CHAPTER - III

RESULTS AND DISCUSSION
This chapter deals with the details of magnetic studies, diffuse reflectance spectra and Infrared spectral interpretation tailored especially to throw light on the structural aspects of the newly synthesised chelate polymers.

GENERAL

Magnetism has played an important role in the development of our understanding of the structural and electronic factors that govern spin exchange phenomena in inorganic and bioinorganic systems[1,2,3]. Thus in the present study magnetic measurements were carried out to obtain information about stereochemistry around the central metal ion. The magnetic properties of coordination compounds arise from the spin and orbital angular momenta of electrons in unfilled orbitals. Molar susceptibility values are used to calculate magnetic moment. These magnetic moments can then be compared with spin-only moments to determine the number of unpaired electrons and hence, the stereochemistry or bond type of a coordinated metal ion.

The electronic spectra often provides a quick and a reliable information about ligand arrangement (i.e. structure of organic molecule) in transition metal complexes. They have been mainly used to get an idea about d-d transitions. The spectrum result from a transition between two different molecular electronic energy levels. The position and shape of the bands in the electronic spectra can be used to assign the transitions in the compound which depends on the geometry of the complex. It is noteworthy, that a study of diffuse reflectance spectra armed with magnetic moment provides the most important information about stereochemistry[4].

In the present course of study the magnetic moment values of Mn (II), Fe(II), Co(II), Ni(II), Cu (II), Zn(II), Cd(II) and Pb(II) chelate polymers were determined at room temperature using Gouy's method. While the diffuse reflectance spectra were studied in the range 400 to 1200 nm. The details of magnetic moment values and assignments of solid state
reflectance spectra of these chelate polymers are incorporated in the subsequent paragraphs and tables.

**CHELATE POLYMERS OF MANGANESE (II),d^6**

Mn(II) forms octahedral, tetrahedral, square planar or lower symmetry compounds, but generally Mn(II) compounds are either octahedral or tetrahedral. Few five coordinated Mn (II) complexes are reported [5].

**Magnetic Properties**

Bivalent manganese is known to form both high spin (S=5/2) and low spin (S=1/2) compounds. The high spin d^6 configuration gives an essentially spin-only magnetic moment of ~ 5.92 B.M., independent of temperature and the type of ligand arrangement around the Mn(II) ion.

Dhumwad et al., Patel et al. and Mishra [6,7,8] reported a magnetic moment value in the range 5.90-5.92 B.M. for Mn (II) chelates. Thomas et al. and other workers [9,10,11] reported a slightly greater magnetic moment value (6.01-6.53 B.M.) for Mn(II) chelate, than the expected spin-only value (5.92 B.M.) but within the limits of spin free values for five unpaired electrons attributing an octahedral geometry.

A very slight decrease of ~ 0.8 B.M. in the magnetic moment values of chelate polymer than the expected value (5.92 B.M.) is of general observation [12,13]. Parihari et al. [14] reported a magnetic moment value in the range (5.78-5.89 B.M.) for Mn(II) Schiff base complexes and suggested an octahedral geometry. Juneja et al. [15] reported 5.66 B.M. value for tetrahedral Mn (II) chelate polymers derived from phenylhydrazides of suberic and sebacis acids. Gandhi et al. [16] and Bhave et al. [17] reported magnetic moment values in the range 5.15 - 5.42 B.M. and 5.13 B.M. for tetrahedral Mn(II) chelate polymers derived from substituted hydroxamic acid and
4,4' - dihydroxy-3,3' - diacetyl biphenyl - 2,6-diaminopyridine respectively. Patel et al.[18] reported magnetic moment values in the range 4.48-4.72 B.M., such low magnetic moments of Mn (II) coordination compounds were attributed to the presence of antiferromagnetic exchange interaction between the manganese atoms in the solid state or due to aerial oxidation of Mn(II) to Mn(III) during the synthesis of the compound.

Klemn and Senff[19] studied Mn(II) pthalocyanine complex and reported magnetic moment 4.51 B.M. and suggested square planar geometry. Mawby and Venanzi[5] reported five coordinated complex of Mn(II) having magnetic moment value very close to 1.60 B.M.

**Electronic Spectra**

High spin Mn(II) complexes have $^6S$ electronic ground state. Since the $^6S$ term is orbitally non-degenerate, it cannot be split by crystal field. Absence of other sextet term implies that the transitions from $^6S$ term are spin forbidden as well as laporte forbidden[20].

Mackay[21] has reported electronic transitions within the 3d configuration for "spin free" Mn(II) species involving multiplicity changes and hence are very weak in intensity. Drago[22] has observed transitions in some cases probably due to vibronic coupling. Shrivastava et al.[23] and Singh et al.[24] have reported spectral assignments for several Mn(II) complexes like transitions from $^6A_g \rightarrow \ ^4T_{1g} (^G)$, $^4T_{2g} (^G)$, $^4E_g$, $^4A_{1g} (^G)$, $^4T_{1g} (^D)$, $^4E_g (^D)$ and $^4T_{1g} (^D)$. These assignments are based on the earlier calculations of Tanabe - Sugano[25] and Orgel[26].

Patel et al.[27] observed weak bands at 13900, 16120 and 25500 cm$^{-1}$ for Mn(II) ion in octahedral environment. Shakir et al.[28] observed two strong bands at 18740 and 22570 cm$^{-1}$ for Mn(II) complexe of N-N' - diphenylhydrazine and their triphenylphosphine derivatives and suggested octahedral geometry. On the basis of two weak bands at 16010 and 23220 cm$^{-1}$. Mishra et al.[29] observed three bands at 20000, 22120 and 25380 cm$^{-1}$ for Mn(II) chelates and suggested tetrahedral environment around Mn(II) ion.
It is worth noting that the spectra of tetrahedral Mn(II) complexes fall into three well defined regions because of the fairly low Dq values involved [30]. The transitions from ground \(^6\text{S}\) solid to excited \(^4\text{G}\) state lie between 21000 and 24000 cm\(^{-1}\), those to \(^4\text{P}\) and \(^4\text{D}\) between 26000 and 29000 cm\(^{-1}\), those to \(^4\text{F}\) lies between 35000 and 38000 cm\(^{-1}\). In tetrahedral Mn(II) complexes due to mixing of p and d- orbitals more intense bands than octahedral complexes are observed[20].

In case of low spin octahedral complexes \(^3\text{T}_{2g}\) is the ground state but the electronic spectra of these complexes and five coordinated derivatives have not been characterized [20]. It is rarely possible to observe the crystal field spectra of Mn(II) complexes with organic ligands, since even very weak tail of ligand absorption falling into the visible region is often sufficient to mask the d-d bands.

**RESULTS AND DISCUSSION**

In the present study, Mn(II) forms coffee or cream coloured amorphous chelates with newly synthesised bis ligands RDP, RDAPDO, MBAA, HMATCH and HCATCH. These are stable towards air and moisture and undergo decomposition at high temperature. Due to their high insolubility in almost all organic solvents, their molecular weights could not be determined by conventional methods. Elemental analysis suggested 1:1 (Metal:Ligand) stoichiometry for all the Mn (II) chelates.

**Magnetic Properties**

Magnetic moment values of the synthesised Mn (II) chelates are found to be in close approximation with the expected spin only value 5.92 B.M. The chelate polymers of Mn (II) with RDAP, RDAPDO and HCATCH exhibit 5.70, 5.60 and 5.11 B.M. respectively. The observed values are slightly less than generally observed for spin free d\(^5\) system. The lower
value of magnetic moments may be due to spin exchange in the solid complexes or due to aerial oxidation of Mn(II) → Mn(III) during synthesis[31]. The low value of magnetic moment is also accounted on the basis of antiferromagnetic interaction between Mn(II) ions in solid state[32].

While the Mn(II) - MBAA, and HMATCH exhibit 6.14 and 6.01 B.M. magnetic moments respectively, these values are slightly greater than the spin only values. However, these values are in the range or limits of spin free values for five unpaired electrons indicating that the chelate polymers are high spin [11,33].

Therefore, on the basis of above finding with respect to magnetic properties the Mn(II) polymers with RDAP,RDAPDO and HCATCH are suggested to have tetrahedral geometry while Mn(II) polymers with MBAA and HMATCH are suggested to have octahedral geometry. Our observed results are in good agreement with those reported [9-17] for magnetic moment studies of Mn(II) complexes.

**Electronic Spectra**

The diffuse reflectance spectra of the Mn(II) chelates under present investigation were studied in the range of 400 to 1200 nm [Fig 3.1]. The absorption bands and tentative assignments for Mn(II) chelate polymers are given in the Table 3.1. The nature of electronic spectra of Mn(II) chelate polymers with all bis ligands in the present study are more or less similar in nature. However the spectra's clearly depicts the important differences in the terms of band intensity and position. Mn (II) - RDAP, RDAPDO, MBAA, HMATCH and HCATCH exhibit bands in the range 22222-25000 cm⁻¹, 16129 - 19230 cm⁻¹ and 12658 - 15873 cm⁻¹. These results are in good agreement with those reported [27,28].

In the present work the low intensities of the bands in case of MBAA and HMATCH for Mn(II) polymers are indicative of octahedral geometry as a consequence of their doubly forbidden
Fig 3.1 DIFFUSE REFLECTANCE SPECTRA OF Mn (II) CHELATE POLYMERS
Table 3.1 Magnetic moments and assignment of solid state reflectance spectra and tentative geometry of Mn(II) chelate polymers

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Bis chelate</th>
<th>µ eff</th>
<th>Absorption band</th>
<th>Assignment</th>
<th>Tentative geometry</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Ligand</td>
<td></td>
<td>m/ cm⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>RDAP</td>
<td>5.70</td>
<td>449 22271</td>
<td>⁶A₁ → ⁴A₂ ⁴E(G)</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>520 19230</td>
<td>⁶A₁ → ⁴T₂ (G)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>564 17730</td>
<td>⁶A₁ → ⁴T₁(G)</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>RDAP DO</td>
<td>5.60</td>
<td>450 22,222</td>
<td>⁶A₁ → ⁴A₁ ⁴E(G)</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>570 17,543</td>
<td>⁶A₁ → ⁴T₂ (G)</td>
<td></td>
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<td></td>
<td></td>
<td>625 16000</td>
<td>⁶A₁ → ⁴T₁(G)</td>
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</tr>
<tr>
<td>3.</td>
<td>MBAA</td>
<td>6.14</td>
<td>405 24691</td>
<td>⁶A₁₂ → ⁴A₁₂ ⁴E (G)</td>
<td>Octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>500 20000</td>
<td>⁶A₁₂ → ⁴T₂ (G)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>560 17857</td>
<td>⁶A₁₂ → ⁴T₁₂ (G)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>770 12987</td>
<td>⁶A₁₂ → ⁴T₁₂ (G)</td>
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</tr>
<tr>
<td>4.</td>
<td>HMATCH</td>
<td>6.01</td>
<td>400 25000</td>
<td>⁶A₁₂ → ⁴A₁₂ ⁴E (G)</td>
<td>Octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>620 16129</td>
<td>⁶A₁₂ → ⁴T₁₂ (G)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>780 12820</td>
<td>⁶A₁₂ → ⁴T₁₂ (G)</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>HCATCH</td>
<td>5.11</td>
<td>400 25000</td>
<td>⁶A₁ → ⁴A₁ ⁴E(G)</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>502 19920</td>
<td>⁶A₁ → ⁴T₂ (G)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>600 16666</td>
<td>⁶A₁ → ⁴T₁(G)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>670 14925</td>
<td>⁶A₁ → ⁴T₁(G)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>790 12658</td>
<td>⁶A₁ → ⁴T₁(G)</td>
<td></td>
</tr>
</tbody>
</table>

73
nature, as expected for octahedral Mn(II) chelate polymers [20,34]. While intense bands in case of RDAP, RDAPDO and HCATCH in the region 22222 - 25000 cm\(^{-1}\) may be due to the tetrahedral environment around Mn(II) ion[15,17]. Thus, on the basis of above observations and magnetic moment data, the Mn(II) chelate polymers of MBAA and HMATCH are suggested to have octahedral geometry, while Mn(II) chelates with RDAP, RDAPDO and HCATCH may have tetrahedral geometry. The experimental observations of earlier workers also support our results [34,35].

**CHELATE POLYMERS OF IRON (II), \(d^6\)**

Iron (II) forms a number of octahedral complexes [36]. Most of them are high spin type. For Fe(II) quite strong ligand fields are required to cause spin-pairing. Fe(II) has lesser tendency to form tetrahedral complexes than Co(II) and Ni(II). However early literature reports tetrahedral [37], five coordinated and planar complexes of Fe(II) [38].

**Magnetic Properties**

The magnetic moment value for high spin octahedral complexes of Fe(II) with \(^3T_2^g\) ground term is expected to be about 5.50 B.M. at room temperature and it is nearly temperature independent [35]. However deviation from regular octahedral symmetry or electron delocalization reduces magnetic moment to the spin only value 4.90 B.M. [39].

Sharma et al. [36] reported the magnetic moment values in the range 4.17-5.16 B.M. for octahedral Fe(II) complexes with N-salicylidene and N-(2-hydroxy-1- naphthylidene) amino acids. Prakash and Sindhu [40] reported magnetic moment values 5.5 and 5.6 B.M. for Fe(II) complexes with 2-amino-3-hydroxy pyridine and some nitrogen donors suggesting an octahedral geometry around the metal ion. Rao et al. [41] reported magnetic moment value 5.10 B.M. for
Fe(II) polychelates and proposed an octahedral geometry. Verma et al. [42] and Prabhakar et al. [43] reported a slightly greater i.e. 5.63 B.M. and 6.11 B.M. value for Fe(II) polychelates with 3-semicarbazone-1-carboxalic acid and (o-hydroxy-benzy1-2-o-hydroxyphenyl) benzimidazole respectively and suggested octahedral geometry. Rana et al.[44] observed a magnetic moment value 6.40 B.M. for Fe(II) octahedral complex and suggested that high value is due to oxidised Fe(II) \( \rightarrow \) Fe(III) species and presence of ferromagnetic impurity in the complex.

For tetrahedral complexes, the magnetic moment value is reported in the range 5.10-5.21 B.M. in view of the \( ^{1}E_{g} \) ground term, owing to the spins of the four unpaired electrons and a small, second order orbital contribution. However, the tetrahedral assignment for Fe (II) complexes, must be viewed with caution, as the magnetic moment of an octahedral complex can be reduced by distortion from regular octahedral symmetry or electron delocalisation towards the ligand [45].

Early literature reveals that planar complexes of Fe(II) exhibit a magnetic moment of about 4.00 B.M. at room temperature[37]. One of the rare example of a planar Fe(II) complex is of ferrous phthalocyanine having magnetic moment 3.96 B.M. at 20°C.[19]

**Electronic Spectra**

The ground state \( ^{5}D \) of a d\(^{6} \) configuration is split by octahedral and tetrahedral ligand field into \( ^{5}T_{2g} \) and \( ^{5}E_{g} \) states, there are no other quintet states, hence only one spin-allowed d-d transitions occur if one of these is the ground state.

In practice, octahedral Fe(II) complexes usually exhibit a number of very small peaks or broad band above 20000 cm\(^{-1} \). The splitting of broad band into small peaks is accounted due to Jahn -Teller effect[39,46].

Sharma et al.[36] and Shakir et al.[28] observed band at 11000cm\(^{-1} \) and 12,350cm\(^{-1} \)
respectively for Fe(II) complexes and assigned a $^1T_{2g}(D) \rightarrow ^3E_g$ transition, suggesting an octahedral geometry. Aswar et al. [42] assigned a tetragonally distorted octahedral geometry to Fe(II) polychelate exhibiting a doublet band at 10,000 - 12,000 cm$^{-1}$. Patel et al. [47] and other workers [20] suggested that such type of doublet bands in Fe(II) complexes could be due to either Jahn-Teller or $D_4h$ distortion. Thus they assigned a tetragonally distorted octahedral geometry to the various high spin Fe(II) complexes with a doublet band in the range 10,000-12,000 cm$^{-1}$.

Rao et al. [41] assigned a band at 28,400 cm$^{-1}$ for Fe(II) N-(4-methyl-8-acetoumbelliferonylidine)-N’-(isonicotinoyl) hydrazine to charge transfer or $t_{2g} \rightarrow \pi^*$. The low spin octahedral Fe(II) complexes have the electronic configuration $t_{2g}^6$. This configuration give rise to $^1A_{1g}$ ground term. Electronic excitation of the $e_g$ orbitals, leads to the configuration $t_{2g}^6 e_g$ which gives rise to spin triplet and spin singlet states. Therefore, two spin allowed transitions are expected i.e. $^1A_{1g} \rightarrow ^3T_{1g}$ (21000-31000 cm$^{-1}$) and $^1A_{1g} \rightarrow ^3T_{2g}$ (26000-37000 cm$^{-1}$). Similarly two $^1A_{1g} \rightarrow ^3T_{1g}$ and $^1A_{1g} \rightarrow ^3T_{2g}$ weaker forbidden transitions are also expected. The $^1A_{1g} \rightarrow ^3T_{2g}$ transition is not usually observed by $d^6$ ions, since it has a very low intensity and is normally obscured by the $^1A_{1g} \rightarrow ^3T_{1g}$ transitions [39,48].

All tetrahedral complexes are high spin. In a tetrahedral field $^3D$ ground term of the Fe(II) split into an upper $^3T_{2g}$ and lower $^3E_g$ states. Spin orbit coupling effects are small, the overall spread of sublevels due to this effect being about 500 cm$^{-1}$ for $^3T_{2g}$ and less than 500 cm$^{-1}$ for $^3E_g$ ground state[33]. Thus in the tetrahedral field only one band i.e. the spin allowed $^3E_g \rightarrow ^3T_{2g}$ transition, is expected for Fe(II) complex occurring at ~40000 cm$^{-1}$. Many compounds in addition show some much weaker bands in the 11000-20,000 cm$^{-1}$ region, these bands are usually appearing as shoulder on the strong charge transfer absorption bands. They are probably due to spin forbidden transitions[48].
RESULTS AND DISCUSSION

Iron(II) chelate polymers in the present course of study have brown or green shade. Their elemental analysis suggest 1:1 (M:L) ratio. The number of water molecules associated with the polymer have been ascertained with the aid of I.R. study and thermal analysis (Chapter III and Chapter IV respectively). All the Fe(II) polychelates are insoluble in common organic solvents.

Magnetic Properties

All the Fe(II) chelates are found to be paramagnetic and magnetic moment values are reported in Table(3.2). The chelate polymers of Fe(II) with RDAP, HCATCH, RDAPDO and MBAA exhibit magnetic moment values in the range 4.39-5.25, which suggests high spin octahedral geometry around the central metal ion. The slightly lower values of magnetic moment can be attributed to the antiferromagnetic interactions or quenching of the orbital contribution as a result of lower site symmetry [49]. The Fe(II) HMATCH exhibit 5.95 B.M. magnetic moment value which is slight greater than the expected value and suggests high spin octahedral geometry. The slightly higher value of magnetic moment can be attributed to the steric volume of the bulky ligand causing an increase in metal-ligand bond distance thereby decreasing Dq sufficiently enough to alter the ground state to the high spin $^3T_2g$ [50]. Our results for high spin octahedral are also supported by other workers [47, 51].

Electronic Spectra

The electronic spectra of Fe(II) with all the bis ligands in the present study exhibit characteristic multiple bands. The bands towards lower cm$^{-1}$ side indicate d-d transition, whereas at higher cm$^{-1}$ charge transfer bands are indicated. Spectra's are displayed in Fig 3.2.
The spectra clearly indicate the absorption band in the 10695-11,904 cm$^{-1}$ region. The band in 10,000 - 11,000 cm$^{-1}$ is a distinguishing feature of Fe(II) high spin octahedral complexes and could be assigned to $^5T_{2g}(D) \rightarrow ^5E_g$ transition [20].

The other two bands at higher cm$^{-1}$ region (i.e. 13,513 - 15,873 cm$^{-1}$ and 20,833 - 23,809 cm$^{-1}$) are observed which are ascribed to either $t_{2g} \rightarrow \pi^*$ transition or charge transfer transition[20].

An astonishing feature exhibited by the spectra's of the Fe(II) - RDAP, RDAPDO , HMATCH and HCATCH chelate polymers under present study is the presence of doublet band in 10,695 - 11,904 cm$^{-1}$ which suggests an tetragonally distorted octahedral geometry around the Fe(II) ion , due to either Jahn-Teller or $D_4h$ distortion .

The order in which the other terms lie above the ground term cannot be predicted by simple manner . However it is possible to calculate the interelectronic repulsion within a configuration to give the energies of the terms above the ground term . Two completely equivalent electronic repulsion parameters can be chosen. The Condon-Shortly parameters can be chosen in one choice Condon-Shortley parameters in which $F_2$ and $F_4$ are selected [53,54] or in another choice the Racah parameters in which $B$ and $C$ are selected [46,55]. The two sets of repulsion parameters are related as

$$B = F_2 - 5F_4 \tag{3.1}$$

and $$C = 35F_4 \tag{3.2}$$

The Racah parameters have an small advantage over the Codon-Shortly parameters and hence are more commonly used by the chemists[20]. In Racah parameters if the separation between terms of the same multiplicity is involved , only one function , $B$ is considered but if separation between terms of different multiplicity is involved both functions $B$ and $C$ are considered. While both the functions $F_2$ and $F_4$ are considered even if the seperation between the
terms of same multiplicity takes place. The Racah interelectronic parameter $B$ is a function of ligand, central ion and stereochemistry. If the $B$ values for metal complexes are compared with the corresponding free ion values, a reduction in $B$ after complexation is observed. This implies both that the mean radial displacement of the d-electrons has increased and the effective charge experienced by these electrons has decreased. Covalency in the metal-ligand bond is given by the formula.

$$\beta = \frac{B \text{ in the complex}}{B \text{ in the free ion}}$$

3.3

The ratio $\beta$ is known as Nephelauxetic ratio.

In the present study crystal field parameters $Dq$, Racah interelectronic repulsion parameters $B, C$ and Nephelauxetic ratio $\beta$ have been calculated by using the following relations [56]

$$E \left( ^{3}T_{2g} \rightarrow ^{3}E_{g} \right) = 10Dq$$

3.4

$$10 Dq = \frac{5}{2} B + 4C$$

3.5

$$= 18.5 B \text{ (Since } C \geq 4 B)$$

$$\beta = \frac{B \text{ in the complex}}{B \text{ in the free ion}}$$

3.6

$B$ value for free ion was taken to be 1060 cm$^{-1}$ as reported [56]. The values of the crystal field parameters are reported in Table 3.2. These values are in favour of octahedral geometry of the Fe(II) chelates. Similar type of crystal field parameters are also reported by Shah et al.[57] and in other literature [58].

In the present work, reduction in $B$ values are observed upon chelation. This indicates that a small amount of the $\sigma$ and $\pi$ electron density on the metal may be transferred on the ligand, such delocalisation will increase the mean distance between d-electrons and thereby reduce B value. In other words a decrease in B value suggests the partial covalent nature of the M-L bond [20].

Thus, the electronic spectra armed with magnetic data suggests an distorted octahedral ($D_{4h}$) geometry for the Fe(II) - RDAP, RDAPDO, HMATCH and HCATCH while octahedral geometry for MBAA chelates under present course of study.
Fig 3.2 DIFFUSE REFLECTANCE SPECTRA OF Fe (II) CHELATE POLYMERS
### Table 3.2 Magnetic moments and assignment of solid state reflectance spectra of Fe(II) chelate polymer with crystal field parameters and tentative geometry

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Bis chelate Ligand</th>
<th>μ_\text{eff}</th>
<th>m</th>
<th>cm</th>
<th>Absorption band cm⁻¹</th>
<th>Assignment</th>
<th>Crystal field Parameters Dq cm⁻¹ B cm⁻¹ β% Ccm⁻¹</th>
<th>Tentative Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>RDAP</td>
<td>4.39</td>
<td>420</td>
<td>17857</td>
<td>23809</td>
<td>C.T.</td>
<td>1190 643 0.61 2572</td>
<td>&quot;Distorted Octahedral&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>560</td>
<td>13513</td>
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<td>C.T.</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>740</td>
<td>840 d</td>
<td>11904</td>
<td>^5T_{2g}(D) → ^3E_g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>RDAPDO</td>
<td>4.65</td>
<td>480</td>
<td>20833</td>
<td>11834</td>
<td>C.T.</td>
<td>1183 639 0.60 2557</td>
<td>&quot;Distorted Octahedral&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>845 d</td>
<td>14,705</td>
<td>11,764</td>
<td>^5T_{2g}(D) → ^3E_g</td>
<td></td>
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<tr>
<td>3</td>
<td>MBAA</td>
<td>5.25</td>
<td>480</td>
<td>20,833</td>
<td>17,241</td>
<td>C.T. or t₂g → π*</td>
<td>1176 636 0.60 2543</td>
<td>&quot;Octahedral&quot;</td>
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<td>580</td>
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<td>14,705</td>
<td>11,764</td>
<td>^5T_{2g}(D) → ^3E_g</td>
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<td>HMATCH</td>
<td>5.95</td>
<td>430</td>
<td>23,255</td>
<td>20,833</td>
<td>C.T.</td>
<td>1190 643 0.61 2573</td>
<td>&quot;Distorted Octahedral&quot;</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>480</td>
<td>15,384</td>
<td>11,904</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>650</td>
<td>840 d</td>
<td>11,764</td>
<td>^5T_{2g}(D) → ^3E_g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>HCATCH</td>
<td>4.45</td>
<td>460</td>
<td>21,739</td>
<td>17,241</td>
<td>C.T.</td>
<td>1176 635 0.59 2540</td>
<td>&quot;Distorted Octahedral&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>580</td>
<td>14,705</td>
<td>11,764</td>
<td>^5T_{2g}(D) → ^3E_g</td>
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</tr>
</tbody>
</table>

*d = doublet*
CHELATE POLYMERS OF COBALT (II), d^7

Divalent cobalt forms numerous complexes of various stereochemical types [11,7]. Octahedral and tetrahedral ones are most common but there are a fair number of square ones as well as some which are five coordination [59-62]. Among most commonly known Co(II) complexes dimethyl glyoximate, which has a square planar structure is well known.

There are more tetrahedral complexes of Co(II) than for other transition metal ions since for the d^7 ion, ligand field stabilization favours the tetrahedral stereochemistry, relative to octahedral one to a small extent than for any other d^n (1 ≤ n ≤ 9) configuration. The tetrahedral complexes of Co(II) have three unpaired electrons and the square planar ones have only one, both as expected for d^7. The octahedral complexes include both high-spin and low-spin cases, the former with three and the latter with one unpaired electron. Since Co(II) occurs in a great variety of structural environments, its electronic structures, hence the spectral and magnetic properties are extremely varied. The stereochemical variations have been discussed in terms of their magnetic and spectral properties by different workers.

Magnetic Properties

For high spin octahedral Co(II) complexes, the magnetic properties are governed by the orbitally degenerate ground term ^4T_{1g}, this provides an orbital contribution to the magnetic moment on the basis of spin orbit coupling constant \( \lambda = -170 \text{ cm}^{-1} \). So that at room temperature high spin Co(II) complexes are expected to give magnetic moments value 5.20 B.M.. The experimental values lie in the range 4.7 - 5.20 B.M. and these values vary appreciably with temperature [63].

Monshi [63] reported magnetic moment value in the range 5.01 - 5.12 B.M. for a series of Co(II) complex of schiff base derived from condensation of 5-[4'-(nitrophenyl)azo]-salicylaldehyde with thiosemicarbazone. Some other workers also reported similar type of
observations and suggested high spin octahedral geometry around the Co(II) ion [64,65]. Singh et al. and Lyall et al. [66,67] suggested an distorted octahedral geometry for Co(II) complexes exhibiting magnetic moment values in the range 4.76 - 5.12 B.M.

Low spin octahedral Co(II) complexes possess $^3E_g$ ground term arising from the $t_{2g}^6e_{g}^2$ electronic configuration. Experimental magnetic moments of these type of complexes usually lie in the range 1.70-1.85 B.M. [68,69], which are close to the spin-only value (1.73 B.M.) and is independent of temperature. Cobalt (II) complexes in tetrahedral environment with the ground term $^4A_{2g}$ are assumed to have no orbital angular momentum. As per spin only formula, the magnetic moment is expected to be equivalent to three unpaired electrons (3.89 B.M.). In the presence of low symmetry ligand field the spin degeneracy of the $^4A_{2g}$ ground term is removed and as a result of this variation in magnetic moment in the range of 4.2 - 4.8 B.M. is observed.

Chaudhary et al. [70] reported magnetic moment values in between 3.98-4.52 B.M. for complexes of bivalent cobalt with hydrazones of morpholine-N-thiahydrazide with benzaldehyde, cinnamaldehyde and cyclohexanone and suggested tetrahedral stereochemistry for them. Patel et al. [71] reported 3.70 B.M. magnetic moment value for Co(II) polychelate of 2,4-dihydroxybenzaldehydeoxime-urea-formaldehyde polymeric ligand and suggested tetrahedral geometry. Tetrahedral bivalent cobalt complexes with benzaldehyde morpholine-N-thiahydrazone and cyclohexanone morpholine-N-thiohydrazone exhibited magnetic moment value between 3.9 - 4.5 B.M. [72]. Similar behaviour in other Co(II) complexes have also been reported [73,74].

All square planar Co(II) complexes are of low spin and with magnetic moment value of 2.2 - 2.7 B.M. at 300 K. Suma et al. [75] observed a significant deviation of $\mu_{\text{eff}}$ value 2.92 B.M. from the normal value 4.7-5.2 B.M. for Co(II) monophenylbutazone (4-butyl-1-
phenyl-3, 5-pyrazolidinedione) complex and suggested a pseudo-octahedral or square-planar stereochemistry. Rai et al. [76] reported Co(II) complex having magnetic moment of 2.0 B.M. indicating planar environment of the ligand atoms around cobalt(II) ion. Similar observations are also reported by other workers [6,77].

Five coordinated Co(II) complexes exhibit both high-spin [78,79,80] (three unpaired electrons) and low-spin [75] (one unpaired electron) configurations for both trigonal bipyramidal and square pyramidal as well as for intermediate configurations. Literature reveals that very few complexes of Co(II) are five coordinated and show magnetic moment associated with one unpaired electron, reviewed by Earnshaw et al.[81].

**Electronic Spectra**

Many octahedral Co(II) complexes are pink or brick red in colour, while tetrahedral complexes are blue. However, the colour is not always a useful criteria of stereochemistry. Generalisations regarding the electronic spectra of Co(II) in various stereochemistry are well known with relatively simple ligands. The spectrum of Co(II) in tetrahedral environment is more intense than that of the octahedral one. Both the octahedral and tetrahedral complexes give rise to electronic spectral band around 20,000 cm⁻¹, although tetrahedral compounds may frequently exhibit maximum near 1500 cm⁻¹.

In the octahedral Co(II) complexes ⁴T₁g and ³E are the spin free and spin paired ground states respectively. A low intensity band observed in the complexes near 8000-10000 cm⁻¹ can be assigned to ⁴T₁g → ⁴T₂g transition. A multiple band observed at 20000 cm⁻¹ is attributed to ⁴T₁g (F)→ ⁴T₁g (P), transition of highest energy, which may be in admixture with spin - forbidden transition. The ⁴T₁g → ⁴A₂g transition is not normally observed as it is a two electron transition. In general two principal regions of absorptions are observed [12,82,83].
Bhaskare et al. [84] used Koning's method [85] to ascertain the correct position of the bands observed in the electronic spectra of Co(II) Schiff base complexes derived from 2-aminothiazole and its derivative with vic-hydroxyaldehydes. They assigned the three observed spectral bands as \( ^{3}T_{2g} \leftarrow ^{3}T_{1g} (v_1) \) \((= 8500)\), \(^{1}A_{2g} \leftarrow ^{3}T_{1g} (v_2) \) \((= 18,000)\) and \(^{3}T_{1g} (P) \leftarrow ^{3}T_{1g} (v_3) \) \((= 20,000 \text{ cm}^{-1})\). Athappan et al. [86] studied the electronic spectra of Co(II) complexes with some conjugated 2-hydroxyacetophenones and observed bands in the 10300, 11500 and 21300-21700 cm\(^{-1}\) regions assigned respectively to \(^{4}T_{1g} \rightarrow ^{4}T_{2g}\) and \(^{4}T_{1g (F)} \rightarrow ^{4}T_{1g} (P)\) transitions characteristic of an octahedral configuration. A number of high spin octahedral complexes of Co(II) have been reported [11,12,86-90].

The tetrahedral complexes of Co(II) with \(^{4}A_{2g}\) ground term are expected to have three transitions. \(^{1}A_{2g} \rightarrow ^{1}T_{2g}, ^{1}A_{2g} \rightarrow ^{1}T_{1g} (F)\) and \(^{1}A_{2g} \rightarrow ^{1}T_{1g} (P)\) corresponding to band frequencies \(v_1, v_2\) and \(v_3\) where \(v_1\) occurs around 30,000-50,000 \(\text{cm}^{-1}\) region which is not well observed. The band corresponding to \(v_2\) is usually broad and appears in the near infrared region. The blue colour characteristics of tetrahedral geometry is due to the intense band of \(v_3\) in the region of 15000-20000 cm\(^{-1}\).

The visible transition observed in both octahedral and tetrahedral cases, but particularly in tetrahedral case, generally have complex envelopes because of number of transitions to doublet excited states occur in the same region, and these acquire same intensity by means of spin-orbit coupling. The electronic spectra of Co(II) tetrahedral complexes have been extensively studied [68,82-84].

Patel et al. [15,91] assigned the bands observed at 8870-8940, 15250-15390 and 23400-24810 cm\(^{-1}\) in the reflectance spectra of Co(II) complexes of \(\alpha\) - oximinoacetooacet-o/p-chloroanilide-\(\beta\)-thiosemi carbazone, to \(^{4}A_{2g} \rightarrow ^{4}T_{1}(F)\), \(^{4}A_{2g} \rightarrow ^{4}T_{1}(P)\) and charge transfer transitions respectively for tetrahedral geometry. The spectral bands in the square planar complexes indicate
two absorption maxima in the visible region and one band in the infrared region with a $^2B_{2g}$ or $^2A_{1g}$ ground state. Many square planar complexes exhibit one band near 20,000 cm$^{-1}$. The visible band is probably due to the $^2A_{1g} \rightarrow ^2B_{1g}$ transition. Patel et al. [15] and Lever [92] observed a band near 20000-21000 cm$^{-1}$ while studying electronic spectra of square planar Co(II) complexes. However, the spectral properties of square planar complexes are not well established.

Dhumwad et al. [6] proposed a square planar geometry for the Co(II) complexes with the ligand $N'-(N$-morpholinocetyl)-$N'-$phenyl thiosemicarbazide and 3,4-methylenedioxy benzaldehyde thiosemicarbazone concluded from the spectral data which exhibited two d-d transition at 9709 and 8333 cm$^{-1}$. Rai et al. [76] observed a broad electronic spectral band centered at 22,000 cm$^{-1}$ for Co(II)-1-pyridylimino-1-phenyl-2-hydroxyiminopropane indicating a planar environment of the ligand atoms around the Co(II) ion. Other workers have also reported a square planar geometry for Co(II) complexes [93,94]. Ciampolini [95] studied the reflectance spectra of five coordinated Co(II) complexes with Co(II) ion with a $^4A_{2g}(F)$ ground term.

RESULTS AND DISCUSSION

The Cobalt (II) chelates under present study have either pale coffee or ash colour. They are stable towards air and, moisture and insoluble in almost all organic solvents. Association of water molecules with the chelate polymers have been confirmed with the help of T G analysis. Elemental analysis revealed 1:1 stoichiometry for all Co(II) chelates.

Magnetic Properties

The newly synthesised Co(II) chelates exhibit a wide range (2.4-6.59 B.M.) of magnetic moment value owing to the existence of Co(II) ion in a variety of structural environment viz octahedral, tetrahedral or square planar (Table 3.3). However the values are in close approximation with expected values for a particular geometry.
The Co(II)-MBAA and HCATCH chelate polymers exhibit 5.10 and 5.59 B.M. magnetic moment values respectively, which satisfactorily lies in the range for high spin octahedral geometry [63]. However, in the present study high value of magnetic moments in the case of HCATCH chelate polymer than the calculated values for three unpaired electrons can be accounted for high orbital contribution [96].

Tetrahedral Co(II) complexes [97] have magnetic moments in the range 4.40-4.80 B.M. The observed magnetic moment for Co(II)-RDAP polymer is 4.15 B.M. at room temperature in the present study is an indicative of tetrahedral geometry. This intermediate value of magnetic moment can be attributed to the equilibrium mixture of two spin states of Co(II) ion with some orbital contribution from super exchange of mobile \( \pi \) - system of ligand. The experimental findings of earlier workers support our results [6, 75-77].

Anomalously low magnetic moment value (2.5 and 2.4 B.M.) for the Co(II)-RDAPDO and HMATCH respectively is observed in the present study suggesting planar geometry. Which is well within the range expected for square planar Co(II) complexes [75-77]. The experimental observations of earlier workers also supported our results [98].

**Electronic Spectra**

The electronic spectra of Co(II) chelates with RDAP, RDAPDO, MBAA, HMATCH and HCATCH are shown in Fig 3.3. Various bands in the electronic spectra are assigned on the basis of literature data available and absorption bands, tentative assignment and proposed geometry for Co(II) chelate polymers are tabulated in Table 3.3.

The reflectance spectra of these chelate polymers exhibit two main absorption maxima in the region 20,000-25,000 cm\(^{-1}\) and 9,000-13,000 cm\(^{-1}\) which corresponds to two spin allowed. \( ^{4}T_{1}(F) \rightarrow ^{4}T_{1}(P) (v_{1}) \) and \( ^{4}T_{1}(F) \rightarrow ^{4}T_{2}(F) (v_{1}) \) transitions respectively. The third transition
\( ^4T_1(F) \rightarrow ^4A_2(F)(v_s) \) is observed in the range 12,000-19,000 cm\(^{-1}\) which is weak. However, the splitting of this band has been observed in Co(II)-MBAA and HCATCH chelate polymers. This splitting may be due to the presence of low symmetry fields [99] and weaker axial interaction in the solid state[100]. The splitting causes a band envelope due to considerable overlap and thus broad bands are observed in the spectra [99]. The electronic spectra of Co(II)-MBAA and HCATCH further reveals that the band of first transition has characteristic splitting into shoulder which makes assignment much difficult. Splitting of this band may be due to lifting of degeneracy of the \( T_{1g}(P) \) level either by spin orbital coupling or by the presence of low symmetry component in the ligand field[101]. Thus, on the virtual appearance of the electronic spectra and the transitions therein indicate octahedral geometry to MBAA, and HCATCH chelate polymers of Co(II).

Crystal field parameters \( Dq \) and \( B \) have been calculated to resolve the problem of the assignment of the shoulder by using the relation derived from the secular determinant in the following form [42].

\[
Dq = \frac{[ (2v_1 - v_3) + (v_3^2 + v_1v_3 - v_1^2)^{1/2} ]}{20} \quad 3.7
\]

\[
B = \frac{v_3 - 2v_1 + 10Dq}{15} \quad 3.8
\]

\[
v_2 = v_1 + 10Dq \quad 3.9
\]

\[
\beta = \frac{B \text{ in the complex}}{B \text{ in the free ion}} \quad 3.10
\]

\[
\beta' = \frac{B \text{ in the free ion} - B \text{ in the complex}}{B \text{ in the free ion}} \times 100 \quad 3.11
\]
To get $D_q$ and $B$, experimental values of $v_1$ and $v_3$ are used. Nephelauxetic ratio $\beta$ was calculated using the above relation. The $B$ value for free ion was taken to be $1120\text{cm}^{-1}$ from the literature [51]. The calculated values of $D_q$, $B$, $\beta$, and $\beta^p$ are tabulated in Table (3.3).

The values of crystal field parameters for Co(II) chelates with MBAA, and HCATCH can be compared with the values reported in literature [63,87,102] for high spin octahedral Co(II) complexes. The transition energy ratio $v_2/v_1$ (1.80, 1.76) come near to the ratio required for an octahedral geometry [103,104].

The calculated value of $v_2 = (v_1 + 10D_q)$ is not in good agreement with experimental value. It is observed that the experimental value is lower than the calculated one which suggests lower symmetry for Co(II) chelates with MBAA, and HCATCH than octahedral geometry. Therefore, it may be concluded that the symmetry of these polymers may be $D_{4h}$.

In $D_{4h}$ symmetry the $^4T_{1g}(P)$ level splits into $^4A_{2g}$ and $^4E_g$ components. Hence the shoulder band around $12,000$-$19,000\text{cm}^{-1}$ may be assigned to $v_2$ transition which may also contain one of the component of $v_1$ transition. Most likely the $^4A_{2g}$ level. The value of $\beta$ in these chelates lies in the range $0.78$-$0.89$ which suggest the partial covalent character to the bond concerned [105].

The reflectance spectra of Co(II) -RDAP exhibits three sharp bands at $21276$, $15384$ and $11,111\text{cm}^{-1}$, which may be assigned to charge transfer, $^4A_{2g} \rightarrow ^4T_{1g}(P)$ and $^4A_{2g} \rightarrow ^4T_{1g}(F)$ respectively [91]. The position of these bands and their high intensity support the tetrahedral stereochemistry [89].

The reflectance spectra of Co(II) RDAPDO and HMATCH chelate polymers exhibit two prominent bands at $20000$-$25000\text{cm}^{-1}$ of high intensity and the other at $12000$-$13000\text{cm}^{-1}$ of low intensity, attributed to $^2A_{1g} \rightarrow ^2E_f$ and $^2A_{1g} \rightarrow ^2B_{1g}$ transitions as expected for an square planar geometry [106]. The relatively high intensity of the first band may be due to contributions.
RDAP
RDAPDO
MBAA
HMATCH
HCATCH

Fig 3.3 DIFFUSE REFLECTANCE SPECTRA OF Co (II) CHELATE POLYMERS
Table 3.3 Magnetic moments and assignment of solid state reflectance spectra of Co(II) chelate polymer with crystal field parameters and tentative geometry

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Bis chelate</th>
<th>μ_{el}</th>
<th>Absorption band</th>
<th>Assignment</th>
<th>Crystal field Parameters</th>
<th>V_{i}</th>
<th>Tentative Geometry</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>Ligand</td>
<td>B.M.</td>
<td>m cm^{-1}</td>
<td></td>
<td>Dq cm^{-1} B_{lg} cm^{-1}</td>
<td>β</td>
<td>ν_{i}/ν_{j}</td>
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<td>1</td>
<td>RDADP</td>
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<td>21276</td>
<td>C.T</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>650</td>
<td>15384</td>
<td>^{4}A_{g} \rightarrow ^{4}T_{_{1g}}(P)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>900</td>
<td>11111</td>
<td>^{4}A_{g} \rightarrow ^{4}T_{_{1g}}(F)</td>
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<td>2</td>
<td>RDAPDO</td>
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<td>825</td>
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<tr>
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<td>21107</td>
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<td>878</td>
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<td>23809</td>
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<td>555</td>
<td>18018</td>
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<td></td>
<td>980</td>
<td>10204</td>
<td>^{4}T_{<em>{1g}}(F) \rightarrow ^{4}E</em>{<em>{2g}}(F)ν</em>{s}</td>
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</table>
by the charge transfer transition appearing in the region 28,000 - 30,000 cm$^{-1}$[107].

Thus the perusal of electronic spectra for Co(II) chelate polymers supplemented by magnetic studies probably confirms a high spin octahedral stereochemistry for MBAA, and HMATCH polymers, a typical tetrahedral orientation for RDAP chelate polymer and a square planar geometry for RDAPDO and HMATCH respectively. The results obtained are in harmony with the literature reported.

**CHELATE POLYMERS OF Ni(II), d$^6$**

Ni(II) ion has a complex array of stereochemistries associated with it. The main structural types being six coordinated octahedral, four coordinated tetrahedral and square planar. A considerable number of five coordinated complexes, both trigonal bipyramidal and square pyramidal occur[108].

A particular characteristic is the existance of complicated equilibria, commonly temperature and concentration dependent, involving different structural types. Owing to very less energy difference between the various structural forms.

To specify, most of the complexes of Ni(II) can be divided into three categories,

i) Six coordinated, octahedral paramagnetic complexes with $^3A_{2g}$ ground term.

ii) Four coordinated, tetrahedral paramagnetic complexes with $^3T_{1g}$ ground term and

iii) Four coordinated, square planar diamagnetic complex with $^1A_{1g}$ spin paired singlet ground term.

**Magnetic Properties**

Magnetically, regular octahedral Ni(II) complexes have relatively simple behaviour. From both d-orbital splitting and energy level diagrams, it follows that they all should have two unpaired electrons. The magnetic moment of octahedral Ni(II) complexes are usually found in the range 2.90 - 3.40 B.M. Consideration of the magnitude of orbital contribution from
\( ^{3}A_{2g} \) to \( ^{3}T_{1g} \) state or spin-orbit coupling gives a somewhat higher magnetic moment than expected 2.83 B.M. spin only value. In certain tetragonally distorted complexes, the magnetic moments have been found to be as high as 3.4 - 3.5 B.M.

Ali et al. [109] observed magnetic moment values between 3.04-3.23 B.M. for different octahedral Ni(II) chelates derived from the schiff bases \( \alpha \)-N-methyl-s-methyl - \( \beta \)-N- (2-pyridyl)-methylendithiocarbazate and its derivatives. Recently Sen et al. [110] reported 2.8 - 3.5 B.M. magnetic moment value range for a new series of complexes of Ni(II) with Schiff bases derived from the condensation of cinnamaldehyde with 4-amino-5-mercapto-S-triazole and 4-amino-5-mercapto-3-methyl-S-triazole and suggested an octahedral symmetry. Ni-complexes having magnetic moment values between 2.54-3.26 B.M. are reported by Naik et al. [111].

Patel et al. [33] reported a magnetic moment value of 2.78 B.M. for Ni(II) polymeric chelate prepared by polycondensation of 2,4-dihydroxypropiophenone with 1,3-propanediol and suggested an octahedral environment around the Ni(II) ion.

The significant deviation of \( \mu_{\text{eff}} \) values 2.63 B.M. from the normal value for Ni(II) with mono phenylbutazone (4-butyl-1-phenyl-3,5-pyrazolidinedione) is observed by Suma et al. [75], and suggested that metal-metal interaction may be presented and that the hydroxyl group may be acting as a bridging group in these complexes.

In tetrahedral symmetry the \( d^9 \) configuration give rise to a \( ^{3}T_{1g}(F) \) ground state, which contributes to much inherent orbital angular momentum and is temperature independent. Thus the magnetic moment of truely tetrahedral Ni(II) should be around ~ 4.2 B.M. at room temperature. However, even slight distortion reduce this markedly (by splitting the orbital degeneracy). Thus, fairly regular tetrahedral complexes have moments of 3.5 to 4.0 B.M., for the more distorted ones the moments are 3.0 to 3.5 B.M. Recently Chaudhary et al. [70] reported a magnetic
moment value between 3.20 - 3.32 B.M. for tetrahedral Ni(II) complexes obtained by condensation of hydrazones of morpholine-N-thiohydrazide with benzaldehyde, cinnamaldehyde and cyclohexanone. Similar observations have been reported by Dwivedi et al.[72] for complexes of Ni(II) with benzaldehyde morpholine-N-thiohydrazone and cinnamaldehyde morpholine-N-thiohydrazone and cyclohexanone morpholine-N-thiohydrazone.

Square planar complexes of Ni(II) are invariably diamagnetic. Since for d^8 configuration, the planar ligand set causes one of the d orbitals (d x^2-y^2) to be uniquely high in energy and the eight electrons can occupy the other four d-orbitals but leave this strongly antibonding one vacant. These complexes are mainly obtained with ligands capable of forming of highly covalent bond with strong σ and π – bonding character. Published literature[63,82,112] reveals several diamagnetic Ni(II) complexes which suggests a square planar four coordinate structure.

A considerable number of Ni(II) complexes having penta-coordinated stereochemistry are found to be diamagnetic [109,113]. Ni(II) complexes also exhibit anomalous magnetic behaviour [114,115]. Large tetragonal distortion may also be found in diamagnetic compounds for which six - fold coordination is claimed.

**Electronic Spectra**

Spectroscopically, the study of Ni(II) complexes is of particular interest because of the large number of stereochemical forms in which the ion occurs. The electronic spectra, when supplemented by magnetic data, provide a valuable insight into the stereochemistry. The colour of the complexes themselves gives an indication of the geometry. For example the square planar complexes are generally red, yellow or brown in colour, while the octahedral complexes are commonly green coloured and the tetrahedral ones are blue.

The octahedral Ni(II) complexes (both regular or distorted) are almost high spin with
The ground term $^1A_g$ is characterized by the presence of three moderately intense bands due to three spin allowed transitions assigned as $^3A_g \rightarrow ^3T_{2g} (F)$, $^3A_g \rightarrow ^3T_{1g} (F)$ and $^1A_g \rightarrow ^3T_{1g} (P)$. These three transitions are commonly observed in the regions 7000-13000 cm$^{-1}$, 11000 - 20000 cm$^{-1}$ and 20000-28000 cm$^{-1}$ respectively [20]. In addition, two spin forbidden bands are frequently observed due to $^3A_g \rightarrow ^1E$ (11000 - 15000 cm$^{-1}$) and $^3A_g \rightarrow ^3T_{1g}$ (17000 - 22000 cm$^{-1}$) transitions.

In tetragonal, $D_{4h}$ symmetry, the ground state $^1A_g$ of course, remains as an orbital singlet, but all the excited states noted above will split into two levels, an orbital singlet and an orbital doublet $E_g$. In descending to $D_{4h}$ symmetry, the octahedral level of $d^8$ molecules, transforms as $^3A_g \rightarrow ^3B_{1g}$, $^1T_{2g} \rightarrow ^3B_{2g}$ and $^3T_{1g} (F) \rightarrow ^1A_g + ^3E_g$. Thus, theoretically our three band spectrum becomes a six band spectrum [116]. It should therefore contain enough information to analyse satisfactorily. However, in practice all six bands are rarely observed.

Recently, Sen et al. [110] reported three absorption bands in the regions 7000-13000, 13000-19000 and 20000-27000 cm$^{-1}$ for $v_1$, $v_2$ and $v_3$, transitions occurring in Ni(II) polychelates indicating octahedral geometry. Rao et al. [117] observed bands at 10640 cm$^{-1}$ ($v_1$), 16130 cm$^{-1}$ ($v_2$), and 26315 cm$^{-1}$ ($v_3$) for Ni(II) complexes with indane 1,3-dione-2-isonicotinoylhydrazone and proposed octahedral structure. They used this spectral data to compute ligand field parameters. Thakur et al. [118] reported three d-d transition bands at 9478-9411 ($v_1$), 16449-16380 ($v_2$) and 21505-21431 cm$^{-1}$ ($v_3$) for Ni(II) chelate obtained by condensation with 4-acyl pyrazolone and 1,4 diamine and suggested an octahedral geometry.

In tetrahedral complexes the transition from the $^3T_{1g} (F)$ ground state to the $^3T_{1g} (P)$ state appears as a very broad band in the visible region (~15000 cm$^{-1}$) with weaker bands on either side of this transition which can be assigned to spin-forbidden bands. In tetrahedral complexes
the intensity of the spectra is significantly greater than in octahedral complexes. The complexes are expected to have three spin allowed transitions $^3T_1(F) \rightarrow ^1T_1(P)$, $^3T_1(F) \rightarrow ^1A_2$ and $^3T_1(F) \rightarrow ^1T_2(F)$. They have three spin forbidden transitions $^3T_1(F) \rightarrow ^1T_2$, $^3T_1(F) \rightarrow ^1E$, $^3T_1(F) \rightarrow ^1T_1$. However, only four transitions are observed these are, $^3T_1(F) \rightarrow ^1T_1 (20,000 \text{ cm}^{-1})$, $^3T_1(F) \rightarrow ^3T_1(P) (15,000 \text{ cm}^{-1})$, $^3T_1(F) \rightarrow ^1E (11,000 \text{ cm}^{-1})$, $^3T_1(F) \rightarrow ^3A_2 (7,000 \text{ cm}^{-1})$. The band due to $^3T_1(F) \rightarrow ^1T_1(P)$ is a strong band of high intensity when compared to others.

Chaudhary et al. [70] reported that the reflectance spectra of Ni(II) complex display one broad and a strong band in visible region, typical of tetrahedral structure.

The square planar complexes do not have any absorption band below 10,000 cm$^{-1}$ due to large crystal field splitting, hence they can be clearly distinguished from octahedral and tetrahedral complexes. Square planar Ni(II) complexes are of low spin type. From the ligand field point of view, three d-d transitions corresponding to excitation from three low lying d - orbitals to the vacant dx$^2$ - y$^2$ orbital can be visualized (i.e. dxy, dzy, dx$^2$, dxz $\rightarrow$ dx$^2$ - y$^2$). The three spin allowed d-d bands, corresponding to the transitions $^1A_{1g} \rightarrow ^1A_{2g}$, $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1F_g$ are expected. Practically, majority of the Ni(II) square planar complexes exhibit a strong absorption in the region of 15,000 - 25,000 and 23,000 - 30,000 cm$^{-1}$ [20,39,119,120]. Singh et al. [67] confirms the square planar geometry to Ni(II) complexes from the two bands observed between 15000-15900 and 19400-2000 cm$^{-1}$ assignable to $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1B_{2g}$ transitions respectively.

**RESULTS AND DISCUSSION**

In the present investigation the Ni(II) chelate polymers have ash or green shade. Insufficient solubilities of these chelate polymers in common organic solvents precluded their determination of molecular weight. Elemental analysis of all the Ni(II) chelates suggests 1:1
(M:L) ratio. Water of hydration is suggested from thermal and I.R. spectral studies.

**Magnetic Properties**

In the present investigation magnetic moment of Ni(II) chelates were measured at room temperature and the values are cited in Table 3.4. Magnetic moment value of Ni(II) chelate polymers with RDAP and RDAPDO is 2.82 and 2.89 B.M. respectively which is found to be in close approximation with the spin only value 2.83 B.M., indicating an octahedral geometry[21,32,75]. Magnetic moment value for Ni(II) chelate with HMATCH is 3.04 B.M. indicating an octahedral geometry [84].

The Ni(II) - MBAA chelate polymer exhibits a magnetic moment of 3.6 B.M. which is higher than "spin only value". The excess value over the spin only value may be due to orbital contribution [121] or spin orbit coupling in \( ^6T_{1g} \) term and some mixing of \( ^6T_{2g} \) and \( ^3A_{2g} \) term [122] or departure from octahedral geometry towards tetragonal \( D_{4h} \) geometry[118].

The Ni(II) chelate of HCATCH is diamagnetic. The diamagnetism is a very strong evidence that the spatial arrangement of the ligand atoms around the Ni(II) ion is a square planar [67,91]. The magnetic moment values for Ni(II) complexes reported in the literature [33,75,110,111] also support our results.

**Electronic Spectra**

The diffuse reflectance spectra's of the Ni(II) chelate polymers under present study display bands in 1000-25000 cm\(^{-1}\). A comparative glance at these spectra clearly reveals that the spectra of Ni (II)- RDAP , RDAPDO , HMATCH have certain similarities , while the spectra of Ni (II) - MBAA and HCATCH have individual distinguishing features.

The spectra of Ni(II) RDAP , RDAPDO and HMATCH bear a close resemblance in profile and band positions to those of octahedral Ni(II) complexes , except that there is a
considerable splitting of bands in the Ni(II) - RDAPDO chelate polymer. In general, the low energy spin allowed band \( \nu_1 \) at 10000 - 12000 cm\(^{-1}\) may be arising due to the splitting of the \( ^1T_{2g}(F) \) state in octahedral symmetry and may be assigned to the transition from \( ^3A_{2g}(F) \) level to the split components of \( ^3T_{2g}(F) \) level. The other two spin free bands observed at 13000-20000 cm\(^{-1}\) and 23000 - 27027 cm\(^{-1}\) can be ascribed to the splitting of the \( ^3T_{1g}(F) \) and \( ^3T_{1g}(P) \) states respectively, they may be assigned to the transition from \( ^3A_{2g}(F) \) level to the split components \( ^3T_{1g}(F) \) for the former and to the split components \( ^3T_{1g}(P) \) for the latter [121]. While in the Ni(II) - RDAPDO, in addition to the above three absorptions observed, the spectra exhibits two spin forbidden bands at 12658 cm\(^{-1}\) and 16666 cm\(^{-1}\) attributable to \( ^1A_g \rightarrow E_r \) and \( ^3A_{2g}(F) \rightarrow ^1T_{1g} \) transitions[123]. The ratio \( \nu_2/\nu_1 \) lies between 1.40 - 1.54 which is in the range of the octahedral Ni(II) chelates [124,125].

Ligand field theory (L.F.T) of spin allowed transitions[85] have been applied to compute the important ligand field parameters. The Racah's electronic repulsion parameter (\( B_{3s} \)) is calculated by using the following equation[85].

\[
B_{3s} = \frac{\nu_2 + \nu_3 - 3\nu_1}{15}
\]  

Using the value of \( B_{3s} \), an attempt have been made to calculate the transition energies by the relations [85].

\[
\nu_2/\nu_1 = 1/2 \left( 15B + 30 Dq \right) \pm 1/2 \left( (15B - 10 Dq)^2 + 12 B \times 10 Dq \right)^{1/2}
\]

In the Ni(II) chelate with an octahedral symmetry, \( \nu_1 = 10 Dq \) is calculated as

\[
\nu_1 = 10 Dq = 1/3 (\nu_2 + \nu_3) - 5 B
\]

Nephelauxetic ratio \( \beta_{3s} \) and \( \beta^0_{3s} \) are calculated using the equation [56,126]

\[
\beta_{3s} = \frac{B_{3s} \text{ in the complex}}{B \text{ in the free ion}}
\]
The various spectral parameters are summarised in Table 3.4 favouring an octahedral symmetry for Ni(II) - RDAP, RDAPDO and HMATCH chelate polymers. The considerable reduction of B\textsubscript{35} values of the free ion from 1080 to 509 - 705 cm\textsuperscript{-1} on chelation indicates the appreciable amount of covalent character of M-L bond.

Approximate value of spin orbit coupling constant "λ" [127] for RDAP, RDAPDO and HMATCH chelates using average value of B\textsubscript{35} (λ = 55.84 cm\textsuperscript{-1}, 104.58 cm\textsuperscript{-1} and 119 cm\textsuperscript{-1}) is calculated by using the equation,

$$\lambda_{\text{eff}} = 2.7 \times B_{35}^2 / 10Dq$$  \hspace{1cm} 3.17

In order to correlate the spectral and magnetic properties μ\textsubscript{eff} values are calculated from the equation[56]

$$\mu_{\text{eff}} = \mu_{\text{eff}}^{so} \times (1 - 4\lambda / 10Dq)$$  \hspace{1cm} 3.18

The experimental room temperature μ\textsubscript{eff} values lie in the range required for octahedral stereochemistry and are in good agreement with the values calculated by substituting the experimental 10Dq and λ in the above equation. The calculated values (2.78, 2.72 and 2.71 B.M.) are found to be slightly less than the experimental value, indicating good correlation between experimental spectral and magnetic properties. Virtually the nature of reflectance spectra of Ni(II) RDAP, RDAPDO and HMATCH match well with those found for octahedral Ni(II) chelates.

The electronic spectra of Ni(II) MBAA exhibit three bands at 10,638 cm\textsuperscript{-1}, 15,873 cm\textsuperscript{-1} and 23,809 cm\textsuperscript{-1} region which are in accordance with octahedral geometry. However the splitting of former (lower energy) and latter (higher energy) is observed. The splitting of the principal three bands into six is a characteristic of D\textsubscript{4h} symmetry [116]. Due to the splitting of the bands
observed the spectra suggests a lower symmetry than octahedral, the $D_{4h}$ symmetry. The first two bands are due to the splitting of one band and can be assigned $^3B_{1g} \rightarrow ^3E_g$ and $^1B_{1g} \rightarrow ^3B_{2g}$ assuming the effective symmetry $D_{4h}$ (components of $^3T_{2g}$ in $D_8$ symmetry). The band at 15873 cm$^{-1}$ may be assigned to $^1B_{1g} \rightarrow ^1A_{2g}(F)$ transition while the higher two bands can be assigned to $^1B_{1g} \rightarrow ^3E_g(P)$ and $^1B_{1g} \rightarrow ^3T_{1g}(P)$ transitions [20].

Crystal field parameters are calculated from the following equations.

\[
10Dq^{XY} = ^2B_{1g} \rightarrow ^2B_{2g} \quad 3.19
\]

\[
D_t (D_{4h}) = 4/7 (Dq^{XY} - Dq^Z) \quad 3.20
\]

\[
10Dq^{XY} - 35. Dt = ^2B_{2g} \rightarrow ^2E_g \quad 3.21
\]

Racah parameter $B$ and Nephelauxetic ratio $\beta$ are calculated by using derivation given by Lever [20]. It is to be noted that $B$ and $\beta$ values are quite low. Their low values suggest the appreciable amount of covalent character in the M-L bond.

The diffused reflectance spectra of Ni(II) Hcatch displays two bands at 15384 cm$^{-1}$ and 22727 cm$^{-1}$ as expected for diamagnetic Ni(II) chelate, indicating a square planar geometry[6]. Appearance of two or three bands in the visible is of general observation for an square planar Ni(II) chelates[82, 112]. The band at 15384 cm$^{-1}$ is attributed to $^1A_{1g} \rightarrow ^1B_{2g}$ while the band at 22727 cm$^{-1}$ is assigned to $^1A_{1g} \rightarrow ^1B_{1g}$ transitions.

It is quite evident, that the observed magnetic moment values for all the Ni(II) chelate polymers under present study are in close agreement with their electronic spectral data. On the basis of which suitable geometries are proposed for Ni(II) chelates.
Fig 3.4 DIFFUSE REFLECTANCE SPECTRA OF Ni (II) CHELATE POLYMERS
Table 3.4 Magnetic moments and assignment of solid state reflectance spectra of Ni(II) chelate polymer with crystal field parameters and tentative geometry

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Bischelate Ligand</th>
<th>μ_m (B.M.)</th>
<th>Absorption band (nm)</th>
<th>Assignment</th>
<th>Crystal field Parameters (Dq cm⁻¹, Bq cm⁻¹, β, β%, ν₁/ν₂)</th>
<th>ν₂ (calcd.cm⁻¹)</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>RDAP</td>
<td>2.82</td>
<td>420 23.970ν_s</td>
<td>'A₂g(F)→'T₁g(P)</td>
<td>1256 509 0.47 52.87</td>
<td>1.40 17648</td>
<td>Octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>615 16.285ν_s</td>
<td>'A₂g(F)→'T₁g(F)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>920 10.869ν_s</td>
<td>'A₂g(F)→'T₁g(F)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>RDAPDO</td>
<td>2.89</td>
<td>400 25.000ν_s</td>
<td>'A₂g(F)→'T₁g(P)</td>
<td>11.11 656 0.60 39.20</td>
<td>1.51 16.870</td>
<td>Octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>550 18.161ν_s</td>
<td>'A₂g(F)→'T₁g(F)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>600 16.666</td>
<td>'A₂g(F)→'T₁g(F)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>790 12.658</td>
<td>'A₂g→E_g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>900 11.111ν_s</td>
<td>'A₂g→'T₁g(F)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>MBAA</td>
<td>3.6</td>
<td>420 23.809ν_s</td>
<td>'B₁g→'T₁g(P)</td>
<td>12820 517 0.48 52.05</td>
<td>1.45 15.527</td>
<td>Octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>460 21.739</td>
<td>'B₁g→'E_g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>630 15.873ν_s</td>
<td>'B₁g→'A₂g(F)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>780 12.820</td>
<td>'B₁g→'B₁g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>940 10.638ν_s</td>
<td>'B₁g→'E_g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>HMATCH</td>
<td>3.04</td>
<td>370 27027ν_s</td>
<td>'A₂g(F)→'T₁g(P)</td>
<td>1123.5 704 0.68 34.75</td>
<td>1.54</td>
<td>Octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>580 17250ν_s</td>
<td>'A₂g(F)→'T₁g(F)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>890 11235ν_s</td>
<td>'A₂g(F)→'T₁g(F)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>HCATCH</td>
<td>Diamagnetic</td>
<td>440 22.727</td>
<td>'A₁g→'B₁g</td>
<td></td>
<td></td>
<td>Square planar</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>650 15.384</td>
<td>'A₁g→'B₁g</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CHELATE POLYMERS OF COPPER (II), d^9

Copper is one of the most extensively studied transition metal ion in terms of complex formation. The dipositive state of copper is the most important oxidation state and the usual coordination numbers adopted by copper (II) are four, five and six. Fairly a large number of six and four coordinated complexes and relatively less number of five coordinated complexes are reported. Distorted octahedral\[128\] geometry for the six coordination, square planar and tetrahedral\[129\] distortions for four coordination and square pyramidal \[130,131\] or trigonal bipyramidal\[132\] arrangements for five coordination have been assigned.

Cu(II) ion with its d^9-electronic configuration in octahedral or tetrahedral environment is highly prone to Jahn-Teller distortion\[46,133\]. Particularly six coordinated complexes are severely distorted from octahedral symmetry to tetragonal arrangement, with majority of them having axially elongated structures as revealed by X-ray studies \(11,134\). In tetrahedral environment also, Jahn-Teller distortion is operative, in spite of the fact that large spin orbit coupling constant might produce sufficient splitting of the \(T_2\) ground state. There are more examples of distorted tetrahedral dispositions, when compared to regular tetrahedral arrangements in Cu(II) complexes \[20\]. Even the five coordinated Cu(II) complexes are no longer novel. Norman et al.\[135\] reported the disposition of square pyramidal geometry towards the trigonal bipyramidal in Cu(II) chloro (glycinato) (1-methylimidazole) polychelate.

**Magnetic Properties**

On the basis of magnetic properties, Cu(II) complexes can be broadly classified into two categories. The first type has essentially temperature independent magnetic moment in the range 1.75-2.20 B.M.\[39\]. These are mononuclear complexes having no major interactions between the electrons on different Cu(II) ions. The second type has moments substantially
below the spin only value which are markedly temperature-dependent. This is due to the coupling of spins of two Cu(II) ions held together in bimetallic complexes. The crystal field predicts that Cu(II) complexes will have a marked contribution to the magnetic moment only when the ground state is orbitally degenerate [136,137].

The observed magnetic moments of many octahedral copper (II) complexes are in the range of 1.8-2.18 B.M. [56]. For the free Cu(II) ion, there is also an interaction with magnetic field due to the orbital momentum, "L" of the electron and the total interaction becomes \( E = (2.0023 + L) \) B.M. The orbital degeneracy is removed by the crystal field and the orbital angular momentum is quenched for the ground states of the copper (II) complexes. Jejurkar et al. [138] reported the magnetic moment value 1.6 and 1.9 B.M. for Cu(II) complexes of Schiff bases, suggesting an octahedral geometry. A slightly higher value of magnetic moment 2.09 B.M. is observed by Rao et al. [117] for the complexes of Cu(II) with indane 1,3-dione-2-isonicotinoylhydrozone.

In square planar complexes the ground state is not degenerate and consequently a planar complex should have a value of \( \mu_{\text{eff}} \) close to the spin only value 1.73 B.M. [136,137]. An examination of the literature data [139,140] of some of the Cu(II) polychelates reveals that the magnetic moment of square planar Cu(II) complexes lies in the range 1.51 B.M. - 1.90 B.M. A higher value of \( \mu_{\text{eff}} \) in the range 1.85 - 2.15 B.M. are expected to be indicative of distortion from square planar geometry [141]. A \( \mu_{\text{eff}} \) in the range of 1.71 - 1.24 B.M. is reported by Shetti et al. [142] for Cu(II) complexes with tridentate ligands having square planar structure.

A perfectly tetrahedral complex, has a degenerate ground state and should have a large orbital contribution. Under these conditions the magnetic moment should vary with temperature and at room temp should be about 2.20 B.M. [143], whereas a distorted tetrahedral complex
Singh et al. [24] reported magnetic moment values 1.93 - 1.95 B.M. for Cu(II) complex of N-phenyl-5-phenyl-1,3,4 oxadiazole-2- sulphonamide and 5-phenyl-1,3,4-oxadiazole-2-imino sulphonamide and suggested tetrahedral environment around Cu(II) ion. Tetragonally coordinated Cu(II) ion with $T_{2g}$ ground term, the anticipated magnetic moment is 2.20 B.M. at room temperature [144].

**Electronic Spectra**

Octahedral complexes without any distortions are expected to have one d-d absorption band corresponding to $^3E_g \rightarrow ^3T_{2g}$ transition [145]. For distorted octahedral complexes, several weak bands are observed around 16,000 cm$^{-1}$ and often a broad tail in the near infrared region due to Jahn-Teller effect. In the axially elongated tetragonal coordination, $^3B_{1g}$ represents the ground state and three absorption bands corresponding to transitions $^3B_{1g} \rightarrow ^3E_g$, $^3B_{1g} \rightarrow ^3B_{2g}$, $^3B_{1g} \rightarrow ^3A_{1g}$ are observed [146].

Bhaskare et al. [84] observed that the electronic spectra of Cu(II) complex shows band at ~15000 cm$^{-1}$, assigned to $^3T_{2g} \leftarrow ^3E_g$ transition and a charge transfer at ~26000 cm$^{-1}$ while a single broad band in the region 13000-17000 cm$^{-1}$ centered at 15037 cm$^{-1}$ which may be due to overlapping of the three transitions $^3B_{1g} \rightarrow ^3B_{2g}$, $^3B_{1g} \rightarrow ^3E_g$ and $^3B_{1g} \rightarrow ^3A_{1g}$ is reported by Pancholi et al. [12] suggesting an distorted octahedral symmetry.

Regular tetrahedral complexes of Cu(II) are very uncommon [20]. In general, nearly regular tetrahedral complexes are expected to give a single broad band corresponding to $^3T_{2g} \rightarrow ^3E_g$ transition, in the near I.R. region and in general they do not have any d-d transition in 10,000 - 20,000 cm$^{-1}$ region in visible spectrum [20]. only low energy charge transfer bands may be observed in this region.
Lielir [147] theoretically predicted that tetrahedral Cu(II) shows no transition in the visible region and distorted octahedral Cu(II) complexes have two transitions near 14700 and 17900 cm\(^{-1}\) region. Singh et al. [24] reported bands at 35088, 20202 and 17241 cm\(^{-1}\) assigned to transitions C.T., \(^3\)B\(_{1g} \rightarrow ^3\)E\(_{1g}\) and \(^3\)B\(_{1g} \rightarrow ^3\)A\(_{1g}\) respectively for Cu(II) complex and assigned a tetrahedral symmetry. In square planar complexes the d-d bands are expected to occur in the range 14000 - 18000 cm\(^{-1}\) [148, 149]. However, when the planar structure is distorted to a tetrahedral configuration the frequency of this band is diminished. The ground term in the square planar geometry is \(^3\)B\(_{1g}\) and three d-d transitions, \(^3\)B\(_{1g} \rightarrow ^3\)B\(_{2g}\), \(^3\)B\(_{1g} \rightarrow ^3\)A\(_{1g}\), and \(^3\)B\(_{1g} \rightarrow ^3\)E\(_{g}\) corresponding transitions are observed [150,151].

Patel et al.[7] observed two bands for Cu(II) polymers with the poly Schiff base, the band at 23240 cm\(^{-1}\) is due to charge transfer from ligand to metal while the band at 14915 cm\(^{-1}\) is due to d-d transition which clearly indicates planar stereochemistry. Several others [63,71,75] have proposed square planar geometry to Cu(II) polychelates. Orgel [152], Byers et al. [153] and Karayannis et al. [154] found a broad band at 16000 cm\(^{-1}\) for square planar Cu(II) complexes.

A number of Cu(II) complexes exhibit five coordination. The trigonal bipyramidal complexes exhibit absorption bands at 8,200 cm\(^{-1}\) and 10,400 cm\(^{-1}\) [155,156]. Zhong - Lin-Lu et al.[157] reported a band at 12400 cm\(^{-1}\) and less intense shoulder band at 15,100 cm\(^{-1}\) in a Cu(II) complex with an asymmetric coordinated 2,2-bipyridine derivative and suggested a trigonal bipyramidal symmetry.

**RESULTS AND DISCUSSION**

The Cu(II)- MBAA, HMATCH have green shades while the others have ash to black shades. All the chelate polymers are non-hygroscopic and stable at room temperature. They are insoluble in almost all common organic solvents. Elemental analysis of all the chelate polymers,
suggests 1:1 metal-ligand stoichiometry, water of hydration is ascertained by thermal and I.R. spectral studies.

**Magnetic Properties**

The room temperature magnetic susceptibility values have been calculated from experimental data and cited in Table 3.5. The data suggests that the copper(II)-chelate polymers under present study are paramagnetic. However, the observed magnetic moment obtained from the above susceptibility values for the Cu(II) chelates with RDAP, MBAA, RDAPDO, HMATCH and HCATCH lies in the range 1.82-2.19 B.M. indicating mononuclear nature of the polymers [39]. All the observed values at room temperature reveals that there is no interaction between the different copper atoms in the polychelates i.e. they are magnetically dilute [39].

The magnetic moment values of Cu(II) - RDAP, RDAPDO and HCATCH lie in the range 2.03-2.17 B.M. These higher values of magnetic moment than the spin only value for one unpaired electron (1.73 B.M.) are indicative of the distortion from square planar geometry [141]. The higher magnetic moment values might be due to the orbital contribution. It could be therefore inferred that the magnetic moment of Cu(II) - RDAP (2.03 B.M.) lies well within the range of square planar or tetragonally distorted octahedral stereochemistry. While the Cu(II) - RDAPDO and HCATCH chelate exhibits 2.19 and 2.17 B.M. values respectively which are in the range expected for a tetragonally distorted octahedral symmetry or approaching the value 2.20 B.M., as expected for a regular tetrahedral geometry. Thus these polychelates may possess either distorted octahedral or tetrahedral structure, but regular tetrahedral complexes of Cu(II) are rare, there is usually a flattening of the tetrahedron due to the Jahn-Teller effect, lifting the degeneracy of the $^3T_g$ ground state [20].

The magnetic moment value of Cu-MBAA and HMATCH polychelate is 1.82 and 1.84 B.M.
respectively. Which is close to spin only value (1.73 B.M.), suggesting that the orbital contribution is almost quenched by the crystal field [158,159]. Thus the Cu(II) MBAA and HMATCH is supposed to have a square planar sterochemistry.

Electronic Spectra

The diffuse reflectance spectra of Cu(II) RDAP chelate polymer indicates that Cu(II) ion is in a tetragonally distorted octahedral environment [160]. The bands near 12903,20408 and 25000 cm⁻¹ region can be assigned to \( ^3B_{1g} \rightarrow ^3B_{2g}, ^3B_{1g} \rightarrow ^3E_g \) and charge transfer respectively.

Electronic spectra of Cu(II) RDAPDO and HCATCH show two broad bands around 25000 cm⁻¹ and 12500-16393 cm⁻¹. The position and shape of the bands indicate that Cu(II) is in a tetragonally distorted octahedral geometry. The intense and broad band noted at 25000 cm⁻¹ is attributed to the charge transfer band. It is a common phenomenon that metal-ligand charge transfer bands occur at markedly higher frequencies, particularly in the UV region as they belong to spin and symmetry allowed transitions. Usually they occur with high intensities similar high intensity bands are also observed in this region due to intra-ligand transition. While the band observed in the 12500-16393 cm⁻¹ region, centered at 15625 and 15384 cm⁻¹ in the Cu(II) RDAPDO and HCATCH polymers may be due to the overlapping of transitions. Since the spectra reveals that the envelope of this broad band is unsymmetrical, seeming to encompass several overlapping transitions[12]. Thus these band are assigned to \( ^3B_{1g} \rightarrow ^3A_{1g}, ^3B_{1g} \rightarrow ^3E_g \) and \( ^3B_{1g} \rightarrow ^3E_g \) transitions expected for an distorted octahedral geometry around Cu(II) ion.

The electronic spectra of Cu(II) chelates with MBAA and HMATCH are recorded in Fig 3.5 and spectral assignements are given in Table 3.5. The electronic spectrum of Cu(II) HMATCH chelate polymer in the present study show three bands in their normally expected region for square planar Cu(II) complexes[161]. The observed bands at 12,987 cm⁻¹ and 20,833 cm⁻¹.
RDAP
RDAPDO
MBAA
HMATCH
HCATCH

Fig 3.5 DIFFUSE REFLECTANCE SPECTRA OF Cu (II) CHELATE POLYMERS
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>BisChelate Ligand</th>
<th>µM</th>
<th>B.M.</th>
<th>Absorption band cm⁻¹</th>
<th>Tentative Assignments</th>
<th>Tentative Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RDAP</td>
<td>2.03</td>
<td>2.19</td>
<td>400, 490, 775, 500, 610, 840</td>
<td>$^{2}E_g \rightarrow ^{2}B_{2g}$, $^{2}B_{1g}$, $^{2}B_{2g}$, $^{2}B_{2g}$, $^{2}B_{1g}$, $^{2}B_{1g}$</td>
<td>Distorted Octahedral</td>
</tr>
<tr>
<td>2</td>
<td>RDAPDOD</td>
<td>400</td>
<td>500</td>
<td>610, 840</td>
<td>$^{2}E_g \rightarrow ^{2}B_{2g}$, $^{2}B_{1g}$, $^{2}B_{2g}$, $^{2}B_{2g}$, $^{2}B_{1g}$, $^{2}B_{1g}$</td>
<td>Distorted Octahedral</td>
</tr>
<tr>
<td>3</td>
<td>MBAA</td>
<td>1.82</td>
<td>1.84</td>
<td>400-590, 480, 600</td>
<td>$^{2}E_g \rightarrow ^{2}B_{2g}$, $^{2}B_{1g}$, $^{2}B_{2g}$, $^{2}B_{2g}$, $^{2}B_{1g}$, $^{2}B_{1g}$</td>
<td>Square planar</td>
</tr>
<tr>
<td>4</td>
<td>IMATCH</td>
<td>2.17</td>
<td>2.50</td>
<td>500, 610, 840, 1250</td>
<td>$^{2}E_g \rightarrow ^{2}B_{2g}$, $^{2}B_{1g}$, $^{2}B_{2g}$, $^{2}B_{2g}$, $^{2}B_{1g}$, $^{2}B_{1g}$</td>
<td>Square planar</td>
</tr>
<tr>
<td>5</td>
<td>HCATCH</td>
<td>2.17</td>
<td>2.50</td>
<td>500, 610, 840, 1250</td>
<td>$^{2}E_g \rightarrow ^{2}B_{2g}$, $^{2}B_{1g}$, $^{2}B_{2g}$, $^{2}B_{2g}$, $^{2}B_{1g}$, $^{2}B_{1g}$</td>
<td>Distorted Octahedral</td>
</tr>
</tbody>
</table>
are consistent with planar structure. These bands are assigned to $^3B_{1g} \rightarrow ^3E_{1g}$, $^3B_{1g} \rightarrow ^3B_{2g}$. The third band around 25,000 cm$^{-1}$ may be attributed to the symmetry forbidden ligand - metal charge transfer transition[162,163]. The diffuse reflectance spectra of Cu(II) MBAA shows a single broad intense band in the 16949 - 25000 cm$^{-1}$ region as expected for a square planar geometry. The broadness of the band observed may be an indication towards lower symmetry[160].

Our experimental results are in good harmony with the earlier work and hence distorted octahedral geometry can be suggested to Cu(II) - RDAP, RDAPDO and HCATCH chelate polymers and a square planar to Cu(II) - MBAA and HMATCH chelate polymer on the basis of spectral studies.

It is worth noting that the magnetic data for all the Cu(II) chelates under present study, substantiate the same view for stereoarrangements.

**CHELATE POLYMERS OF Zn(II), d$^{10}$**

Zn(II) ion forms numerous complexes of various stereochemical types, having 4, 5, or 6 coordination number. Their chelate polymers are diamagnetic as it has d$^{10}$ configuration and the d-d transitions are not observed. Zn(II) complexes with monomeric and polymeric structures have been reported [164,165].

The tetrahedral complexes are predominant [70,166,167]. Patel et al.[83] proposed a tetrahedral geometry for Zn(II) - 7- (α- phenyl - α- o/m - chloroanilinomethyl )-8- quinolinol complex. Zn(II) complexes achieve five coordination by dimerisation[168,169].

Zn(II) forms trigonal bipyramidal complexes with one axial and three equitorial positions and the fifth one is occupied anion like isothiocyanide or chloride etc. Bhattacharya et al.[170] suggested trigonal bipyramidal geometry for Zn(II) complexes of two new potentially pentadentate ligands based on methyl 2- aminocyclopent-1-ene-1-dithiocarboxylate with pendent...
pyrazolyl groups. Square pyramidal complexes are also reported [170]. The square pyramidal geometry is common in Zn(II) complexes. However, a few cases of fourcoordinate square planar Zn(II) complexes are also known i.e. bis(glycinyl)Zn(II) [171].

A few octahedral complexes of Zn(II) are also reported [11,39,172]. Mohanty et al. [65] proposed an octahedral symmetry to the Zn(II) complex, in consonance with their analytical conductance and infrared spectra data. Eaborn et al. [173] reported a three coordinated Zn(II) complex.

RESULTS AND DISCUSSIONS

The Zn(II) - RDAP, RDAPDO, MBAA, HMATCH and HCATCH chelate polymers synthesised and are coloured amorphous solids and stable at room temperature. Their elemental analysis gives 1:1 (M:L) ratio. They are insoluble in almost all organic solvents. Water of hydration is suggested from thermal and I.R. spectral studies.

Magnetic Properties

The room temperature magnetic susceptibilities have been calculated from experimental data. The data suggests that the Zn(II) chelate polymers under present study are diamagnetic. This is in accordance with the d^10 (i.e. completely filled 'd' subshells) configuration of the Zn(II) ion. A survey of literature reveals [33,110] that all the Zn(II) chelates show diamagnetic nature.

Electronic Spectra

The diffuse reflectance spectra was recorded in the range 400-1200 nm. A perusal of the electronic spectra revealed no d-d transitions as expected for d^10 system and do not furnish any relevant information [166,167].

Thus the Zn(II) chelates under present study are found to be diamagnetic. On the basis of the elemental analysis, magnetic and electronic spectral results, most probable geometry of the chelate polymers may be tetrahedral. Our observations are in good agreement with the reported literature.
CHELATE POLYMERS OF Cd (II), d^{10}

Cd(II) ion with d^{10} configuration forms chelate polymers. The Cd(II) ion in the complexes generally have four, five, or six coordination number. It forms rather stable four coordinated complexes than Zn(II) in six coordination; due to its larger size. However, the tetrahedral complexes are more common [39]. The Cd(II) -1-(3',5' - dinitro -2' - hydroxyphenylazo)-2-napthol-4-sulphonic acid complex is suggested to be four coordinated with a tetrahedral stereochemistry around the metal ion, on the basis of analytical and IR spectral data by Mahapatra et al.[166]. Choudhary et al.[70] proposed a tetrahedral structure to a Cd(II) complex with hydrazones of morpholine - N - thiahydrazide with benzaldehyde, cinnamaldehyde and cyclohexanone. On the basis of stoichiometry, Mohanty et al.[65] suggested an octahedral structure for the Cd(II) complexes.

RESULTS AND DISCUSSION

The Cd(II) chelate polymers with the newly synthesised ligands in the present study are found to be coloured. They are insoluble in almost all common organic solvents. Their elemental analysis give 1:1 (M:L) ratio. They were subjected to I.R. and thermal studies so as to ascertain the associated water of hydration.

Magnetic Properties

The Cd(II) chelate polymers under present investigation were found to be diamagnetic from the magnetic susceptibility measurement data at room temperature. General magnetochemistry of Cd(II) complexes [27,72,73] reveals that Cd(II) complexes show diamagnetism due to the completely filled 'd' subshell. Further, since there are no unpaired electrons, the complexes of Cd(II) are expected to be diamagnetic.
Electronic Spectra

The diffuse reflectance spectra of Cd(II) polymers do not furnish any relevant information towards their stereochemistry as expected for d^10 system, hence are not reported in the present investigation.

So on the basis of analytical, I.R. spectral data and TGA (to be discussed later) Cd (II) chelates with RDAP, RDAPDO, MBAA, Hmatch and HCATCH are supposed to have tetrahedral geometry which is the most favoured structure for elements with d^10 electronic system[39]. Our observations are also supported by the reported literature.

CHELATE POLYMERS OF Pb(II), d^10.

The chemistry of Pb(II) is much less extensive than the transition metal ions. However, a number of Pb(II) complexes can be prepared [174,175]. Variety of different coordination geometries have been observed in these complexes including an octahedral coordination complex. The lead ion in the complexes have three, four or six coordination number. The six coordinated complex has highly distorted structure, while the four coordinated has a stable stereoarrangement[176]. η⁶- benzene complex [Pb⁶⁺(AlCl)₂(η⁶-C₆H₆)]C₆H₆ in which Pb(II) is in a distorted pentagonal bipyramidal site is reported [177]. Various stereoarrangement around the Pb(II) ion in complexes containing tris(pyrazolyl)methane ligands, like trigonally distorted octahedral, highly asymmetric distorted square base pyramid have been proposed by Reger recently[178], on the basis of X-ray crystallographic studies and concluded that the geometry about the lead and even the coordination number can be controlled by variations in the ligand charge and substitution with these versatile tris(pyrazolyl)methane/Poly-(pyrazolyl) borate ligands.
RESULTS AND DISCUSSION

The Pb(II) coordination polymers in the present study are found to be coloured. All the polymers are non-hygroscopic and stable at room temperature. They are insoluble in almost all common organic solvents. Their elemental analysis suggests 1:1 stoichiometry. Water of hydration is suggested from thermal and I.R. spectral studies.

Magnetic Properties

The magnetic susceptibility studies of Pb(II) chelate polymers carried out at room temperature, suggests that the complexes are diamagnetic. This observed diamagnetic property of Pb(II) ion is in good agreement with d^{10} system having completely filled d-subshell.

Electronic Spectra

A perusal of the electronic spectra revealed no d-d transitions as expected for d^{10} system and do not furnish any relevant information. Therefore these spectras are not reported in the present investigation.

The Pb(II) chelate polymers in the present investigation are found to be diamagnetic. On the basis of elemental analysis, magnetic and electronic spectral studies, most probable geometry for these chelates may be tetrahedral.
INFRARED SPECTRA

The infrared spectra of a ligand results on excitation of the ligand vibrations, by absorption of photons in the spectral region. However, when a ligand is coordinated to a metal atom, one additional atom is introduced into the vibrating system of the ligand. This causes the bond length, bond angles and interatomic forces within the ligand to undergo modifications to a certain extent.

In principle, therefore it should be possible to correlate the change in the spectrum with the structure of the coordination compound. The difference between the spectra of the free ligand and the chelates are usually of the following types,

1) Changes in the band position.
2) Changes in the relative intensities and appearance of new bands.
3) Splitting of a single peak into several closely spaced bands in the complex.
4) Disappearance of few band frequencies.

An unique interpretation of the observed changes in the spectra is not possible because of several uncertain factors which would influence the vibrational modes of the molecules. The usual method is to compare the ligand spectrum with that of the chelate, in which the ligand is coordinated in a known way as given in the literature. It has been observed that the vibrational bands associated with stretching of a bond involving coordinated atoms are shifted either to a lower or higher frequencies upon coordination. Vibrations involving coordinate bond stretching and bending modes generally appear in the low frequency region. Metal-nitrogen, metal-oxygen and metal-sulphur vibrations are very difficult to assign on an empirical basis, since their frequencies are sensitive to both the metal and the ligand and they often couple with other low frequency modes in metal complexes. The solid state spectra becomes complicated because of distortion caused by adjacent molecules in the lattice.
The I.R. spectra of all the bischelating ligands and their chelate polymers have been scanned with an objective of obtaining information about the coordinating atoms in the ligands, which would help in arriving at the stereochemistry of chelate polymers. The assignments of vibrational frequencies are mainly based on the data available in the literature and therefore empirical and tentative. The discussion is therefore very brief and cursory. So as to economise the space, the spectra of only interested frequency in the present investigation are displayed in Fig 3.6 - 3.10 while the assignments of the ligands and their chelate polymers are cited in Table 3.6 - 3.10.

RESULTS AND DISCUSSION

RDAP and its chelate polymers. (Table 3.6, Fig. 3.6)

The I.R. spectrum of RDAP and its chelates are found to be comparable with each other and suggests a definite difference from that of the coordinating ligand. The ligand exhibits a band in the range 2900-3000 cm\(^{-1}\) which may be due to the stretching vibrations of-OH group. The existence of this band at higher frequencies than expected for phenolic-OH frequency may be due to intramolecular hydrogen bonding\[179,180\] between phenolic hydrogen atom and the carbonyl oxygen atom. It is further observed that this band in the chelates has been replaced by a broad hump ranging between 3398-3433 cm\(^{-1}\). It appears, as if the \(v\)OH band in the chelates shifted to higher frequency when compared to ligand. From a general survey of the I.R. spectra \[181,182,183\] of metal chelates, such a shift may suggest (a) the disappearance of \(v\) O-H band in the range 2900-3000 cm\(^{-1}\) due to the coordination of phenolic group to the metal ion after deprotonation and (b) appearance of a new hump between 3398-3433 cm\(^{-1}\) due to the subsequent induction of water molecules in the chelate\[183\]. Nature of water molecules (coordinated/lattice) is confirmed by TG analysis.
Presence of coordinated water molecules is further confirmed from the appearance of diagnostic bands due to rocking and wagging vibrational modes at 799-853 cm\(^{-1}\). While the other band expected at \(\sim 1540\) cm\(^{-1}\) seems to merge into the \(\nu\text{C}=\text{O}\) and \(\text{C}=\text{C}\) bands. This is inferred from the medium broad bands of \(\text{C}=\text{O}\) observed in Fe(II),Ni(II) and Cu(II)-RDAP chelates as compare to RDAP and other chelates which exhibits sharp bands. Similarly, the coordination of phenolic oxygen to the metal ion after deprotonation may be inferred from, (1) the shift of phenolic \(-\text{C}=\text{O}\) from 1257 to 1264 cm\(^{-1}\) [184] (2) by the appearance of a new band at 1100-1256 cm\(^{-1}\) of \(\nu\text{C}-\text{O}-\text{M}\) in the spectra's of chelates [88] which is not noted in the free ligand spectra.

The band positioned at 1660 cm\(^{-1}\) in the I.R. spectra of the free ligand is seen to split into two components in all the chelates. Between the resultant one, one is observed invariably at 1588 cm\(^{-1}\). In view of its low intensity as compared with the second, it has been assigned to \(\nu\text{C}=\text{C}\) of the benzene ring. The position of the second component is variable and is of higher intensity. This is attributed to \(\nu\text{C}=\text{O}\) bond. The carbonyl stretching frequency has undergone a downward shift by 50-70 cm\(^{-1}\) in all the chelates. This clearly indicates the participation of the carbonyl group in coordination i.e. indicating coordination of the metal ion through an oxygen atom of the carbonyl group [185,186,187].

Altogether, different new band appeared in the lower frequency region (700-400 cm\(^{-1}\)) of the spectra which was not observed in the free ligand spectrum. Vibrations involving metal coordinated bond stretching and bending modes generally appear in the lower frequency region because of the relatively heavy mass of the metal and weak nature of the coordinate bond. Thus the non-ligand band observed at \(\sim 576\) to \(\sim 601\) cm\(^{-1}\) in the chelate spectra's have been assigned to M-O stretching frequency [188].

Thus the perusal of the I.R spectra reveals that the RDAP acts as a dibasic tetradeinate
Fig 3.6  I R SPECTRA OF RDAP AND ITS CHELATE POLYMERS

A = RDAP, B = Mn(II) RDAP, C = Fe(II) RDAP, D = Co(II) RDAP,
E = Ni (II) RDAP, F = Cu (II) RDAP, G = Zn (II) RDAP, H = Cd (II) RDAP, I = Pb (II) RDAP
Table 3.6 Infrared spectral data of RDAP and its chelate polymers

<table>
<thead>
<tr>
<th>Ligand/Chelate Polymer</th>
<th>OH --O cm(^{-1})</th>
<th>C=O cm(^{-1})</th>
<th>-C-O cm(^{-1})</th>
<th>C-O-M cm(^{-1})</th>
<th>C=C cm(^{-1})</th>
<th>M - O cm(^{-1})</th>
<th>vH(_2)O cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RDAP]</td>
<td>2900-3000b</td>
<td>1660</td>
<td>1257s</td>
<td>--</td>
<td>1588sh</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>[Mn(II)(RDAP)](_n)</td>
<td>--</td>
<td>1555</td>
<td>1262s</td>
<td>1213</td>
<td>1598sh</td>
<td>585</td>
<td>--</td>
</tr>
<tr>
<td>[Fe(II)(RDAP).2H(_2)O](_n)</td>
<td>--</td>
<td>1605mb</td>
<td>1264s</td>
<td>1256</td>
<td>1588sh</td>
<td>578</td>
<td>3422b. 839</td>
</tr>
<tr>
<td>[Co(II)(RDAP).2H(_2)O](_n)</td>
<td>--</td>
<td>1553</td>
<td>1264s</td>
<td>1200</td>
<td>1595sh</td>
<td>600</td>
<td>3433b</td>
</tr>
<tr>
<td>[Ni(II)(RDAP).2H(_2)O](_n)</td>
<td>--</td>
<td>1605mb</td>
<td>1262s</td>
<td>1211</td>
<td>1537sh</td>
<td>592</td>
<td>3420b. 799</td>
</tr>
<tr>
<td>[Cu(II)(RDAP).2H(_2)O](_n)</td>
<td>--</td>
<td>1528mb</td>
<td>1264s</td>
<td>1224</td>
<td>1586sh</td>
<td>576</td>
<td>3424b. 853</td>
</tr>
<tr>
<td>[Zn(II)(RDAP).2H(_2)O](_n)</td>
<td>--</td>
<td>1602</td>
<td>1264s</td>
<td>1198</td>
<td>1535sh</td>
<td>593</td>
<td>3398b</td>
</tr>
<tr>
<td>[Cd(II) (RDAP)](_n)</td>
<td>--</td>
<td>1596</td>
<td>1264s</td>
<td>1100</td>
<td>1500sh</td>
<td>600</td>
<td>--</td>
</tr>
<tr>
<td>[Pb(II) (RDAP)](_n)</td>
<td>--</td>
<td>1572</td>
<td>1264s</td>
<td>1247</td>
<td>1534sh</td>
<td>586</td>
<td>--</td>
</tr>
</tbody>
</table>

b = broad, mb = medium broad, s = sharp, sh = shoulder
OO-OO ligand towards all the metal ions, coordinating through both deprotonated phenolic and carbonyl oxygens. It is worth noting that each molecule of RDAP possesses two phenolic and carbonyl groups, maintaining a functional similarity on either side of the benzene ring. Thus the ligand is of specific structural interest exhibiting a symmetric bidentate OO-OO donor system, resulting in polymer chelates.

**RDAPDO and its chelate polymers.** (Table 3.7, Fig. 3.7)

On comparison of infrared spectra of ligand and its polymers, it is inferred that they are virtually identical with each other, however, they show important differences. The ligand spectra exhibits a band in the range 2900-3100 cm⁻¹ which is attributed to a νO-H stretching. It is reasonable to expect hydrogen bonding O-H---N between phenolic hydrogen atom and azomethine nitrogen atoms.[69,189]

Further this band disappears in all the chelates indicating that phenolic (OH) group gets deprotonated in metal chelates. The band at 1180 cm⁻¹ in the spectrum of free ligand may due to νC-O stretching vibrations. The positive shifting of this vibration in the spectra of chelates confirm the coordination through phenolic oxygen atom to the metal ion[190,191].

At the same time a medium broad peak observed in the free ligand at 3407 cm⁻¹ may be assigned to νO-H of oxime [192] is also observed in all the chelates in the range of 3408-3422 cm⁻¹, as a wide band. The strong band present at 1641 cm⁻¹ in the ligand which is also retained in the spectra of the chelates may be due to oximic νC=N[193]. The shifting of C=N band in the chelates to a lower frequency 10-50 cm⁻¹ may be caused by drainage of the electrons from the nitrogen atom to the metal atom upon chelation[194]. Thus it has been concluded that coordination through the azomethine nitrogen has taken place.

While the strong band present in the ligand around 1039 cm⁻¹ can be assigned to νN-O
Fig 3.7  \textit{I} \textit{R} SPECTRA OF RDAPDO AND ITS CHELATE POLYMERS

A = RDAPDO, B = Mn(II) RDAPDO, C = Fe(II) RDAPDO, D = Co(II) RDAPDO, E = Ni (II) RDAPDO
F = Cu (II) RDAPDO, G = Zn (II) RDAPDO, H = Cd (II) RDAPDO, I = Pb (II) RDAPDO
### Table 3.7 Infrared spectral data of RDAPDO and its chelate polymers

<table>
<thead>
<tr>
<th>Ligand/Chelate Polymer</th>
<th>OH--N cm(^{-1})</th>
<th>-C-O cm(^{-1})</th>
<th>NO-H cm(^{-1})</th>
<th>C = N cm(^{-1})</th>
<th>C-O-M cm(^{-1})</th>
<th>N-O cm(^{-1})</th>
<th>M-O cm(^{-1})</th>
<th>M-N cm(^{-1})</th>
<th>vH(_2)O cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RDAPDO]</td>
<td>2900-3100(^{b})</td>
<td>1180s</td>
<td>3407mb</td>
<td>--</td>
<td>1039</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>[Mn(II)(RDAPDO)](_n)</td>
<td>--</td>
<td>1278s</td>
<td>3422</td>
<td>1592</td>
<td>1187s</td>
<td>1052</td>
<td>549</td>
<td>487</td>
<td>--</td>
</tr>
<tr>
<td>[Fe(II)(RDAPDO).2H(_2)O(_l)](_n)</td>
<td>--</td>
<td>1182s</td>
<td>3408</td>
<td>1596</td>
<td>1141s</td>
<td>1019</td>
<td>503</td>
<td>471</td>
<td>1552,830</td>
</tr>
<tr>
<td>[Co(II)(RDAPDO).2H(_2)O(_l)](_n)</td>
<td>--</td>
<td>1264s</td>
<td>3421</td>
<td>1595</td>
<td>1189s</td>
<td>1053</td>
<td>550</td>
<td>425</td>
<td>--</td>
</tr>
<tr>
<td>[Ni(II)(RDAPDO).2H(_2)O(_l)](_n)</td>
<td>--</td>
<td>1329s</td>
<td>3420</td>
<td>1599</td>
<td>1199s</td>
<td>1045</td>
<td>529</td>
<td>486</td>
<td>1540,840</td>
</tr>
<tr>
<td>[Cu(II)(RDAPDO).2H(_2)O(_l)](_n)</td>
<td>--</td>
<td>1269s</td>
<td>3408</td>
<td>1595</td>
<td>1062s</td>
<td>1053</td>
<td>585</td>
<td>479</td>
<td>1545,770</td>
</tr>
<tr>
<td>[Zn(II)(RDAPDO)](_n)</td>
<td>--</td>
<td>1257s</td>
<td>3408</td>
<td>1599</td>
<td>1190s</td>
<td>1027</td>
<td>510</td>
<td>420</td>
<td>--</td>
</tr>
<tr>
<td>[Cd(II)(RDAPDO)](_n)</td>
<td>--</td>
<td>1246s</td>
<td>3408</td>
<td>1590</td>
<td>1116s</td>
<td>1028</td>
<td>510</td>
<td>420</td>
<td>--</td>
</tr>
<tr>
<td>[Pb(II)(RDAPDO)](_n)</td>
<td>--</td>
<td>1280s</td>
<td>3408</td>
<td>1590</td>
<td>1183s</td>
<td>1019</td>
<td>515</td>
<td>425</td>
<td>--</td>
</tr>
</tbody>
</table>

\(^{b}\) = broad, s = sharp, mb = moderate band
stretching frequency. This band has undergone an upward shift by 10-15 cm\(^{-1}\) in the chelates of Mn(II), Co(II), Ni(II) and Cu(II), and a downward shift by 10-20 cm\(^{-1}\) in the chelates of Fe(II), Cd(II), Pb(II), and Zn(II). This change in band position may be due to an increase in the ionic character of the N-O bond. The sharp non-ligand bands observed at 1062-1199 cm\(^{-1}\) may be due to C-O-M stretching frequency. The band normally observed for the water of hydration in the complexes at 3600-3200 cm\(^{-1}\) region seems to be merged into the band observed for vOH of oxime [195]. However, the weaker bands in the region 770-850 cm\(^{-1}\) and 1530-1550 cm\(^{-1}\) indicate the presence of coordinated water molecules. The new non-ligand bands observed at 420-487 cm\(^{-1}\) and 503-600 cm\(^{-1}\) are assigned to vM-N and vM-O respectively. From the spectral data it has been concluded that the RDAPDO act as a dibasic tetradentate ON-NO donor coordinating through the phenolic oxygen atoms and nitrogen of oximino group.

**MBAA and its chelate polymers** (Table 3.8, Fig. 3.8)

The I.R spectra of the ligand and their chelate polymers are quite informative. The assignment for the frequencies of different groups in the chelates corresponding to those considered for ligand have been proposed tentatively and arrived on the basis of literature data.

I.R. spectrum of MBAA reveals a broad multiplet spreading over 3500-2500 cm\(^{-1}\) with its centre at ~ 3000 cm\(^{-1}\), may be assigned to the combined mode of vNH\(_2\) and vOH of -COOH. The broad multiplet band shows splitting into two sharp bands of medium strength at 3487 and 3374 cm\(^{-1}\) region assignable to v\(_{\text{as}}\) NH\(_2\) modes and the one at 2923 cm\(^{-1}\) to v\(_{\text{s}}\) NH\(_2\) [63]. However, the band at 3487 cm\(^{-1}\) disappears in the chelate polymers. While the bands at 3374 cm\(^{-1}\) and 2923 cm\(^{-1}\) shows a negative and a positive shift respectively. The shifting of the N-H bands in the chelates implies the participation of nitrogen of the amino group in coordination [196]. Further evidence for the N-bonding of the NH\(_2\) group to the central metal ion stems from the shift to lower
Fig 3.8  I R SPECTRA OF MBAA AND ITS CHELATE POLYMERS

A = MBAA, B = Mn(II) MBAA, C = Fe(II) MBAA, D = Co(II) MBAA, E = Ni (II) MBAA,
F = Cu (II) MBAA, G = Zn (II) MBAA, H = Cd (II) MBAA, I = Pb (II) MBAA
Table 3.8 Infrared spectral data of MBAA and its chelate polymers

<table>
<thead>
<tr>
<th>Ligand/Chelate Polymer</th>
<th>NH₂ v as cm⁻¹</th>
<th>-OH v scm⁻¹</th>
<th>C = O v cm⁻¹</th>
<th>COO⁻ vas cm⁻¹</th>
<th>vs cm⁻¹</th>
<th>C-N cm⁻¹</th>
<th>C-O-M cm⁻¹</th>
<th>M-O cm⁻¹</th>
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<th>νH₂O cm⁻¹</th>
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<td>2900mb</td>
<td>1665</td>
<td>--</td>
<td>--</td>
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</tr>
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<td>3133s</td>
<td>--</td>
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<td>1161</td>
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<td>416</td>
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<td>3137s</td>
<td>--</td>
<td>1543</td>
<td>1618</td>
<td>1588</td>
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<td>1163</td>
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<td>3134s</td>
<td>--</td>
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<td>1616</td>
<td>1591</td>
<td>1176</td>
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<td>3125s</td>
<td>--</td>
<td>1546</td>
<td>1618</td>
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<td>1160</td>
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<tr>
<td>[Cu(II)(MBAA)]ₙ</td>
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<td>--</td>
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<td>1601</td>
<td>1211</td>
<td>1143</td>
<td>489</td>
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<tr>
<td>[Zn(II)(MBAA)].2H₂O]ₙ</td>
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<td>3127s</td>
<td>--</td>
<td>1545</td>
<td>1618</td>
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<td>[Cd(II)(MBAA)]ₙ</td>
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<td>3139s</td>
<td>--</td>
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<td>1620</td>
<td>1587</td>
<td>1200</td>
<td>1162</td>
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<tr>
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<td>2928s</td>
<td>--</td>
<td>1508</td>
<td>1615</td>
<td>1574</td>
<td>1211</td>
<td>1156</td>
<td>499</td>
<td>440</td>
</tr>
</tbody>
</table>

s = sharp, nb = medium broad, vas = asymmetric stretching frequency, and vs = symmetric stretching frequency
frequency by 25-60 cm\(^{-1}\) of \(\nu\) C-N band in all chelates observed at 1236 cm\(^{-1}\) in the I.R. spectra of the free ligand. Further the broad band at 2900 cm\(^{-1}\) due to the \(\nu\)OH of-COOH is absent in chelates indicating deprotonation of carboxylic group [197]. A strong absorption band at 1665 cm\(^{-1}\) assigned to \(\nu\)C=O of free COOH group [198] shifted in all the chelates, indicating the absence of free COOH groups [199, 200]. In chelates the \(\nu_{\infty}\) and \(\nu_\alpha\) vibration of the COO\(^-\) group appearing in the range 1615-1620 cm\(^{-1}\) and 1574 - 1601 cm\(^{-1}\) respectively indicate that carboxylate group acts as unidentate coordinating agent [36, 201]. The appearance of a new band at 1163-1156 cm\(^{-1}\) of \(\nu\)C-O-M in the spectra of the chelates [41], confirms the coordination by the carboxylate group. This band is absent in the spectra of the free ligand. The doublet band at 2849 cm\(^{-1}\) can be assigned to the C-H stretching frequency of the methylene group.

A perusal of the I.R. spectra of the ligand and their chelate polymers in the region 400-700 cm\(^{-1}\), with a view to obtain information regarding metal-ligand vibration, reveals new weak band at 416 - 440 cm\(^{-1}\) and 489 - 517 cm\(^{-1}\). These bands are assigned to metal-nitrogen and metal-oxygen stretching vibrations respectively [202]. A broad band observed only in the chelates at 3406-3494 cm\(^{-1}\) region may be attributed to coordinated water [188]. The two weaker vibrations in the region 750-820 cm\(^{-1}\) and 1530 cm\(^{-1}\) are assigned to O-H rocking and wagging bands respectively of coordinated water in the chelates. Such bands have also been observed by Shukla et al. [203] in the region 900-650 cm\(^{-1}\).

Thus the foregoing facts suggests that the ligand MBAA acts as a tetradeutate NO-ON donor ligand with the amino nitrogen and carboxylate oxygen atom as the bonding sites.

**HMATCH and its chelate polymers** (Table 3.9, Fig. 3.9)

The I.R spectra of HMATCH and its chelate polymers have been studied on the basis of literature data. The coordination sites of the ligand, involved in bonding with metal ion have
been determined by careful comparison of the I.R spectrum of the chelates with that of the parent ligand. Some important bands and their assignments are discussed below.

I.R spectra of HMATCH exhibits band at 3187 cm\(^{-1}\) which is assignable to weakly hydrogen bonded phenolic O-H stretching frequency. However, this band is not seen in the spectra of chelate polymers indicating that proton of the O-H group is released as a result of chelation.

The C-O stretching frequency observed at about 1264 cm\(^{-1}\) in the ligand has shifted towards higher wavenumber by 10-20 cm\(^{-1}\) in the chelate polymers which further supports the formation of metal-ligand chelates through OH proton [203]. A sharp but moderate band at about 1613 cm\(^{-1}\) in the ligand due to v C = N shows either a positive shift [204] or negative shift [205] in chelate polymers. Such shifting of bands after the complexation indicates the coordination of metal atom to ligand through the azomethine nitrogen atom [206,207]. The non-ligand bands observed at 1140-1164 cm\(^{-1}\) may be attributed to the presence of C-O-M stretching frequency. The ligand band at 918 cm\(^{-1}\) (N-N) shifts to higher frequency upon chelation. A shift to a higher frequency in v N-N is expected due to the reduction of lone-pair repulsive forces of the adjacent nitrogen atom. The magnitude of this shift indicates the monodentate coordination of the >N-N< residue, as the shift greater than 50 cm\(^{-1}\) is usually observed in bidentate coordination [208]. The medium band around 3030 cm\(^{-1}\) in the ligand due to thioimido vNH shows a slight negative shift in chelate polymers. Such shifting of band after complexation may due to drain of electron density towards the electronegative azomethine nitrogen. The two bands at 1489 and 823 cm\(^{-1}\) are assigned to vC=S vibrations [209] in the free ligand. These bands are also observed in the chelate polymers without any shift, which reveals that thioketo group is not involved in coordination. A broad band observed in all the chelate polymers at 3421-3439 cm\(^{-1}\) region may be attributed to vOH of lattice water molecules [210] and a band at 770-780 cm\(^{-1}\) indicating the presence of coordinated
Fig 3.9  IR SPECTRA OF HMATCH AND ITS CHELATE POLYMERS

A = HMATCH, B = Mn(II) HMATCH, C = Fe(II) HMATCH, D = Co(III) HMATCH, E = Ni (II) HMATCH,
F = Cu (II) HMATCH, G = Zn (II) HMATCH, H = Cd (II) HMATCH, I = Pb (II) HMATCH
### Table 3.9 Infrared spectral data of HMATCH and its chelate polymers

<table>
<thead>
<tr>
<th>Ligand/Chelate Polymer</th>
<th>OH--N cm⁻¹</th>
<th>-C-O cm⁻¹</th>
<th>C=N cm⁻¹</th>
<th>N-N cm⁻¹</th>
<th>-C-N-H S cm⁻¹</th>
<th>N-H cm⁻¹</th>
<th>C=S cm⁻¹</th>
<th>C-O-M cm⁻¹</th>
<th>M-O cm⁻¹</th>
<th>M-N cm⁻¹</th>
<th>vH₂O cm⁻¹</th>
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<td>[HMATCH]</td>
<td>3187 b</td>
<td>1264s</td>
<td>1613mb</td>
<td>918</td>
<td>3030</td>
<td>2918</td>
<td>1489,823</td>
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<td>--</td>
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</tr>
<tr>
<td>[Mn(II)(HMATCH)₂H₂O]ₙ</td>
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<td>942</td>
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<td>1559,820</td>
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<td>560</td>
<td>410</td>
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<tr>
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<td>950</td>
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<td>478</td>
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<td>776</td>
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<td>950</td>
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<td>2921</td>
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<td>490</td>
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<td>770</td>
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<td>1569,823</td>
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<td>580</td>
<td>490</td>
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<td>770</td>
</tr>
<tr>
<td>[Cu(II)(HMATCH)]ₙ</td>
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<td>1616</td>
<td>920</td>
<td>3025</td>
<td>2920</td>
<td>1490,822</td>
<td>1142</td>
<td>570</td>
<td>480</td>
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</tr>
<tr>
<td>[Zn(II)(HMATCH)]ₙ</td>
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<td>1615</td>
<td>920</td>
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<td>2918</td>
<td>1566,822</td>
<td>1151</td>
<td>580</td>
<td>490</td>
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</tr>
<tr>
<td>{[Cd(II)(HMATCH)]₂H₂O]ₙ</td>
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<td>950</td>
<td>3025</td>
<td>2918</td>
<td>1565,823</td>
<td>1140</td>
<td>560</td>
<td>458</td>
<td>3429b</td>
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<td>[Pb(II)(HMATCH)]ₙ</td>
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<td>1603</td>
<td>940</td>
<td>3024</td>
<td>2918</td>
<td>1490,822</td>
<td>1164</td>
<td>587</td>
<td>490</td>
<td>--</td>
<td>---</td>
</tr>
</tbody>
</table>

b = broad, s = sharp, mb = moderate band
water molecules [183]. This is further confirmed by the TG studies.

I.R spectra of the bis ligand and their chelate polymers were also examined in the 400-700 cm\(^{-1}\) region with a view to obtain information regarding metal-coordinating atom vibrations. The M-O stretching frequency appear in the range 553-600 cm\(^{-1}\) and observed band in neighbourhood at 410-490 cm\(^{-1}\) may be identified as M-N stretching frequency[210].

In the light of the above discussion it may be concluded that the ligand HMATCH behaves as a tetradentate bis chelating agent coordinating through, (a) oxygen of phenolic group and (b) tertiary nitrogen of azomethine linkage.

**HCATCH and its chelate polymers** (Table 3.10, Fig.3.10)

The FTIR spectral data of the chelate polymers in comparison with those of the uncomplexed (HCATCH) give some information about the bonding site of the ligand moieties to the central metal ion.

The ligand spectra shows a strong and a broad band centered around 3266 cm\(^{-1}\), assignable to the hydrogen bonded phenolic OH vibration. As is anticipated this band disappears in the spectra of chelates, indicating that the proton of the -OH group is replaced by the metal ion upon chelation. Medium broad band at about 1618 cm\(^{-1}\), may be due to C=N mode of azomethine linkage. The positive and negative shifting of this vibration in the spectra of the chelates suggests the coordination of the azomethine nitrogen to the metal ion [207]. The perusal of I.R spectrum of ligand, depicts a two bands at 1479 and 814 cm\(^{-1}\) indicating the presence of C=S group [209]. These band remained unaltered in the spectra of the chelates indicating the non involvement of sulphur atom of thione group. A medium to strong band observed at 1282 cm\(^{-1}\) in the free ligand is attributed to phenolic -C-O vibration [211]. This band shifted towards higher frequency side indicating the formation of metal - ligand chelate. The non- ligand bands observed at
Fig 3.10  I R SPECTRA OF HCATCH AND ITS CHELATE POLYMERS

A = HCATCH, B = Mn(II) HCATCH, C = Fe(II) HCATCH, D = Co(II) HCATCH, E = Ni (II) HCATCH,
F = Cu (II) HCATCH, G = Zn (II) HCATCH, H = Cd (II) HCATCH, I = Pb (II) HCATCH
Table 3.10 Infrared spectral data of HCATCH and its chelate polymers

<table>
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<tr>
<th>Ligand/ Chelate Polymer</th>
<th>OH—N cm⁻¹</th>
<th>-C=O cm⁻¹</th>
<th>C=N cm⁻¹</th>
<th>N-N cm⁻¹</th>
<th>-C-N-H cm⁻¹</th>
<th>N-H cm⁻¹</th>
<th>C=S cm⁻¹</th>
<th>C-O-M cm⁻¹</th>
<th>C-Cl cm⁻¹</th>
<th>M-O cm⁻¹</th>
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<td>868</td>
<td>3037</td>
<td>2921</td>
<td>1479,814</td>
<td>--</td>
<td>779</td>
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<td>2924</td>
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<td>526</td>
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<td>1616</td>
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<td>1492,814</td>
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<td>2918</td>
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<td>1199</td>
<td>777</td>
<td>518</td>
<td>470</td>
<td>--</td>
</tr>
</tbody>
</table>

b = broad, s = sharp, mb = moderate band
1142 -1199 cm\(^{-1}\) may be attributed to the presence of C-O-M stretching frequency. The ligand band at 868 cm\(^{-1}\) (vN-N) shifts to higher frequency upon chelation, may be due to the reduction of lone-pair repulsive forces of the adjacent nitrogen atom. A medium intensity band around 3037 cm\(^{-1}\) due to the thioimido group shows a slight negative shift upon chelation. A broad band in the range 3425-3450 cm\(^{-1}\) which may due to the presence of vOH water[211]. A band observed at \(~779\) cm\(^{-1}\) may be asigned to C-Cl stretching frequency.

The stretching frequencies of metal-nitrogen and metal-oxygen bands are usually noted in the far I.R region, (600-400 cm\(^{-1}\))[212,213]. The position of these bands depend on the nature of the donor atoms and other stereochemical factors.

In the present investigation, from a correlation of the far I.R spectrum of the complexes with that of the free ligand (Fig 3.10), the bands observed at 457-490 cm\(^{-1}\) and 500-526 cm\(^{-1}\) may be attributed to vM-N and vM-O respectively. The I.R spectrum thus reveals that the ligand acts as a tetradentate in all chelates. The similarity of the I.R spectrum of chelate polymers suggests that the mode of coordination of the ligand is same in all the chelates irrespective of the metal ion used.
REFERENCES


134) Joestan, M.D., Inorg. Chem. 9, 151(1972)
154) Karayannis,N.M., Mukulshi, C.M., Putlewski, L.L. and Lebes, M.M.,


196) Rivas, B.L. and Seguel, G.V., Polymer Bulletein, Springer Verlag (1996).


