.61 | 39.08 | 50 |
|        |                                                     | 14470 | $^3T_{1g}(F)$ |
|        |                                                     | 23620 | $^3T_{1g}(P)$ |
|        |                                                     | 34315 | $\rightarrow \text{CT}$ |
| 3.     | $[\text{Ni}_4(\text{BHEFPAD})_2(\text{H}_2\text{O})_8]$ | 2.2 | 9100 | $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ | 910 | 622.6 | 0.598 | 1.84 | 67.22 |
|        |                                                     | 16750 | $^3T_{1g}(F)$ |
|        |                                                     | 19890 | $^3T_{1g}(P)$ |
| 4.     | $[\text{Ni}_2(\text{BHBFADM})_2(\text{H}_2\text{O})_8]$ | 2.3 | 10250 | $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ | 1025 | 651.6 | 0.625 | 1.70 | 50.0 |
|        |                                                     | 17425 | $^3T_{1g}(F)$ |
|        |                                                     | 23100 | $^3T_{1g}(P)$ |
5. $[\text{Ni}_3(\text{HAHNA})_2 \text{ (H}_2\text{O})_{10}]$ 3.2

- $3\text{A}_{2g}(F) \rightarrow 3\text{T}_{2g}(F)$ 112 636 0.610 1.72 63.93
- $19150 \rightarrow 3\text{T}_{1g}(F)$
- $23750 \rightarrow 3\text{T}_{1g}(P)$
- $32350 \rightarrow \text{CT}$

6. $[\text{Ni}_3(\text{CPAHNA})_2 \text{ (H}_2\text{O})_{10}]$ 3.2

- $3\text{A}_{2g}(F) \rightarrow 3\text{T}_{2g}(F)$ 1089 700 0.672 1.82 48.80
- $19920 \rightarrow 3\text{T}_{1g}(F)$
- $23250 \rightarrow 3\text{T}_{1g}(P)$

7. $[\text{Ni}_2(\text{BHANB}) \text{ (H}_2\text{O})_4]$ -

- $1\text{A}_{1g} \rightarrow 1\text{E}_{1g}$ - - - - - -
- $18120 \rightarrow 1\text{E}_{1g}$

8. $[\text{Ni}_2(\text{BDHAD}) \text{ Cl}_2(\text{H}_2\text{O})_2]$ -

- $1\text{A}_{1g} \rightarrow 1\text{E}_{1g}$ - - - - - -
- $18325 \rightarrow 1\text{E}_{1g}$

9. $[\text{Ni}_2(\text{BHAH}) \text{ Cl}_2(\text{H}_2\text{O})_{10}]$ 3.1

- $3\text{A}_{2g}(F) \rightarrow 3\text{T}_{2g}(F)$ 1047.5 763.3 0.712 1.55 40.4
- $16245 \rightarrow 3\text{T}_{1g}(F)$
- $26630 \rightarrow 3\text{T}_{1g}(P)$
- $34350 \rightarrow \text{CT}$

10. $[\text{Ni}_2(\text{BHCAD}) \text{ (H}_2\text{O})_8]$ 3.2

- $3\text{A}_{2g}(F) \rightarrow 3\text{T}_{2g}(F)$ 1017 779.6 0.748 1.55 33.68
- $15855 \rightarrow 3\text{T}_{1g}(F)$
- $26365 \rightarrow 3\text{T}_{1g}(P)$
- $38225 \rightarrow \text{CT}$
| 11. $\left[N_{2}(BHFA) Cl_{2}(H_{2}O)_{2}\right]$ | - | 16350 | $^1A_{1g} \rightarrow ^1E_{1g}$ | - | - | - | - | - | - |
| | | 17430 | $^1E_{1g}$ | - | - | - | - | - | - |
| 12. $\left[N_{2}(BAAD) Cl_{2}(H_{2}O)_{2}\right]$ | - | 16250 | $^1A_{1g} \rightarrow ^1E_{1g}$ | - | - | - | - | - | - |
| | | 17435 | $^1E_{1g}$ | - | - | - | - | - | - |
ELECTRONIC SPECTRA AND MAGNETIC PROPERTIES OF COPPER(II) COMPLEXES.

Copper(II) ion has a $3d^9$ configuration which gives rise to a $^2D$ ground state and split into two terms under the influence of an octahedral field (spin-orbit coupling being ignored). Jahn-Teller distortion effect leads to appreciable tetragonal distortion of Copper(II) complexes, are regarded as distorted octahedral or approximately square planar complexes. The energy splitting is shown in (Fig. 453), where the $^2T_{2g}$ term is placed higher than $^2E_g$ term because the behaviour of a $d^9$ electronic configuration is mostly described as a $d^1$ hole configuration. If there is no further distortion, we would expect three transitions whether the symmetry is essentially square planar or distorted octahedral.

The visible absorption spectra of acetylacetone and ethylacetoacetone chelates of Copper(II) in solution in several polar and non-polar solvents have examined by Belford et al. and have divided it into three gaussian components. The observed bands are assigned considering the field effect expected to be due to solvent molecules. Graddon has pointed out a band of intermediate intensity ($\lambda = 300$) in the region 27,000 cm$^{-1}$ in the spectra of ethylacetoacetate complexes of copper(II), later on Ferguson accepted the assignment of the band of 27,000 cm$^{-1}$ but pointed out that it was incorrect to treat the ligand field as having $D_{4h}$ symmetry and suggested that $D_{2h}$ or $C_{2v}$ to be a much better approach. This would remove the degeneracy of the doublet and gives rise to four transitions. The finding of Cotton and Wise on the analogous Cu(dmg) which does have ideal molecular alignment, have apparently resolved the discrepancy.
Basu and his coworkers have reported that the spectrum of single crystal of di(3-phenylacetylacetonato) Copper(II) at liquid nitrogen temperature contain four partially resolved bands in the visible region which have ascribed to be due to required d-d transitions and a more intense band at 23,000 cm\(^{-1}\) corresponds to that observed by Graddon. At room temperature this band persists but the four former bands are replaced by two broad bands with maxima at 16,000 and 19,000 cm\(^{-1}\) respectively. Johnson and his coworkers have reported a broad asymmetric band for hydroxy ammidine complexes of Copper(II) which could be divided into two gaussian components at room temperature. The phosphine oxide complex, \([(\text{Ph}_3\text{PO})_4 \text{Cu}]^{2+}\) is an example of a square planar Cu(II) complex having a broad band at about 14,300 cm\(^{-1}\).

In the crystal spectra of \([\text{Cu(CH}_3\text{COO})_2 \text{H}_2\text{O}]\) the acetate ion acts as bridging ligand has also been reported where these bands are observed at 11,400 and 27,000 cm\(^{-1}\). The band at 11,400 cm\(^{-1}\) is assigned to the transition \(dz^2/dxy \rightarrow dx^2-y^2\) and the band at 14,400 cm\(^{-1}\) to \(dz^2/dy^2 \rightarrow dx^2-y^2\). The band at 27,000 cm\(^{-1}\) is not a d-d transition. The ultraviolet and visible spectral studies of several schiff base complexes of copper(II), believed to be planar, have been carried out in different inter and polar solvents and the bands are located in the region 15,000 - 19,000 cm\(^{-1}\).

Electronic spectra of the complexes \([\text{Cu(TSC)}_2 x^2]\) (\(x = \text{ClO}_4, \text{NO}_3, \text{Cl, Br}\)) show two maxima at 15,000 and 19,000 cm\(^{-1}\) which is reported to be due to \([\text{Cu(TSC)}_2]^{2+}\) chromophore. Blumberg and peisach have proposed with certain intensity absorbing copper proteins, that inspite of the high intensity, the bands at 20,000
cm\(^{-1}\) are due to d–d transitions. The spectra of Cu(KTS)\(^{6+}\) and a number of closely related Cu(II) bis(thiosemicarbazone) complexes\(^{69}\) have two bands at 20,000 cm\(^{-1}\) and 30,000 cm\(^{-1}\). Livingstone and his coworkers have reported\(^{70}\) a number of complexes with tridentate SNN ligands of the type Cu\(X_2(SNN\text{Me})\) (\(X = \text{Cl}^-, \text{Br}^-, \text{SCN}^-\)). They found two bands in the region 6,925 – 13,700 cm\(^{-1}\). The spectra of another complex of the type [Cu (SNN\text{Me})\(_2\)] (BF\(_2\)) show two d–d transition bands at 10,420 and 16,130 cm\(^{-1}\).

MAGNETIC PROPERTIES:

Figgis and Martin have reported\(^{71}\) the values of the exchange integral in copper acetate and copper acetate monohydrate at 302 and 286 cm\(^{-1}\) respectively. While postulating the exchange to take place between the copper atoms by means of the overlap of the \(d\) \(x^2-y^2\) orbital to form bond, these authors emphasize the weakness of these bond and important role of the interaction occurs by super exchange mechanism via carboxylate group. Copper(II) acetate monohydrate and anhydrous copper(II) acetate have \(\mu^2\) eff value 1.39 and 1.40 B.M. respectively at room temperature\(^{72-73}\). Copper(II) acetates are dimers\(^{74}\) and their magnetic properties have been studied over a wide range of temperature\(^{75}\).

Martin and Watermann have studied\(^{76}\) the magnetic properties of copper(II) formate tetrahydrate over the temperature range 80 – 300 K. It possess \(\mu^2\) eff = 1.66 B.M. at 295°K and \(\Theta = -173\) K. These workers have explained the super exchange mechanism in terms of a prior \(T_{2g} \rightarrow A_g\) excitation followed by \(T_{2g} \rightarrow T_{1g}\) exchange through which cupric ions are linked in chains.
Kato and his coworkers have studied the copper(II) complexes with sub-normal magnetic moments (below 1.73 B.M.) several copper compounds such as CuO, CuF₂, CuS, CuCl₂, CuBr₂, CuSO₄, and KCuF₃ are known to exhibit intermolecular magnetic exchange. Besides this, there is a number of complexes where the exchange is presumably intramolecular due to the formation of Cu-Cu bands.

The low magnetic moments (μ_eff. = 1.4 B.M.) of bivalent copper with substituted acetic acid, benzoic acid, L, w - dicarboxylic acids and manycupric alkanoates indicate anti-ferromagnetism in these systems. The ferromagnetic interactions take place along symmetrically bridged halogen chain and antiferromagnetic interactions along asymmetrically bridged halogen chains. The copper complexes with 2,3-dimethylquinoxaline and semicarbazide ligands exhibit antiferromagnetism.

RESULTS AND DISCUSSION:

The electronic spectral data and the magnetic moment values of all the complexes reported in the present investigation are recorded in (Table - 27).

The electronic spectra of all the copper(II) complexes except [Cu₂(BDHAD)Cl₂(H₂O)₂] show one broad asymmetric band in the region 11110 cm⁻¹ 15670 cm⁻¹ and another band at Ca 28450 cm⁻¹ - 35105 cm⁻¹. The former band can be assigned to the transition 2E_g → 2T₂g in a distorted octahedral geometry and the latter band can be ascribed to a CT band. The width and asymmetry provide evidence for tetragonal distortion and Jahn-Teller effect.
The copper(II) complex $[\text{Cu}_2(\text{BDIIAD})\text{Cl}_2(\text{H}_2\text{O})_2]$ the electronic spectral observed at 16550 cm$^{-1}$ which can be assigned to the transition $^2\text{A}_1 \rightarrow ^2\text{E}$ suggestive of a square planar stereochemistry around the Cu(II) ions. The complex $[\text{Cu}_2(\text{HPAN})_2\text{Cl}_2]$ exhibits bands at 13885 and 11295 which can be assigned to transition $^2\text{E}_1 \rightarrow ^2\text{B}_2$ and $^2\text{E}_1 \rightarrow ^2\text{A}_1$ respectively is in conformity with earlier observations for penta-coordinated square pyramidal Cu(II) complex.

The $\mu$$_{\text{eff}}$ values of all the complexes except $[\text{Cu}_2(\text{HPAN})_2\text{Cl}_2]$ $[\text{Cu}_4(\text{BAHD})(\text{H}_2\text{O})_8]$, $[\text{Cu}_4(\text{BHEFPAD})_2(\text{H}_2\text{O})_8]$ and $[\text{Cu}_4(\text{BHEFADM})_2(\text{H}_2\text{O})_8]$ lies in the range 1.8 - 1.9 B.M. in accordance with octahedral geometry. The $\mu$$_{\text{eff}}$ values of the above complexes are found to be subnormal (1.4 - 1.5 B.M.) indicating the presence of antiferromagnetic exchange interaction between Cu-Cu ions in a dinuclear structure (Table - 27).
### Table 27
Electronic spectra, Magnetic moments and ligand field parameters of Cu(II) complexes.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Complexes</th>
<th>$\mu_{\text{eff.}}$</th>
<th>E.M. at room temp.</th>
<th>Electronic Spectral bands</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$\left[ \text{Cu}_2(\text{HPAN})_2 \text{Cl}_2 \right]$</td>
<td>1.5</td>
<td>13885, 11295</td>
<td>$^2B_1 \rightarrow ^2E_2$</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>$\left[ \text{Cu}_4(\text{BAHD})(\text{H}_2\text{O})_8 \right]$</td>
<td>1.5</td>
<td>14350, 32210</td>
<td>$^3E_g \rightarrow ^2T_{2g}$</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>$\left[ \text{Cu}_4(\text{DHBFPAD})_2(\text{H}_2\text{O})_8 \right]$</td>
<td>1.5</td>
<td>11110, 14250, 20450</td>
<td>$^2B_{1g} \rightarrow ^2E_{1g}$</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>$\left[ \text{Cu}_4(\text{DHBFADM})_2(\text{H}_2\text{O})_8 \right]$</td>
<td>1.4</td>
<td>11210, 13950, 20350</td>
<td>$^2B_{1g} \rightarrow ^2E_{1g}$</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>$\left[ \text{Cu}_3(\text{HAHNA})_2(\text{H}<em>2\text{O})</em>{10} \right]$</td>
<td>1.9</td>
<td>14100-14915, 28450</td>
<td>$^2E_g \rightarrow ^2T_{2g}$</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>$\left[ \text{Cu}_3(\text{CPAHNA})_2(\text{H}<em>2\text{O})</em>{10} \right]$</td>
<td>1.9</td>
<td>14200-14850, 28550</td>
<td>$^2E_g \rightarrow ^2T_{2g}$</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>$\left[ \text{Cu}_2(\text{BHAND})(\text{H}_2\text{O})_4 \right]$</td>
<td>1.8</td>
<td>14380, 31210</td>
<td>$^2E_g \rightarrow ^2T_{2g}$</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>$\left[ \text{Cu}_2(\text{EDHAD}) \text{Cl}_2(\text{H}_2\text{O})_2 \right]$</td>
<td>1.8</td>
<td>16550</td>
<td>$^2A_{1g} \rightarrow ^2E_g$</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>$\left[ \text{Cu}_2(\text{BHAD}) \text{Cl}_2(\text{H}_2\text{O})_6 \right]$</td>
<td>1.8</td>
<td>14250-15670, 35105</td>
<td>$^2E_g \rightarrow ^2T_{2g}$</td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>$\left[ \text{Cu}_2(\text{BHFA}) \text{Cl}_2(\text{H}_2\text{O})_6 \right]$</td>
<td>1.8</td>
<td>13440-15535, 14380, 33450</td>
<td>$^2E_g \rightarrow ^2T_{2g}$</td>
<td>$\rightarrow$ CT</td>
</tr>
</tbody>
</table>
11. \[\text{Cu}_2(\text{BHPAD})\text{Cl}_2(\text{H}_2\text{O})_6\] 1.8 \[13450-15530\] \(2\text{E}_g \rightarrow 2\text{T}_{2g}\)
\[34360\] \(\rightarrow \text{CT}\)
\[32370\]

12. \[\text{Cu}_2(\text{BAAD})\text{Cl}_2(\text{H}_2\text{O})_6\] 1.8 \[13210-15350\] \(2\text{E}_g \rightarrow 2\text{T}_{2g}\)
\[34470\] \(\rightarrow \text{CT}\)

2-hydroxy-3-(phenylazo)-1-naphthaldehyde (HPANH); 4,4'-bis (3-formyl-2-hydroxynaphthyl-1-azo)-3,3'-dimethylbenzidine (BAADH2);
4,4'-bis (2-hydroxy-5-bromo-3-formylphenylazo) diphenyl (BHBFPADH2);
4,4'-bis (2-hydroxy-5-bromo-3-formylphenylazo) diphenyl methane (BHBFPADH2);
4-(2'-hydroxyphenyl-1'-azo)-1-hydroxy-2-naphthoic acid (HANAH2);
4-(2'-carboxyphenyl-1'-azo)-1-hydroxy-2-naphthoic acid (CPAHNAH2);
4,4'-bis (4-hydroxy-1-azo-2-naphthoic acid) 3,3'-dimethyldiphenyl (BHANDH2);
4,4'-bis (2,4-dinitro-6-hydroxy phenyl-1-azo) 3,3'-dimethyl diphenyl (BDHADH2);
4,4'-bis (2-hydroxynaphthyl-1-azo) 3,3'-dimethyl diphenyl (BHADH2);
4,4'-bis (4-hydroxy-5-carboxyphenyl-1-azo) 3,3'-dimethyldiphenyl (BHCADH2);
4,4'-bis (4-hydroxy-5-formyl phenyl-1-azo) 3,3'-dimethyldiphenyl (SHFADH2);
4,4'-bis [(acetylacetonyl-3')-azo] 3,3'-dimethyldiphenyl (BAAD).
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