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 synthesized 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 [1-3]. Thus in the present study magnetic measurements were carried out to obtain information about stereochemistry around the central metal ion. The magnetic properties of a coordination compound arise from the spin and orbital angular moment 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 spectrum often provides quick and reliable information about ligand arrangement (i.e. structure of organic molecules) in transition metal complexes. They have been mainly used to get an idea about d-d transitions. The spectrum results 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 geometry of the complexes. 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) and Cd(II) polychelates were determined at room temperature using Gouy's method. Whereas 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 the polychelates are incorporated in the subsequent paragraphs and tables.

**CHELATE POLYMERS OF MANGANESE (II) d⁵**

Mn(II) forms octahedral, tetrahedral, square planer or lower symmetry compounds but generally Mn(II) compounds are either octahedral or tetrahedral. Few five coordinated Mn(II) complexes are also reported [5]. Manganese (II) ion is largest and have no ligand field stabilization energy in complex when compared with other complexes.

**Magnetic Properties:**

Bivalent manganese is known to form both high spin \(s=5/2\) and low spin \(s=1/2\) compounds. The high spin d⁵ configuration gives as essentially spin only, magnetic moment for five unpaired electrons 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 [6-8] have reported, magnetic moment value in the range 5.90-5.92 B.M. for Mn (II) chelates. Thomas et al and other worker [9-11] reported slightly greater magnetic moment value (6.01-6.53) B.M. for Mn(II) chelate than the expected spin (5.92 B.M.) but within the limits of spin free value for five unpaired electrons attributing an octahedral geometry.

A very slight decrease of ~ 0.88 B.M. in the magnetic moment value of chelate polymer than the expected value (5.92) B.M. is a general observation [12,13]. Parihani 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 Mn(II) coordination polymers derived from phenyhydrizine of suberic and sebacis acids and suggested tetrahedral geometry. Gandhi et al [16] and Bhave et al [17] reported magnetic moment value in the range...
5.15-5.42 B.M. and 5.13 B.M. for tetrahedral Mn(II) chelate polymers derived from substituted hydroximic acid 4,4' dihydroxy-3,3'-diacetylphenyl-2,6-diaminopyridine respectively. Patei et al. [18] reported magnetic moments value in the range 4.48-4.72 B. M., low magnetic moments of Mn(II) coordination compounds were attributed to the presence of antiferromagnetic exchange interaction between the magnetic atom in solid state or due to arrival oxidation of Mn(II) to Mn(III) during the synthesis of the compound.

Kelman and Sneff [19] studied Mn(II) phthalocyanine complexes and reported magnetic moments 4.51 B.M. and suggested square planar geometry. Mawby and Vehanzi [20] reported five coordinated complexes of Mn(II) having magnetic moment value very close to 1.60B.M.

**Electronic Spectra:**

Manganese (II) ion has d⁵ configuration and is capable of forming spin free as well as spin pair complexes. Due to additional stability of the half filled d-shell spin free complexes are more predominant.

High spin Mn (II) complexes have ⁵S electronic ground state. Since the ⁵S term is orbitally non-degenerate and therefore it cannot split by a crystal field. The absence of any other spin sextet term implies that are crystal field transitions from the ⁵S term will be spin as well as laporte forbidden[20]. The crystal field spectra of high spin d⁵ complexes are therefore expected to be very weak. At low temperature it is possible to obtain sharp and accurate measurement of electronic transition energies with d⁵ complex. The spectral assignment for several Mn(II) complex are reported [21]. It is observed that transitions to spin doublet levels are highly forbidden. The intensities of the octahedral Mn(II) complex [21] are very low (E~ 10⁴-10⁻¹ L cm⁻¹ mol⁻¹ ) as a consequence of their doubly forbidden nature. The tetrahedral complex exhibit spectra with molar extinction coefficient in the range 1-10 cm⁻¹ mol⁻¹. 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 in to the visible
region is often enough to mask the d-d bands. In case of low spin octahedral complexes $^2T_{1g}$ is the ground state but the electronic spectra of these complexes and five coordinate derivations have not been characterized [30].

Drago [22] and Singh [24] have reported spectral assignment for several Mn(II) complex like transitions from $^5A_{1g} \rightarrow ^4T_{1g}(^4G)$, $^4T_{2g}(^4G)$, $^4A_{1g}(^4G)$, $^4T_{1g}(^4D)$ and $^4T_{1g}(^2D)$. These assignments are based on the earlier calculations of Tanabe–Sugano [25] and Orgel [26].

Patel et al [27] have observed weak bands at 13,900, 16,120 and 25,500 cm$^{-1}$ for Mn(II) in octahedral environment. Shakir et al [28] observed two strong bands at 18,870 and 22570 cm$^{-1}$ for Mn (II) complexes of N'N diphenylhydrazine and their triphenyl-phosnine derivatives and suggested octahedral geometry. On the basis of two weak bands observed at 16,010 and 23,220 cm$^{-1}$, Mishra et al [29] observed three bands at 20,000, 22,120 and 25,380 cm$^{-1}$ for Mn(II) chelate and suggested tetrahedral environment around Mn(II) ion.

**Results and discussion:**

In the present study Mn(II) forms brown coloured chelates with bis-bidentate ligands BNPSAP, BNBSAP, BIPSAP and BNESAP, respectively. These are stable toward air and moisture and undergoes decomposition at high temperature. Due to their high insolubility in almost all organic solvents their molecular weight 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 value of synthesized Mn(II) chelates are found to be in close approximation with the expected spin only value 5.92 B.M. The chelates polymers of Mn(II) with BNPSAP, BNBSAP, BIPSAP and BNESAP exhibit 5.80, 5.85, 5.48 and 5.73 B.M. respectively. The observed value 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) \( \rightarrow \) Mn(III) during synthesis [30]. The low value of magnetic moment is also accounted on the basis of antiferromagnetic interaction between Mn(II) ions in solid state [31].

Therefore, on the basis of above finding with respect to magnetic moment of Mn(II) polymers with BNPSAP, BNBSAP, BIPSAP and BNESAP are suggested to have octahedral geometry. Our observations results are in good agreement with those reported for magnetic moments studies of Mn(II) complexes [9-17].

**Electronic Spectra:**

The diffuse reflectance spectra of the Mn(II) chelate under present investigation were studied in the range of 400-1200 nm fig (3.1). The absorption bands and tentative assignments for Mn(II) chelates polymers are given in the table 3.1. The nature of electronic spectra of Mn(II) chelates polymers with all the bis-bidentate ligands in the present study are more or less similar in nature. However the spectra clearly depicts the important difference in the terms of band intensity and position, Mn(II) - BNPSAP, BNBSAP, BIPSAP and BNESAP exhibit bands in the range 15000-18700, 19000-23000 and 24000-25500 cm\(^{-1}\) is distinguishing feature of Mn(II) high spin octahedral complexes and could be assigned to \( ^{6}A_{19} \rightarrow ^{4}T_{1g}(^{4}G) \), \( ^{6}A_{1g} \rightarrow ^{4}T_{2g}(^{4}G) \), \( ^{6}A_{1g} \rightarrow ^{4}A_{1g}, ^{4}E_{g}(^{4}G) \), transitions respectively. These results are in good agreements with those reported in literature [27,28,31].

In the present work the low intensities of the bands in case of BNPSAP, BNBSAP, BIPSAP and BNESAP polymers are indicate of octahedral geometry as a consequence of their doubly forbidden nature as expected for octahedral Mn(II) chelates. Thus on the basis of above observation and magnetic moment data the Mn(II) chelate polymers of BNPSAP, BNBSAP, BIPSAP and BNESAP are suggested have octahedral geometry. The experimental observation of earlier workers also support our results.
Table 3.1 Magnetic moments, assignment of solid-state reflectance spectra and tentative geometry of Mn (II) chelate polymers.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Bis-chelate Ligand</th>
<th>$\mu_{\text{eff}}$ (BM)</th>
<th>Absorption band</th>
<th>Assignments</th>
<th>Geometry</th>
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<td></td>
<td></td>
<td>nm</td>
<td>cm$^{-1}$</td>
<td></td>
</tr>
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<td>1</td>
<td>BNPSAP</td>
<td>5.80</td>
<td>529</td>
<td>18,870</td>
<td>$^6A_{1g} \rightarrow ^4T_{1g}(^4G)$, Octahedral</td>
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<td>435</td>
<td>22,981</td>
<td>$^6A_{1g} \rightarrow ^4T_{2g}(^4G)$</td>
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<td></td>
<td></td>
<td></td>
<td>395</td>
<td>25300</td>
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</tr>
<tr>
<td>2</td>
<td>BNBSAP</td>
<td>5.85</td>
<td>666</td>
<td>15,000,</td>
<td>$^6A_{1g} \rightarrow ^4T_{1g}(^4G)$, Octahedral</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>526</td>
<td>19,000</td>
<td>$^6A_{1g} \rightarrow ^4T_{2g}(^4G)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>408</td>
<td>24,500</td>
<td>$^6A_{1g} \rightarrow ^4A_{1g}(^E_0)$</td>
</tr>
<tr>
<td>3</td>
<td>BIPSAP</td>
<td>5.48</td>
<td>666</td>
<td>15,000,</td>
<td>$^6A_{1g} \rightarrow ^4T_{1g}(^4G)$, Octahedral</td>
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<td></td>
<td>512</td>
<td>19,500</td>
<td>$^6A_{1g} \rightarrow ^4T_{2g}(^4G)$</td>
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<td></td>
<td></td>
<td></td>
<td>400</td>
<td>24,500</td>
<td>$^6A_{1g} \rightarrow ^4A_{1g}(^E_0)$</td>
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<td>4</td>
<td>BNESAP</td>
<td>5.73</td>
<td>689</td>
<td>14,500,</td>
<td>$^6A_{1g} \rightarrow ^4T_{1g}(^4G)$, Octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>526</td>
<td>19,000</td>
<td>$^6A_{1g} \rightarrow ^4T_{2g}(^4G)$</td>
</tr>
<tr>
<td></td>
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<td>400</td>
<td>25,000</td>
<td>$^6A_{1g} \rightarrow ^4A_{1g}(^E_0)$</td>
</tr>
</tbody>
</table>
Fig. 3.1: Diffuse Reflectance Spectra of Mn(II) Chelates.
CHELATE POLYMERS OF IRON (II) d^{6}

Iron(II) forms a number of octahedral complexes [32] and most of them are high-spin type. For Fe(II) quite strong ligand field 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 [33], five coordinated and planar complexes of Fe(II) [34].

Magnetic Properties:

The magnetic moment value for high-spin octahedral complexes of Fe(II) with \(^5T_2g \) 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 reduce magnetic moment to the spin only 4.90 B.M. [36].

Mostafa et al. [37] reported the magnetic moment value in the range 4.75 B.M. for Fe(II) complex with phenylacetyl-4-phenyl-3 thiosemicabazr. Prakash and Shindhu [38] reported, magnetic moment value 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. Patel et al [39] reported the magnetic moment value of Fe(II) complex 5.19 B.M. and this value characteristics of a high-spin octahedral geometry of Fe(II) complex with 2,2'-bipyridylamine Schiff base.

For tetrahedral shows complex, the magnetic moment value is reported in the range 5.20 to 5.21 B.M. in the view of the \(^5E_g \) ground term owing to the spins of the four unpaired electron and a small, second order orbital contribution. However the tetrahedral assignment for Fe(II) complex 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 [40].

Early literature that planer complex of Fe(II) exhibit a magnetic moment of about 4.00 B.M. at room temperature [33] one of the example of planer Fe(II) complex is of ferrous phthalocyanine having magnetic moment 3.98 B.M. at 20°C [19].

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Electronic Spectra:

The ground state term $^5D$ of a d$^6$ configuration is split by octahedral and tetrahedral ligand field in to $^5T_{2g}$ and $^5E_g$ states. There are no other quintet state hence only one spin of allowed d-d-transitions $^5T_{2g} \rightarrow ^5E_g$ occurs if one of these is the ground state.

Sharma et al [32] and Shakier [28] observed bands at 10000 and 12350 cm$^{-1}$ respectively for Fe(II) complex and assigned to $^5T_{2g}$ (D) $\rightarrow ^5E_g$ transition suggesting an octahedral geometry. Patel et al [41] and other worker suggested a number of very small peaks or broad bands 20000 cm$^{-1}$ and splitting of such bands into small peaks is due to either Jahn –Teller or $D_{4h}$ distortion. They also assigned a tetragonally distorted octahedral geometry to the various high spin Fe(II) complex with a double band in the range 1000 -12000 cm$^{-1}$.

The low spin octahedral Fe(II) complex have the electronic configuration $^1T_{2g}$. This configuration give rise to $^1A_{1g}$ ground term. Electronic excitation of the $e_g$ orbitals leads to the configuration $^3T_{2g}$, $e_g$ which gives rise to spin triplet and spin singlet states. Therefore two spin allowed transitions are expected i.e. $^1A_{1g} \rightarrow ^1T_{1g}$ (21000-31000 cm$^{-1}$) and $^1A_{1g} \rightarrow ^1T_{2g}$ (26000,37000 cm$^{-1}$). Similarly two $^1A_{1g} \rightarrow ^3T_{1g}$ and $^1A_{1g} \rightarrow ^3T_{2g}$ weak forbidden transitions are also expected. The $^1A_{1g} \rightarrow ^3T_{2g}$ transition is not usually observed by the d$^6$ ions. Since it has a very low intensity and is normally observed by the $^1A_{1g} \rightarrow ^1T_{1g}$ transition [36,42].

All the tetrahedral complexes are high spin. In a tetrahedral field $^5D$ ground term of the Fe(II) split in to an upper $^5T_{2g}$ and lower $^5E_g$ state spin orbit coupling effect are small, the overall spread of sublevel due to this effect being about 500 cm$^{-1}$ for $^5T_{2g}$ and less than 500 cm$^{-1}$ for the $^5E_g$ ground state [43]. Thus in the tetrahedral field only one band i.e. the spin allowed $^5E_g \rightarrow ^5T_{2g}$ transition is expected for Fe(II) complex occurring at ~40000 cm$^{-1}$. Many compounds show some much weaker bands in the 11000-20000 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 [42].

**Results and discussion:**

Iron (II) chelate polymers in the present's course of study are golden brown in coloured. Their elemental analysis suggest 1:1 (metal:ligand) ratio. The number of water molecular associated with the polymers have been ascertained with the aid of IR study are thermal analysis. All the Fe(II) polymers are insoluble in water and common organic solvents.

**Magnetic Properties:**

All the Fe(II) chelates are found to be paramagnetic and magnetic moment are reported in table 3.2. The chelate polymers of Fe(II) with BNPSAP, BNBSAP, BIPSAP and BNESAP exhibit magnetic moment in the range 5.78-5.99 B.M. which suggest high spin octahedral geometry around the central metal ion. The slightly lower value of magnetic moment can be attributed to the antiferromagnetic interactions or quenching of the orbital contribution as a results of lower site symmetry [44].

**Electronic Spectra:**

The electronic spectra of Fe(II) with all the bis-ligands in the present study exhibits characteristic multiple bands. The multiple bands towards lower energies side indicate d-d transitions, whereas higher energy charge transfer bands are indicated. The spectra clearly indicate the absorption band in the 10,980–19,840 cm⁻¹ region. The band in the region 10,000-11,000 cm⁻¹ is distinguishing feature of Fe(II) high spin octahedral complexes and could be assigned to $^{5}T_{2g} \rightarrow ^{5}E_{g}$ transition. The other two bands at higher cm⁻¹ region (13,513-15873 cm⁻¹ and 20,833-23,809 cm⁻¹) are observed which are ascribed to either $^{5}T_{2g} \rightarrow \pi$, transition or charge transfer transition.

The order in which the other terms lie above the ground term cannot be predicated 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 parameter can be chosen. The Condon-Shortley parameter in
which \( F_2 \) and \( F_4 \) are selected [45,46] or in another choice in Racah
parameter in which \( B \) and \( C \) selected [47,48]. The two sets of repulsion
parameter are relatives.

\[
B = F_2 - 5F_4 \quad \text{and} \quad C = 35F_4
\]

The Racah parameters have a small advantage over the Coden-
Shortley parameter and hence are more commonly used by the chemists
[20]. In Racah parameters if the separation between form of the same
multiplicity involved only one formulation \( B \) is considered but if separation
between terms of different multiplicity is involved both function \( B \) and \( C \)
are considered while both the factions \( F_2 \) and \( F_4 \) are considered even if
the separation between the, terms of same multiplicity takes place. The
Racah interelectronic parameter \( B \) is function of ligand, central ion and
stereochemistry. If the \( B \) value 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 radical displacement of the d-
electron has increased and effective charge experienced by these electron
has decreased. Covalency in the metal -ligand bond is given by the
formula.

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

The ratio \( \beta \) is know as Nephelauxetic ratio.

In the present study crystal field parameter \( Dq,B \) (Racah
interelectron repulsion parameter), and \( \beta \) (Nephelauxetic ratio) have been
calculated by using the following relations [49].

\[
E(5T_2 \rightarrow 5E_g) = 10Dq
\]
\[
10Dq = 5/2 B + 4C
\]
\[
= 18.5B (\text{since } C = 4B)
\]
Table 3.2 Magnetic moments, assignment of solid-state reflectance spectra and tentative geometry of Fe (II) chelates polymers.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Bis-chelate (BM)</th>
<th>$\mu$ eff</th>
<th>Absorption band</th>
<th>Assignments</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand</td>
<td></td>
<td></td>
<td>nm</td>
<td>cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>BNPSAP</td>
<td>5.99</td>
<td>910</td>
<td>10,980</td>
<td>$^3T_{2g} \rightarrow ^5E_g$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>504</td>
<td>19,840</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>BNBSAP</td>
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<td>1086</td>
<td>9,200</td>
<td>$^3T_{2g} \rightarrow ^5E_g$</td>
</tr>
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<td></td>
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<td></td>
<td>526</td>
<td>19,000</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>BIPSAP</td>
<td>5.48</td>
<td>869</td>
<td>11,500</td>
<td>$^3T_{2g} \rightarrow ^5E_g$</td>
</tr>
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<td></td>
<td>392</td>
<td>25,500</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>BNESAP</td>
<td>5.73</td>
<td>884</td>
<td>11,300</td>
<td>$^3T_{2g} \rightarrow ^5E_g$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>384</td>
<td>26,000</td>
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</table>
Fig. 3.2: Diffuse Reflectance Spectra of Fe(II) Chelates
CHELATE POLYMERS OF COBALT (II) d^7

Divalent cobalt forms numerous complexes of various stereochemical types [11, 7]. Generally Co(II) complexes are obtained in tetrahedral and octahedral environment and much less frequently in planar environment. There are a fair number of square ones as well as some, which are five coordination [50-53]. Among most common known Co(II) complex dimethyl glyoximate ,which has a square planar structure is well known.

Tetrahedral complexes are usually more favorable for Co(II) than any other transitions metal ion because the ligand field stabilization favours the tetrahedral stereochemistry relative to octahedral one. The tetrahedral complexes of Co(II) have three unpaired electrons and the square planar one have only one, both as expected for d^7. The octahedral complexes include both high spin and low spin cases the forms with three and the latter with one unpaired electron. Since Co(II) occurs in a great variety of structural environments it electron structure, hence the spectral and magnetic properties are extremely varied. The stereochemical variations have been discussed in term of their magnetic and spectral properties by different workers.

**Magnetic Property**

The Co(II) ion has 3d^7 configuration with free ion ground term 4F in high spin complexes and 2G in low spin complexes. The magnetic properties high spin octahedral Co(II) complexes, are governed by the orbitally degenerate ground term 4T_{1g}, this provides an orbital contribution to the magnetic moment. So that at room temperature magnetic moments value are found to lie in the range of 4.30 -5.20B.M. and hence these values very appreciably with change in temperature [54].

Monshi et al [54] reported magnetic moment value in the range 5.01-5.12 B.M. for series of Co(II) complexes of Schiff bases derived from condensation 5-[4'-(nitrophenyl)azo]-salicylaldoxide and thiosemicarbazide.

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Some other worker also reported similar type of observation and suggested high spin octahedral geometry around the Co(II) ion [55,56]. Dolakiya et al [57] reported magnetic moments value 4.71 and 4.60 B.M. for a series of Co(II) complexes of Schiff base derived from condensation of 5-chlorosalicylaldehyde and p-anisidine and 5-bromo salicylaldehyde and p-anisidine.

Low spin octahedral Co(II) complexes have \(^{2}\text{Eg}\) ground term arising from \(t_{2g}^{6},e_{g}\) electronic configuration. Experimental magnetic moments of these type of complexes usually lie in the range 1.70-1.85 B.M. [58,59], which are close to give spin only value (1.73 B.M.) and is independent of temperature. Cobalt(II) complexes in tetrahedral environment with the ground term \(^{4}\text{A}_{2g}\) and the magnetic moment is expected to the spin only value modified by the found (1-4\(\lambda/10Dq\)) and TIP term from higher ligand field level. The spin only magnetic moments is expected to the equivalent of three unpaired electron (3.89 B.M.). In the presence of low symmetry ligand field the spin degeneracy of the \(^{4}\text{A}_{2g}\) ground term is removed and as a result of this variation in magnetic moment values in between 3.98-4.52 B.M. observed.

Patel et al [60] reported 3.70 B.M. magnetic moments value for Co(II) polychelate of 2,4-dihydroxybenzaldehydeoxime-urea-formaldehyde polymeric ligand and suggesting tetrahedral geometry. Tetrahedral cobalt complexes with benzaldehyde morpholine-N-thiohydrozone and cyclohexanone morpholine-N-thiohydrozone exhibited magnetic moments value between 3.9-45 B.M. [61]. Similar behavior in the other Co(II) complexes have also been reported [62,63].

Five coordinated Co(II) complexes exhibit both high spin with three unpaired electron and low spin with (One unpaired electron) [64,65,67]. Configurations for both trigonal bipyramidal and square pyramidal as well as for intermediates configuration are known. Literature reveals that very few complexes of Co(II) are five coordinated and show magnetic moments associated with one unpaired electron reviewed by Earnshaw et al [68].
Electronic Spectra:

The Co(II) ion has the electronic configuration d⁷ and its ground state configuration in an octahedral field may be either t⁵₂, e²_g in weak field or t⁵₂, e¹_g in strong field. Generally Co(II) complex are obtained in tetrahedral and octahedral environment and much less frequency in planar environments. The electronic transitions of Co(II) in various stoerechemistry are briefly mentioned here. The ground state of Co(II) in octahedral environment is ⁴T₁⁰ and ²E₉ depending on whether the complexes is high spin or low spin. Most of the octahedral Co(II) complex are pink redish brown in colour [69], while tetrahedral complex are blue. However the colour is not always a useful criteria of stoerechemistry. The electronic spectrum of Co(II) complexes in tetrahedral environment is more intense than that of the octahedral one. Both type octahedral and tetrahedral complexes give rise to electronic spectral band around 20,000 cm⁻¹ although tetrahedral compounds frequently exhibits maximum near 15,0000 cm⁻¹.

Octahedral coordinated Co(II) ion has three spin allowed d-d-transitions those from the ground state ⁴T₁⁰ (F) to a that ⁴T₂⁰, ⁴T₁⁰ (P) and ⁴A₂₉ (F) states respectively. A low energy band in the complexes near 8000-10000 cm⁻¹ can be assigned to ⁴T₁⁰ → ⁴T₁⁰ transition. A multiple band observed at 20,0000cm⁻¹ is attributed to transition ⁴T₁⁰ → ⁴T₂⁰ transition higher energy which may be admixture with spin forbidden transitions. The ⁴T₁⁰ → ⁴A₂₉ transition is not normally observed as it is a two electron transition [12,70-71]. Theoretically the ν₂/ν₁ ratio is of nearly constant (1.85-2.20) and therefore ν₂ can be readily predicted if ν₁ is measured.

The ground state of Co(II) ion tetrahedral configuration is ⁴A₂₉. The lowest energy band corresponding to ⁴A₂₉ → ⁴T₂⁰ transition is not often observed since it is weak and lie in the infrared region other transitions ⁴A₁₉ → ⁴T₁⁰ (F), ⁴T₂⁰ → ⁴T₁⁰ (P). The electronic spectra of Co(II) tetrahedral complex have been extensively studied [58,68-72].
Patel et al [27,73] have observed the bands at 8870-8940, 12,250-15390 and 23,400-24,810 cm\(^{-1}\) in the reflectance spectra of Co(II) complexes of \(\alpha\)-oximinoacetacet -o/P-chloroaniline-\(\beta\)-thiosemicabazone these are assigned to to \(^4A_{2g} \rightarrow ^4T_{1g}\) (F), \(^4A_{2g} \rightarrow ^4T_{1g}\) (P) and charge transfer transitions respectively and suggest tetrahedral geometry. Planar coordination has observed in very few complexes [74]. The spectral bands in the square planer complexes indicate two absorption maxima in the visible region one band in the infrared region with \(^2B_{2g}\) or \(^2A_{1g}\) ground state. Many square planer Co(II) complexes exhibit one bands near 20,000 cm\(^{-1}\). The visible band is probably due to \(^2A_{1g} \rightarrow ^2B_{1g}\) transition.

Patel et al [7] and lever [20] have observed a bands near 2,000-21,000 cm\(^{-1}\) while studying the electronic spectra of square planer Co(II) complexes.

A number of ligands are now known to give rises to high -spin and low spin free coordinated complexes of Co(II). In the group \(D_{3h}\), four principle absorption bands have been assigned to \(^4A_2\) (F) \(\rightarrow ^4E\) (5,500 cm\(^{-1}\), \(^4A_2\) (F) \(\rightarrow ^4E\) (12,400 cm\(^{-1}\)) \(\rightarrow ^4A_1\) (15,6000-16,000 cm\(^{-1}\)), \(^4A_2\) (F) \(\rightarrow ^4E\) (P) (20,000 cm\(^{-1}\)) transition respectively [75].

**Results and discussions:**

The Co(II) chelates under present study are dark brown coloured. They are stable towards air and moisture and insoluble in almost all organic solvents. Association of water molecular with the chelate polymers have been confirmed with the help of TGA analysis. Elemental analysis suggest (M:L)1:1 stoichimentry for all Co(II) chelates.

**Magnetic Property:**

In present work the magnetic moment values of Co(II) chelates are presented in table 3.3. The magnetic moment values for Co(II) chelates have been used as criteria to determine the type of coordination around the metal ion. Due to the intrinsic orbital angular momentum in the
ground state, there is consistently a considerable orbital contribution and the effective magnetic moment value of Co(II) BNPSAP, BNBSAP, BIPSAP and BNESAP chelates lies between 5.01-5.09 B.M., which are greater than the spin only value, and satisfactorily lies in the range for octahedral geometry [54].

Electronic Spectra:

The electronic spectra of Co(II) chelates with BNPSAP, BNBSAP, BIPSAP and BNESAP are shown in fig. 3.3. Various bands in the electronic spectra are assigned on the basis of the literature data available. Absorption bands tentative assignment and proposed geometry for Co(II) chelate polymers are tabulated in table 3.3

The reflectance spectra exhibit the bands of medium intensity at 9,000 and 18,000 cm\(^{-1}\), which are assigned to \(^{4}T_{1g}(F) \rightarrow ^{4}T_{2g}\) \((v_1)\) and \(^{4}T_{1g}(F) \rightarrow ^{4}T_{1g}(P)\) \((v_3)\) transitions, respectively. The third \(^{4}T_{1g}(F) \rightarrow ^{4}A_{2g}\) \((F)\) \((v_1)\) is observed at \(\sim 19000\) cm\(^{-1}\) which is weak. However, the splitting of this band has been observed in Co(II) BNPSAP, BNBSAP, BIPSAP and BNESAP chelate polymers.

The splitting of \(v_3\) band may be the presence of low symmetry field [74] and weaker axial interaction in the solid state [74]. The electronic spectra of Co(II) BNPSAP, BNBSAP, BIPSAP and BNESAP chelates further reveal that the band of light transition has characterization splitting in to shoulder which makes assignments much different splitting of this band and may be due to lifting of degeneracy of \(T_{1g}(P)\) level either by spin orbital coupling or by presence of low symmetry component in the ligand field [76]. Thus on the virtual appearance of the electronic spectra and the transitions their in indicate octahedral geometry of BNPSAP, BNBSAP, BIPSAP and BNESAP chelates of Co(II). An attempts has been made to utilize electronic spectral data to compute the important ligand field and repulsion parameters using the ligand field theory of spin allowed transitions.
All important ligand field and repulsion parameters are calculated using following equation.

\[
Dq = \left[ \frac{(2\nu_1 - \nu_2) + \nu_3^2 + \nu_1 \nu_3 - \nu_1^2)}{20} \right]^{1/6}
\]

\[
B = \nu_1 - 2\nu_1 + 10Dq
\]

\[
\nu_2 = \nu_1 + 10Dq
\]

\[
\beta = B \text{ in complex}
\]

\[
\beta^* = B \text{ in the free ion} - B \text{ in the complex \times 100}
\]

The calculated value of \(Dq\), \(B\), \(\beta\), and \(\beta^*\) are tabulated in Table 3.3.

The value of crystal field parameters for Co(II) chelates with BNPSAP, BNBSAP, BIPSA, and BNESAP can be compared with the values reported in literature [54, 78, 79] for high spin octahedral Co(II) complexes. The transition energy ratio \(\nu_2/\nu_1\) (1.80 / 1.76), which is found in the range for octahedral geometry [80-81].

The value of \(\beta\) in these chelates lies in the range 0.78-0.89 which suggest the practical covalent character to the bond concerned [82].

On the basis of electronic spectral data and magnetic moment value octahedral structure are proposed for the Co (II) polychelates.
Table 3.3 Magnetic moments, assignment of solid state reflectance spectra and tentative geometry of Co(II) chelate polymers.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Bis-chelate Ligand</th>
<th>$\mu_{\text{eff}}$ (BM)</th>
<th>Absorption band</th>
<th>Assignments</th>
<th>Dq</th>
<th>B</th>
<th>$\beta$</th>
<th>$\beta^0$</th>
<th>$\nu_2/\nu_1$</th>
<th>Geometry</th>
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<td>BNPSAP</td>
<td>5.08</td>
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<td>607</td>
<td>0.698</td>
<td>30.00</td>
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<td></td>
<td>555</td>
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<td>2</td>
<td>BNBSAP</td>
<td>5.07</td>
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<td>9,200 $^1T_{1g}(F) \rightarrow ^4T_{2g}(\nu_3)$</td>
<td>1032</td>
<td>728</td>
<td>0.749</td>
<td>23.10</td>
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<td></td>
<td>563</td>
<td>19,000 $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)(\nu_3)$</td>
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<td>1100</td>
<td>9,090 $^4T_{1g}(F) \rightarrow ^4T_{3g}(\nu_3)$</td>
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<td>751</td>
<td>0.773</td>
<td>22.70</td>
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<td>520</td>
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<td>4</td>
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<td>724</td>
<td>0.748</td>
<td>25.38</td>
<td>1.95</td>
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<td></td>
<td></td>
<td>509</td>
<td>19,630 $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)(\nu_3)$</td>
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</table>

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Results and discussion

All important ligand field and repulsion parameters are calculated using following equation.

\[
Dq = \left[ \frac{(2\nu_2 - \nu_3) + (\nu_3^2 + \nu_1\nu_3 - \nu_1^2)}{20} \right]^{\frac{1}{6}}
\]

\[
B = \frac{v_2 - 2v_1 + 10Dq}{15}
\]

\[
v_2 = v_1 + 10Dq
\]

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

\[
\beta^o = \frac{B\text{ in the free ion} - B\text{ in the complex} \times 100}{B\text{ in the free ion}}
\]

The calculated value of \(Dq\), \(B\), \(\beta\), and \(\beta^o\) are tabulated in table 3.3.

The value of crystal field parameters for Co(II) chelates with BNPSAP, BNBSAP, BIPSAP and BNESAP can be compared with the values reported in literature [54,78,79] for high spin octahedral Co(II) complexes. The transition energy ratio \(v_2/v_1\) (1.80 / 1.76), which is found in the range for octahedral geometry [80-81].

The value of \(\beta\) in these chelates lies in the range 0.78-0.89 which suggest the practical covalent character to the bond concerned [82].

On the basis of electronic spectral data and magnetic moment value octahedral structure are proposed for the Co (II) polychelates.
Fig. 3.3: Diffuse Reflectance Spectra of Co(II) Chelates
CHELATE POLYMERS OF NICKEL (II) d^8

The Ni(II) form a large number of complexes 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 have been reported [83]. Most of the complexes of Ni(II) can be divided in to three categories

1) Six coordinated, octahedral paramagnetic complexes with $^3A_{1g}$ ground term.
2) Four coordinated, tetrahedral paramagnetic complex with $^3T_{1g}$ ground term and .
3) Four coordinated square planar diamagnetic complexes with $^1A_{1g}$ spin paired singlet ground term.

Magnetic Properties:

In a regular octahedral complex of nickel (II). The magnetic moment of octahedral Ni(II) complex are usually found in the range 2.80-3.40 B.M. Consideration of spin–orbit coupling and contribution from $^3A_{1g}$ and the next higher $^3T_{2g}$ state give a somewhat higher magnetic moment value than expected 2.83 B.M. spin only value. In certain tetragonally distorted complex, the magnetic moments have been found to be high as 3.40-3.50 B.M. For the stereochemistry of the nickel (II) complexes the magnetic data are specially significant. Since the stereochemistry of the attached ligand affects the quenching of orbital magnetism, the size of the latter may in suitable cases be used as a guide to stereochemistry.

Dholakiya et al [57] observed magnetic moment value between 2.74-2.98 B.M. for several Ni(II) chelates derived from the Schiff bases bis[(benzylidene)ethylene diamine]] and their derivatives. Panchal et al [27] reported 2.98-3.01 B.M. magnetic moment for a new series of complexes of Ni(II) with Schiff base derived from di[(benzylidene)-1-8-diaminonaphthalene]] and suggested an octahedral geometry. Ni(II) complexes having magnetic moment value between 2.54-3.26 B.M. for
Ni(II) polymeric chelates prepared by polycondensation of 2,4-dihydroxypropionone with 1,3-propanediol and suggested an octahedral environment around the Ni(II) ion.

In tetrahedral symmetry the d⁶ configuration give to ³T₁g (F) ground state, which contributes to much inherent orbital angular momentum and its 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 spitting the orbital degeneracy). Thus fairly regular tetrahedral complexes have moment of 3.0-3.5 B.M. Recently Chadhury et al [84] reported a magnetic moment value between 3.20-3.30 B.M. for tetrahedral Ni(II) complexes obtained by condensation of hydrazones of morphine-N-thiohydrazide with benzaldehyde, cinnamaldehyde and cyclohexanone.

Square planar complexes of Ni(II) are essentially diamagnetic. Since for d⁶ configuration the planar ligand set course on of the d-orbital d(x² - y²) to be uniquently high in energy and the eight electrons can occupy the other four d-orbital but leave this strongly antibonding one vacant, these complexes are mainly obtained with ligand capable of forming of highly covalent bond with strong σ and π bonding character [34,70,85].

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 in to the stereochemistry. The colour of the complexes themselves give an indication of the tetryahedron. The square planar complexes of Ni(II) are generally orange, red, yellow or brown but purple and green coloured examples are also known while, the octahedral complexes are commonly green coloured and tetrahedral one are blue.

The octahedral Ni(II) complexes are almost high spin complexes having either regular or distorted octahedral stereochemistry. Octahedral...
Ni(II) complexes with $^3\text{A}_2g$ ground term are characterized by the presence of three moderately intense bands due to the three spin allowed transitions $^3\text{A}_2g \rightarrow ^3\text{T}_{1g}(F)$, $^3\text{A}_2g \rightarrow ^3\text{T}_{1g}(F)$ and $^3\text{A}_2g \rightarrow ^3\text{T}_{1g}(P)$, respectively. These transitions are commonly observed in the regions 7000-13000 cm$^{-1}$, 14000-20000 cm$^{-1}$ and 20000-25000 cm$^{-1}$ respectively [20]. In addition two spin forbidden bands are frequently observed due to the $^3\text{A}_2g \rightarrow ^1\text{E}_{1g}(11000-15000\text{cm}^{-1})$ and $^3\text{A}_2g \rightarrow ^3\text{T}_{1g} (17000-22000\text{cm}^{-1})$ transitions.

In tetragonal $D_{4h}$ symmetry the ground state $^3\text{A}_2g$ 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 levels of $d^8$ molecule transforms as $^3\text{A}_2g \rightarrow ^3\text{B}_{1g}$, $^3\text{T}_{2g}(F) \rightarrow ^3\text{E}_{2g}$, $^3\text{E}_{g}$ and $^3\text{T}_{1g} \rightarrow ^3\text{A}_{2g}$, $^3\text{E}_{g}$. Thus theoretically our three bands spectrum becomes a six band spectrum and it should therefore, contain enough information to analyses the spectra satisfactorily. However in practice all six bands are rarely observed.

The tetrahedral Ni(II) complexes have a multiple bands at 15000-180000 cm$^{-1}$, which is assigned to $^3\text{T}_{1}(F) \rightarrow ^3\text{T}_{1}(P)$ transitions with weak bands on either side of this transitions which can be assigned to are spin forbidden transition assigned to components of $^1\text{D}$ and $^1\text{G}$ levels respectively. A bands at 8000-10000 cm$^{-1}$ assigned as $v_2$ transition $^3\text{T}_{1}(F) \rightarrow ^3\text{A}_2 (F)$. In contrast to tetrahedral cobalt, this band is not unusually split, presumably because the excited state concerned in an orbital singlet. The $v_1$ band corresponding to $^3\text{T}_{1}(F) \rightarrow ^3\text{A}_2$ in observed only in certain circumstances. The visible spectra of tetrahedral Ni(II) differ slightly from that of tetrahedral Co(II) although it is true to say that molar extinction coefficient are usually lower in the former case. Choudhary et al [84] reported the reflectance spectra of Ni(II) complex display one broad and strong band in visible region typical of tetrahedral structure.
Results and discussion:
In present investigation the Ni(II) chelate polymers have brown shade, insufficient solubility of these chelate polymers in common organic solvents. Precluded their determination of molecular weight. Elemental analysis of all the Ni(II) chelates suggest 1:1 (m:l) ratio.

Magnetic Properties:
In the present investigation magnetic moment of Ni(II) chelates have been measured at room temperature and values are incorporated in Table 3.4. The magnetic moment values for Ni(II) BNPSAP, BNBSAP, BIPSAP and BNESAP are observed in the range 2.88-2.97B.M. Corresponding to two unpaired electrons. The magnitude of magnetic moment clearly indicated that Ni(II) ion has paramagnetic nature in all the polyhedral with octahedral structure. This slight variation in magnetic moment values for a high spin Ni(II) complex depend on the magnitude of the orbital contribution expected for similar hexa coordinate Ni(II) ions [21, 31, 54].

Electronic spectra:
The diffuse reflectance spectra of the Ni(II) chelates polymer under present study display bands in the range 10000-25000 cm⁻¹.
The spectra of Ni(II) polychelates with BNPSAP, BNBSAP, BIPSAP and BNESAP bear a close resemblance in profile and band positions to these of octahedral Ni(II) complexes. The solid reflectance spectra of the Ni(II) polychelates are consistent with the formation of an octahedral geometry [87] with the appearance of three bands in the range 10,382-10,800, 16,970-17,490 and 24,5000-26,3000 cm⁻¹ corresponding to the transitions \(3A_2g(F) \rightarrow 3T_{1g} (F)\), \(3A_2g(F) \rightarrow 3T_{1e}(F)\) and \(3A_2g(F) \rightarrow 3T_{2g}(P)\) transitions respectively. The ratio \(\nu_2/\nu_1\) lies between 1.40-1.54 B.M. which in the range of the octahedral Ni(II) chelates [84, 85, 124, 125]. An attempt has been made to utilize electronic spectral data to complete the important ligand and repulsion parameters using the ligand field theory.

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Results and discussion

[L.F.T.] of spin allowed transition [90]. The Racah interelectronic repulsion parameter (B_{35}) is calculated by using the following equation [90]

\[ B_{35} = \frac{u_3 + u_2 - 3 u_1}{15} \] \hspace{1cm} 3.12

Using the value B_{35} an attempt have been made to calculate the transition energies u_2 and u_3 by the relation.

\[ \frac{u_2}{u_3} = \frac{1}{2} \left[ (15B+30Dq) + \frac{1}{2} \left[ (15B-10Dq)^2 + 12B \times 10Dq \right] \right]^{1/2} \] \hspace{1cm} 3.13

The Ni(II) chelate with an octahedral symmetry v_1 = 10Dq is calculated as

\[ v_1 = 10Dq = 1/3 (u_2 + u_3 - 5B) \] \hspace{1cm} 3.14

Nephelauxetic ratio \( \beta_{35} \) and \( \beta_{0,35} \) are calculated using the equation [49,91]

\[ \beta_{35} = \frac{B_{35} \text{ in the complex}}{B \text{ in the free ion}} \] \hspace{1cm} 3.15

\[ \beta_{0,35} = \frac{B - B_{35} \times 100}{B} \] \hspace{1cm} 3.16

The various spectral parameters have been summarized in table 3.4, which are favours an octahedral symmetry to Ni(II) BNPSAP, BNBSAP, BIPSAP and BNESAP chelates. The considerable reduction of B_{35} values of free ion from 1080 cm\(^{-1}\) to 609-705 cm\(^{-1}\) on chelation indicate the appreciable amount of covalent characterize in the metal-ligand bond. On the basis of spectral data an octahedral structure are proposed for all the nickel polychelates.
Fig. 3.4: Diffuse Reflectance Spectra of Ni(II) Chelates
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Bis-chelate Ligand</th>
<th>$\mu$ eff (BM)</th>
<th>Absorption band nm</th>
<th>Assignments</th>
<th>Dq</th>
<th>B</th>
<th>$\beta^\alpha$</th>
<th>$\nu_2/\nu_1$</th>
<th>Geometry</th>
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<tbody>
<tr>
<td>1</td>
<td>BNPSAP</td>
<td>2.88</td>
<td>925 10,800</td>
<td>$^3A_{2g} \rightarrow ^3T_{2g}(\nu_1)$</td>
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<td></td>
<td>1080 707 0.670</td>
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<td>581 17,200</td>
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<td>380 26,300</td>
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<td>408 24,500</td>
<td>$^3A_{2g} \rightarrow ^3T_{1g}(P)(\nu_3)$</td>
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<td>1058 676 0.676</td>
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<td>408 24,500</td>
<td>$^3A_{2g} \rightarrow ^3T_{1g}(P)(\nu_3)$</td>
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CHELATE POLYMERS OF COPPER (II) d^9

Copper is one of the most extensively studied transition metal ion in term of complex formation. The Cu(II) ion with d^9 configuration is most susceptible to Jahn-teller distortion. The dipositive state copper is most important oxidation state and the usual coordination numbers adopted by copper (II) are four, five and six. Fairly large number of six and four coordinated complexes and relative less number of five coordinated complex are reported. The six coordinated complex of Cu(II) are unusually distorted due to Jahn-Teller effect. Through d^9 ion in tetrahedral environment is subjected to Jahn-teller distortion, the large spin orbit coupling constant for Cu(II) might produce sufficient splitting of the ground T_{2g} term make Jahn-teller effect in to operation [92-96]. There are several example of distorted tetrahedral geometry, which is determined by the steric factor of the ligand.

Magnetic Properties :

On the basis of magnetic properties Cu(II) complexes can be broadly classified in to two categories. The first type has essentially temperature independent magnetic moment in the range 1.75-2.20 B.M. [36]. These are mononuclear complexes having no major interaction between the electrons on different Cu(II) ion. The second type has moments suitably below the spin only values which are markedly temperature dependent. This is due to the coupling of spin of two Cu(II) ion held together in bimetallic complexes. The crystal field predicts that Cu(II) complexes will have marked contribution to the magnetic moment only when the ground state is orbitally degenerate [97,98].

In square planar complexes the ground state is not degenerate and subsequently planer complexes should have value close to the spin only value 1.73 B.M. [7,8,96-97] An examination of the literature data [9,10,98-99] of some of the Cu(II) polychelates reveal that the magnetic moment of square planar Cu(II) complexes lies in the range 1.77-1.74
Chapter-3

Results and discussion

B.M. is respectively by Shetty [100] for Cu(II) complex with tridentate ligand having square planer structure.

A perfectly tetradebate complex has a degenerate ground state and should have a large orbital contribution. Under these condition the magnetic moment should vary with temperature and at room temperature should be about 2.20 B.M. [101] whereas, distortate tetrahedral complex should vary lower value of $\mu_{\text{eff}}$ [97].

Singh et al [24] reported magnetic moment value 1.9-1.95 B.M. for Cu(II) complexes of N-phenyl-5-phenyl1,3,4-coxidazole-2-sulphonoamide and 5 phenyl-1-3-4-oxozole-2-imino sulphonamide and suggested tetrahedral environment around Cu(II) ion. Tetragonally coordinate Cu(II) ion with T$_{2g}$ ground term the anticipated magnetic moment is 2.20 B.M. at room temperature[102].

Electronic spectra:

The ground state of a cubic octahedral coordinated copper (II) ion is $^2$E$_g$ in tetrahedral complex is $^2$T$_{1g}$ whereas for the square planar complexes is $^2$B$_{1g}$. The d$^9$ configuration gives rise to the $^2$D free ion term, which splits in a regular octahedral field into a lower doublet $^2$E$_g$ level and an upper triplet $^2$T$_{2g}$ level. Thus only one spin allowed d-d transition $^2$E$_g$ $\rightarrow$ $^2$T$_{2g}$ is expected in visible spectra of Cu(II) complexes. [16]. For distorted octahedral complex, several weak bands are observed at 16000 cm$^{-1}$ and often a broad tail near infrared region due to John–Teller effect. However the d$^9$ configuration is highly Jahn-Teller sensitive and the resulting tetragonal distortion (D$_{4h}$) led to the further splitting of the $^2$E$_g$ and $^2$T$_{2g}$ levels into $^2$B$_{1g}$, $^2$A$_{1g}$ and $^2$B$_{2g}$, $^2$E$_g$ levels respectively. In the axially, elonganated tetragonal coordination $^2$B$_{1g}$ respectively the ground state and three absorption bands corresponding to transitions $^2$B$_{1g}$ $\rightarrow$ $^2$A$_{1g}$, $^2$B$_{1g}$ $\rightarrow$ $^2$B$_{2g}$ and $^2$B$_{1g}$ $\rightarrow$ $^2$E$_{1g}$ are observed [17].

Bhaskar et al [72] studied that the electronic spectra of Cu(II) complexes and observed band at 15000 cm$^{-1}$ assigned to $^2$T$_{2g}$ $\rightarrow$ $^2$E$_g$ transition and charge transfer transition at~26000 cm$^{-1}$ while a single
broad band in the region 13000-17000 cm\(^{-1}\) center at 15037 cm\(^{-1}\) which may be due to overlapping of the three transitions \(^2B_{1g} \rightarrow ^2B_{2g}\), \(^2B_{1g} \rightarrow ^2E_g\) and \(^2B_{1g} \rightarrow ^2A_{1g}\) are reported by Pancholi et al [12] and suggested a distorted octahedral symmetry Regular tetrahedral complex of Cu(II) are very uncommon [20]. In general nearly regular tetrahedral complex are expected to give a single broad band corresponding to \(^2E_g \rightarrow ^2E_g\) transition in the near IR region and in visible spectra [20] only low energy charge transition band may be observed in this region.

Singh et al [24] reported bands at 35088 and 20220, 17241 cm\(^{-1}\) which are assigned to transitions CT, \(^2B_{1g} \rightarrow ^2E_{1g}\) and \(^2B_{1g} \rightarrow ^2A_{1g}\), respectively, for Cu(II) complex and assigned a tetrahedral symmetry. In square planar complex the d-d bands are expected to occur in the range 14000-18000 cm\(^{-1}\) [147-148]. The ground term in the a square planar geometry is \(^2B_{1g}\) and three d-d transition \(^2B_{1g} \rightarrow ^2B_{2g}\), \(^2B_{1g} \rightarrow ^2A_{1g}\) and \(^2B_{1g} \rightarrow ^2B_{2g}\) are observed [104-105].

Patel et al. [7] observed two bands for Cu(II) polymer with the poly Schiff base. The band at 23,240 cm\(^{-1}\) is due to charge transfer ligand to metal while the band at 14915 cm\(^{-1}\) is due to d-d transition which clearly indicated planar stereochemistry several other workers [54,60,64] have proposed square planar geometry to Cu(II) polychelates. Orgel [106] and Kerayannis and [107] and found a broad band at 16000 cm\(^{-1}\) for square planar Cu(II) complexes. Five coordinated complexes exhibit two bands near at 8200 and 10200 cm\(^{-1}\).

**Results and discussion**

**Magnetic Properties**

All the Cu(II) polychelates in the present course of study are air stable coloured solid and insoluble in water and most of the organic solvents. Elemental analysis suggest 1:1 metal: Ligand stoichiometry. The room temperature susceptibility value have been calculated from experimental data and given in table 3.5. The data suggest that copper (II) chelate polymers under present study are paramagnetic. The observed
magnetic moment value for the Cu(II) chelates with BNPSAP, BNBSAP, BIPSAP and BNESAP lie in the range 1.80-1.87 B.M. indicating mononuclear nature of chelates [20]. These values are close to the spin-allowed moment than spin only value 1.73 B.M. might. The higher magnetic be due to orbital contribution Thus the Cu(II) polychelates with BNPSAP, BNBSAP, BIPSAP and BNESAP may have square planar geometry.

Electronic spectra:

The diffuse reflectance spectra of Cu(II) chelates with BNPSAP, BNBSAP, BIPSAP and BNESAP are recorded in Fig. 3.5 and spectral assignment are given in the table 3.5. The electronic spectra of Cu(II) BNPSAP, BNBSAP, BIPSAP and BNESAP chelate in the present study show three bands in their normally expected region for square planer Cu(II) complexes (16000, 25000 cm⁻¹) [108]. These bands are assigned as \(^2B_{1g} \rightarrow ^2A_{1g} \), \( ^2B_{1g} \rightarrow ^2B_{2g} \) and \( ^2B_{1g} \rightarrow ^2E_g \) transition respectively. Our experimental results are in good with earlier work and square planer to Cu(II) Chelate polymer on the basis of spectral studies.
Table 3.5 Magnetic moments, assignment of solid state reflectance spectra and tentative geometry of Cu(II) chelates polymers.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Bis-chelate Ligand</th>
<th>( \mu_{\text{eff}} ) (BM)</th>
<th>Absorption band (nm, cm(^{-1}))</th>
<th>Assignments</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BNPSAP</td>
<td>1.80</td>
<td>565 17,690 ( ^2B_{1g} \rightarrow A_{1g} )</td>
<td></td>
<td>Square Planar</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>520 19,210 ( ^2B_{1g} \rightarrow ^2B_{2g} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>402 24,830 ( ^3B_1 \rightarrow ^3E_0 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>BNBSAP</td>
<td>1.85</td>
<td>565 17,690</td>
<td>( ^2B_{1g} \rightarrow A_{1g} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>520 19,210 ( ^3B_1 \rightarrow ^3E_0 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>402 24,830 ( ^1G \rightarrow ^3B_{2g} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>BIPSAP</td>
<td>1.86</td>
<td>565 17,690</td>
<td>( ^2B_{1g} \rightarrow A_{1g} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>520 19,210 ( ^2B_{1g} \rightarrow ^2B_{2g} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>402 24,830 ( ^2B_1 \rightarrow ^2E_0 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>BNESAP</td>
<td>1.87</td>
<td>565 17,690</td>
<td>( ^2B_{1g} \rightarrow A_{1g} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>520 19,210 ( ^2B_{1g} \rightarrow ^2B_{2g} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>402 24,830 ( ^3B_1 \rightarrow ^3E_0 )</td>
<td></td>
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</tbody>
</table>
Fig. 3.5: Diffuse Reflectance Spectra of Cu(II) Chelates
CHELATE POLYMERS OF ZINC (II) d^{10}

Zn(II) ion forms numerous complexes of various stericchemical types having 4, 5 and 6 coordination numbers. Its 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 structure have been reported [110,111].

The tetrahedral complexes are predominant [84,111-112]. Patel et al [70] proposed tetrahedral geometry for Zn(II)-7-(α-phenyl-α-o/m-chloro-aniline methyl)-8-quinolinol complexes Zn(II) complexes achieve five coordination by dimerisation [110-112].

Zn(II) form trigonal bipyramidal complexes with one axial and three equatorial positions the fifth one is occupied anion like isothiocyanide or chloride etc. Bhattacharya et al [113] suggested trigonal bipyramidal geometry for Zn(II) complexes of two potentially pentadentate ligand based on methyl-2-aminocyclopent-1-ene-dithiocarboxylate with pendent pyrazole group. Square pyramidal complexes are also reported [114].

A few octahedral complexes of Zn(II) are also reported [11,36,115]. Mohanty et al [56] proposed an octahedral symmetry to the Zn(II) complexes in conjugation with their analytical, conductance and infrared spectral data.

Results and discussion:

The Zn (II) complexes of BNPSAP, BNBSAP, BIPSAP and BNESAP chelate polymers have been synthesized and are coloured amorphous solid and stable at room temperature. Their elemental analysis indicate 1:1 (Metal: ligand) ratio. They are insoluble in water and almost all organic solvents.

Magnetic Properties:

The room temperature magnetic susceptibilities have been calculated from experimental data. The data suggest that the Zn(II)
chelate polymer under present study are diamagnetic. This is in accordance with the $d^{10}$ (i.e. completely filled 'd' sub shells) configuration of Zn(II) ion. A survey of literature reveals that all the Zn(II) chelates show diamagnetic nature.

**Electronic Spectra:**

The diffuse reflectance spectra were 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.

The Zn(II) chelates under present study are found to be diamagnetic. On the basis of elemental analysis, magnetic and electronic spectra results most probable geometry for Zn(II) the chelate polymer may be tetrahedral. Our observation are in good agreement with the reported literature.

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

Cd(II) ion with $d^{10}$ configuration forms several chelate polymers. The Cd(II) ion in the complexes generally have four, five or six coordination number. It forms rather stable four coordinate complexes them Zn (II) in six coordination due to large size. However the tetrahedral complexes are more common [36]. The Cd(II) α (3,3'-dinitro2-hydrophenylazo)-2-naphthol-4-sulphonicacid complexes is suggested to be four coordinated with a tetrahedral stereochemistry around metal ion on the basis the analytical and IR spectral data by Mahapatra et al [111] Chaudhary et al [84] proposed a tetrahedral structure to Cd(II) complexes with hydrazones of morpholine–N-thiohyazole with benzaldehyde, cinnamaldehyde and cyclohexanone on the basis stiochomentry. Mohonty et al [56] suggested an octahedral structure for the Cd(II) complexes.
Magnetic Properties:

The Cd(II) chelate polymers, under investigation, were found to be diamagnetic from the magnetic susceptibility measurement data at room temperature. General magnetochemistry of Cd(II) complexes 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 diamagnetic.

Electronic Spectra:

The diffuse reflectance spectra of Cd (II) polymers do not furnish any relevant information towards their stereochemistry. So an the basis of analytical, IR spectral and TGA the Cd(II) chelate with BNPSAP, BNBSAP, BIPSAP and BNESAP are supported to have tetrahedral geometry which is most favourable structure for elements with $d^{10}$ electronic system.

Results and discussion:

Magnetic Properties-

The room temperature magnetic susceptibilities have been calculated from experimental data. The data suggest that the Cd(II) chelates polymer under pressure study are diamagnetic. This is in acceptances with the $d^{10}$ (i.e., completely filled 'd' subshells). Configuration of Cd (II) ion a study of literature reveal that all the Cd (II) chelates show diamagnetic nature.

Electronic Spectra:

The diffuse reflectance spectrum 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.

The Cd (II) chelates under present study are found to be diamagnetic. On the basis of elemental analysis, magnetic and electronic spectra results, Most probable geometry of the chelates polymer may be tetrahedral. Our observation are in good agreement with the reported literature.
INFRARED SPECTROCOPY

Infrared spectroscopy provides one of the most versatile and useful techniques for the quantitative and qualitative characterization of most of materials found in the solid, liquid or gases state. When a ligand is coordinated to a metal ion, one additional atom is introduced into the vibrating system of the ligand. This causes the bond length, bond angles and intratonic forces within the ligand to undergo modification a certain extent. Radiation in IR region can be utilized inorganic structure determination by making of the fact that it is absorption atomic bonds in organic compounds. Chemical bonds in different environment will absorb varying intensities and varying frequencies. Thus IR spectroscopy involves collecting absorption information and analyzing it in the form of a spectrum. The frequencies at which there are absorption of IR radiation. The principle therefore it should be possible to correct the change in the spectrum with the structure of the coordination compounds. The difference between the spectra of the free ligand and the complex are usually of the following types.

1) Change in the band position
2) Change in the relative intensities and appearance of new bands.
3) Shifts of single peak in to several closely spaced bands in the complexes.
4) Disappear of few band frequencies.

A unique interpretation of the observed change is not possible because of several uncertain factors which would influence of the vibrational modes of the molecules. The usual method is to compare the ligand spectrum with that of the compound in which the ligand is coordinated in a known way as given in the literature. It has been observed that vibrational bands associated with stretching of a bond involving coordinated atoms are usually shifted to lower frequency on coordination. A shift to higher energy on coordination is also possible. Coordination normally reduces the effective symmetry of the ligand which
may cause appearance of new bands and the spitting of bands which may be degenerated in the free ligand. Vibration involving coordination bond, stretching and bending modes generally appear in the low frequency region. Metal-nitrogen and metal-oxygen vibrations are very difficult to assign on an empirical basis, since their frequencies are sensitive to both the metal and ligand and they often couple complex with other low frequencies modes in metals complex. The coordination bond stretching vibrations are usually assigned by comparison between infrared spectra of the free ligand and its metal complexes.

The IR spectra of polychelates studies in the present investigation were taken with a limited objective of obtaining information about the coordinating atoms in the ligands which would help in arriving at the stereochemistry of the polychelates. The discussion give below, therefore is very briefly and cursor. The assignment of vibration at frequencies are mainly based on the data available in the literature and therefore empirical and tentative.

The IR spectra of all the ligand and their polychelates have been scanned. However to economies the space the spectra of only interested frequencies the present course of coordination study are showed in fig 3.6 to 3.9 which the assignment of all the ligand and their polychelates are tabulated in table 3.6 to 3.9

**BNPSAP and its Polychelates:**

The coordination sites involved in bonding with metal ion have been determined by carefully comparing the infrared spectra of the polychelates with that of free ligand. The IR spectra of the polychelates show significant changes as compared to the free ligand. The ligand spectrum exhibits a band at 2952 cm\(^{-1}\) which is attributed to a \(\nu(\text{OH})\) stretching. It is reasonable to expect hydrogen bonding between phenolic hydrogen atom and azomethine C=N nitrogen atom [115]. Further this band disappears in the spectra all chelates indicating the phenolic (OH) group gets deprotonated in metal chelates and coordination of phenolic oxygen to the

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Fig. 3.6: IR Spectra of BNPSAP and its Chelates
Chapter 3

Results and discussion

metal ion. This is further supported by the shift in the stretching frequency of the phenolic (C-O) to the higher side by ∼ 30-85 cm⁻¹ [116-117]. The characteristic \( v(C=\text{N}) \) vibration reported to appears at 1625 cm⁻¹ in the free ligand, undergoes a shift to lower frequency on complexation and appears at 1600 in the polychelates suggesting coordination through the azomethine nitrogen atom of the Schiff base [119]. The band generally observed in the region 3200-3600 cm⁻¹ is attributed to water of hydration in the complexes. Further the weaker bands in the region 770-850 cm⁻¹ and 1530-550 cm⁻¹ are indicate the presence of these water as coordinated. The non ligand band observed at 420-487 cm⁻¹ and 503-600 cm⁻¹ are assigned to M-N and \( v(M-O) \) modes respectively. The appearance of N=N band in the spectrum of ligand and its polychelates remain unchanged indicate its non-involvements in coordination [119]. From the IR spectra data its has been concluded that BNPSAP act as bis-bidentate ONNO donor coordinating through the phenolic oxygen and azomethine nitrogen atoms.

BNBSAP and its Polychelates:

The preminarily identification of the complex formation were done obtained from the IR spectra (Table 3.7) IR spectrum of BNBSAP exhibits band at 2925 cm⁻¹, which is assigned to the intramolecular hydrogen bonded phenolic OH stretching frequency. However this band absent in the spectra of chelate polymers indicating that proton of the OH group is released as a result of chelation. The C-O stretching frequency observed at about 1281 cm⁻¹ in the ligand has been shifted towards higher wave number by 10-25 cm⁻¹ in the chelate polymers which further supports the formation of metal–ligand bond through OH group [121]. A strong band observed at about 1634 cm⁻¹ in the ligand spectrum due to C=\text{N} shows either a positive [119] or negative shift [118] in spectra of chelates a such shifting of bands after the complexation indicates the coordination of metal atom to ligand through the azomethine nitrogen atom. The appearance of N\(=\text{N} \) band in the spectrum of ligand and its polychelates more or less at the same position after complexation indicating its non-

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### Table No. 3.6: Infrared Spectra data of BNPSAP and its chelate Polymers

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Compound</th>
<th>$\nu$(OH) cm$^{-1}$</th>
<th>$\nu$(C=N) cm$^{-1}$</th>
<th>$\nu$(C-O) cm$^{-1}$</th>
<th>$\nu$(M-O) cm$^{-1}$</th>
<th>$\nu$(M-N) cm$^{-1}$</th>
<th>$\nu$(H$_2$O) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BNPSAP</td>
<td>2952</td>
<td>1625</td>
<td>1290</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>2</td>
<td>[Mn (BNPSAP)(H$_2$O)$_2$]$_n$</td>
<td>-----</td>
<td>1595</td>
<td>1375</td>
<td>510</td>
<td>460</td>
<td>3440,805</td>
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<tr>
<td>3</td>
<td>[Fe (BNPSAP)(H$_2$O)$_2$]$_n$</td>
<td>-----</td>
<td>1602</td>
<td>1387</td>
<td>514</td>
<td>490</td>
<td>3430,803</td>
</tr>
<tr>
<td>4</td>
<td>[Co (BNPSAP)(H$_2$O)$_2$]$_n$</td>
<td>-----</td>
<td>1590</td>
<td>1360</td>
<td>525</td>
<td>470</td>
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<tr>
<td>5</td>
<td>[Ni (BNPSAP)(H$_2$O)$_2$]$_n$</td>
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<td>1595</td>
<td>1367</td>
<td>520</td>
<td>457</td>
<td>3427,804</td>
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<tr>
<td>6</td>
<td>[Cu (BNPSAP)]$_n$</td>
<td>-----</td>
<td>1580</td>
<td>1350</td>
<td>526</td>
<td>485</td>
<td>-----</td>
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<tr>
<td>7</td>
<td>[Zn (BNPSAP)]$_n$</td>
<td>-----</td>
<td>1592</td>
<td>1325</td>
<td>521</td>
<td>488</td>
<td>-----</td>
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<td>8</td>
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<td>1590</td>
<td>1320</td>
<td>578</td>
<td>470</td>
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Fig. 3.7: IR Spectra of BNBSAP and its Chelates
Table No. 3.7: Infrared Spectra data of BNBSAP and its chelate Polymers

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Compound</th>
<th>$v$(OH) cm$^{-1}$</th>
<th>$v$(C=N) cm$^{-1}$</th>
<th>$v$(C-O) cm$^{-1}$</th>
<th>$v$(M-O) cm$^{-1}$</th>
<th>$v$(M-N) cm$^{-1}$</th>
<th>$v$(H$_2$O) cm$^{-1}$</th>
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<td>1634</td>
<td>1292</td>
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<td>560</td>
<td>420</td>
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<td>533</td>
<td>478</td>
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<td>585</td>
<td>490</td>
<td>3423,770</td>
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<td>[Ni (BNBSAP)(H$_2$O)$_2$]$_n$</td>
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<td>1336</td>
<td>570</td>
<td>480</td>
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<td>1624</td>
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<td>580</td>
<td>490</td>
<td>-----</td>
</tr>
<tr>
<td>7</td>
<td>[Zn (BNBSAP)]$_n$</td>
<td>-----</td>
<td>1622</td>
<td>1335</td>
<td>560</td>
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<td>1598</td>
<td>1387</td>
<td>587</td>
<td>490</td>
<td>-----</td>
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</table>
involvements in coordination. A broad band observed in all the chelates polymers in the range 3389-3391 cm\(^{-1}\) may be attributed to \(\nu(OH)\) of water molecules [124] and bands at 770-780 cm\(^{-1}\) indicating the presence of these water as coordinated water molecules.

IR spectra of ligand and its chelates polymers were also examined in the 400-600 cm\(^{-1}\) region with a view to obtained information regarding metal-coordinating atom vibration. The M-O stretching frequency appears at 553-600 cm\(^{-1}\) and observed band in neighborhood of 410-490 cm\(^{-1}\) may be identified as M-N stretching frequency [125].

In the light of the above discussion it may be concluded that the ligand BNBSAP behave as bis-bidentate chelating agent coordinating through oxygen of phenolic group and nitrogen of azomethine linkage.

**BIPSAP and its Polychelates:**

The infrared spectra of ligand and its polychelates have been studied on the basis of literature data. The coordination sites of ligand involved in bonding with metal ion have been determined by careful comparison of the IR spectra of polychelates with that of the ligand (BIPSAP).

The ligand spectrum shows a band around at 3025 cm\(^{-1}\) assigned to the hydrogen bonded phenolic OH vibration. As anticipated this band disappears in the spectra of chelates indicating the proton of the OH group is replaced by the metal ion upon chelation. Medium band observed at 1630 cm\(^{-1}\) in the ligand spectrum due to C=N made of azomethine linkage. The positive and negative shifting of the \(\nu(C=N)\) band vibration in the spectra of the chelate suggests the coordination of the azomethine nitrogen to metal [126]. A broad band in the range 3425-3450 cm\(^{-1}\) due to the presence of \(\nu(OH)\) water [127]. The position of N=N band in the spectrum of ligand and its polychelates remain unchanged indicating its non-involvement in coordination. The stretching frequency of metal nitrogen and metal-oxygen band are usually noted in the far IR region 600-400 cm\(^{-1}\) [128].

_Deptt of Chemistry, S.G.B. Amravati University, Amravati (M.S.)_
Table No. 3.8: Infrared Spectra data of BIPSAP and its chelate Polymers

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Compound</th>
<th>$\nu$(OH) cm$^{-1}$</th>
<th>$\nu$(C=N) cm$^{-1}$</th>
<th>$\nu$(C-O) cm$^{-1}$</th>
<th>$\nu$(M-O) cm$^{-1}$</th>
<th>$\nu$(M-N) cm$^{-1}$</th>
<th>$\nu$(H$_2$O) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BIPSAP</td>
<td>2923</td>
<td>1630</td>
<td>1281</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>2</td>
<td>[Mn (BIPSAP) (H$_2$O)$_2$]$_n$</td>
<td>------</td>
<td>1617</td>
<td>1300</td>
<td>506</td>
<td>416</td>
<td>3404,753</td>
</tr>
<tr>
<td>3</td>
<td>[Fe (BIPSAP) (H$_2$O)$_2$]$_n$</td>
<td>------</td>
<td>1595</td>
<td>1379</td>
<td>514</td>
<td>430</td>
<td>34394,817</td>
</tr>
<tr>
<td>4</td>
<td>[Co (BIPSAP)(H$_2$O)$_2$]$_n$</td>
<td>------</td>
<td>1597</td>
<td>1381</td>
<td>516</td>
<td>465</td>
<td>3425,812</td>
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<tr>
<td>5</td>
<td>[Ni (BIPSAP)(H$_2$O)$_2$]$_n$</td>
<td>------</td>
<td>1599</td>
<td>1325</td>
<td>517</td>
<td>440</td>
<td>3427,756</td>
</tr>
<tr>
<td>6</td>
<td>[Cu (BIPSAP)]$_n$</td>
<td>------</td>
<td>1599</td>
<td>1350</td>
<td>513</td>
<td>425</td>
<td>------</td>
</tr>
<tr>
<td>7</td>
<td>[Zn (BIPSAP)]$_n$</td>
<td>------</td>
<td>1597</td>
<td>1325</td>
<td>512</td>
<td>430</td>
<td>------</td>
</tr>
<tr>
<td>8</td>
<td>[Cd (BIPSAP)]$_n$</td>
<td>------</td>
<td>1590</td>
<td>1322</td>
<td>510</td>
<td>440</td>
<td>------</td>
</tr>
</tbody>
</table>
In the present investigation from a correlation of the for IR spectra of the complexes with that of the free ligand. (fig. No. 3.3). The bands observed at 457-480 and 500-526 cm\(^{-1}\) may attribute to \(\nu\) (M-O) and \(\nu\) (M-O) modes respectively. The IR data revealed that the ligand act as bis bidentate molecule in all chelates.

**BNESAP and its Polychelates:**

The IR spectrum of BNESAP and its polychelates 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 3200-3300 cm\(^{-1}\) which may be due to the stretching vibration of OH group. The existence of the band at lower frequencies for phenolic OH frequencies may be due to intra molecular hydrogen bonding [137] between phenolic hydrogen atom and the azomethine C=N group. The disappearance of this band in the spectra of polychelates indicate deprotonation of the phenolic hydroxyl group and coordination of phenolic oxygen to the metal ion [130]. The appearance of a new hump between 3391-3485 cm\(^{-1}\) due to water molecules in the chelate [131]. Nature of water molecular coordinated confirmed from the appearance of diagnostic bands due to rocking and wagging modes at 795-853 cm\(^{-1}\). Similarly the coordination of phenolic oxygen to the metal ions after protonation may be inferred from the shift of phenolic C-O from 1100-1256 cm\(^{-1}\) [132] to the appearance of new band at 1279-1294 cm\(^{-1}\) of \(\nu\) (C-O) in the spectra of chelates [132]. The appearance of N=N band in the spectrum of ligand and its polychelates remain unchanged indicating non-involvements in coordination. Altogether, difference new band appearance in the lower frequency region 700-400 cm\(^{-1}\) of the spectra which was not observed in the free ligand spectrum. Vibrations involving metal coordination bond stretching bonding modes generally appearance in the lower frequency region because of the relatively heavy mass and weak nature of the coordinated bond. This non -ligand band observed at 576-601 cm\(^{-1}\) in the spectrum have been assigned to M-O stretching frequencies [133].
Table No. 3.9: Infrared Spectra data of BNESAP and its chelate Polymers

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Compound</th>
<th>$\nu$(OH) cm(^{-1})</th>
<th>$\nu$(C=N) cm(^{-1})</th>
<th>$\nu$(C-O) cm(^{-1})</th>
<th>$\nu$(M-O) cm(^{-1})</th>
<th>$\nu$(M-N) cm(^{-1})</th>
<th>$\nu$(H(_2)O) cm(^{-1})</th>
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<tbody>
<tr>
<td>1</td>
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<td>1635</td>
<td>1279</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
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<td>$[\text{Mn (BNESAP)}(\text{H}_2\text{O})_2]_n$</td>
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<td>1578</td>
<td>1310</td>
<td>503</td>
<td>471</td>
<td>3447,851</td>
</tr>
<tr>
<td>4</td>
<td>$[\text{Co (BNESAP)}(\text{H}_2\text{O})_2]_n$</td>
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<td>1550</td>
<td>1325</td>
<td>529</td>
<td>486</td>
<td>3450,835</td>
</tr>
<tr>
<td>5</td>
<td>$[\text{Ni (BNESAP)}(\text{H}_2\text{O})_2]_n$</td>
<td>-----</td>
<td>1595</td>
<td>1329</td>
<td>520</td>
<td>425</td>
<td>3452,840</td>
</tr>
<tr>
<td>6</td>
<td>$[\text{Cu (BNESAP)}]_n$</td>
<td>-----</td>
<td>1580</td>
<td>1350</td>
<td>585</td>
<td>485</td>
<td>-----</td>
</tr>
<tr>
<td>7</td>
<td>$[\text{Zn (BNESAP)}]_n$</td>
<td>-----</td>
<td>1552</td>
<td>1372</td>
<td>510</td>
<td>488</td>
<td>-----</td>
</tr>
<tr>
<td>8</td>
<td>$[\text{Cd (BNESAP)}]_n$</td>
<td>-----</td>
<td>1590</td>
<td>1320</td>
<td>515</td>
<td>470</td>
<td>-----</td>
</tr>
</tbody>
</table>
Fig. 3.9: IR Spectra of BNESAP and its Chelates
REFERENCES


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