CHAPTER II

ADVANCE SUMMARY OF THE PRESENT INVESTIGATION
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The metal ions selected for the present investigation are cobalt(II) \([3d^7]\), nickel(II) \([3d^8]\), copper(II) \([3d^9]\), zinc(II) \([3d^{10}]\), cadmium (II) \([4d^{10}]\) and mercury(II) \([5d^{10}]\). These metal ions are reacted with multidonor azodyes. The azodye ligands synthesized in our laboratory behave as tridentate chelating ligand having \(\text{O} \text{O} \text{N}\) potential donor atoms, bis-bidentate ligands with \(\text{O} \text{N} - \text{O} \text{O}, \text{O} \text{O} - \text{O} \text{O}, \text{O} \text{N} - \text{N} \text{O}\) donor atoms and bis-tridentate ligands having \(\text{O} \text{O} \text{N} - \text{N} \text{O} \text{O}\) donor atoms. Using these multidentate azo dye ligands, a number of polymeric (dimeric, trimeric and tetrameric) complex compounds have been synthesized.

This thesis has been divided into ten chapters. In chapter I, a brief introduction of coordination chemistry has been presented. An advanced summary of the present investigation has been presented in chapter II. In chapter III a general survey of metal complexes has been described. The preparation of azo-dye and their metal complexes have been discussed in chapter IV. The infrared spectra of the ligands and the metal complexes have been discussed in chapter V. The probable structure of the complex compounds have been suggested basing upon their electronic spectra and magnetic measurement data which have been presented in chapter VI. The \(^1\text{H}\) NMR spectral data of a few ligands and ESR spectra of some copper complexes have been included in chapter VII. Thermal analysis and XRD- study of a few complex compounds have been included in the chapter VIII. Analysis and physical measurement find their place in chapter IX. A list of specialised reference books along with a list of publications have been mentioned in chapter X.
The present work describes the synthesis and characterisation of a number of polynuclear metal complexes with the following azodyes.

1. 2-hydroxy-3-(phenylazo)-1-naphthaldehyde. [HPANH]

2. 4,4-bis (3-formyl-2-hydroxynaphthyl-1-azo)-3,3 dimethylbenzidine. [BAHDH₂]

3. 4,4-bis (2-hydroxy-5-bromo-3-formyl phenylazo)diphenyl. [BHBFPADH₂]
4. $\text{Br} \quad \text{OH} \quad \text{N} \quad \text{OH} \quad \text{CH}_2 \quad \text{Br} \quad \text{N} \quad \text{OH}

$4,4\text{-bis (2-hydroxy-5-bromo-3-formyl phenyl azo)diphenyl methane.}$

5. 

$\text{COOH} \quad \text{N} \quad \text{N} \quad \text{OH} \quad \text{COOH}

$4\text{-}(2\text{-hydroxy phenyl-1-azo)-1-hydroxy-2-naphthoic acid.}$

6. 

$\text{COOH} \quad \text{COOH}

$4\text{-}(2\text{-carboxy phenyl-1-azo)-1-hydroxy-2-naphthoic acid.}$

7. 

$\text{CH}_3 \quad \text{CH}_3 \quad \text{OH} \quad \text{COOH}

$4\text{,4\text{'-bis(4-hydroxy-1-azo-2-naphthoic acid)3,3\text{'-dimethyldiphenyl.}}$

$[\text{BH} \text{HNDH}_4]$
8. \[
\begin{array}{c}
\text{NO}_2 \\
\text{NO}_2 \\
\text{N=N} \\
\text{N=N} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{N=N} \\
\text{N=N} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{N=N} \\
\text{N=N} \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\]

4,4'-bis(2,4-dinitro-6-hydroxy phenyl-1-azo)3,3' dimethyldiphenyl. \( \text{[BDHADH}_2] \)

9. \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{N=N} \\
\text{N=N} \\
\text{OH} \\
\text{OH} \\
\text{N=N} \\
\text{N=N} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{N=N} \\
\text{N=N} \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\]

4,4'-bis(2-hydroxynaphthyl-1-azo)3,3' dimethyldiphenyl. \( \text{[BHADH}_2] \)

10. \[
\begin{array}{c}
\text{COOH} \\
\text{HO} \\
\text{N=N} \\
\text{N=N} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{N=N} \\
\text{N=N} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{N=N} \\
\text{N=N} \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\]

4,4'-bis(4-hydroxy-5-carboxyphenyl-1-azo)3,3' dimethyldiphenyl. \( \text{[BHCADH}_4] \)

11. \[
\begin{array}{c}
\text{CHO} \\
\text{HO} \\
\text{N=N} \\
\text{N=N} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{N=N} \\
\text{N=N} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{N=N} \\
\text{N=N} \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\]

4,4'-bis(4-hydroxy-5-formyl phenyl-1-azo)3,3' dimethyldiphenyl. \( \text{[BHFADH}_2] \)

12. \[
\begin{array}{c}
\text{O=C} \\
\text{CH} \\
\text{N=N} \\
\text{N=N} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{O=C} \\
\text{CH}_3 \\
\text{C=O} \\
\text{C=O} \\
\text{C=O} \\
\text{C=O} \\
\end{array}
\]

4,4'-bis[ (acetylacetonyl-3')-azo]3,3' dimethyldiphenyl. \( \text{[BAAD]} \)
PREPARATION OF AZO DYES:

The aromatic amines used for the preparation of azodyes are aniline, O-tolidine (3,3'-dimethylbenzidine), benzidine, 4,4' diaminodiphenylmethane, O-aminophenol, anthranic acid. These amines are treated with conc. HCl and sodium nitrite solution at 0°C to form corresponding diazonium chlorides. The alkaline solution of 2 hydroxy-1-naphthaldehyde, 5-Bromosalicylaldehyde, 1-hydroxy-2-naphthoic acid, 2,4-dinitrophenol, p-naphthol, salicylic acid, salicylaldehyde and acetyl-acetone at 0°C are separately treated with respective diazonium chlorides, when different coloured azodyes separated out. The azo dyes behave as tridentate, bis-tridentate and bis-bidentate ligands coordinating to the metal ions through azo nitrogen, phenolic oxygen, carboxyl oxygen, aldehydic oxygen, ketonic oxygen and enolic oxygen atoms.

The ligand, 2-hydroxy-3-(phenyl-azo)-1-naphthaldehyde coordinates to the metal ions through one of azo nitrogen atoms, one aldehydic oxygen atom and phenolic oxygen atom which acts as a bridge between two metal ions favouring the formation of dinuclear structure. Thus it serves as a tridentate ligand having \( \text{N} \text{O} \text{O} \) donor atoms with bridging phenolic oxygen atom (Fig. 1).

The azodye, 4,4'-bis(3-formyl-2-hydroxyphenyl-1-azo)-3,3'-dimethylbenzidine coordinates to the metal atoms through its two azonitrogen, two aldehydic oxygen and two phenolic bridging oxygen atoms. It behaves as a bis-tridentate ligand with \( \text{O} \text{N} \text{O} \text{C} \) donor atoms (Fig. 2).
The azodye, $4,4'\text{-bis}(2\text{-hydroxy}-5\text{-bromo}-3\text{-formylphenylazo})\text{-diphenyl}$ coordinates to the metal ions in an analogous manner as in the previous case and hence behaves as a bis-tridentate ligand with $0\text{N} \overset{\infty}{\sim} \text{N} 0\text{O} 0$ donor atoms. (Fig-3).

The bis-tridentate azo dye, $4,4'\text{-bis}(2\text{-hydroxy}-5\text{-bromo}-3\text{-formyl phenylazo})\text{-diphenylmethane}$, is bounded to the metal ions through two azo nitrogens, two aldehydic oxygens and two phenolic oxygen atoms (Fig-4).

The azo dyes, $4-(2'\text{-hydroxy phenyl}-1'\text{-azo})\text{-1-hydroxy-2-}naphthoic$ and $4-(2'\text{-carboxyphenyl}-1'\text{-azo})\text{-1-hydroxy-2-naphthoic}$ acid coordinate to the metal ions through phenolic oxygen, carboxyl oxygen and one azo nitrogen atoms. Thus these two dyes serve as bis-bidentate ligands with $0\text{N} \overset{\infty}{\sim} \text{O} $ donor atoms (Fig-5).

The azodyes, $4,4'\text{-bis}(4\text{-hydroxy-1-azo-2-naphthoic acid})\text{-3,3'-}dimethyl diphenyl$ and $4,4'\text{-bis}(4\text{-hydroxy-5-carboxyphenyl-1-azo})\text{-3,3'-}dimethyl diphenyl$ coordinate to the metal ions through phenolic oxygen and carboxyl oxygen atoms only. These two azodyes behave as bis-bidentate ligands with $0\text{N} \overset{\infty}{\sim} \text{O} $ donor atoms (Fig-6).

The azodyes, $4,4'\text{-bis}(2,4\text{-dinitro-6-hydroxyphenyl -1-azo})\text{-3,3'-}dimethyl diphenyl$ and $4,4'\text{-bis}(2\text{-hydroxynaphthyl-1-azo})\text{-3,3'-}dimethyl diphenyl$ are bonded to the metal ions through two azo nitrogen and two phenolic oxygen atoms. Both the dyes serve as bis-bidentate ligand with $0\text{N} \overset{\infty}{\sim} \text{N} 0$ potential donor atoms as represented by Fig- 7 & Fig-8 respectively.
The azo dye, 4,4'-bis(4-hydroxy-5-formylphenyl-1-azo)-3,3'-dimethyl diphenyl coordinates to the metal ions through two phenolic oxygen atoms and two aldehydic oxygen atoms thus behaving as bis-bidentate ligands with $\text{O} \equiv \text{C} - \text{O}^{-}$ donor atoms (Fig-9).

The azo dye, 4,4'-bis [acetylacetone-3'-azo]-3,3'-dimethyl diphenyl is bonded to the metal ions through two ketonic oxygen and two enolic oxygen atoms. It behaves as a bis-bidentate ligand having $\text{O} \equiv \text{C} - \text{C}^{-}$ donor atoms (Fig-10).

**PREPARATION OF METAL COMPLEXES:**

The metal complexes have been prepared by adding the chloride salts of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) dissolved in ethanol to the solution azodyes in suitable organic solvents like methanol, ethanol, dioxane or dimethylformamide in 1:1, 1:2 or 2:3 molar ratio. The conc. ammonia is then added drop by drop with stirring when metal complexes separated out in neutral medium. The complexes thus isolated are then filtered, washed successively with ethanol and ether and dried in vacuo. Most of the complexes are amorphous in nature, have high melting points and are insoluble in common organic solvents but sparingly soluble in DMF, suggestive of a polymeric nature of the complexes.

**INFRARED SPECTRA OF THE COMPLEXES:**

The preparation of multinucleared metal complexes using multidentate azo dyes as ligands and their characterisation is the main aim of this work. The chelating azodyes coordinate to the metal ions through phenolic, enolic, carbonyl, carboxyl oxygen and azo nitrogen atoms.
In the i.r. spectra of the ligand, 2-hydroxy-3-(phenylazo)-1-naphthaldehyde, weak bands are observed at 2880 cm\(^{-1}\) and 3070 cm\(^{-1}\) due to phenolic OH group and the lowering is attributed to the intramolecular hydrogen bonding, O - H .... O. The disappearance of these bands in the metal chelates indicates the removal of the phenolic proton and the formation of M-O bond. In the ligand \(\gamma (C=O)\) and \(\gamma (-N=N-)\) appear at 1640 cm\(^{-1}\) and 1590 cm\(^{-1}\) respectively and in the metal complexes at ca 1630 and ca 1540 cm\(^{-1}\) indicating the bonding of carbonyl oxygen and one of the azo nitrogen atoms to the metal ions. In the ligand \(\gamma (C=O)\) vibration appears at 1510 cm\(^{-1}\) and the positive shift of 10-15 cm\(^{-1}\) in the metal complexes supports the formation of M-O bridge in a dimeric structure. The conclusive evidence of bonding of oxygen and nitrogen atoms in the complexes is further provided by the appearance of \(\gamma (M-O)\) and \(\gamma (M-N)\) at ca 480 cm\(^{-1}\) and ca 410 cm\(^{-1}\) respectively. Thus the azo dye behaves as a O O N donor tridentate ligand with the phenolic oxygen atom acting as a bridge between two metal atoms favouring the formation of a dinuclear structure (Fig-11).

In the i.r. spectrum of the ligand, 4,4'-bis(3-formyl-2-hydroxynaphthyl-1-azo)3,3'-dimethyldiphenyl, the bands observed at 1620 cm\(^{-1}\), 1545 cm\(^{-1}\) and 1380 cm\(^{-1}\) can be assigned to \(\gamma (C=O)\), \(\gamma (-N=N-)\) and \(\gamma (C=O)\) vibrations respectively. The negative shift of ca 10-20 cm\(^{-1}\) of the first bands in the metal complexes indicates the bonding of carbonyl oxygen and azo nitrogen atoms to the metal atoms. The positive shift of the C-O band in the metal chelates can be assigned to the presence of a bridging oxygen (M - O M) atoms.
The presence of coordinated water molecules in Co(II), Ni(II) and Cu(II) complexes is shown by the appearance of a broad hump at ca 3400 cm\(^{-1}\) followed by a sharp peak at ca 830 cm\(^{-1}\) assignable to OH stretching and rocking vibrations respectively. Thus the azo dye behaves as a bis-tridentate ligand (Fig-12).

The azo dye ligands, 4,4\(^{\prime}\)-di-(2-hydroxy-5-bromo-3-formylphenyl azo) -diphenyl and 4,4\(^{\prime}\)-di(2-hydroxy-5-bromo-3-formylphenylazo) diphenylmethane behave as bis-tridentate ligands having donor atoms. In the ligands the bands appearing at 1605 cm\(^{-1}\) and 1595 cm\(^{-1}\) can be assigned to \(\nu(N-N)\) vibrations respectively. Shifting of this band by ca 70-80 cm\(^{-1}\) in the metal complexes indicates the bonding of one of the azo nitrogen atoms to the metal ions. The bands observed at 1670 cm\(^{-1}\) and 1645 cm\(^{-1}\) can be ascribed to \(\nu(C=O)\) vibration. In the metal chelates a decrease of ca 40-45 cm\(^{-1}\) occurs indicating the bonding of the carbonyl oxygen atoms to the metal ions. The bands observed at 1535 cm\(^{-1}\) and 1530 cm\(^{-1}\) in the ligands can be assigned to \(\nu(C=O)\) vibration and a positive shift of ca 10-20 cm\(^{-1}\) in the metal chelates indicates the bridging phenolic oxygen atom (\(\text{M} \rightleftharpoons \text{M}\)). The far i.r. spectra of the complexes show medium sharp bands at ca 405-415 cm\(^{-1}\) and 510-515 cm\(^{-1}\) assignable to \(\nu(N-N)\) and \(\nu(M=O)\) vibrations respectively (Fig-13).

The azo dyes, 4-(2'-hydroxyphenyl-1'-azo)-1-hydroxy-2-naphthoic acid and 4-(2'-carboxyphenyl-1'-azo)-1-hydroxy-2-naphthoic acid behave as doubly-bidentate donor ligands. The bands observed at 1595 cm\(^{-1}\), 1605 cm\(^{-1}\), 1280 cm\(^{-1}\) and 1270 cm\(^{-1}\), in the ligands can be assigned to \(\nu(N=N)\) and \(\nu(C=O)\) vibrations respectively and
a negative shift of ca 30-40 cm⁻¹ in the former case and ca 30-50 cm⁻¹ in the latter case indicate the bonding of azo nitrogen and phenolic oxygen atoms to the metal ions. In the ligands the band observed at 1630 cm⁻¹ and 1670 cm⁻¹ can be assigned to \( \nu_{as}(\text{COO}) \) vibration and a bathochromic shift of ca 200 cm⁻¹ in the metal complexes indicates the unidentate coordination of carboxylate group. The presence of coordinated water molecules in all the metal complexes is indicated from the double humps and broad bands at ca 3120-3420 cm⁻¹ followed by a sharp peak at ca 810-840 cm⁻¹ assignable to OH stretching and rocking vibrations respectively. The evidence of bonding is further proved by the appearance of \( \nu(M-O) \) and \( \nu(M-N) \) at ca 445 cm⁻¹ and ca 410 cm⁻¹ respectively (Fig-14).

The azo dye, 4,4'-bis(4-hydroxy-1-azo-2-naphthoic acid)3,3' -dimethyldiphenyl behaves as a doubly-bidentate \( \text{O} \)-(\( \text{O} \)) donor ligand. In the ligand the band observed at 1460 cm⁻¹ can be assigned to \( \nu(C-O) \) vibration. In the metal chelates this band has been shifted down by 10-30 cm⁻¹ indicating the bonding of phenolic oxygen atoms. In the ligand, the \( \nu_{as}(\text{COO}^-) \) and \( \nu_{s}(\text{COO}^-) \) bands appear at 1650 cm⁻¹ and 1410 cm⁻¹ respectively and in the metal chelates these bands are found at \( \sim 1600 \) cm⁻¹ and 1380-1400 cm⁻¹ with a difference of \( \sim 200 \) cm⁻¹ in support of monodentate nature of the carboxylate group. In the metal chelates broad bands are observed at \( \sim 3200-3400 \) cm⁻¹ followed by sharp peak at \( \sim 850 \) cm⁻¹ attributed to OH stretching and rocking vibrations respectively thus showing the presence of coordinated water molecules in the complexes (Fig-15.)

The azo dyes, 4,4'-bis(2,4-dinitro-6-hydroxyphenyl-1-azo)3,3' -dimethyldiphenyl and 4,4'-bis(2'-hydroxynaphthal-1-azo)-3,3' -
dimethyldiphenyl, behave as doubly-bidentate ligand having \( \text{O} - \text{N}-\text{N} \text{O} \) donor atoms. In the ligands the sharp band observed at 1620 cm\(^{-1}\) and 1635 cm\(^{-1}\) can be assigned to \( \nu (-\text{N}=-\text{N}) \) vibration respectively. In the metal chelates these bands appear at ca 1600 cm\(^{-1}\) and ca 1620 cm\(^{-1}\) indicative of azo nitrogen coordination to the metal ions. In the ligands the bands observed at 1490 cm\(^{-1}\) and 1470 cm\(^{-1}\) can be assigned to \( \nu (\text{C}-\text{O}) \) vibration and a decrease of 10-30 cm\(^{-1}\) of this band in the metal chelates shows the bonding of phenolic oxygen atoms to the metal ions. The presence of coordinated water molecules in the complexes is suggested by the appearance of broad bands and double humps at a band 3450 cm\(^{-1}\) followed by a sharp peak at 850 cm\(^{-1}\) attributed to stretching and nocking vibrations respectively (Fig. 16 & 17).

The azo dyes, \( 4,4'\text{-bis}(2\text{-hydroxy-naphthyl-1-azo})-3,3'\text{-dimethyldiphenyl} \) and \( 4,4'\text{-bis}(4\text{-hydroxy-5-carboxyphenyl-1-azo})-3,3'\text{-dimethyldiphenyl} \), behave as doubly-bidentate \( \text{O} - \text{N}-\text{N} \text{O} \) donor ligand. In the ligands the bands at 1465 cm\(^{-1}\) and 1485 cm\(^{-1}\) can be assigned to \( \nu (\text{C}-\text{O}) \) vibration which undergo a negative shift of 10-15 cm\(^{-1}\) in the metal chelates indicating coordination of phenolic oxygen atoms to the metal ions. In the former ligand the \( \nu_{as}(\text{COO}^-) \) and \( \nu_s(\text{COO}^-) \) bands appear at 1680 cm\(^{-1}\) and 1420 cm\(^{-1}\) respectively and in the metal chelates these bands are found at 1600 cm\(^{-1}\) and 1385 - 1400 cm\(^{-1}\) with a difference of \( \sim 205 \text{ cm}^{-1} \) in support of monodentate nature of carboxylate group. In the latter ligand. In case of latter ligand the band appeared at 1665 cm\(^{-1}\) can be ascribed to \( \nu (\text{C}=\text{O}) \) vibration which has been shifted down by 10-15 cm\(^{-1}\) in the metal chelates indicating bonding of carbonyl oxygen atoms to
the metal ions. The conclusive evidence of bonding of oxygen atoms
is provided by the appearance of a band at $\sim 500 \text{ cm}^{-1}$ (M-O) (Fig-
18 & 19).

The azo dye, 4,4'-bis [(acetylacetonyl-3')-azo] 3,3'-dimethyl-
diphenyl, can exist in two keto and enol tautomeric forms (Fig-20).
In the ligand four important bands at 1670,1610,1180 and 1620 cm$^{-1}$
have been assigned. In the complexes the former three frequencies
show negative shifts indicating the coordination of ketonic and
enolic oxygen atoms to the metal ions. The fourth band remains un-
affected in the metal chelates showing non-coordination of the azo
nitrogen atoms. The presence of coordinated water molecules in all
the complexes is indicated by the appearance of a broad band at
$\sim 3300 - 3500 \text{ cm}^{-1}$ followed by a sharp peak between 835-845 cm$^{-1}$
assignable to OH stretching and rocking vibrations respectively. Thus
the azo dye behaves as a bis-bidentate ligand with $\text{donor}$

**ELECTRONIC SPECTRA AND MAGNETIC PROPERTIES OF METAL COMPLEXES :**

**COBALT(II) COMPLEXES:**

The electronic spectra of the Cobalt(II) complexes except
$\text{Co}_2(\text{HPAN})_2\text{Cl}_2$ show mostly three d-d transitions in the region
$8400 - 9022 \text{ cm}^{-1}, 16460 - 18405 \text{ cm}^{-1}$ and $19230-21685 \text{ cm}^{-1}$ assignable
to $^4T_{1g}(F) \rightarrow ^4T_{2g}(F \chi\gamma_1), ^4T_{1g}(F) \rightarrow ^4A_{2g}(F) (~\gamma_2 ~)$ and $^4T_{1g}(F)\rightarrow$
$^4T_{1g}(F)(\gamma_3)$ transitions respectively. The spectral parameters like
$D_1, B, \gamma_2/\gamma_1$ and $\sigma$ have been calculated using Underhill and Billing
equation. These values along with higher $\mu^2_{\text{eff.}}$ values in the range
5.0 -- 5.1 B.M. support an octahedral stereochemistry for the complexes.
In some complexes charge transfer bands are also observed in the region 31150 - 35500 cm\(^{-1}\).

The electronic spectrum of the complex \([\text{Co}_2(\text{HPAN})_2\text{Cl}_2]\) displays three bands 11450 cm\(^{-1}\) (\(\gamma_2\)), 15300 cm\(^{-1}\) (\(\gamma_3\)) and 19560 cm\(^{-1}\) (\(\gamma_4\)) in conformity with earlier observation for penta coordinated square pyramidal Co(II) complex.

The magnetic moments of the complexes except \([\text{Co}_4(\text{BAHD})_2(\text{H}_2\text{O})_8]\), \([\text{Co}_4(\text{BHBFPAD})_2(\text{H}_2\text{O})_8]\) and \([\text{Co}_4(\text{BHFADM})_2(\text{H}_2\text{O})_8]\) fall in the range 5.0 - 5.1 B.M. expected for high spin octahedral Cobalt(II) complexes. 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 (M\(\bigtriangleup\)O\(\bigtriangleup\)M). These complexes have been suggested to possess octahedral geometry basing upon their spectral band position and values of spectral parameters which are in agreement with those reported in 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 subnormal magnetic moment is due to metal-metal interaction in a dimeric structure. The dimerisation is achieved through the phenolic oxygen atoms acting as a bridge between two Cobalt atoms and the lowering of magnetism is attributed to antiferromagnetism via super exchange mechanism.

**NICKEL COMPLEXES**:

The visible electronic spectra of the red coloured complexes \([\text{Ni}_2(\text{BHAN})_4(\text{H}_2\text{O})_4]\), \([\text{Ni}_2(\text{BDHAD})_2(\text{H}_2\text{O})_2]\), \([\text{Ni}_2(\text{BHFAD})_2(\text{H}_2\text{O})_2]\)
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 supported by the dimagnetic 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 bands occurs 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 transition \(3\text{A}_{2g}(\text{F}) \rightarrow 3\text{T}_{2g}(\text{F})(\gamma_1)\), \(3\text{A}_{2g}(\text{F}) \rightarrow 3\text{T}_{1g}(\text{F})(\gamma_2)\) and \(3\text{A}_{2g}(\text{F}) \rightarrow 3\text{T}_{1g}(\text{F})(\gamma_3)\) respectively. In addition to it the complexes also exhibit a band in the range of 32350 -- 34350 cm\(^{-1}\) which may be assigned to the L→M charge transfer bands.

The complex \([\text{Ni}_2(\text{HPAN})_2\text{Cl}_2]\) exhibits bands at 8215 cm\(^{-1}\), 15450 cm\(^{-1}\) and 24470 cm\(^{-1}\) which can be assigned to transition \(3\text{B}_1 \rightarrow 3\text{B}_2\), \(3\text{B}_1 \rightarrow 3\text{E}^a\), \(3\text{B}_1 \rightarrow 3\text{A}_2\) and \(3\text{B}_1 \rightarrow 3\text{E}^b\) respectively, is in conformity with earlier observations for pentacoordinated square pyramidal structure.

All the nickel complexes except \([\text{Ni}_2(\text{BHAN})(\text{H}_2\text{O})_4]\), \([\text{Ni}_2(\text{BHAD})\text{Cl}_2(\text{H}_2\text{O})_2]\), \([\text{Ni}_2(\text{BAAD})\text{Cl}_2(\text{H}_2\text{O})_2]\) 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.
COPPER (II) COMPLEXES:

The electronic spectra of all the copper(II) complexes except \([\text{Cu}_2(\text{BDHAD})\text{Cl}_2(\text{H}_2\text{O})_2]\) and \([\text{Cu}_2(\text{HPAN})_2\text{Cl}_2]\) show one broad asymmetric band in the region \(11110 \text{ cm}^{-1} - 15670 \text{ cm}^{-1}\) and another band at ca \(28450 \text{ cm}^{-1}, 25105 \text{ cm}^{-1}\). The former band can be assigned to the transition \(2_{E_g} \rightarrow 2_{T_{2g}}\) 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.

In the copper(II) complex \([\text{Cu}_2(\text{BDHAD})\text{Cl}_2(\text{H}_2\text{O})]\) the electronic spectral band observed at \(16550 \text{ cm}^{-1}\), can be assigned to the transition \(2_{A_{1g}} \rightarrow 2_{E_g}\) 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 \(13085\) and \(11295\) which can be assigned to transitions \(2_{B_1} \rightarrow 2_{B_2}\) and \(2_{B_1} \rightarrow 2_{A_1}\) respectively is in conformity with earlier observations for pentacoordinated square pyramidal Cu(II) complex.

The \(J^{\text{eff.}}\) values of all the complexes except \([\text{Cu}_2(\text{HPAN})_2\text{Cl}_2]\), \([\text{Cu}_4(\text{BAHD})(\text{H}_2\text{O})_8]\), \([\text{Cu}_4(\text{BHFPA}_{\text{D}})(\text{H}_2\text{O})_8]\) and \([\text{Cu}_4(\text{BHFPA}_{\text{D}})(\text{H}_2\text{O})_8]\) lie in the range \(1.8 - 1.9 \text{ B.M.}\) in accordance with octahedral geometry. The \(J^{\text{eff.}}\) values of the above complexes are found to be subnormal \((1.4 - 1.5 \text{ B.M.})\) indicating the presence of antiferromagnetic exchange interaction between Cu-Cu ions in a dinuclear structure by superexchange phenomenon.
PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA:

The $^1$H nmr spectra of a few ligands have been scanned on a EM-390 NMR spectrophotometer (90 MHz) using acetone $d_6$ as the solvent and tetramethyl silane as the internal standard.

In the $^1$H nmr spectra of the azo dye ligands the six ligands (HPANH), (DHBFADH$_2$), (HAHNAH$_3$), (BHADH$_2$), (BHFADH$_2$), (BADD) give an unsymmetrical pattern around the region $\delta = 6.6 - 8.5$ (ppm) indicating presence of aromatic protons. The keto-enol tautomeric forms in the ligands BAAD can be explained due to the presence of a sharp peak at $\delta 3.2$ which are not changed on dilution indicating the presence of O-H...O intramolecular hydrogen bonding in the enolic forms of the ligand. In the ligand HPANH and DHBFADH$_2$ the peaks observed at $\delta$ 10.56, 12.6 and 9.8, 10.9 respectively show the presence of one phenolic proton, one aldehydic proton and two phenolic, two aldehydic proton respectively. In the ligand BHADH$_2$ and BHFADH$_2$ the peak observed at $\delta 2.3$ are assigned to six methyl protons and the latter the peak observed at $\delta 9.9$ can be assigned to two aldehydic proton.

ELECTRON SPIN RESONANCE SPECTRA:

The e.s.r. spectra of ten polycrystalline Copper(II) complexes have been recorded at bands 'X' at room temperature with a varian E$_4$ ESR spectrometer. For all the complexes, the principal 'g' values and axial symmetry parameter 'G' values are calculated. To get further information about the ground state, another useful parameter 'R' has been calculated.
In the e.s.r. spectrum of the complex \( \left[ \text{Cu}_2(\text{BDHAD})\text{Cl}_2(\text{H}_2\text{O}) \right] \) the 'g' values \( g_1, g_2, g_3 \) are found to be 2.0266, 2.0868 and 2.2251 respectively. These values show that there may be either severe distortion from Oh or rhombic symmetry supporting a planar configuration. The 'R' value is found out to be less than one indicating ground state to be predominantly \( d_{x^2-y^2} \). The axial symmetry parameter 'G' is found out to be 3.96 which indicates that the 'g' values will be nearer to the molecular 'g' values. In the complex the 'g' values is less than 2.3 which show that the complex is largely covalent. Further these values is consistent with the mixed Cu-N and Cu-O bonded copper complex.

The e.s.r. spectrum of the complex \( \left[ \text{Cu}_2(\text{BHCAD})(\text{H}_2\text{O})_8 \right] \) shows that the symmetry around the Cu(II) ion in the unit cell is tetragonal (elongated octahedral) with \( g_1 = 2.0933 \) and \( g_{11}=2.2022 \). The axial symmetry parameter 'G' comes out to be 2.16. The 'R' value is found out to be less than one indicating the ground state to be predominantly a \( d_{x^2-y^2} \) orbital.

The e.s.r. spectrum of the complex \( \left[ \text{Cu}_2(\text{HPAN})_2\text{Cl}_2 \right] \) the 'g_av' value is found to be 2.1008 using Kneubuhls method. This type of spectrum appears due to extensive coupling operating between two copper ions in a dinuclear structure.

In the e.s.r. spectrum of the complexes \( \left[ \text{Cu}_4(\text{DHBFAD})_2(\text{H}_2\text{O})_8 \right] \), \( \left[ \text{Cu}_4(\text{DHBFAD})_2(\text{H}_2\text{O})_8 \right] \), \( \left[ \text{Cu}_3(\text{HAHNA})_2(\text{H}_2\text{O})_{10} \right] \), \( \left[ \text{Cu}_3(\text{CPAHNA})_2(\text{H}_2\text{O})_{10} \right] \), \( \left[ \text{Cu}_2(\text{BHFAD})\text{Cl}_2(\text{H}_2\text{O})_6 \right] \), \( \left[ \text{Cu}_2(\text{BAAD})\text{Cl}_2(\text{H}_2\text{O})_6 \right] \) the 'g_av' value are found to be 2.10947, 2.11546, 2.1306, 2.1311, 2.123 respectively. These spectra are isotropic consisting of a single line, character-
istic of a regular octahedral geometry. The type of spectrum may result due to the fact that a regular octahedral stereochemistry undergoing a dynamic or pseudorotational type of Jahn-Teller distortion.

In the e.s.r. spectrum of the complex $[\text{Cu}_2(\text{BHAD})\text{Cl}_2(\text{H}_2\text{O})_6]$ the $g_{av}$ value calculated to be 2.1118 by applying Kneubuhl's method. This type of spectrum may result when a regular octahedral stereochemistry undergoes a dynamic or pseudo-rotational type of Jahn-Teller distortion or due to grossly misaligned tetragonal axes which may be reducing the symmetry or a chromophore of symmetry lower than octahedral may undergo free rotation.

THERMAL ANALYSIS:

The thermal analysis (DTA, TGA) of the complex compounds under report has been carried out by Hungarian Optical Works, Hungary in the temperature range $0^\circ$C to $1000^\circ$C at a heating rate of $10^\circ$C/min. The complex $[\text{Cd}_2(\text{BHFA})\text{Cl}_2(\text{H}_2\text{O})_2]$ is stable up to $160^\circ$C indicating the co-ordinated nature of two water molecules. The compound registers a mass loss of $12.45\%$ ($13.24$ theoretical) at $200^\circ$C as evident from the break on the TGA curve which corresponds to the loss of two water molecules and two chlorine atoms. It is supported by a sharp exothermic peak at $210^\circ$C on the DTA curve. Thereafter the compound loses its mass with the rise of temperature and at $340^\circ$C loses $\frac{1}{4}$th of the ligand molecule with a total loss of $30.82\%$ ($29.21\%$ theoretical). Supported by a sharp peak at $320^\circ$C on the DTA curve. Thereafter the compound suffers a total mass loss of $60.57\%$ ($61.15\%$ theoretical) between $440^\circ$C-$630^\circ$C which corresponds to the loss of another half of the ligand moiety. It is supported by the sharp
exothermic peak at 660°C on the DTA curve. At 800°C on the TGA curve there is almost a total loss of the compound 98.9% which is further supported by the exothermic peak at 800°C on the DTA curve. Thereafter the thermogram becomes a straight line.

The complex \( \text{[CO}_2\text{(HPAN)}_2\text{Cl}_2 \] is quite stable at room temperature. The complex does not lose its mass upto 210°C. At 210°C the complex loses 10.25% of its mass equivalent to the mass loss of two chlorine atoms (9.59% theoretical). It is supported by the small exothermic peak on DTA curve and a sharp break on TGA curve. Thereafter the compound loses its mass gradually with the rise of temperature with a total loss of 79.13% (79.72% theoretical) mass upto 500°C which is equal to the rest of the ligand moiety with the formation of \( \text{CoO} \). Thereafter the thermogram becomes a straight line suggesting the stable nature of the product.

The complex \( \text{[Ni}_3\text{(CPAHNA)}_2\text{(H}_2\text{O)}_{10} \] is observed no mass loss upto 140°C indicating coordinated nature of all the water molecule. With the rise of temperature this complex suffers a mass loss of 10.4% at 200°C against the theoretical value of 10.56% which corresponds to six water molecules. Thereafter the complex suffers a gradual mass loss of 8.2% (7.87% theoretical) with the rise of temperature upto 320°C which corresponds to the loss of four water molecules. Thereafter the compound loses its mass slowly with the rise of temperature. The compound loses the ligand moiety at 580°C. The total mass loss is 84.78% (theoretical value 82.77%) which show the formation of \( \text{NiO} \).
X-RAY DIFFRACTION STUDY:

The x-ray diffraction study (powder pattern) of two complexes $[\text{Ni}_2(\text{HPAN})_2 \text{Cl}_2]$ and $[\text{Cu}_2(\text{BDHAD}) \text{Cl}_2(\text{H}_2\text{O})_2]$ have been indexed in a PW 1130/00 model x-ray diffractometer supplied by M/S Phillips Holland. The unit cell parameter like $a, b, c, \alpha, \beta, \gamma$ and volume have been calculated with the help of a computer with model IBM PC AT 286 with coprocessor. Basing upon unit cell dimension (in $\text{Å}^0$ unit) and three axes ($\alpha, \beta, \gamma$) values the complexes $[\text{Ni}_2(\text{HPAN})_2 \text{Cl}_2]$ and $[\text{Cu}_2(\text{BDHAD}) \text{Cl}_2(\text{H}_2\text{O})_2]$ are suggested to be rhombohedral and monoclinic crystallographic system respectively.