Chapter 4

Study of

Transition Metal complexes

With

Pyrazolone Derivatives
4.1 Copper(II) complexes

4.1.1] Introduction:

Copper is an important transition metal. It forms complexes with various ligands. Copper shows +1 and +2 oxidation states. A large number of Cu(II) complexes with nitrogen, oxygen containing ligands and with pyrazolone derivatives have been reported. Several studies have centered on synthesis of pyrazolone derivatives containing bidentate, tridentate ligands (N, O donor atoms) due to their biological activities. Copper(II) complexes as anti-inflammatory drugs are often more active than the parent ligand themselves.

The complex of Cu(II) with 1-isonicotinyl-3-methyl pyrazol-5-one and 1-isonicotinyl-3-methyl-4-hydroxybenzylidine pyrazol-5-one has anti-tumor activity.

Neutral complexes of Cu(II) with 1-phenyl-2,3-dimethyl-4-amino pyrazol-5-one derivatives has anti-microbial activities. The complexes of Cu(II) with pyrazolone derivatives are anti-pyretic and analgetics. A large number of pyrazolone derivatives and their complexes with Cu(II) are important in dye industries.

M. Alaudeen reported the copper complexes with pyrazolone based ligand having anti-bacterial activities.

Copper(II) with d^9 system is stereochemically flexible. It forms a tetra, penta and hexa coordinate complexes.

Tetra-coordinate complexes have either tetrahedral or square planar structure. Hexa co-ordinate complexes have octahedral structure. However, a penta coordinate have a trigonal-bipyramidal, square pyramidal, or intermediate structures. The copper(II) ion with its d^9 electronic configuration in both octahedral
and tetrahedral environment is highly susceptible to Jahn-Teller distortion.\textsuperscript{20-22}

Only few Cu(II) complexes have regular geometries.\textsuperscript{23} A large number of hexa-coordinated octahedral complexes are severely distorted to tetragonal elongation or tetragonal compressions are revealed by X-ray analysis.\textsuperscript{24-26} Most of square planar complexes have weakly coordinating group in axial positions.\textsuperscript{27} Even in tetrahedral environment, John Teller distortion is operative.\textsuperscript{30}

In the dinuclear Cu(II) with 1, 3-diphenyl-4-(salicylidene hydrazono) -phenyl ethylene pyrazolone, two Cu(II) are bonded with two tridentate ligands and the geometries around the metal ions are slightly distorted square planar.

In this section, the synthesis, properties and characterization of Cu(II) complexes derived from HBMP, ABMP, BMP, HBDPP, ABDPP and BDPP have been discussed.

4.1.2 Synthesis of Complexes:

0.02 moles of ligand (in slight excess) was taken in round bottom flask containing 30ml of methanol. 0.01 moles of copper (II) chloride dissolved in 20ml of methanol and was gradually added into the solution of ligand. Ten percent alcoholic ammonia solution was added drop wise till precipitation of complex was obtained. The pH of precipitation of complexes was noted.

The precipitated complex was digested for one hour. Any change in pH if observed was readjusted and digested for one more hour. The precipitate of complex was filtered in hot condition. It was washed with alcohol followed by petroleum ether (40–60° C) and dried in vacuum desiccators over calcium chloride.
Table 4.1.1 Analytical data of Copper(II) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mol. Formula</th>
<th>Formula Weight</th>
<th>Dec. Temp.</th>
<th>Colour</th>
<th>Yield</th>
<th>Calculated (Found)</th>
<th>( \Lambda_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>[Cu(HBMP)]_2</td>
<td>C(<em>{22})H(</em>{18})Cu(<em>{4})N(</em>{6})O(_{6})</td>
<td>497.95</td>
<td>287</td>
<td>Green</td>
<td>87%</td>
<td>53.06 (53.05)</td>
<td>3.64 (3.628)</td>
</tr>
<tr>
<td>[Cu(ABMP)]_2</td>
<td>C(<em>{22})H(</em>{20})Cu(<em>{6})N(</em>{4})O(_{4})</td>
<td>495.98</td>
<td>301</td>
<td>Greenish blue</td>
<td>60%</td>
<td>53.28 (53.27)</td>
<td>4.06 (4.02)</td>
</tr>
<tr>
<td>[Cu(BMP)]<em>2Cl(</em>{2})</td>
<td>C(<em>{22})H(</em>{20})Cl(<em>{2})Cu(</em>{4})N(<em>{4})O(</em>{4})</td>
<td>538.87</td>
<td>220</td>
<td>Dark green</td>
<td>80%</td>
<td>49.03 (49.00)</td>
<td>3.74 (3.75)</td>
</tr>
<tr>
<td>[Cu(HBDPP)]_2</td>
<td>C(<em>{30})H(</em>{22})Cu(<em>{4})N(</em>{8})O(_{8})</td>
<td>630.06</td>
<td>321</td>
<td>Greenish blue</td>
<td>82%</td>
<td>57.19 (57.18)</td>
<td>3.52 (3.51)</td>
</tr>
<tr>
<td>[Cu(ABDPP)]_2</td>
<td>C(<em>{30})H(</em>{24})Cu(<em>{6})N(</em>{6})O(_{6})</td>
<td>628.09</td>
<td>273</td>
<td>Greenish blue</td>
<td>72%</td>
<td>57.37 (57.29)</td>
<td>3.85 (3.82)</td>
</tr>
<tr>
<td>[Cu(BDPP)]<em>2Cl(</em>{2})</td>
<td>C(<em>{30})H(</em>{24})Cl(<em>{2})Cu(</em>{4})N(<em>{6})O(</em>{6})</td>
<td>670.98</td>
<td>260</td>
<td>Greenish blue</td>
<td>88%</td>
<td>53.70 (53.72)</td>
<td>3.61 (3.58)</td>
</tr>
</tbody>
</table>

HBMP → 1-(2-hydroxybenzoyl)-3-methyl-pyrazol-5-one, ABMP → 1-(2-aminobenzoyl)-3-methyl-pyrazol-5-one, BMP → 1-benzoyl-3-methyl-pyrazol-5-one, HBDPP → 3,6-dimethyl-1-(2-hydroxybenzoyl)-pyrano[4,3-c]pyrazol-4(1H)-one, ABDPP → 1-(2-aminobenzoyl)-3,6-dimethyl-pyrano[4,3-c]pyrazol-4(1H)-one, BDPP → 1-benzoyl-3,6-dimethyl-pyran[4,3-c]pyrazol-4(1H)-one.
Result And Discussion

4.1.3] Properties:
All the Copper(II) complexes are colored solids, stable to air and moisture. The complexes do not have sharp melting point, but decomposed on heating beyond 220°C. Copper(II) complexes are insoluble in water, methanol, ethanol, acetone, ethyl acetate, petroleum ether, 1,4-dioxane but soluble in DMSO. The chloride is determined by Volhard's test.

Analytical data given in Table 4.1.1 suggest that the metal-ligand stoichiometry is 1:2 and the complexes are monomeric in nature.

The limited solubility of these complexes in suitable organic solvents did not permit the determination of their molecular weight.

The molar conductance ($\Lambda_m$) values of the complexes in DMSO ($10^{-3}$ M) lie in the range 14 to 24 ohm$^{-1}$cm$^2$ mol$^{-1}$. These low values indicates that the complexes are non electrolytes.$^{32-34}$

4.1.4] Magnetic susceptibility of Cu(II) complexes:
The magnetic moment in Cu(II) complexes does not give the information about exact stereochemistry.

The magnetic moment of octahedral Cu(II) complexes fall in the range 1.8 to 2.1 B.M. Lower magnetic moment value is due to distorted octahedral geometry. On the basis of magnetic moment, octahedral copper(II) complexes are broadly divided into two categories; one is that the magnetic moment of complexes is independent on temperature in the range 1.75-2.2 B.M.$^{35-39}$ These are mononuclear complexes without any interaction of an electron on the different Cu(II) ions.

The second category is that complexes have temperature dependent lower magnetic moment than spin only value due to spin coupling of Cu(II) ions pair.
The magnetic moments of polynuclear Cu(II) complexes were observed in the range 1.53-1.86 B.M. Polynuclear copper complexes show variable temperature magnetic susceptibility with weak ferromagnetic coupling ($J=+16$ cm).

The tetra coordinated complexes of Cu(II) are divided into two groups, The first with the magnetic moment range 1.72 B.M.-1.83 B.M. having a square planar geometry and the second with magnetic moment in the range 1.9-2.00 B.M. having tetrahedral geometry.

Table 4.1.2: Magnetic moments and Electronic spectral data of Copper(II) complexes

<table>
<thead>
<tr>
<th>Cu(II) Complexes</th>
<th>Magnetic Moment $\mu_{\text{eff}}$ in B.M.</th>
<th>$\lambda_{\text{Max}}$ in cm$^{-1}$ ($\lambda_{\text{Max}}$ in nm)</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(HBMP)$_2$]</td>
<td>1.84</td>
<td>16207 (617 nm)</td>
<td>$^{2}B_{1g}\rightarrow ^{2}B_{2g}$</td>
</tr>
<tr>
<td>[Cu(ABMP)$_2$]</td>
<td>1.86</td>
<td>-</td>
<td>$^{2}B_{1g}\rightarrow ^{2}E_{g}$</td>
</tr>
<tr>
<td>[Cu(BMP)$_2$Cl$_2$]</td>
<td>1.78</td>
<td>16393 (610 nm)</td>
<td>$^{2}B_{1g}\rightarrow ^{2}A_{g}$</td>
</tr>
<tr>
<td>[Cu(HBDPP)$_2$]</td>
<td>1.87</td>
<td>16260 (615 nm)</td>
<td></td>
</tr>
<tr>
<td>[Cu(ABDPP)$_2$]</td>
<td>1.90</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[Cu(BDPP)$_2$Cl$_2$]</td>
<td>1.82</td>
<td>15773 (634 nm)</td>
<td></td>
</tr>
</tbody>
</table>

In the present work, the room temperature magnetic susceptibility indicates that Copper(II) complexes exhibit magnetic moment values (1.78-1.90 B.M.) within the normal range for octahedral field. The values of magnetic moment of Cu(II) complexes are represented in the table 4.1.2.
Slightly higher value of magnetic moments of these complexes higher than the spin only value (1.73 B.M.) can be attributed to spin orbit coupling. The values of the magnetic moment suggest that Copper(II) complexes under investigation are paramagnetic in nature with one unpaired electron.

### 4.1.5 Electronic spectral study of Cu(II) complexes:

A complex with the d⁹ configuration of the metal ion is expected to experience Jahn–Teller distortion which leads to further splitting of the \( ^2E_g \) and \( ^2T_{2g} \) levels into \( ^2B_{1g}, ^2A_g \) and \( ^2B_{2g}, ^2E_g \) levels respectively.\(^{46}\) Octahedral complexes without distortion are expected to have only one transition \( (^2E_g \rightarrow ^2T_{2g}) \). But, due to John–Teller effect, a broad band with several components is observed at 16000 cm⁻¹ in the visible region and often broad tail into the near infra-red region.\(^{47,48}\)

The spectra of distorted octahedral complexes should consist of three bands corresponding to the transitions \( ^2B_{1g} \rightarrow ^2A_{1g}, ^2B_{1g} \rightarrow ^2B_{2g} \) and \( ^2B_{1g} \rightarrow ^2E_g \) (weakly distorted) and \( ^2B_{1g} \rightarrow ^2B_{2g}, ^2B_{1g} \rightarrow ^2E_g \) and \( ^2B_{1g} \rightarrow ^2A_g \) (strongly distorted) in order to increase energy.

These bands are very close together but transition \( ^2B_{1g} \rightarrow ^2E_g \) takes place in ultra-violet region. Generally, such complexes exhibit a broad structure less band with or without shoulder between 14000–18000 cm⁻¹ depending upon the strength of in-plane and axial ligands.\(^{49,51}\) This is caused by Jahn–Teller effect.

The five coordinated trigonal-bipyramidal Cu(II) complexes exhibit a strong low energy band followed by weak band to higher energy but in square pyramidal Cu(II) complexes, band with greater intensity absorption to higher energy.\(^{52}\)

As distortion proceed from regular square-pyramidal to trigonal-bipyramidal, the band intensity shift to higher energy.\(^{53}\)
Cu(II) system with square planar stereochemistry will have no electronic absorption below 10000 cm\(^{-1}\).

A nearly regular tetrahedral Cu(II) complexes give a single band near IR region without the absorption in the region 10000-20000 cm\(^{-1}\) corresponding to \(^{2}T_{2} \rightarrow ^{2}E\). However, Low energy charge transfer bands are observed in the visible region.\(^{54-55}\)

The electronic spectrum alone is not definite tool to distinguish between square planar and tetrahedral geometries.

In the present work, Electronic absorption spectrum of Cu(II) complexes were recorded by preparing its solution in DMSO solvent. The electronic absorption spectra of Cu(II) complexes are represented as figures 4.1.1-4.1.4 and their absorption in Table 4.1.2.

The spectra of synthesized Cu(II) complexes should consist of only single broad band in the region 15773-16393 cm\(^{-1}\) has been observed hence it is concluded that all three transitions \(^{2}B_{1g} \rightarrow ^{2}B_{2g}\), \(^{2}B_{1g} \rightarrow ^{2}E_{g}\) and \(^{2}B_{1g} \rightarrow ^{2}A_{g}\) be within this broad envelope. This band is characteristic of distorted octahedral Cu(II) complexes.\(^{56-57}\)
4.1 Copper(II) Complexes

Figure 4.1.1 Electronic spectra of $[\text{Cu(HBMP)}_2]$.

Figure 4.1.2 Electronic spectra of $[\text{Cu(BMP)}_2\text{Cl}_2]$.
4.1 Copper(II) Complexes

Figure 4.1.3 Electronic spectra of $[\text{Cu(HBDPP)}_2]$
4.1.6] Infrared spectral study of Cu(II) complexes

The infrared spectra of the solid complexes display changes that may give a reasonable idea about the structure of these complexes.

A] Stretching vibration due to Hydroxyl group:

In the free ligand HBMP and HBDPP, the broad band in the region 3478–3100 cm\(^{-1}\) have been assigned to \(\nu(\text{OH})\) vibrations.

The broad band in the region 3478–3100 cm\(^{-1}\) along with a narrow band of medium intensity (1230-1250 cm\(^{-1}\)) assigned to the phenolic OH groups.

The absence of broad band in the infrared spectrum of Cu(II) complex with HBMP as well as in the infrared spectrum of Cu(II) complex with HBDPP indicate that it coordinate through the oxygen of the phenolic group after deprotonation. The phenolic OH group on deprotonation forms covalent bond with central metal atom through oxygen atom.

The phenolic oxygen participation was further confirmed by the shift of \(\nu(\text{C-O})\) by \(~10\) cm\(^{-1}\).\(^{58-59}\)

B] Stretching vibration due to amino group:

The infrared spectrum of Cu(II) complex with ABMP and ABDPP has singlet in the region 3283-3370 cm\(^{-1}\) which shows that metal cation is bound to a deprotonated NH\(_2\) group.\(^{60-61}\)

The IR spectrum of ABMP and ABDPP shows C-N stretching,\(^{62}\) near 1300 cm\(^{-1}\) are shifted to lower wave numbers by \(~30\) cm\(^{-1}\) in the spectrum of complexes.

C] Stretching vibration due to Carbonyl groups:

The absorptions in the range 1723-1700 cm\(^{-1}\) and 1641-1683 cm\(^{-1}\) in the free ligands can be attributed to C=O stretching vibrations are shifted to a lower by 11-41 cm\(^{-1}\) which shows the involvement of carbonyl
groups. Similarly the band to $v$(C-O) stretching vibration shifted to up field by $\sim$10 cm$^{-1}$ in the IR spectrum of Cu(II) complexes. Both indicate the participation of oxygen atom as donor atoms.$^{63-64}$

**D] Stretching vibration due to C=N group:**

The absorption band in the region 1596 cm$^{-1}$, 1603 cm$^{-1}$ and 1603 cm$^{-1}$ of C=N of ligands HBDPP, ABDPP and BDPP respectively, is moved towards lower wave numbers by 17-33 cm$^{-1}$ in the spectra of the complexes, which confirms the coordination of the nitrogen atom to the metallic ion.$^{65}$

**E] Stretching vibration due to Cu-N and Cu-O:**

The spectra of copper complexes exhibit bands in the ranges 512–540 cm$^{-1}$. This may be assigned to $v$(Cu–N) stretching frequencies, in other words, these bands are possibly due to the formation of coordinate bonds between the donor atom (N) and the central Cu(II) ion.$^{66-67}$

The spectra of Cu(II) complexes exhibit bands in the range 409–464 cm$^{-1}$. This may be assigned to $v$(Cu–O) stretching frequencies.$^{68}$

**Table 4.1.3: Infrared spectral data of Cu(II) complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$v$NH$_2$</th>
<th>$v$C=O</th>
<th>$v$C=O</th>
<th>$v$C-N</th>
<th>$v$C-O</th>
<th>$v$Cu-N</th>
<th>$v$Cu-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(HBMP)$_2$]</td>
<td>-</td>
<td>1700</td>
<td>1630</td>
<td>-</td>
<td>1240</td>
<td>540</td>
<td>409</td>
</tr>
<tr>
<td>[Cu(ABMP)$_2$]</td>
<td>3157</td>
<td>1678</td>
<td>1629</td>
<td>-</td>
<td>-</td>
<td>512</td>
<td>427</td>
</tr>
<tr>
<td>[Cu(HBDPP)$_2$]</td>
<td>-</td>
<td>1682</td>
<td>1629</td>
<td>1584</td>
<td>1262</td>
<td>527</td>
<td>417</td>
</tr>
<tr>
<td>[Cu(ABDPP)$_2$]</td>
<td>3247</td>
<td>1686</td>
<td>1647</td>
<td>1570</td>
<td>-</td>
<td>528</td>
<td>464</td>
</tr>
<tr>
<td>[Cu(BDPP)$_2$Cl$_2$]</td>
<td>-</td>
<td>1673</td>
<td>1631</td>
<td>1578</td>
<td>-</td>
<td>526</td>
<td>423</td>
</tr>
</tbody>
</table>
Figure 4.1.5 Infrared spectrum of [Cu(HBMP)₂]
Figure 4.1.6 Infrared spectrum of $[\text{Cu(ABMP)}_2]$
Figure 4.1.7 Infrared spectrum of [Cu(H2DDP)] 2+ (DPP = diphenylphosphine)
Chapter 4: Study of transition metal complexes with pyrazolone derivatives

4.1 Copper(II) Complexes

Spectrum Name: Cu-ADBPP (KBr)
Date Created: Dec 17 14:01:59 2005

Figure 4.1.8 Infrared spectrum of $[\text{Cu(ABDPP)}_2]$
Chapter 4: Study of transition metal complexes with pyrazolone derivatives

4.1 Copper(II) Complexes

Figure 4.1.9 Infrared spectrum of [Cu(BDPP)₂Cl₂]
4.1.7] **ESR spectral study of Cu(II) complexes:**

ESR is a valuable tool in all branches of Science and Technology, for studying chemical species that have one or more unpaired electrons, such as organic and inorganic free radicals or inorganic complexes possessing a transition metal ion.

Electron Spin Resonance (ESR) was discovered in Kazan State University by the Soviet physicist Yevgeny Zavoisky in 1944, and was developed independently at the same time by Brebis Bleaney at Oxford University.

ESR spectrum is obtained by absorption of microwave frequency by paramagnetic substances to induce transitions between magnetic energy levels of electrons with unpaired spins. This technique is used to detect the presence of unpaired electron in a complex.

For an electron of spin value $S = \pm 1/2$, the spin angular momentum quantum number will have values $m_s = \pm 1/2$ which leads to doubly degenerate spin energy state. The degeneracy can be resolved in presence of strong and uniform magnetic field. The application of magnetic field leads to the formation of two non degenerate energy levels. The low energy state will have spin magnetic moment aligned with the field and corresponding to the quantum number. The high energy state will have spin magnetic moment opposed to the field and corresponding to quantum number, $m_s = \pm 1/2$.

In general if an electron possessing an electronic spin $S$ and orbital angular momentum $L$, in units of $(h/2\pi)$ ($h$ is the Planck's constant, $6.62619 \times 10^{-27}$ erg sec) is considered. Then the total angular momentum will be $L+S=J$ \hspace{1cm} (I)

The magnetic dipole $\mu$ is proportional to the total angular momentum $J$, $^{70}$

Hence $\mu = -g \beta J$ \hspace{1cm} (II)
\[ g = l + J (J+1) + S (S+1) - L (L+1)/2J (J+1) \]

Where \( g \) is the Lande's splitting factor for free ion and \( \beta = \frac{e^2 h}{4 \pi m c} \)

\[ = 9.274096 \times 10^{-27} \text{ erg/gauss} \]

is the Bohr-magnetron.

In addition, the critical examination of ESR spectra can provide useful information about interaction of metal ion with its ligand environment and covalency factor of chemical bonding.

Traditionally, ESR results are presented as 'g' values which represent energy level separation corresponding to microwave energy. It may arise from combination of microwave and zero field splitting. Each paramagnetic ion contributes magnetic moment which is reflected in the ESR spectrum. The ESR spectrum can provide individual contribution from an electron to the magnetic moments.

In the simplest ESR of a paramagnetic ion, the 'g' value is 2.0023 for a free electron spin with quenched orbital contribution. The value of 'g' depends upon the orientation of the molecule having unpaired electron and applied magnetic field.

The ESR spectrum can be characterized by the position, intensity and shape of its component lines.

The \( H_\parallel \ and \ H_\perp \) values were measured from the spectrum and used to calculate \( g_\parallel \) and \( g_\perp \) values.

The values of \( g_\parallel \), \( g_\perp \), \( g_{avg} \) and magnetic susceptibility from ESR spectrum are tabulated in Table 4.1.4. The original spectrums are reproduced as Figure 4.1.10 and 4.1.11. The pattern can be used to calculate splitting factor 'g' and hyperfine splitting factor 'A'. The value of paramagnetic ion situated in a crystal of low symmetry depends upon the orientation of the crystal.

The average \( g_{avg} \) values can be obtained by using the formula (III) \(^71\)

\[ g_{avg} = \frac{1}{3}(g_\parallel + 2g_\perp) \]

\[ ------ (III) \]
The higher g value is due to higher elongation in the Z axis of the compound.

The values of the hyperfine splitting parameters $A_||$ and $A_\perp$ are calculated by taking one third of the line widths at half height and which are indicative of the presence of the unpaired electron of orbitals.

$$A_{av} = 1/3 \left[ A_|| + 2A_\perp \right] \quad \text{(IV)}$$

The axial symmetry parameter $(G)$ is calculated from the expression which measures the interaction between copper centers in the unit cells.\(^7\)

$$G = \frac{g_\perp - 2.003}{g_\perp - 2.003} \quad \text{(V)}$$

If $G$ is less than 4.0, the ligand forming the Cu(II) compound is regarded a strong field ligand.

The in plane covalency parameter $(\alpha^2)$ is calculated by using the following expression (VI)\(^7\)

$$\alpha^2 = A_\perp / 0.036 + (g_\perp - 2.0023) + 3/7 (g_\perp - 2.0023) + 0.04 \quad \text{(VI)}$$

The $\alpha^2$ value accounts for a fraction of the unpaired electron density on the Cu(II) ion.\(^7\)

The term containing the factor $\alpha^2$ arises from the dipole-dipole interaction between the magnetic moments associated with the spin motion of the electron and the nucleus.\(^7\)

If the unpaired electron is delocalized to the neighboring atom, the contribution is reduced as decreases from unity. This quantity $\alpha^2$ is a function which depends upon the nature of the Cu-ligand bond.

For Cu(II) complexes, $\alpha^2 = 0.5$ indicates complete covalent bonding but $\alpha^2 = 1.0$ suggests complete ionic bonding.

The smaller the value of $\alpha^2$, more covalent in bonding.\(^7\)
The out of plane $\sigma$ covalency parameter ($\alpha^2$) has been calculated\textsuperscript{76} by using the expression (VII).

\[
\alpha^2 + \alpha^2 - 2\alpha^1 \alpha S = 1 \quad \text{(VII)}
\]

Where, $S$ is the overlap integral (0.76).

The $\alpha^2$ value increases with the corresponding decrease in $\alpha^2$, indicating that the axial $\sigma$ bonding decrease with corresponding increase in the in-plane $\sigma$ bonding.\textsuperscript{76}

The larger the value of $\alpha^2$ indicates more covalent bonding where as $\alpha^2 = 0$ indicates complete ionic bonding.

The Fermi contact interaction term ($K$) can be calculated\textsuperscript{77} from the expression (VIII).

\[
K = A_{av}/0.0036 + (g_{av} - 2.303) \quad \text{(VIII)}
\]

This term has its origin in a non-vanishing probability of finding the unpaired electron at the site of nucleus. It is a term which is an independent property of the central ion and is also isotropic in the present study.

The magnetic moment of Cu(II) complexes can be calculated from $g_{av}$ value as computed from ESR spectral data by using the expression:

\[
\mu_{eff} = g_{av} \left[ S (S+1) \right]^{1/2} \quad \text{(IX)}
\]

In the present work, ESR spectral data supports the covalent nature of bonding and the stereochemistry proposed for the present Cu(II) complexes.

The $g_{||}$ value is suggest the existence of sufficient covalency in the Cu(II) complex of HBMP and HBDPP. Analysis of these data show that in all cases $g_{||} > g_{\perp}$ which suggest a $d_{x^2-y^2}$ ground state for the Cu(II) ion in these complexes.

The axial spectrum with $g_{||} > g_{\perp} > 2.03$ is consistent with a distorted octahedral geometry around the Copper(II) ion.\textsuperscript{73} The spectra exhibited
pronounced peak at $g_\perp = 2.07 \pm 0.02$ and a broad and shallow quadruplet at $g_\parallel = 2.23 \pm 0.02$, the later arising from the splitting of $g_\parallel$. Such spectral features are characteristic of the Cu$^{2+}$ ions present in axially distorted octahedral sites.\textsuperscript{72}

The calculated $G$ value for the present complexes appeared in the range 3.38 and 3.85 indicate the existence of a negligible exchange interaction between copper, as $G < 4$.\textsuperscript{71}

The calculated In plane covalency parameter ($\alpha^2$) value for the present complexes are in the range 0.46 - 0.44 and value of Out of plane covalency parameter ($\alpha'^2$) are 0.60-0.62 and indicates covalent bonding in Cu(II) complexes\textsuperscript{76}

The magnetic moment of Cu(II) complexes 1.68 and 1.69 B.M. indicates the presence of one unpaired electron.

<table>
<thead>
<tr>
<th>Complex</th>
<th>ESR Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$g_{|}$</td>
</tr>
<tr>
<td>A</td>
<td>2.23</td>
</tr>
<tr>
<td>B</td>
<td>2.30</td>
</tr>
</tbody>
</table>

Where $A \rightarrow [\text{Cu(HBMP)}_2]$ and $B \rightarrow [\text{Cu(HBDPP)}_2]$. 

\[ \text{108} \]
Chapter 4: Study of transition metal complexes with pyrazolone derivatives

4.1 Copper(II) Complexes

Figure 4.1.10 ESR spectrum of [Cu(HBMP)₂]
Figure 4.1.11 ESR spectrum of [Cu(HBDPP)₂]
4.1.8] X-ray diffraction:

X-ray diffraction technique can be used to determine the crystallinity of the complexes. Thus by matching the pattern recorded for the sample with that in the standard X-ray diffraction pattern, the unknown compound can be identified. The solids can basically be divided in two categories, amorphous and crystalline.

In crystalline materials the atomic or molecular spades are ordered in three-dimensional array called lattice, within the solid. This ordering of molecular components is lacking in the non-crystalline materials. The relatively random arrangement of molecules in non-crystalline materials makes them poor coherent scatterers of X-rays, resulting in broad diffused maxima in their diffraction patterns.

The X-ray patterns of the amorphous materials are quite distinguishable from those of crystalline specimen which give sharply defined diffraction patterns.

When the compounds are exposed to radiation then they may absorb radiation resulting into X-ray absorption spectra. However a solid substance can diffract these X-rays resultinginto diffractograms. The incident angle of X-radiation is related to crystal having fixed inter-nuclear distance which is related to the wavelength of reflected radiation.

The monochromatic incident radiation is generally used and the angle at which the radiation is diffracted from the crystal can be related to atomic spacing in a crystal with Bragg's equation,

\[ n\lambda = 2d \sin \theta \]

Where 'n' is the order of diffraction and is usually assumed as unity. 'λ' is the wavelength of monochromatic X-rays and 'd' is the inter-planar spacing
The phenomena of X-ray crystallography originates when a scattered beam of X-ray is bombarded on an array of atoms in a crystal. Each layer produces reflected beams of X-ray. The distance traveled by reflected beam from a successive layer differs by an integral multiple of wavelength.

The distance $d$ between the two successive planes in the crystal is determined experimentally by X-ray diffraction. X-rays are high energy radiations produced by the bombardment of high energy electrons on heavy metal targets (anode) such as Cu, Mo, Cr etc. The high energy electrons incident on the target knock off electrons from the orbit close to the nucleus and the electrons from the higher level jump into these vacancies giving high energy X-rays. These are termed the characteristic X-rays. The wavelengths of these X-rays are in the range 0.01 to 10 nm.

Each diffractograms is well resolved into sharp refluxes suggesting highly crystalline nature for the complexes.

The position of each reflux was accurately measured and by using Bragg’s equation the interplanar distance $d$ was calculated. The $d$-spacing values of each reflux were used to calculate lattice parameters assuming the probable crystal system.

All calculations were performed by using computerized software program Powder-X developed by Cheng Dang. The data obtained and reciprocal lattice $(h, k, l)$ are listed in the Table 4.1.5 to 4.1.7.

On the basis of the results and the support of literature, the Cu(II) complexes with HBMP and HBDPP are crystalline in nature due to sharp refluxes shown, (Figures.4.1.12 to 4.1.13) and have been assigned monoclinic.
Table 4.1.5 XRD data of Cu[HBMP]$_2$

<table>
<thead>
<tr>
<th>$h$</th>
<th>$k$</th>
<th>$l$</th>
<th>d(Calc.)</th>
<th>d(Exp.)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>4.27460</td>
<td>4.27944</td>
<td>19.60</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3.60933</td>
<td>3.60926</td>
<td>18.82</td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>1</td>
<td>3.35159</td>
<td>3.35376</td>
<td>97.52</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2.62841</td>
<td>2.62958</td>
<td>16.21</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2.54683</td>
<td>2.54633</td>
<td>15.06</td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>2.21120</td>
<td>2.21044</td>
<td>19.21</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2.12365</td>
<td>2.12314</td>
<td>14.71</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0</td>
<td>1.82122</td>
<td>1.82133</td>
<td>15.16</td>
</tr>
<tr>
<td>-5</td>
<td>2</td>
<td>0</td>
<td>1.54175</td>
<td>1.54184</td>
<td>16.34</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>1</td>
<td>1.52859</td>
<td>1.52845</td>
<td>14.28</td>
</tr>
</tbody>
</table>

Crystal system: Monoclinic
Radiation: Cu
Lattice Parameter: $a = 8.682128$ $b = 7.098841$ $c = 4.438337$
Lattice Parameter: $\alpha = 90.00000$ $\beta = 99.66561$ $\gamma = 90.00000$

Figure 4.1.12 XRD spectrum of Cu[HBMP]$_2$
Table 4.1.6 XRD data of Cu[HBDPP]$_2$

Crystal system: Monoclinic  
Lattice Type: P  
Radiation: Cu  
Wavelength: 1.540598

<table>
<thead>
<tr>
<th>$h$</th>
<th>$k$</th>
<th>$l$</th>
<th>$D$(Cal)</th>
<th>$D$(Obs.)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>4.18051</td>
<td>4.25807</td>
<td>16.17</td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>1</td>
<td>1.99488</td>
<td>1.98109</td>
<td>87.86</td>
</tr>
<tr>
<td>-3</td>
<td>0</td>
<td>0</td>
<td>1.41013</td>
<td>1.41936</td>
<td>31.52</td>
</tr>
<tr>
<td>-3</td>
<td>3</td>
<td>2</td>
<td>1.26122</td>
<td>1.25679</td>
<td>43.27</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>1</td>
<td>1.15113</td>
<td>1.15379</td>
<td>35.55</td>
</tr>
</tbody>
</table>

Figure 4.1.13 XRD spectrum of Cu[HBDPP]$_2$
4.2: NICKEL(II) COMPLEXES

4.2.1 Introduction:
Nickel has characteristic electronic configuration $3d^84s^2$ and shows (2+) common oxidation state. It forms a large number of complexes with coordination numbers 3 to 6. However, majority of Ni(II) complexes have coordination number 4 and 6 and many show coordination number 5. The coordination numbers 3, 7 and 8 are still quite rare.

A number of Ni(II) complexes with pyrazolone based ligands containing nitrogen, oxygen as donor atoms have been reported. The most common geometry of Ni(II) complexes being octahedral. The other geometries like square pyramidal, trigonal-bipyramidal, tetrahedral and square planar are also studied. Slightly distorted octahedral Ni(II) complexes have been reported by many workers, but trigonal-bipyramidal Ni(II) complexes has been reported rarely.

One of the characteristics of stereochemistry of Ni(II) complexes is that, equilibria between the different structural types often exist in solution and these equilibria are generally temperature dependent and sometimes concentration dependent.

The electronic structure and stereochemistry of Ni(II) complexes have been reviewed. Electronic spectra of Ni(II) complexes in conjunction with magnetic data provide a better insight into the stereochemistry.

The color of the complexes themselves gives an indication of the geometry in many instances. Octahedral Ni(II) complexes and sometimes tetrahedral are blue, purple and green whereas planar complexes are commonly red, or brown but few purple or green colours.

Riggle et al. have been synthesized green and orange octahedral Ni(II) complexes.
In this section, the synthesis, properties and characterization of Ni(II) complexes derived from HBMP, ABMP, BMP, HBDPP, ABDPP and BDPP have been discussed.

4.2.2] Synthesis of Complexes:

0.02 moles of ligand (in slight excess) was taken in round bottom flask containing 30ml of methanol. 0.01 moles of nickel (II) chloride dissolved in 20ml of methanol and was gradually added into the solution of ligand. Ten percent alcoholic ammonia solution was added drop wise till precipitation of complex was obtained. The pH of precipitation of complexes was noted.

The precipitated complex was digested for one hour. Any change in pH if observed was readjusted and digested for one more hour. The precipitate of complex was filtered in hot condition. It was washed with alcohol followed by petroleum ether (40–60°C) and dried in vacuum desiccators over calcium chloride.

4.2.3] Properties:

All the Nickel(II) complexes are colored solids, stable to air and moisture. The complexes do not have sharp melting point, but decomposed on heating beyond 247°C. Nickel(II) complexes are insoluble in water, methanol, ethanol, chloroform, carbon tetrachloride, acetone, ethyl acetate, petroleum ether, diethyl ether, 1,4-dioxane but soluble in DMSO. The chloride is determined by Volhard's method. Analytical data given in Table 4.2.1 suggest that the metal-ligand ratio is 1:2 and the complexes are monomeric in nature. The molar conductance ($\Lambda_m$) values of the complexes in DMSO ($10^{-3}$ M) lie in the range 11 to 18 ohm$^{-1}$ cm$^2$ mol$^{-1}$ shows that complexes are non electrolytes.97
<table>
<thead>
<tr>
<th>Complex</th>
<th>Mol. Formula</th>
<th>Calculated (Found)</th>
<th>Δ_m</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Ni</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(HBMP)_2]</td>
<td>C_{22}H_{18}NiN_{2}O_{6}</td>
<td>493.09</td>
<td>280°C</td>
<td>53.59</td>
<td>3.68</td>
<td>11.90</td>
<td>11.36</td>
<td>16</td>
</tr>
<tr>
<td>[Ni(ABMP)_2]</td>
<td>C_{22}H_{18}NiN_{2}O_{6}</td>
<td>491.12</td>
<td>257°C</td>
<td>53.80</td>
<td>4.10</td>
<td>11.95</td>
<td>17.11</td>
<td>18</td>
</tr>
<tr>
<td>[Ni(BMP)Cl]</td>
<td>C_{22}H_{20}NiN_{2}O_{4}</td>
<td>534.01</td>
<td>292°C</td>
<td>53.80</td>
<td>4.09</td>
<td>11.94</td>
<td>17.10</td>
<td>18</td>
</tr>
<tr>
<td>[Ni(BMP)Cl]</td>
<td>C_{22}H_{20}NiN_{2}O_{4}</td>
<td>534.01</td>
<td>292°C</td>
<td>53.80</td>
<td>4.09</td>
<td>11.94</td>
<td>17.10</td>
<td>18</td>
</tr>
<tr>
<td>[Ni(HBDPP)_2]</td>
<td>C_{30}H_{26}NiN_{2}O_{6}</td>
<td>625.21</td>
<td>315°C</td>
<td>57.63</td>
<td>3.55</td>
<td>9.39</td>
<td>8.96</td>
<td>15</td>
</tr>
<tr>
<td>[Ni(HBDPP)_2]</td>
<td>C_{30}H_{26}NiN_{2}O_{6}</td>
<td>625.21</td>
<td>315°C</td>
<td>57.63</td>
<td>3.55</td>
<td>9.39</td>
<td>8.96</td>
<td>15</td>
</tr>
<tr>
<td>[Ni(HBDPP)_2]</td>
<td>C_{30}H_{26}NiN_{2}O_{6}</td>
<td>625.21</td>
<td>315°C</td>
<td>57.63</td>
<td>3.55</td>
<td>9.39</td>
<td>8.96</td>
<td>15</td>
</tr>
<tr>
<td>[Ni(HBDPP)_2]</td>
<td>C_{30}H_{26}NiN_{2}O_{6}</td>
<td>625.21</td>
<td>315°C</td>
<td>57.63</td>
<td>3.55</td>
<td>9.39</td>
<td>8.96</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 4.2.1 Analytical data of Ni(II) complexes

Chapter 4: Study of transition metal complexes with pyrazolone derivatives

<table>
<thead>
<tr>
<th>Complex</th>
<th>For Wt. Dec.Temp</th>
<th>Colour</th>
<th>Yield</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Ni</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(HBMP)_2]</td>
<td>493.09</td>
<td>Orange</td>
<td>64%</td>
<td>53.59</td>
<td>3.68</td>
<td>11.90</td>
<td>11.36</td>
<td>16</td>
</tr>
<tr>
<td>[Ni(ABMP)_2]</td>
<td>491.12</td>
<td>Orange</td>
<td>68%</td>
<td>53.80</td>
<td>4.10</td>
<td>11.95</td>
<td>17.11</td>
<td>18</td>
</tr>
<tr>
<td>[Ni(BMP)Cl]</td>
<td>534.01</td>
<td>Orange</td>
<td>76%</td>
<td>49.48</td>
<td>3.77</td>
<td>10.99</td>
<td>10.95</td>
<td>10.49</td>
</tr>
<tr>
<td>[Ni(BMP)Cl]</td>
<td>534.01</td>
<td>Orange</td>
<td>76%</td>
<td>49.48</td>
<td>3.77</td>
<td>10.99</td>
<td>10.95</td>
<td>10.49</td>
</tr>
<tr>
<td>[Ni(HBDPP)_2]</td>
<td>625.21</td>
<td>Orange</td>
<td>71%</td>
<td>57.63</td>
<td>3.54</td>
<td>(9.38)</td>
<td>(8.94)</td>
<td>15</td>
</tr>
<tr>
<td>[Ni(HBDPP)_2]</td>
<td>625.21</td>
<td>Orange</td>
<td>71%</td>
<td>57.63</td>
<td>3.54</td>
<td>(9.38)</td>
<td>(8.94)</td>
<td>15</td>
</tr>
<tr>
<td>[Ni(HBDPP)_2]</td>
<td>625.21</td>
<td>Orange</td>
<td>71%</td>
<td>57.63</td>
<td>3.54</td>
<td>(9.38)</td>
<td>(8.94)</td>
<td>15</td>
</tr>
<tr>
<td>[Ni(HBDPP)_2]</td>
<td>625.21</td>
<td>Orange</td>
<td>71%</td>
<td>57.63</td>
<td>3.54</td>
<td>(9.38)</td>
<td>(8.94)</td>
<td>15</td>
</tr>
<tr>
<td>[Ni(HBDPP)_2]</td>
<td>625.21</td>
<td>Orange</td>
<td>71%</td>
<td>57.63</td>
<td>3.54</td>
<td>(9.38)</td>
<td>(8.94)</td>
<td>15</td>
</tr>
</tbody>
</table>

HBMP → 1-(2-hydroxybenzoyl)-3-methyl-pyrazol-5-one, ABMP → 1-(2-aminobenzoyl)-3-methyl-pyrazol-5-one, BMP → 1-benzoyl-3-methyl-pyrazol-5-one, HBDPP → 3,6-dimethyl-1-(2-hydroxybenzoyl)pyrano[4,3-c]pyrazol-4-(1H)-one, ABDPP → 1-(2-aminobenzoyl)-3,6-dimethyl-pyrano[4,3-c]pyrazol-4-(1H)-one, BDPP → 1-benzoyl-3,6-dimethyl-pyrano[4,3-c]pyrazol-4-(1H)-one.
4.2.4] Magnetic susceptibility of Ni(II) complexes:

Magnetic susceptibility measurements at room temperature give information of the geometries about the Ni(II) complexes.

The magnetic moments of octahedral Nickel(II) complexes fall in the range 2.9-3.4 B.M. These values of magnetic moments are slightly higher than the expected spin only value 2.83 B.M. This could be explained, taking into account the spin orbit coupling contribution from \( ^3A_{2g} \) and the next higher \( ^3T_{2g} \) state.\(^{98-99}\)

The magnetic moments are still higher (3.4-3.5 B.M.) in some tetragonally distorted complexes.\(^{100}\)

The magnetic moments of tetrahedral Ni(II) complexes are in the range of 3.5 to 4.00 B.M. indicating higher orbital contribution due to an orbitally degenerate \( ^3T_I(P) \) term of tetrahedral ligand fields of Ni(II) complexes.\(^{101}\) This is temperature dependent. Distortion from tetrahedral to tetragonal stereochemistry results in the low orbital contribution and magnetic moment value fall to 3.2 B.M.

Square planar Ni(II) complexes are generally diamagnetic or paramagnetic due to temperature independent paramagnetism.

Syamal and co-workers \(^{102}\) reported octahedral Ni(II) complexes with magnetic moment 3.15-3.25 B.M.

In the present work, the room temperature magnetic susceptibility indicates that Nickel(II) complexes exhibits magnetic moment values (2.9-3.1 B.M.) within the required range for octahedral field.\(^{103}\)

Slightly higher value of magnetic moments of these complexes higher than the spin only value (2.83 B.M.) can be attributed to spin orbit coupling. The values of the magnetic moment suggest that nickel(II) complexes under investigation are paramagnetic in nature with two unpaired electron.\(^{104}\)
Table 4.2.2: Magnetic Moment and Elect. Spec. data of Ni(II) complexes

<table>
<thead>
<tr>
<th>Ni(II) Complexes</th>
<th>Magnetic Moment in B.M.</th>
<th>$\lambda_{\text{Max}}$ in cm$^{-1}$</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\nu_1$</td>
<td>$\nu_2$</td>
</tr>
<tr>
<td>[Ni(HBMP)$_3$]</td>
<td>2.93</td>
<td>11550</td>
<td>18480</td>
</tr>
<tr>
<td>[Ni(ABMP)$_3$]</td>
<td>3.01</td>
<td>11510</td>
<td>19567</td>
</tr>
<tr>
<td>[Ni(BMP)$_2$Cl$_2$]</td>
<td>3.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(HBDPP)$_3$]</td>
<td>2.98</td>
<td>11495</td>
<td>17817</td>
</tr>
<tr>
<td>[Ni(ABDPP)$_3$]</td>
<td>3.05</td>
<td>11400</td>
<td>18240</td>
</tr>
<tr>
<td>[Ni(BDPP)$_2$Cl$_2$]</td>
<td>3.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.2.5] Electronic spectral study of Ni(II) complexes:

Electronic spectra of Ni(II) complexes with magnetic data provide a better information about the stereochemistry of complexes.

In octahedral complexes, Ni(II) with $^3F$ ground state which was split into triplet terms ($^3A_{2g}$, $^3T_{2g}$, $^3T_{1g}$) and to give three spin allowed transitions $^3A_{2g} \rightarrow ^3T_{2g}$, $^3A_{2g} \rightarrow ^3T_{1g}(F)$ and $^3A_{2g} \rightarrow ^3T_{1g}(P)$ in the range 7000-13000 cm$^{-1}$, 11000-20000 cm$^{-1}$ and 20000-28000 cm$^{-1}$ respectively.\(^{105-106}\)

In addition, two spin forbidden transitions corresponding to $^3A_{2g} \rightarrow E_g$ and $^3A_{2g} \rightarrow ^1T_{2g}$ in the region 11000-17000 cm$^{-1}$ are also observed.\(^{107}\)

The tetrahedral Ni(II) complexes have intense blue color due to the presence of an absorption band in the red part of the visible region. three spin allowed transitions $^3T_1(F) \rightarrow ^3T_1(P)$, $^3T_1(F) \rightarrow ^3A_2$, $^3T_1(F) \rightarrow ^3T_2$ and two spin forbidden transitions $^3T_1(F) \rightarrow ^1T_2$ and $^3T_1(F) \rightarrow ^1E$ are possible.

However, only four bands corresponding to the following transitions are observed $^3T_1(F) \rightarrow ^1T_2$ (~20000 cm$^{-1}$), $^3T_1(F) \rightarrow ^3T_1(P)$ (~15000 cm$^{-1}$), $^3T_1(F) \rightarrow ^1E$ (~11000 cm$^{-1}$) and $^3T_1(F) \rightarrow ^3A_2$ (~7000 cm$^{-1}$)
Chapter 4: Study of transition metal complexes with pyrazolone derivatives

4.2 Nickel (II) Complexes

Figure 4.2.1: Electronic spectra of [Ni(HBMP)_2]

Figure 4.2.2: Electronic spectra of [Ni(ABMP)_2]
4.2 Nickel (II) Complexes

Figure 4.2.3: Electronic spectra of [Ni(HBDPP)$_2$]

Figure 4.2.4: Electronic spectra of [Ni(BDPP)$_2$Cl$_2$]
Of all the above, $^3T_1(F) \rightarrow ^3T_1(P)$ band is a strong one with high intensity when compared to other band.\textsuperscript{108}

The electronic spectra of paramagnetic tetrahedral Ni(II) complexes with $^3T_1(F)$ ground term show more intense bands when compared to octahedral complexes.\textsuperscript{109}

Ni(II) complexes with square planar geometry show three absorptions in the range of 21800 to 22471 cm\textsuperscript{-1}, 23000 to 30000 cm\textsuperscript{-1} and 15000 to 23000 cm\textsuperscript{-1} which are assigned to transitions $^1A_{1g} \rightarrow ^1B_{1g}$, $^1A_{1g} \rightarrow ^1A_{2g}$ and $^1A_{2g} \rightarrow ^1E_g$ respectively.\textsuperscript{110}

The square planar Ni(II) complexes do not show any absorption below 10000 cm\textsuperscript{-1} due to large crystal field splitting hence they can be distinguished from octahedral complexes and tetrahedral complexes.\textsuperscript{111-112}

In the present investigation, Electronic absorption spectrum of selected Ni(II) complexes were recorded by preparing its solution in DMSO solvent.

The results of the electronic absorption spectrum of Ni(II) complex is reported in Table 4.2.2 and spectra as figure 4.2.1 to 4.2.4. The electronic absorption of complexes shows a regular pattern of absorption in three regions 11400-11550 cm\textsuperscript{-1}, 17817-19567 cm\textsuperscript{-1} and 26666-27900 cm\textsuperscript{-1}. This pattern of absorption may be assigned to transitions $^3A_{2g} \rightarrow ^3T_{2g}(v_1)$, $^3A_{2g} \rightarrow ^3T_{1g}(F)/(v_2)$ and $^3A_{2g} \rightarrow ^3T_{1g}(P)/(v_3)$ respectively.

These observed transitions may be assigned to the characteristic three spin-allowed transitions of octahedral complexes.\textsuperscript{113-116} The $v_2/v_1$ ratio for synthesized Ni(II) complexes occur in 1.61-1.67 range which lie within the range 1.5-1.8 of octahedral complexes.\textsuperscript{117}

\textbf{4.2.6] Infrared spectral study of Ni(II) complexes:}

The IR spectrums of the complexes were compared with that of the free ligand. The characteristic absorption bands of the free ligands are
shifted and new vibrational bands are appeared on complexation. The IR spectra of Ni(II) complexes are represented as figure 4.2.5-4.2.8.

(1) **Stretching vibration due to Hydroxyl group:**

The absence of broad band in region 3200-3400 cm\(^{-1}\) of infrared spectrum of \([\text{Ni(HBMP)}_2]\) and \([\text{Ni(HBDPP)}_2]\) shows that it coordinate via the O of the phenolic group after deprotonation.\(^{58}\)

2) **Stretching vibration due to amino group:**

The infrared spectrum of Ni(II) complex with ABMP has singlet at 3382 cm\(^{-1}\) which shows that Ni(II) cation is bound to a deprotonated NH\(_2\) group.\(^{62}\)

3) **Stretching vibration due to Carbonyl groups:**

The absorptions in the region 1700-1723 cm\(^{-1}\) and 1641-1683 cm\(^{-1}\) in the free ligands can be attributed to (C=O) stretching vibrations are shifted to a lower by 24-41 cm\(^{-1}\) which indicates the involvement of carbonyl groups.\(^{63}\)

4) **Stretching vibration due to C=N group:**

A shift to lower wave numbers by 21 cm\(^{-1}\) in \(v(C=N)\) suggesting involvement of the N in coordination with metal ion in complexes.\(^{118-119}\)

5) **Stretching vibration due to Ni-N and Ni-O:**

The bands in the ranges 520-565 cm\(^{-1}\) and 426-499 cm\(^{-1}\) are \(v(\text{Ni-N})\) and \(v(\text{Ni-O})\) stretching frequencies.\(^{46-47}\)
Figure 4.2.5 Infrared spectrum of $[\text{Ni(HBMP)}_2]$
Chapter 4: Study of transition metal complexes with pyrazolone derivatives

4.2 Nickel (II) Complexes

Comment: Ni

User: Chemistry

Date/Time: 4/18/2007 4:46:46 PM

Figure 4.2.6: Infrared spectrum of [Ni(ABMP)2]
Figure 4.2.7: Infrared spectrum of [Ni(BMP)\(_2\)]Cl\(_2\)
Figure 4.2.8 Infrared spectrum of [Ni(HBDPP)₂].

Data File: S-34
Comment: Ni-Dhbpp

Chapter 4: Study of transition metal complexes with pyrazolone derivatives
4.2 Nickel (II) Complexes
4.2.7] **XRD:**

X-ray diffraction technique can be used to determine the crystallinity of the complexes. Thus by matching the pattern recorded for the sample with that in the standard X-ray diffraction pattern, the unknown compound can be identified.

X-Ray diffractometric study of metal complexes provides information about their crystallization. The position of each reflex was accurately measured and by using Bragg's equation the interplanar distance \( d \) was calculated. The \( d \)-spacing values of each reflex were used to calculate lattice parameters assuming the probable crystal system.

Each diffractograms is well resolved into sharp reflexes suggesting highly crystalline nature for the complexes.

The position of each reflex was accurately measured and by using Bragg's equation the interplanar distance \( d \) was calculated. The \( d \)-spacing values of each reflex were used to calculate lattice parameters assuming the probable crystal system

All calculations were performed by using computerized software program *Powder-X* developed by Cheng Dang. The data obtained and reciprocal lattice \((h, k, l)\) are listed in the Table 4.2.4.

Thus, on the basis of the results and the support of literature The Ni(II) complex with HBMP are crystalline in nature due to sharp reflexes shown, (Figs.4.2.9) and have been assigned monoclinic.\(^{79}\)
### Table 4.2.4: XRD data of [Ni(HBMP)\(_2\)]

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>[Ni(HBMP)(_2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Lattice Type</td>
<td>P</td>
</tr>
<tr>
<td>Radiation</td>
<td>Cu</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.540598</td>
</tr>
<tr>
<td>Lattice Parameter</td>
<td>(a = 4.9168) (b = 4.9168) (c = 5.4089)</td>
</tr>
<tr>
<td>Lattice Parameter</td>
<td>(\alpha = 90.0000) (\beta = 99.6656) (\gamma = 90.0000)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2(\theta) Start</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(\theta) End</td>
<td>99.98</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>D(Cal)</th>
<th>D(Obs)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>4.29783</td>
<td>4.25807</td>
<td>46.16</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2.66884</td>
<td>2.70445</td>
<td>57.76</td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>1</td>
<td>1.96668</td>
<td>1.98109</td>
<td>45.34</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>2</td>
<td>1.68359</td>
<td>1.67286</td>
<td>13.75</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>3</td>
<td>1.64956</td>
<td>1.66027</td>
<td>10.33</td>
</tr>
<tr>
<td>-2</td>
<td>3</td>
<td>0</td>
<td>1.62214</td>
<td>1.60940</td>
<td>20.64</td>
</tr>
<tr>
<td>-3</td>
<td>1</td>
<td>2</td>
<td>1.38458</td>
<td>1.38303</td>
<td>15.69</td>
</tr>
</tbody>
</table>

![Figure 4.2.9: XRD spectrum of Ni\([\text{HBMP}]_2\)\(\_\)](image-url)
4.3: Cobalt(II) complexes

4.3.1] Introduction:

The Cobalt(II) ion has [Ar]3d7 electronic configuration. Cobalt is biologically important element. Vitamin B$_{12}$, cyanocobalmin, contains cobalt in oxidation state +3. Cobalt(II) forms a large number of complexes with various stereochemical types.$^{120-121}$ Octahedral and tetrahedral ones are most common structure having usually pale-red or blue color respectively.$^{122-123}$

Cobalt(II) ion prefers to form tetrahedral complexes than any other transition metal ion; because of small energy difference in crystal field stabilization energies between octahedral and tetrahedral cobalt(II) complexes.$^{124}$

Because of the small stability difference between octahedral and tetrahedral Co(II) complexes, there are several cases in which the two types with the same ligand are both known and may be in equilibrium. An example is that there is always some $[\text{Co(H}_2\text{O)}_4]^{2+}$ in equilibrium with $[\text{Co(H}_2\text{O)}_6]^{2+}$ in aqueous solution. Five coordinated Co(II) complexes has trigonal-bipyramidal or square-pyramidal geometry, in limited cases many have an intermediate.$^{125-127}$

Tetrahedral complexes are generally formed with monodentate anionic ligands such as Cl$^-$, Br$^-$, I$^-$, SCN$^-$, N$_3^-$ and OH$^-$ or with ligands that are bidentate mono-anions or with the less hindered ligands. Planar complexes are formed with several bidentate such as dimethylglyoximate, dithioacetylacetonate and dithiolate-type ligands.

R.A Bailey has been reported an octahedral complexes of Co(II) with pyrazolone based ligands.$^{88}$

A number of pyrazolone and pyrano-pyrazolone based tridentate ligand forms coordination complexes with Co(II) ion.$^{128-131}$
In this section, the synthesis, properties and characterization of Cobalt(II) complexes derived from HBMP, ABMP, BMP, HBDPP, ABDPP and BDPP have been discussed.

4.3.2] Synthesis of Complexes:

0.02 moles of ligand (in slight excess) was taken in round bottom flask containing 30ml of methanol. 0.01 moles of cobalt chloride dissolved in 20ml of methanol and was gradually added into the solution of ligand. Ten percent alcoholic ammonia solution was added drop wise till precipitation of complex was obtained. The pH of precipitation of complexes was noted.

The precipitated complex was digested for one hour. Any change in pH if observed was readjusted and digested for one more hour. The precipitate of complex was filtered in hot condition. It was washed with alcohol followed by petroleum ether (40–60°C) and dried in vacuum desiccators over calcium chloride.

Result And Discussion

4.3.3] Properties:

All the synthesized Co(II) complexes are colored solids, stable to air and moisture. The complexes do not have sharp melting point, but decomposed on heating beyond 292°C. Complexes are insoluble in water, methanol, ethanol, chloroform, carbon tetrachloride, ethyl-acetate, petroleum ether, diethyl ether, 1,4-dioxane but soluble in DMSO. The chloride is determined by Volhard's test.\textsuperscript{132}

Analytical data given in Table 4.3.1 suggest that the metal-ligand stoichiometry is 1:2 and the complexes are monomeric in nature.

The molar conductance (\(\Lambda_m\)) values of the complexes in DMSO (10\(^{-3}\)M) lie in the range 10 to 18 ohm\(^{-1}\)cm\(^2\) mol\(^{-1}\) therefore the complexes are considered to be non electrolytes.\textsuperscript{133}
### Table 4.3.1 Analytical data of Cobalt(II) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mol. Formula</th>
<th>Formula Weight</th>
<th>Dec. Temp.</th>
<th>Colour</th>
<th>Yield</th>
<th>Calculated</th>
<th>Found</th>
<th>( \Lambda_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(HBMP)_2]</td>
<td>C(<em>{22})H(</em>{18})CoN(_4)O(_6)</td>
<td>493.33</td>
<td>292</td>
<td>pale pink</td>
<td>87%</td>
<td>53.56</td>
<td>(3.68)</td>
<td>(11.95)</td>
</tr>
<tr>
<td>[Co(ABMP)_2]</td>
<td>C(_{22})H(_20)CoN(_6)O(_4)</td>
<td>491.36</td>
<td>302</td>
<td>pale pink</td>
<td>60%</td>
<td>53.78</td>
<td>(4.10)</td>
<td>(11.99)</td>
</tr>
<tr>
<td>[Co(BMP)_2Cl]</td>
<td>C(<em>{22})H(</em>{20})Cl(_2)CoN(_4)O(_4)</td>
<td>534.25</td>
<td>287</td>
<td>pale pink</td>
<td>80%</td>
<td>49.46</td>
<td>(3.77)</td>
<td>(11.03)</td>
</tr>
<tr>
<td>[Co(HBDPP)_2]</td>
<td>C(<em>{30})H(</em>{22})CoN(_4)O(_8)</td>
<td>625.45</td>
<td>308</td>
<td>pale pink</td>
<td>82%</td>
<td>57.61</td>
<td>(3.55)</td>
<td>(9.42)</td>
</tr>
<tr>
<td>[Co(ABDPP)_2]</td>
<td>C(_{30})H(_24)CoN(_6)O(_6)</td>
<td>623.48</td>
<td>320</td>
<td>pale pink</td>
<td>72%</td>
<td>57.79</td>
<td>(3.88)</td>
<td>(9.45)</td>
</tr>
<tr>
<td>[Co(BDPP)_2Cl]</td>
<td>C(<em>{30})H(</em>{24})Cl(_2)CoN(_4)O(_6)</td>
<td>666.37</td>
<td>298</td>
<td>pale pink</td>
<td>88%</td>
<td>54.07</td>
<td>(3.63)</td>
<td>(8.84)</td>
</tr>
</tbody>
</table>

**Notes:**

HBMP → 1-(2-hydroxybenzoyl)-3-methyl-pyrazol-5-one, ABMP → 1-(2-aminobenzoyl)-3-methyl-pyrazol-5-one, BMP → 1-benzoyl-3-methyl-pyrazol-5-one, HBDPP → 1-(2-aminobenzoyl)-3,6-dimethyl-pyrazol-4(1H)-one, ABDPP → 1-(2-aminobenzoyl)-3,6-dimethyl-pyrazol-4(1H)-one, BDPP → 1-benzoyl-3,6-dimethyl-pyrazol-4(1H)-one.
4.3.4] Magnetic susceptibility of Co(II) complexes:

The magnetic moment (μ) of a transition metal ion can give important information about the number of unpaired electrons present in the metal ion and help to indicate the structure of the complex.

In octahedral field the ground state \( ^4T_{1g} \) is three fold orbitally degenerate state and causes an orbital contribution to the magnetic moment on the basis of spin orbital coupling constant \( n = 170 \text{ cm}^{-1} \), high spin Co(II) complexes are expected to show magnetic moments in the range 4.7 - 5.2 B.M.\(^{134}\)

For low spin octahedral complexes of Co(II) possessing \(^2E_g\) ground term, the magnetic moment is observed in the range of 1.8 - 1.9 B.M. which is very close to the spin only value (1.73 B.M.) and is temperature dependent.\(^{135}\) Low spin octahedral complexes are expected only with the ligands of strong fields at the far end of the spectrochemical series.

S.A. Abdel-Latif et al. have been synthesized octahedral Co(II) complexes with pyrazolone derivatives having magnetic moment 4.7 - 4.9 B.M.\(^{29}\) Eanrshaw and co-workers \(^{136}\) have reviewed the chemistry of five coordinated complexes of Co(II). Five coordinate's complexes have shown the magnetic moment value about 2.3B.M.

The square planar complexes of Co(II) are low spin with magnetic moment values in the range 2.2 to 2.9B.M. at room temperature. Fitzgerald et al. suggested that \( dz^2 \) orbital have unpaired electron in square planar complexes.\(^{137}\)

Tetrahedral Co(II) complexes with \(^4A_g\) ground term are assumed to have angular moments. The expected spin only value for three unpaired electrons is 3.89 B.M. In presence of low symmetry ligand field the spin degeneracy of the \(^4A_2\) ground term is removed and as a result, variation in magnetic moments in the range of 4.2 - 4.8 B.M. is observed.\(^{138}\)
In the present work, the magnetic moment of Co(II) complexes were determined by using Gouy’s method and results of these measurements are tabulated in Table no.4.3.2.

The room temperature magnetic susceptibility indicates that Cobalt(II) complexes has magnetic moment values (3.94 - 4.11 B.M.) within the normal range for octahedral field and indicating the presence of three unpaired electrons per metal ion.\textsuperscript{139}

Slightly higher value of magnetic moments of these complexes higher than the spin only value (3.92 B.M.) can be attributed to spin orbit coupling.

**Table 4.3.2: Mag. Moment and Elect. Spectral data of Co(II) complexes**

<table>
<thead>
<tr>
<th>Co(II) Complexes</th>
<th>Magnetic Moment in B.M.</th>
<th>$\lambda_{\text{Max}}$ in cm(^{-1})</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(HBMP)}_3])</td>
<td>3.94</td>
<td>17200, 21850, 28500 (581, 458, 351)</td>
<td>16800-18000 cm(^{-1}) (4T_1g(F) \rightarrow 4T_2g(F))</td>
</tr>
<tr>
<td>([\text{Co(ABMP)}_3])</td>
<td>3.98</td>
<td>-</td>
<td>21800-22360 cm(^{-1}) (4T_1g(F) \rightarrow 4T_1g(P))</td>
</tr>
<tr>
<td>([\text{Co(BMP)}_2\text{Cl}_2])</td>
<td>4.11</td>
<td>16800, 22360 (595, 447)</td>
<td>28500-29200 cm(^{-1}) (Charge Transfer)</td>
</tr>
<tr>
<td>([\text{Co(HBDPP)}_3])</td>
<td>3.93</td>
<td>17500, 21800, 29200 (571, 459, 342)</td>
<td></td>
</tr>
<tr>
<td>([\text{Co(ABDPP)}_3])</td>
<td>3.96</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>([\text{Co(BDPP)}_2\text{Cl}_2])</td>
<td>3.98</td>
<td>18000, 22100 (556, 452)</td>
<td></td>
</tr>
</tbody>
</table>
4.3.5] Electronic spectral study of Co(II) complexes:

The Co(II) ion has $3d^7$ electronic configuration which in octahedral fields gives rise to either high spin $t_{2g}^5e_g^2$ complexes or low spin $t_{2g}^6e_g^1$ complexes. High spin octahedral complexes show ground term $^4T_{1g}$ arising from $t_{2g}^5, e_g^2$ configuration. In general, it is observed that the spectra of octahedral complexes show a band in the near infrared region around 8000-10000 cm$^{-1}$ assigned to the lowest energy transition $^4T_{1g} \rightarrow ^4T_{2g}$ and a band in the visible region due to $^4T_{1g} \rightarrow ^4T_{1g}(P)$ transition around 20000 cm$^{-1}$.

Most of the time $^4T_{1g} \rightarrow ^4A_{2g}$ transition band is not seen. The other two transitions have the normal intensities of octahedral spin allowed, napolate forbidden bands with $^4A_{2g}$ state derived from $t_{2g}^3, e_g^4$ configuration and $^4T_{1g}$ (F) state derived from $t_{2g}^5, e_g^2$ configuration. The visible band frequently has a shoulder or a fine structure to it, and is attributed to $^4T_{1g} \rightarrow ^4A_{2g}$ transition. A regular octahedral symmetry giving rise to distorted geometry is indicated by enhancement of intensities of electronic absorption spectra.

The tetrahedral complexes of Co(II) with $^4A_2$ ground term are expected to have following three transitions $^4A_2 \rightarrow ^4T_2$ (3000-5000 cm$^{-1}$), $^4A_2 \rightarrow ^4T_1(F)$ (near infrared region) and $^4A_2 \rightarrow ^4T_1(P)$ (15000-20000 cm$^{-1}$). The electronic spectra of tetrahedral complexes have been extensively studied by Ferguson, Cotton and Goodgam. Tetrahedral complexes significantly differ from octahedral absorption in their much greater intensities and thus allowing a ready distinction between the two stereochemistries.

The square planar stereochemistry of Co(II) is rare. Square planar complexes of Co(II) can be distinguished from tetrahedral complexes both by spectroscopically and magnetically.
Figure 4.3.1 Electronic spectra of [Co(HBMP)₂]
Figure 4.3.2 Electronic spectra of [Co(BMP)₂Cl₂]

Chapter 4: Study of transition metal complexes with pyrazolone derivatives

4.3 Co(II) complexes
4.3 Co(II) complexes

Figure 4.3.3 Electronic spectra of [Co(HBDPP)$_2$]

Figure 4.3.4 Electronic spectra of [Co(BDPP)$_2$Cl$_2$]
Low spin square planar complexes exhibit a narrow band at 8100-8600 cm\(^{-1}\) and a stronger as well as broader band at 20000 cm\(^{-1}\). However, the spectra of square planar complexes are not fully understood. Many square planar complexes exhibit one band near 20000 cm\(^{-1}\). The visible band is probably a transition \(^{2}A_{lg} \rightarrow ^{2}B_{lg}\). The square planar complexes which were studied are of low spin configuration with ground term \(^{2}E_{2g}\) or \(^{2}A_{lg}\). Ciampolini reviewed the spectra of five coordinated Co(II) complexes.\(^{144}\)

In the present investigation, Electronic absorption spectrum of selected Co(II) complexes were recorded by preparing its solution in DMSO solvent. The results of the electronic absorption spectrum of Co(II) complex is reported in Table no.4.3.2.

The Co(II) complexes exhibit absorption bands in the region 16800-18000 cm\(^{-1}\) and a strong high-energy band at 21800-22360 cm\(^{-1}\) are assigned to the transitions \(^{4}T_{lg}(F) \rightarrow ^{4}T_{2g}(F)\) and \(^{4}T_{lg}(F) \rightarrow ^{4}T_{lg}(P)\) respectively for a high-spin octahedral geometry. A high-intensity band in the region 28565–29215 cm\(^{-1}\) was assigned to the charge transfer.\(^{115,145}\)

These observed transitions are characteristic of octahedral complexes.

4.3.6] **Infrared spectral study of Co(II) complexes:**

The IR spectrums of the complexes were compared with that of the free ligand. The characteristic absorption bands of the free ligands are shifted and new vibrational bands are appeared on complexation.

(1) **Stretching vibration due to Hydroxyl group:**

The absence of broad band in the infrared spectra of Co(II) complexes with HBMP and with HBDPP shows that it coordinate to the oxygen of the phenolic group after deprotonation.

The phenolic oxygen participation was further confirmed by the blue shift of \(\nu(C-O)\).\(^{58}\)
2) **Stretching vibration due to amino group:**

The infrared spectrum of Co(II) complex with ABMP and ABDPP has singlet in the region 3213-3388 cm\(^{-1}\) which shows that metal cation is bound to a deprotonated NH\(_2\) group.\(^{61}\)

3) **Stretching vibration due to Carbonyl groups:**

The absorptions in the region 1700-1723 cm\(^{-1}\) and 1641-1683 cm\(^{-1}\) in the free ligands can be attributed to (C=O) stretching vibrations are shifted to a lower which is shows the involvement of carbonyl groups.\(^{34}\)

4) **Stretching vibration due to C=N group:**

On comparison of the IR spectra of the ligands with their Co(II) complexes, show a shift to lower wave numbers by 13-22 cm\(^{-1}\) in \(\nu\)(C=N) suggesting involvement of the N in coordination with the Co(II).\(^{38}\)

5) **Stretching vibration due to Co-N and Co-O:**

The spectra of Cobalt complexes exhibit bands in the ranges 520-565 cm\(^{-1}\) of \(\nu\)(Co–N) stretching frequencies and bands in the ranges 438-499 cm of \(\nu\)(Co–O) stretching frequencies.\(^{65}\)

> **Table 4.3.4: Infrared spectral data of Co(II) complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\nu) NH(_2)</th>
<th>(\nu) C=O</th>
<th>(\nu) C=O</th>
<th>(\nu) C-N</th>
<th>(\nu) C-O</th>
<th>(\nu) Co-N</th>
<th>(\nu) Co-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(HBMP)(_2)]</td>
<td>-</td>
<td>1691</td>
<td>1622</td>
<td>-</td>
<td>1241</td>
<td>565</td>
<td>499</td>
</tr>
<tr>
<td>[Co(ABMP)(_2)]</td>
<td>3388</td>
<td>1682</td>
<td>1621</td>
<td>-</td>
<td>-</td>
<td>563</td>
<td>493</td>
</tr>
<tr>
<td>[Co(BMP)(_2)Cl(_2)]</td>
<td>-</td>
<td>1682</td>
<td>1642</td>
<td>-</td>
<td>-</td>
<td>528</td>
<td>458</td>
</tr>
<tr>
<td>[Co(HBDPP)(_2)]</td>
<td>-</td>
<td>1687</td>
<td>1637</td>
<td>1581</td>
<td>1261</td>
<td>520</td>
<td>438</td>
</tr>
<tr>
<td>[Co(ABDPP)(_2)]</td>
<td>3213</td>
<td>1682</td>
<td>1652</td>
<td>1590</td>
<td>-</td>
<td>541</td>
<td>472</td>
</tr>
<tr>
<td>[Co(BDPP)(_2)Cl(_2)]</td>
<td>-</td>
<td>1673</td>
<td>1634</td>
<td>1576</td>
<td>-</td>
<td>554</td>
<td>442</td>
</tr>
</tbody>
</table>
Figure 4.3.5 Infrared spectrum of [Co(HBMP)\textsubscript{2}]
Chapter 4: Study of transition metal complexes with pyrazolone derivatives

4.3 Co(II) complexes

Figure 4.3.6 Infrared spectrum of [Co(ABMP)₂]
Figure 4.3.7 Infrared spectrum of \([\text{Co(HBDPP)}_2]\)

Comment: Co-DHBPP

Date/Time: 9/18/2007 5:06:42 PM
User: Chemistry
4.3.7] XRD:

X-ray diffraction technique can be used to determine the crystallinity of the complexes. X-Ray diffractometric study of metal complexes provides information about their crystallization.

The position of each reflux was accurately measured and by using Bragg's equation the interplanar distance $d$ was calculated. The $d$-spacing values of each reflux were used to calculate lattice parameters assuming the probable crystal system.

All calculations were performed by using computerized software program *Powder-X* developed by Cheng Dang. The data obtained and reciprocal lattice $(h, k, l)$ are listed in the Table 4.3.4. The Co(II) complex with HBMP is crystalline in nature (Figures.4.3.8) and have been assigned monoclinic.79

Table 4.3.4 XRD data of Co[HBMP]$_2$

<table>
<thead>
<tr>
<th>Sample Name [Co(HBMP)$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system: Monoclinic</td>
</tr>
<tr>
<td>Lattice Type: P</td>
</tr>
<tr>
<td>Radiation: Cu</td>
</tr>
<tr>
<td>Lattice Parameter:</td>
</tr>
<tr>
<td>$a = 4.9168$</td>
</tr>
<tr>
<td>$b = 4.9168$</td>
</tr>
<tr>
<td>$c = 5.4089$</td>
</tr>
<tr>
<td>$\alpha = 90$</td>
</tr>
<tr>
<td>$\beta = 90$</td>
</tr>
<tr>
<td>$\gamma = 120$</td>
</tr>
<tr>
<td>2Theta Start= 10</td>
</tr>
<tr>
<td>2Theta End= 99.98</td>
</tr>
<tr>
<td>Density= 1.641g/cm$^3$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H</th>
<th>K</th>
<th>L</th>
<th>d  (Exp.)</th>
<th>d  (Calc.)</th>
<th>Intensity (Exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>5.28216</td>
<td>5.40890</td>
<td>81.08</td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>4.89073</td>
<td>4.91680</td>
<td>136.28</td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>4.68930</td>
<td>4.91680</td>
<td>91.81</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>3.40179</td>
<td>3.47670</td>
<td>334.08</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>2.96590</td>
<td>2.92464</td>
<td>35.88</td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>2.50071</td>
<td>2.45840</td>
<td>55.60</td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>2.48145</td>
<td>2.45840</td>
<td>118.50</td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>2.44178</td>
<td>2.45840</td>
<td>57.55</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>2.37457</td>
<td>2.36964</td>
<td>35.97</td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>1</td>
<td>2.28701</td>
<td>2.23807</td>
<td>74.89</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>2</td>
<td>2.15147</td>
<td>2.13466</td>
<td>77.33</td>
</tr>
</tbody>
</table>
Chapter 4: Study of transition metal complexes with pyrazolone derivatives

4.3 Co(II) complexes

Figure 4.3.8 XRD spectrum of [Co(HBMP)₂]
4.4: Iron(II) Complex

4.4.1 introduction:

Iron is an important transition metal with a functional role in living systems. Most of the iron in the body is present as iron containing proteins such as hemoglobin, myoglobin and ferridoxin perform role in oxygen transport and electron transfer process.

Iron(II) complexes are known in a wide variety of stereochemistry and spin states including seven, six, five, four and three coordination. Fe(II) has a lower tendency to form tetrahedral complexes than has Co(II) or Ni(II) but a number of these are known. The [FeX₄]²⁻ ions exist in salts with several large cations and FeL₂X₂. Iron(II) tetrahedrally coordinated by sulfur atoms occurs in the protein rubredoxin.

A moderate number of five-coordinate complexes are known with high-spin distorted trigonal-bipyramidal or with low-spin square-pyramidal geometry.

Iron(II) forms a number of complexes in which the coordination number is six. Most of the complexes have octahedral structure.

The hexacyanoferrate(II) ion, commonly called ferrocyanide, is stable and well-known complex of iron(II).

Fe(II) forms a number of complexes with pyrazolone based ligands. Jadeja R.N. and Parmar N.J reported octahedral Fe(II) chelates from O,N,N,O donor ligands. The octahedral complexes of Fe(II) with 2, 3-dimethyl-1-phenylpyrazole-5-one (antipyrine) have been prepared and characterized by Prabhakaran C.P. and Patel C.C.

In this section, the synthesis, properties and characterization of Iron(II) complexes derived from HBMP, ABMP, BMP, HBDPP, ABDPP and BDPP have been discussed.
4.4.2] Synthesis of Complexes:

0.02 moles of ligand (in slight excess) was taken in round bottom flask containing 30ml of methanol. 0.01 moles of ferrous chloride dissolved in 20ml of methanol and was gradually added into the solution of ligand. Ten percent alcoholic ammonia solution was added drop wise till precipitation of complex was obtained. The pH of precipitation of complexes was noted.

The precipitated complex was digested for one hour. Any change in pH if observed was readjusted and digested for one more hour. The precipitate of complex was filtered in hot condition. It was washed with alcohol followed by petroleum ether (40–60°C) and dried in vacuum desiccators over calcium chloride.

### Result And Discussion

4.4.3] Properties:

All the complexes are brown colored solids, stable to air and moisture. The complexes do not have sharp melting point, but decomposed on heating beyond 252°C.

Fe(II) complexes are insoluble in water, methanol, ethanol, chloroform, carbon tetrachloride, acetone, ethyl acetate, petroleum ether, diethyl ether, 1,4-dioxane but soluble in DMSO. The chloride content was estimated gravimetrically as AgCl by using Volhard's method.¹³²

Analytical data given in Table 4.4.1 suggest that the metal: ligand stoichiometry is 1:2 and the complexes are monomeric in nature.

The molar conductance ($\Lambda_m$) values of the complexes in DMSO ($10^{-3}$M) lie in the range 13 to 24 ohm⁻¹cm² mol⁻¹ indicate non electrolytes nature.¹⁵⁶⁻¹⁵⁷
Table 4.4.1 Analytical data of Iron(II) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mol. Formula</th>
<th>For Wt</th>
<th>Dec. Temp</th>
<th>Colour</th>
<th>Yield</th>
<th>Calculated (Found)</th>
<th>$\Lambda_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>[Fe(HBMP)$_2$]</td>
<td>C$<em>{22}$H$</em>{18}$FeN$_4$O$_6$</td>
<td>490.24</td>
<td>252</td>
<td>brown</td>
<td>69%</td>
<td>53.90</td>
<td>3.70</td>
</tr>
<tr>
<td>[Fe(ABMP)$_2$]</td>
<td>C$<em>{22}$H$</em>{20}$FeN$_6$O$_4$</td>
<td>488.27</td>
<td>268</td>
<td>brown</td>
<td>64%</td>
<td>54.12</td>
<td>4.13</td>
</tr>
<tr>
<td>[Fe(BMP)$_2$Cl$_2$]</td>
<td>C$<em>{22}$H$</em>{20}$Cl$_2$FeN$_4$O$_4$</td>
<td>531.16</td>
<td>281</td>
<td>brown</td>
<td>70%</td>
<td>49.75</td>
<td>3.80</td>
</tr>
<tr>
<td>[Fe(HBDPP)$_2$]</td>
<td>C$<em>{30}$H$</em>{22}$FeN$_8$O$_8$</td>
<td>622.36</td>
<td>284</td>
<td>brown</td>
<td>74%</td>
<td>57.90</td>
<td>3.56</td>
</tr>
<tr>
<td>[Fe(ABDPP)$_2$]</td>
<td>C$<em>{30}$H$</em>{24}$FeN$_6$O$_6$</td>
<td>620.39</td>
<td>298</td>
<td>brown</td>
<td>71%</td>
<td>58.08</td>
<td>3.90</td>
</tr>
<tr>
<td>[Fe(BDPP)$_2$Cl$_2$]</td>
<td>C$<em>{30}$H$</em>{24}$Cl$_2$FeN$_6$O$_6$</td>
<td>663.28</td>
<td>301</td>
<td>brown</td>
<td>78%</td>
<td>54.32</td>
<td>3.65</td>
</tr>
</tbody>
</table>

HBMP → 1-(2-hydroxybenzoyl)-3-methyl-pyrazol-5-one , ABMP → 1-(2-aminobenzoyl)-3-methyl-pyrazol-5-one , BMP → 1-benzoyl-3-methyl-pyrazol-5-one , HBDPP → 3,6-dimethyl-1-(2-hydroxybenzoyl)-pyrano[4,3-c]pyrazol-4(1H)-one , ABDPP → 1-(2-aminobenzoyl)-3,6-dimethyl-pyrazol-5-one , BDPP → 1-benzoyl-3,6-dimethyl-pyrazol-4(1H)-one.
4.4.4] Magnetic susceptibility of Fe(II) complexes:

The magnetic moment of Fe(II) complex was determined by using Gouy’s balance method. Results of this measurement are tabulated in Table no. 4.4.2

In Tetrahedral complexes the magnetic moments are normally 5.0-5.2 B.M., owing to the spins of the four unpaired electrons and a small, second-order orbital contribution\(^{153}\)

In low spin octahedral iron(II) complexes, spin-pairing occurs and Fe(II) have the electronic configuration \(t_{2g}^6\) with \(A_{1g}\) ground state. These complexes are diamagnetic but \([\text{Fe(dipy)}_3]^{2+}\) and \([\text{Fe(phen)}_3]^{2+}\) has very low magnetic moments due to the presence of iron(III) impurities. For high spin octahedral complexes of iron(II), the magnetic moments are \(~\) 4.8 B.M. at room temperature. The spin-orbit coupling constant, \(\lambda = -100\ \text{cm}^{-1}\) and the magnetic moment is independent on temperature.

Nalanda S. L. et al have been reported high spin octahedral Fe(II) complex having magnetic moment 5.09 B.M.\(^{158}\)

Table 4.4.2: Mag. Moments and Elect. Spect. data of Fe(II) complexes

<table>
<thead>
<tr>
<th>Fe(II) Complexes</th>
<th>Magnetic Moment in B.M.</th>
<th>(\lambda_{\text{Max}}) in cm(^{-1}) ((\lambda_{\text{Max}}) in nm)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe(HBMP)}_3])</td>
<td>4.98</td>
<td>11500 ((870))</td>
<td></td>
</tr>
<tr>
<td>([\text{Fe(ABMP)}_3])</td>
<td>4.88</td>
<td>11450 ((873))</td>
<td></td>
</tr>
<tr>
<td>([\text{Fe(BMP)}_2\text{Cl}_2])</td>
<td>4.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Fe(HBDPP)}_3])</td>
<td>4.92</td>
<td>11850 ((844))</td>
<td>(5T_{2g} \rightarrow 5E_g)</td>
</tr>
<tr>
<td>([\text{Fe(ABDPP)}_3])</td>
<td>4.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Fe(BDPP)}_2\text{Cl}_2])</td>
<td>4.88</td>
<td>11600 ((862))</td>
<td></td>
</tr>
</tbody>
</table>
Mohammad Shakir et al. synthesized octahedral Fe(II) complexes with magnetic moment 5.40-5.80 B.M.\textsuperscript{159}

In the present work, the room temperature magnetic susceptibility indicates that Fe(II) complexes exhibits magnetic moment values (4.82 – 4.98 B.M.) within the required range for octahedral field.

### 4.4.5 Electronic spectral study of Fe(II) complexes:

In high spin octahedral complexes, the ground state $^5D$ split into high energy $^5T_{2g}$ and low energy $^5E_g$ levels. There are no other quintet states and hence only one spin-allowed $^5T_{2g} \rightarrow ^5E_g$ transition occurs in the visible or near infrared region but in excited state, is subjected to Jahn-Teller distortion and shows broad absorption.\textsuperscript{160}

C. P. Prabhakaran et al. reported octahedral iron(II) complexes with antipyrine with band 10,000 - 10,400 cm$^{-1}$ of $^5T_{2g} \rightarrow ^5E_g$ transition.\textsuperscript{161}

In low spin octahedral complexes, the ground state is $^1A_{1g}$ hence two relatively low lying spin allowed transitions to $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ takes place.\textsuperscript{162}

All the tetrahedral complexes Fe(II) complexes are high spin complexes and the band occurs at 4000 cm$^{-1}$.

In the present investigation, Electronic absorption spectrum of selected Fe(II) complexes were recorded by preparing its solution in DMSO solvent.

The results of the electronic absorption spectrum of Fe(II) complex is reported in Table 4.4.2 and spectra as figure 4.4.1 to 4.4.4.

The electronic spectra of the iron complexes exhibit a weak intensity ($d$-$d$) transition in the region 11,450-11,850 cm$^{-1}$, which may be reasonably assigned to the $^5T_{2g} \rightarrow ^5E_g$ transition, consistent with a high-spin octahedral environment around iron(II) ion.\textsuperscript{159}
4.4.1: Electronic spectra of [Fe(HBMP)₂]

4.4.2: Electronic spectra of [Fe(ABMP)₂]
4.4 Iron(II) complexes

4.4.3: Electronic spectra of [Fe(HBDPP)$_2$]

4.4.4: Electronic spectra of [Fe(BDPP)$_2$Cl$_2$]
Figure 4.4.5 Infrared spectrum of [Fe(HBMP)$_2$]
Chapter 4: Study of transition metal complexes with pyrazolone derivatives

4.4 Iron(II) complexes

Figure 4.4.6 Infrared spectrum of $[\text{Fe(ABMP)}_2$...]
Figure 4.4.7 Infrared spectrum of [Fe(HBDPP)₂]
Figure 4.4.8 Infrared spectrum of [Fe(BDPP)₂]
4.4.6] **Infrared Spectral Study of Iron(II) Complexes:**

The comparison of IR spectrum data of Fe(II) complex with the corresponding ligands helps in determining the bonding pattern in the complexes.

**A) Stretching vibration due to Hydroxyl group:**

On complexation, phenolic OH stretching disappears in the infrared spectra of Fe(II) complexes. The phenolic oxygen participation was confirmed by the blue shift of ν(C-O) stretching.\(^{59}\)

**B) Stretching vibration due to amino group**

The infrared spectrum of Fe(II) complex with ABMP has singlet at 3280 cm\(^{-1}\) which indicate that involvement of deprotonated NH\(_2\) group in complexation.\(^{60}\)

**Table 4.4.3: Infrared spectral data of Fe(II) complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>(v)NH(_2)</th>
<th>(v)C=O</th>
<th>(v)C=O</th>
<th>(v)C-N</th>
<th>(v)C-O</th>
<th>(v)Fe-N</th>
<th>(v)Fe-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(HBMP)(_2)]</td>
<td>-</td>
<td>1685</td>
<td>1625</td>
<td>-</td>
<td>1262</td>
<td>534</td>
<td>498</td>
</tr>
<tr>
<td>[Fe(ABMP)(_2)]</td>
<td>3280</td>
<td>1678</td>
<td>1630</td>
<td>-</td>
<td>-</td>
<td>537</td>
<td>498</td>
</tr>
<tr>
<td>[Fe(HBDPP)(_2)]</td>
<td>-</td>
<td>1681</td>
<td>1638</td>
<td>1585</td>
<td>1261</td>
<td>531</td>
<td>498</td>
</tr>
<tr>
<td>[Fe(BDPP)(_2)Cl(_2)]</td>
<td>-</td>
<td>1671</td>
<td>1625</td>
<td>1572</td>
<td>-</td>
<td>503</td>
<td>498</td>
</tr>
</tbody>
</table>

**C) Stretching vibration due to Carbonyl groups**

The stretching vibrations of (C=O) is shifted to a lower by 22-33 cm\(^{-1}\) which is shows the involvement of carbonyl groups.\(^{64}\)
D] **Stretching vibration due to C=N group**

The absorption bands of C=N of ligands HBDPP, ABDPP and BDPP is decreases by 17-18 cm\(^{-1}\) in the spectra of the complexes, The lowering in the position of such band suggests linkage between donor nitrogen atom with Fe(II) metal ion.\(^{163}\)

E] **Stretching vibration due to Fe-O and Fe-N:**

The \(v\) (Fe–O) and \(v\) (Fe–N) stretching bands exhibits in the ranges 503 – 537 cm\(^{-1}\) and 498 cm\(^{-1}\) respectively.\(^{67}\)

4.4.7] **X-Ray Diffraction Study of Iron(II) Complexes.**

X-Ray diffractometric study of metal complexes provides information about their crystallization. Each diffractograms is well resolved into sharp refluxes suggesting highly crystalline nature for the complexes.

The position of each reflux was accurately measured and by using Bragg's equation the interplanar distance \(d\) was calculated. The \(d\)-spacing values of each reflux were used to calculate lattice parameters assuming the probable crystal system.

All calculations were performed by using computerized software program **Powder-X** developed by Cheng Dang.

The data obtained and reciprocal lattice \((h, k, l)\) are listed in the Table 4.4.4 and XRD spectrum is represented as Figure.4.4.9

The literature suggests that the transition metal complexes derived from different ligands can crystallize in different crystal systems. The present mononuclear complexes have been reported with the probable Miller Indices using X-ray diffractograms.

Thus, on the basis of the results and the support of literature The Fe(II) complex with HBDPP is crystalline in nature due to sharp refluxes shown, and have been assigned monoclinic.\(^{164-165}\)
Table 4.4.4 XRD data of Fe[HBDPP]$_2$

<table>
<thead>
<tr>
<th>$h$</th>
<th>$k$</th>
<th>$l$</th>
<th>$D(\text{Cal})$</th>
<th>$D(\text{Obs})$</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>3.24497</td>
<td>3.34573</td>
<td>121.04</td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>1</td>
<td>1.98964</td>
<td>1.98109</td>
<td>181.24</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0</td>
<td>1.62527</td>
<td>1.60940</td>
<td>85.06</td>
</tr>
<tr>
<td>-3</td>
<td>0</td>
<td>0</td>
<td>1.40828</td>
<td>1.41936</td>
<td>43.66</td>
</tr>
<tr>
<td>-3</td>
<td>3</td>
<td>2</td>
<td>1.25992</td>
<td>1.25679</td>
<td>69.31</td>
</tr>
</tbody>
</table>

Figure 4.4.9 XRD spectrum of Fe[HBDPP]$_2$
4.5 Manganese(II) complexes

4.5.1 Introduction:

Manganese is an important transition metal. The Mn(II) ion has $d^5$ configuration. The divalent state of manganese is the most stable oxidation state. Mn(II) ion is largest and have low ligand field stabilization energy in the complexes when compared with Fe(II), Co(II), Ni(II) and Cu(II) complexes hence most of the Mn(II) complexes show high spin behaviour.

Manganese(II) complexes have received considerable interest in the synthesis due to their diversity in coordination behavior and geometry and these complexes were found to act as catalysts for a variety of organic reactions. Mn(II) forms complexes with various ligands. A number of four coordinated Mn(II) complexes with tetrahedral or square planar geometry are also known.¹⁶⁶ These complexes are usually not very stable in polar solvents but however the tetrahedral geometry is preserved in less polar solvents.

Five-coordinated Mn(II) complexes containing two bidentate ligands with a square pyramidal coordination geometry ¹⁶⁷ or trigonal-bipyramidal geometry ¹⁶⁸ have been reported. The common coordination number of Mn(II) is six with octahedral geometry.¹⁶⁹

Tetrahedral Mn(II) complexes has green-yellow color and intense than the pink octahedral complexes.

A large number of Mn(II) complexes with nitrogen, oxygen containing ligands ¹⁷⁰-¹⁷¹ and with pyrazolone derivatives ¹⁷²-¹⁷⁵ have been reported.

Octahedral Mn(II) complexes with derivatives of 3-methyl-1-phenyl-pyrazol-5-one (antipyrine) have been prepared and characterized in which the ligands are coordinated through O,O and N.⁶³
In this section, the synthesis, properties and characterization of Mn(II) complexes derived from HBMP, ABMP, BMP, HBDPP, ABDPP and BDPP have been discussed.

4.5.2] Synthesis of Complexes:

0.02 moles of ligand (in slight excess) was taken in round bottom flask containing 30ml of methanol. 0.01 moles of manganous chloride dissolved in 20ml of methanol and was gradually added into the solution of ligand. Ten percent alcoholic ammonia solution was added drop wise till precipitation of complex was obtained. The pH of precipitation of complexes was noted.

The precipitated complex was digested for one hour. Any change in pH if observed was readjusted and digested for one more hour. The precipitate of complex was filtered in hot condition. It was washed with alcohol followed by petroleum ether (40–60°C) and dried in vacuum desiccators over calcium chloride.

4.5.3] Properties:

The Mn(II) complexes synthesized from pyrazolone based ligands. These are brown colored. They are stable to air and moisture. They decompose at high temperature.

These complexes are insoluble in common polar and non-polar solvents but soluble in DMSO. The chloride is checked Volhard's test.

Analytical data given in Table 4.5.1 suggest that the metal-ligand stoichiometry is 1:2 and the complexes are monomeric in nature. The limited solubility of these complexes in suitable organic solvents did not permit the determination of their molecular weight.

The molar conductance ($\Lambda_m$) of the synthesised Mn(II) complexes in DMSO ($10^{-3}$ M) are 14 to 24 ohm$^{-1}$ cm$^2$ mol$^{-1}$ indicate that the complexes are non electrolytes.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Mol. Formula</th>
<th>For Wt</th>
<th>Dec.Temp</th>
<th>Colour</th>
<th>Yield</th>
<th>Calculated (Found)</th>
<th>$\Lambda_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>[Mn(HBMP)$_2$]</td>
<td>C$<em>{22}$H$</em>{18}$Mn$_4$O$_6$</td>
<td>489.33</td>
<td>310</td>
<td>Brown</td>
<td>69%</td>
<td>54.00</td>
<td>3.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(53.95)</td>
<td>(3.72)</td>
</tr>
<tr>
<td>[Mn(ABMP)$_2$]</td>
<td>C$<em>{22}$H$</em>{20}$Mn$_6$O$_4$</td>
<td>487.37</td>
<td>318</td>
<td>Brown</td>
<td>72%</td>
<td>54.22</td>
<td>4.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(54.10)</td>
<td>(4.10)</td>
</tr>
<tr>
<td>[Mn(BMP)$_2$Cl$_2$]</td>
<td>C$<em>{22}$H$</em>{20}$Cl$_2$Mn$_4$O$_4$</td>
<td>530.26</td>
<td>294</td>
<td>Brown</td>
<td>64%</td>
<td>49.83</td>
<td>3.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(49.81)</td>
<td>(3.78)</td>
</tr>
<tr>
<td>[Mn(HBDPP)$_2$]</td>
<td>C$<em>{30}$H$</em>{22}$Mn$_4$O$_8$</td>
<td>621.45</td>
<td>347</td>
<td>Brown</td>
<td>68%</td>
<td>57.98</td>
<td>3.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(57.85)</td>
<td>(3.56)</td>
</tr>
<tr>
<td>[Mn(ABDPP)$_2$]</td>
<td>C$<em>{30}$H$</em>{24}$Mn$_6$O$_6$</td>
<td>619.48</td>
<td>339</td>
<td>Brown</td>
<td>62%</td>
<td>58.16</td>
<td>3.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(58.14)</td>
<td>(3.89)</td>
</tr>
<tr>
<td>[Mn(BDPP)$_2$Cl$_2$]</td>
<td>C$<em>{30}$H$</em>{24}$Cl$_2$Mn$_4$O$_6$</td>
<td>662.37</td>
<td>285</td>
<td>Brown</td>
<td>74%</td>
<td>54.40</td>
<td>3.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(54.40)</td>
<td>(3.63)</td>
</tr>
</tbody>
</table>

4.5.4] Magnetic susceptibility of Mn(II) complexes:

The room temperature magnetic susceptibility for the metal complexes can be determined by Gouy's method. The weak octahedral field complexes are expected to have the spin only moment 5.92 B.M. because the crystal field or spin orbit coupling alone is unable to lift the six fold degeneracy of the \( ^6A_{lg} \) state and five unpaired electrons. Many researcher have been reported the octahedral manganese complexes having magnetic moment in the range of 5.81-5.89 B.M.\(^{159,178}\)

However, in many complexes, the observed magnetic moments fall in the range of 4.7 to 5.7 B.M. at room temperature. The subnormal moments are due to the presence traces of Mn(III) species and spin exchange in solid state.\(^{179}\)

The magnetic moments of tetrahedral complexes have been found to be close to the spin only value.\(^{180-181}\)

Table 4.5.2: Mag. moments and Elec. Spec. data of Mn(II)complexes

<table>
<thead>
<tr>
<th>Mn(II) Complexes</th>
<th>Magnetic Moment in B.M.</th>
<th>( \lambda_{\text{Max}} ) in cm(^{-1} ) (( \lambda_{\text{Max}} ) in nm)</th>
<th>Mn(II) Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mn(HBMP)}_3])</td>
<td>5.88</td>
<td>18350 cm(^{-1}) (544 nm), 22800 cm(^{-1}) (438 nm)</td>
<td>( ^6A_{lg} \rightarrow ^4T_{lg} )</td>
</tr>
<tr>
<td>([\text{Mn(ABMP)}_3])</td>
<td>5.90</td>
<td>-</td>
<td>18100-18900 cm(^{-1})</td>
</tr>
<tr>
<td>([\text{Mn(BMP)}_2\text{Cl}_2])</td>
<td>5.80</td>
<td>18100 cm(^{-1}) (552 nm), 22200 cm(^{-1}) (450 nm)</td>
<td>( ^6A_{lg} \rightarrow ^4T_{2g}(G) )</td>
</tr>
<tr>
<td>([\text{Mn(HBDPP)}_3])</td>
<td>5.92</td>
<td>18900 cm(^{-1}) (529 nm), 23500 cm(^{-1}) (425 nm)</td>
<td>22200-23500 cm(^{-1})</td>
</tr>
<tr>
<td>([\text{Mn(ABDPP)}_3])</td>
<td>5.85</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>([\text{Mn(BDPP)}_2\text{Cl}_2])</td>
<td>5.83</td>
<td>18450 cm(^{-1}) (542 nm), 22290 cm(^{-1}) (448 nm)</td>
<td></td>
</tr>
</tbody>
</table>
In present work, the Mn(II) complex synthesized from the pyrazolone and pyrano-pyrazolone derivatives shows magnetic moment in the range 5.80-5.92 B.M. at room temperature suggesting octahedral geometry. The Mn(II) complex have magnetic moment substantially that of spin only value expected for an S = 5/2 system.

The above magnetic moment value is indicative of the presence of $^6A_{1g}$ ground state associated with an octahedral structure and may be due to the absence of Mn$^{3+}$ species.

**4.5.5] Electronic spectral study of Mn(II) complexes:**

Many high spin Mn(II) complexes are very light colored and intensities of transitions are extremely low due to spin forbidden as well as Laporate forbidden. However, four bands are observed in the visible region corresponding to $(^6A_{1g} \rightarrow ^4T_{1g})$, $(^6A_{1g} \rightarrow ^4T_{2g})$, $(^6A_{1g} \rightarrow ^2E_g)$ and $(^6A_{1g} \rightarrow ^4A_{ig})$ transitions having octahedral geometry.

Electronic spectra of tetrahedral Mn(II) complexes show weak absorption at about 20,000 cm$^{-1}$ and 26,000 cm$^{-1}$ assignable to $^6A_{1g} \rightarrow ^4T_{2g}$ and $^6A_{1g} \rightarrow ^4E_g, ^4A_{ig}(G)$ transitions in the visible region. Tetrahedral Mn(II) complexes has yellow-green color and more intense than the light pink colored octahedral Mn(II) complexes. The high intensity of color of Tetrahedral Mn(II) complexes is probably due to overlap of the metal 3d orbitals with ligand orbitals.

The selected electronic spectra of synthesized Mn(II) complexes are represented as figure no. 4.5.1-4.5.4 and their absorption bands are summarized in Table 4.5.2.

In the present study, the Mn(II) complexes shows two spin forbidden $d$-$d$ bands 18100 - 18900 cm$^{-1}$ and 22200-23500 cm$^{-1}$ are assigned to $^6A_{ig} \rightarrow ^4T_{1g}$ and $^6A_{ig} \rightarrow ^4T_{2g}(G)$ transitions respectively. These transitions are characteristics of octahedral structure.
Figure 4.5.1 Electronic spectra of \([\text{Mn(HBMP)}_2]\)

Figure 4.5.2 Electronic spectra of \([\text{Mn(BMP)}_2\text{Cl}_2]\)
Figure 4.5.3: Electronic spectra of [Mn(HBDPP)$_2$]

Figure 4.5.4: Electronic spectra of [Mn(BDPP)$_2$Cl$_2$]
4.5.6] Infrared spectral study of Mn(II) complexes:
The infrared spectra of the solid complexes exhibit changes that may give
idea about the structure of these complexes.

1) Stretching vibration due to Hydroxyl group:

The infrared spectrum of Mn(II) complexes with HBMP and with
HBDPP shows that it coordinate through the oxygen of the phenolic
group after deprotonation.\(^{26}\)

2) Stretching vibration due to amino group:

The infrared spectrum of Mn(II) complex with ABMP and ABDPP
has singlet in the region 3125-3217 cm\(^{-1}\) which shows that metal cation is
bound to a deprotonated NH\(_2\) group.\(^{27}\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\nu\text{NH}_2)</th>
<th>(\nu\text{C}=\text{O})</th>
<th>(\nu\text{C}=\text{O})</th>
<th>(\nu\text{C-N})</th>
<th>(\nu\text{C-O})</th>
<th>(\nu\text{Mn-N})</th>
<th>(\nu\text{Mn-O})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(HBMP)(_2)]</td>
<td>-</td>
<td>1690</td>
<td>1622</td>
<td>-</td>
<td>1242</td>
<td>535</td>
<td>420</td>
</tr>
<tr>
<td>[Mn(ABMP)(_2\text{Cl}_2)]</td>
<td>3125</td>
<td>1681</td>
<td>1639</td>
<td>-</td>
<td>-</td>
<td>535</td>
<td>431</td>
</tr>
<tr>
<td>[Mn(HBDPP)(_2)]</td>
<td>-</td>
<td>1681</td>
<td>1639</td>
<td>1596</td>
<td>1251</td>
<td>527</td>
<td>498</td>
</tr>
<tr>
<td>[Mn(ABDPP)(_2)]</td>
<td>3217</td>
<td>1681</td>
<td>1653</td>
<td>1590</td>
<td>-</td>
<td>541</td>
<td>458</td>
</tr>
</tbody>
</table>

3) Stretching vibration due to Carbonyl groups:

The C=O stretching vibrations is shifted to a lower by 28-32 cm\(^{-1}\)
which is shows the involvement of carbonyl groups in complexation.\(^{28}\)

4) Stretching vibration due to C=N group:

The absorption bands of C=N of ligands HBDPP, ABDPP and BDPP
are moved towards lower wave numbers by 7-13 cm\(^{-1}\) in the complexes,
which confirms the coordination of the N to the metallic ion.\(^{29}\)

5) Stretching vibration due to Mn-N and Mn-O:

The Mn-O and Mn-N stretching frequencies exhibit bands in the
ranges 527-41 and 420-498 cm\(^{-1}\) respectively.\(^{33,34}\)
Figure 4.5.5 Infrared spectrum of [Mn(HBMP)₂]
Figure 4.5.6 Infrared spectrum of [Mn(ABMP)$_2$]
Figure 4.5.7 Infrared spectrum of [Mn(HBDPP)$_2$]
Figure 4.5.8 Infrared spectrum of [Mn(ABDPP)$_2$]
4.5.7] XRD

X-ray diffraction technique can be used to determine the crystallinity of the complexes. X-Ray diffractometric study of metal complexes provides information about their crystallization. Each diffractograms is well resolved into sharp reflexes suggesting highly crystalline nature for the complexes. The position of each reflux was accurately measured and by using Bragg's equation the interplanar distance \( d \) was calculated. The \( d \)-spacing values of each reflux were used to calculate lattice parameters assuming the probable crystal system.

All calculations were performed by using computerized software program *Powder-X* developed by Cheng Dang. The data obtained and reciprocal lattice \( (h, k, l) \) are listed in the Table 4.5.4.

The literature suggests that the transition metal complexes derived from different ligands can crystallize in different crystal systems. The present mononuclear complexes have been reported with the probable Miller Indices using X-ray diffractograms. Thus, on the basis of the results and the support of literature, the Mn(II)complex with HBDPP is crystalline in nature due to sharp reflexes shown, (Figure 4.5.9) and have been assigned monoclinic.\(^{189-190}\)
Table 4.5.4 XRD data of Mn[HBDPP]₂

<table>
<thead>
<tr>
<th>H</th>
<th>K</th>
<th>L</th>
<th>D (Exp.)</th>
<th>D (Calc.)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>5.57374</td>
<td>5.40890</td>
<td>6.44</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>4.30167</td>
<td>4.25807</td>
<td>35.95</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2.67069</td>
<td>2.70445</td>
<td>45.86</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>2</td>
<td>2.28948</td>
<td>2.28291</td>
<td>6.34</td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>1</td>
<td>1.96962</td>
<td>1.98109</td>
<td>35.59</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>2</td>
<td>1.68615</td>
<td>1.67286</td>
<td>11.32</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>3</td>
<td>1.67833</td>
<td>1.67286</td>
<td>9.12</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>3</td>
<td>1.65151</td>
<td>1.66027</td>
<td>8.80</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>1</td>
<td>1.15613</td>
<td>1.15379</td>
<td>6.34</td>
</tr>
</tbody>
</table>

Crystal system: Monoclinic  
Lattice Type: P  
Radiation: Cu  
Wavelength: 1.540598  
Lattice Parameter: a = 4.9168, b = 4.9168, c = 5.4089  
Lattice Parameter: α = 90.00, β = 90.00, γ = 120.00  
θ Start = 10  
θ End = 99.98

Figure 4.5.9 XRD spectrum of Mn[HBDPP]₂
4.6 Conclusion:

On the basis of above discussion and information available in literature, it is found that as synthesized metal complexes are stable at room temperature.

1] The ligands HBMP, ABMP, HBDPP and ABDPP acts as monobasic tridentate ligands where as ligands BMP and BDPP are neutral bidentate ligands forms octahedral complexes.

2] Analytical data shows that complexes are monomeric and metal and ligands are in the ratio 1:2.

3] The conductivity measurements of the present Metal(II) complexes shows that complexes are non electrolytes.

4] The magnetic moment values of metal(II) complexes are within the required range for octahedral field.

5] Octahedral structures of complexes further confirmed by electronic spectra of complexes.

6] From infrared spectra, it is concluded that Metal(II) ion is coordinated to ligand HBMP by O,O,O., to ligand HBDPP and ABMP by N,O,O., to ligand BMP by O,O., to ligand ABDPP by N,N,O., and BDPP by N,O.

7] Ligands BMP and BDPP are bidentate ligands forms octahedral complexes having Cl atoms at axial positions.

8] The g\textsubscript{||} value suggests that the existence of covalency in the Cu(II) complex of HBMP. Analysis of these data show that in all cases
$g_\parallel > g_\perp$ which indicates $d_{x^2-y^2}$ ground state for the Cu(II) ion in these complexes.

The axial spectrum with $g_\parallel > g_\perp > 2.03$ is consistent with a distorted octahedral geometry around the copper(II) ion.

9] XRD study shows the metal(II) complexes with synthesized ligands are crystalline in nature and have been assigned monoclinic.
Structure of Metal(II) Complexes

Metal(II) Complex of HBMP

Metal(II) Complex of ABMP

Metal(II) Complex of BMP
Structure of Metal(II) Complexes

Metal(II) Complex of HBDPP

Metal(II) Complex of ABDPP

Metal(II) Complex of BDPP
Chapter 4: Study of transition metal complexes with pyrazolone derivatives

4.8 References:


15) James F Huheey, Ellen A Keiter & Richard L Keiter,


85) Feng Bao, Rui Ma, Xingqiang Lu, Guoqiu Gui and Qing Wu


90) Feng Bao, Rui Ma, Xingqiang Lu, Guoqiu Gui and Qing Wu


126) James F Huheey, Ellen A Keiter & Richard L Keiter, 


164) Ko Yoneda et al., *Polyhedron*, 24, 16-17 (2005) 2442


172) Rajendra N Jadeja, Narsidas J Parmar, and Jayant R Shah


