4

COMPOSITION OF METAL CHELATES
COMPOSITION OF METAL CHELATES

The composition and the structure of the ligands and the chelates as well, were investigated. The composition of the chelates prepared has been determined on the basis of

(A) Percentage estimation of elements.

(B) Molecular weight determination by Rasch method.

(C) Conclusions drawn from Job's method of continuous variation.


(E) From the results of magnetic susceptibility.

The theoretical and experimental study of several organic ligands having the general structure (I) and the corresponding metal chelate having structure (II) have been reported (1 to 9). They have been found identical with the ligands and chelates under investigation.
(A) Percentage estimation of elements:

Several methods are adopted for determining the percentage of elements in given chelates. The percentages of metals in the chelates have been determined either by weighing metal...
oxide (10-14) or by weighing metal (15) obtained after ignition of a known weight of the chelate.

They were also quantitatively analysed for determination of percentage of carbon by combustion method. Nitrogen content was determined by using Kjeldahl's method.

The present thesis describes the determination of percentage of metal like Cu$^{2+}$, Ni$^{2+}$, Fe$^{2+}$ and Fe$^{3+}$ in the chelates formed with ligands (i) 2-hydroxy-5-methylacetophenonehydrazone and (ii) 2-hydroxy-5-methylpropiophenonehydrazone by weighing metal oxide method. However in the case of Co$^{2+}$-chelate the percentage estimation of cobalt was determined using anthranilic acid method.

(a) **Estimation of Copper as copper oxide from its chelates**:

(i) Copperbis-2-hydroxy-5-methylacetophenonehydrazone (0.200 gm) was ignited in a crucible. The ignited mass was then treated with a drop of concentrated nitric acid and then excess of acid was evaporated to dryness.
It was cooled and the residue was weighed as copper oxide. (ii) The same procedure was followed for copperbis-2-hydroxy-5-methylpropio phenonehydrazone.

The results are tabulated below.

<table>
<thead>
<tr>
<th>Chelates</th>
<th>Weight of chelate obtained in gm.</th>
<th>Weight of metal oxide ignited in gm.</th>
<th>Percentage of Metal</th>
<th>Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Cu(C₉H₁₁N₂O₂)₂</td>
<td>0.200</td>
<td>0.041</td>
<td>16.30</td>
<td>16.50</td>
<td></td>
</tr>
<tr>
<td>ii) Cu(C₁₀H₁₃N₂O₂)₂</td>
<td>0.200</td>
<td>0.038</td>
<td>15.31</td>
<td>15.00</td>
<td></td>
</tr>
</tbody>
</table>

(b) Estimation of Nickel as nickel oxide from its chelates:

(i) Nickelbis-2-hydroxy-5-methylaceto phenonehydrazone (0.200 gm) was ignited in a crucible, treated with concentrated nitric acid, excess of acid was evaporated to dryness, residue was cooled and weighed as nickel oxide. (ii) The same procedure was followed for nickelbis-2-hydroxy-5-methylpropio phenonehydrazone.
The results are tabulated below.

<table>
<thead>
<tr>
<th>Chelates</th>
<th>Weight of chelate ignited in gm.</th>
<th>Weight of metal oxide obtained in gm.</th>
<th>Percentage of Metal Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Ni(C₉H₁₁N₂O)₂</td>
<td>0.200</td>
<td>0.040</td>
<td>15.26</td>
<td>15.70</td>
</tr>
<tr>
<td>ii) Ni(C₁₀H₁₃N₂O)₂</td>
<td>0.200</td>
<td>0.036</td>
<td>14.22</td>
<td>14.00</td>
</tr>
</tbody>
</table>

(c) Estimation of Ferrous and Ferric as ferric oxide from its chelates:

(i) Ferrous-2-hydroxy-5-methylacetophenone-hydrazone (0.200 gm.) was ignited in a crucible. A drop of concentrated nitric acid was added and evaporated to dryness. It was cooled and then weighed as ferric oxide. The same procedure was followed for

(ii) Ferrous-2-hydroxy-5-methylpropiophenone-hydrazone.

(iii) Ferric-2-hydroxy-5-methylacetophenone-hydrazone.

(iv) Ferric-2-hydroxy-5-methylpropiophenone-hydrazone.
The results are tabulated below.

<table>
<thead>
<tr>
<th>Chelates</th>
<th>Weight of chelate metal oxide in gm.</th>
<th>Weight of metal oxide ignited in gm.</th>
<th>Percentage of metal obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ferrous Chelate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i) Fe(C₉H₁₁N₂O)</td>
<td>0.200</td>
<td>0.073</td>
<td>25.57</td>
</tr>
<tr>
<td>ii) Fe(C₁₀H₁₃N₂O)</td>
<td>0.200</td>
<td>0.069</td>
<td>24.03</td>
</tr>
<tr>
<td><strong>Ferric Chelate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iii) Fe(C₉H₁₁N₂O)</td>
<td>0.200</td>
<td>0.074</td>
<td>25.57</td>
</tr>
<tr>
<td>iv) Fe(C₁₀H₁₃N₂O)</td>
<td>0.200</td>
<td>0.068</td>
<td>24.03</td>
</tr>
</tbody>
</table>

(d) Estimation of Cobalt as cobalt anthranilate

(i) Cobaltbis-2-hydroxy-5-methylacetophene nonehydrazone (0.200 gm) was ignited in a crucible. The ignited mass was then treated with a drop of concentrated nitric acid. The excess of the acid was evaporated to dryness by heating the crucible with small amount of sulphuric acid at low flame. The residue was extracted with dilute hydrochloric acid and the extract was evaporated to dryness. The residue
was again dissolved in hydrochloric acid. It was then diluted to 100 ml. and warmed up to boiling. The pH was adjusted between 3.5 and 4.5, and treated with 3% solution of sodium anthranilate and further boiled for five minutes. It was then allowed to stand for ten minutes. Precipitates of cobalt anthranilate were filtered, washed with a solution of sodium anthranilate (0.15%), followed by alcohol, dried at 105°C and finally weighed.

(ii) Cobaltbis-2-hydroxy-5-methylpropiophenone-hydrazone (0.200 gm.) was ignited and the same procedure followed.

The results are tabulated below.

<table>
<thead>
<tr>
<th>Chelates</th>
<th>Weight of chelate ignited in gm.</th>
<th>Weight of chelate anthranilate obtained in gm.</th>
<th>Percentage of Metal Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Co(C_{9H_{11}N_{2}O})_2</td>
<td>0.200</td>
<td>0.174</td>
<td>15.30</td>
<td>15.50</td>
</tr>
<tr>
<td>ii) Co(C_{10H_{13}N_{2}O})_2</td>
<td>0.200</td>
<td>0.163</td>
<td>14.27</td>
<td>14.50</td>
</tr>
</tbody>
</table>

...188
(e) Besides, the percentage estimation of Carbon by Combustion method and Nitrogen by Kjeldahl's method of the said chelates are carried out and the results are tabulated below.

<table>
<thead>
<tr>
<th>Chelates</th>
<th>% of Carbon</th>
<th>% of Nitrogen</th>
<th>% of Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=CH₃R₂=CH₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(C₈H₁₁N₂O)₂</td>
<td>55.46</td>
<td>14.25</td>
<td>16.30</td>
</tr>
<tr>
<td></td>
<td>55.48</td>
<td>14.25</td>
<td>16.50</td>
</tr>
<tr>
<td>Ni(C₉H₁₂N₂O)₂</td>
<td>56.15</td>
<td>14.30</td>
<td>15.20</td>
</tr>
<tr>
<td></td>
<td>56.10</td>
<td>14.56</td>
<td>15.70</td>
</tr>
<tr>
<td>Co(C₉H₁₂N₂O)₂</td>
<td>56.12</td>
<td>14.55</td>
<td>15.30</td>
</tr>
<tr>
<td></td>
<td>56.15</td>
<td>14.35</td>
<td>15.50</td>
</tr>
<tr>
<td>Fe(C₉H₁₂N₂O)²</td>
<td>49.32</td>
<td>12.79</td>
<td>25.57</td>
</tr>
<tr>
<td></td>
<td>49.30</td>
<td>12.85</td>
<td>25.55</td>
</tr>
</tbody>
</table>

| R=CH₃R₂=C₂H₅  |             |               |            |
| Cu(C₁₀H₁₃N₂O)₂| 57.49       | 13.41         | 15.31       |
|               | 57.50       | 13.60         | 15.00       |
| Ni(C₁₀H₁₃N₂O)₂| 58.15       | 13.57         | 14.22       |
|               | 58.20       | 13.70         | 14.00       |
| Co(C₁₀H₁₃N₂O)₂| 58.13       | 13.56         | 14.27       |
|               | 58.15       | 13.80         | 14.50       |
| Fe(C₁₀H₁₃N₂O).| 51.50       | 12.02         | 25.57       |
|               | 51.55       | 11.90         | 25.90       |

It is clear from the above table that the metal : ligand ratio being 1:2 in case of Cu²⁺, Ni²⁺, Co²⁺ chelates and 1:1 in case of Fe²⁺, Fe³⁺ chelates.
The molecular weights of the chelates were determined by Rasch method using pure camphor. The results are recorded in the following table.

Weight of complex = 0.200 gm.
Weight of camphor = 2.0 gm.
\( K_f \) of camphor = 39.68°C/100 ml.

<table>
<thead>
<tr>
<th>Chelates</th>
<th>Depression in F.P.</th>
<th>Molecular Weights</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Experimental</td>
</tr>
<tr>
<td></td>
<td>( T_c )</td>
<td>( T_o )</td>
</tr>
<tr>
<td>Cu( (C\textsubscript{9}H\textsubscript{11}N\textsubscript{2}O)\textsubscript{2} )</td>
<td>10.19</td>
<td>10.5</td>
</tr>
<tr>
<td>Cu( (C\textsubscript{10}H\textsubscript{13}N\textsubscript{2}O)\textsubscript{2} )</td>
<td>9.50</td>
<td>9.5</td>
</tr>
<tr>
<td>Ni( (C\textsubscript{9}H\textsubscript{11}N\textsubscript{2}O)\textsubscript{2} )</td>
<td>10.32</td>
<td>10.5</td>
</tr>
<tr>
<td>Ni( (C\textsubscript{10}H\textsubscript{13}N\textsubscript{2}O)\textsubscript{2} )</td>
<td>9.62</td>
<td>9.6</td>
</tr>
<tr>
<td>Co( (C\textsubscript{9}H\textsubscript{11}N\textsubscript{2}O)\textsubscript{2} )</td>
<td>10.31</td>
<td>10.3</td>
</tr>
<tr>
<td>Co( (C\textsubscript{10}H\textsubscript{13}N\textsubscript{2}O)\textsubscript{2} )</td>
<td>9.61</td>
<td>9.6</td>
</tr>
<tr>
<td>Fe( (C\textsubscript{9}H\textsubscript{11}N\textsubscript{2}O) )</td>
<td>18.12</td>
<td>18.0</td>
</tr>
<tr>
<td>Fe( (C\textsubscript{10}H\textsubscript{13}N\textsubscript{2}O) )</td>
<td>17.03</td>
<td>17.0</td>
</tr>
</tbody>
</table>

The results are in agreement with the composition of the chelates.
(C) Job's method of continuous variation

Since chelates under investigation obey Beer's law, Job's method of Continuous Variation can be applied for confirming metal: ligand ratio.

In a chemical reaction of the type -

\[ M + n.A = M A_n \]

In which the complex \( M A_n \) is formed from the metal ions "M" and the ligand "A" having same molar concentrations are mixed in varying proportions.

Now \( M + n.A = M A_n \) ...........(i)

Therefore, \( K = \frac{[M A_n]}{[M] x (A)^n} \) ...........(ii)

If we impose the restriction, \( [M] + [A] = \) Constant, where \( [M] \& [A] \) denote conc. of M & A respectively.

It can be shown that when concentration of chelate \( [M A_n] \) is maximum,

then \( \frac{d[M A_n]}{d[M]} = 0 \) ...........(iii)

or \( \frac{[A]}{[M]} = n \) ...........(iv)
In other words for a constant total concentration of a metal and the chelating agent in a solution, the concentration of the chelate is the greatest, when the metal and the chelating agent are brought together in the same ratio in which they exist in the chelate. This can be evaluated in terms of Optical density. If a solution of a ligand 'A' is mixed with a solution of metal ion 'M' so that the total molar concentration of the ligand plus that metal is maintained constant, then

\[
[M] = M_t - [MA_n] \quad \ldots\ldots (v)
\]

\[
[A] = A_t - n[MA_n] \quad \ldots\ldots (vi)
\]

\[
[M_t] + [A_t] = \text{constant} \quad \ldots\ldots (vii)
\]

Where \([M_t]\) and \([A_t]\) are the total molarities of 'M' and 'A' respectively. The optical density 'D' of the solution at a given wavelength represents the total absorption by all the species in the solution.

\[
D = 1 \left[ (E_1(M) + E_2(A) + E_3[MA_n]) \right] \quad \ldots (viii)
\]
Where 'l' is the length of the lightpath through the solution and $E_1$, $E_2$, $E_3$ are respective molar extinction coefficients of 'M', 'A' and 'MA' respectively.

Now

$$Y = l[(E_1(M) + E_2(A) + E_3(MA)) - l(E_1M + E_2A)]$$

Function 'Y' represents the difference in the Optical density 'D' shown by equation (viii) and the corresponding optical density that would have resulted if no reaction occurred.

Where the chelating agent (ligand) is transparent to the given wavelength, the equation (ix) may be simplified by assuming $E_2 = 0$. If the cell path (l) is 1 cm, the function 'Y' is defined by the relationship.

$$Y = E_1(M) + E_3(MA) - (E_1M)$$

Differentiating the equation (x) with respect to ($A_t$) gives
\[ \frac{\text{d}y}{\text{d}[A_t]} = E_1 \frac{\text{d}[M]}{\text{d}[A_t]} - \frac{\text{d}[Mt]}{\text{d}[A_t]} + E_3 \frac{\text{d}[Man]}{\text{d}[A_t]} \ldots \ (xi) \]

Now according to equation (v)

\[ [M] = [M_t] - [Mn] \]

differentiating with respect to \( A_t \)

\[ \frac{\text{d}[M]}{\text{d}[A_t]} = \frac{\text{d}[M_t]}{\text{d}[A_t]} - \frac{\text{d}[Mn]}{\text{d}[A_t]} \]

\[ \ldots \frac{\text{d}[M]}{\text{d}[A_t]} - \frac{\text{d}[M_t]}{\text{d}[A_t]} = \frac{-\text{d}[Mn]}{\text{d}[A_t]} \ldots (xii) \]

Putting this value in equation (xi)

\[ \frac{\text{d}y}{\text{d}[A_t]} = E_3 \frac{\text{d}[Mn]}{\text{d}At} - \frac{E_1 \text{d}[Mn]}{\text{d}[A_t]} \]

\[ \frac{\text{d}y}{\text{d}[A_t]} = [E_3 - E_1] \frac{\text{d}[Mn]}{\text{d}At} \ldots (xiii) \]

Equation (xiii) represents the base for the Job's method of continuous variation.
Though Cu$^{+2}$, Ni$^{+2}$, Co$^{+2}$ solutions are coloured but the concentrations of said ions taken for analysis so low that they appeared nearly colourless.

If the chelate is the only coloured substance present, the optical density of the solution is proportional to the concentration of the chelate. Hence the graph of optical density against the volume of the solutions of metal ion as well as that of the ligand would give curve with the maximum at the composition corresponding to the formula of the chelate. If the substance present which absorb light in the same region as does chelate, it is necessary to make an allowance for the same. Job\textsuperscript{(16)} observed that this method is not applicable to a system in which more than one compounds are formed.

This method has been used to determine the composition of Cu$^{+2}$, Fe$^{+2}$, Fe$^{+3}$ and Co$^{+2}$ chelates with salicylic acid derivatives.
Foley and Anderson\(^{(17)}\), Turner and Anderson\(^{(18)}\), Yoe and Harvey\(^{(19)}\), Moss and Mellob\(^{(20)}\) employed this method for iron and kojic acid. Pandya\(^{(9)}\) and Amin\(^{(10)}\) used this method to determine the composition of \(-O\)-hydroxy ketoxime chelates with \(\text{Cu}^{+2}\), \(\text{Ni}^{+2}\) and \(\text{Co}^{+2}\).

In the present work this method was adopted. The solutions of the metal ions and ligands were prepared having same molar concentrations. The solutions of the metal ions and the ligands were mixed in molar ratios of 1:9, 2:8, 3:7, ..., and buffered to the required pH. The chelates formed were extracted by adding 15 ml of \(\text{CHCl}_3\) and the optical density of the chloroform extract was measured. The results showed that in the case of \(\text{Cu}^{+2}\), \(\text{Ni}^{+2}\) and \(\text{Co}^{+2}\), there was a maxima when the metal:ligand ratio was 1:2.

The above results indicate that the chelates of these ligands with \(\text{Cu}^{+2}\), \(\text{Ni}^{+2}\) and \(\text{Co}^{+2}\) should have the following structure.
Feigl and Bondi\(^{(21)}\), Cox, Wardlaw and Webster\(^{(22)}\) have reported that at a higher pH salicylaldoxime give 1:1 chelate with Cu\(^{2+}\). This is probably due to the stronger dianionic ligand of structure (ii) produced from structure (I) giving 1:1 complex having structure (III).

With Fe\(^{2+}\) and Fe\(^{3+}\).

\[
\begin{align*}
\text{Fe}^{2+} & \quad \text{Fe}^{3+} \\
\text{C} &= \text{N} \quad \text{C} &= \text{N} \\
\text{R} & \quad \text{R} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

(I) (II) (III)
The reagent under investigation formed complexes with Fe$^{2+}$ and Fe$^{3+}$ at higher pH having metal:ligand ratio 1:1. The complex has been assigned the structure (III). The 1:1 composition is supported by element composition and the result of Job's method of continuous variation\(^{23}\).

In the present work, 0.0025 M solutions of all the metal salts were prepared and standardized as described earlier, and 0.0025M ethanolic solutions of the reagents were used. The solutions of the metal salts and the reagents were mixed in various proportions as under, solution of metal salt:solution of reagent.

1:9, 2:8, 3:7, 4:6, 5:5 etc.

and maintaining the pH 4.5 for Cu$^{2+}$, pH=5.5 for Ni$^{2+}$, pH = 6.5 for Co$^{2+}$, pH = 7.5 for Fe$^{2+}$ and pH = 7.0 for Fe$^{3+}$. The precipitated complex in each case was extracted by adding 25 ml. chloroform. The chloroform layer was separated. Water droplets were avoided using centrifuge.
The percentage transmission and optical density of the extracted solution of the chelate was determined in each case at wavelengths 440 nm. and 570 nm. Optical densities and percentage transmission at various concentrations are tabulated and optical density against concentration of the components were plotted and composition of the chelate determined from the graphs. (Fig. 1 - 10)
JOB’S METHOD FOR COPPER BIS 2-HYDROXY-5-METHYLACETOPHENONEHYDRAZONE

<table>
<thead>
<tr>
<th>Copper solution taken ml.</th>
<th>Reagent solution ml.</th>
<th>Percentage Transmission 440 nm</th>
<th>Percentage Transmission 570 nm</th>
<th>Optical Density 440 nm</th>
<th>Optical Density 570 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>63.0</td>
<td>85.5</td>
<td>0.200</td>
<td>0.070</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>48.0</td>
<td>79.0</td>
<td>0.315</td>
<td>0.100</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>37.0</td>
<td>73.0</td>
<td>0.430</td>
<td>0.135</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>35.0</td>
<td>71.0</td>
<td>0.450</td>
<td>0.150</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>40.0</td>
<td>72.0</td>
<td>0.400</td>
<td>0.140</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>51.0</td>
<td>79.0</td>
<td>0.290</td>
<td>0.100</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>61.5</td>
<td>85.0</td>
<td>0.210</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Reagent = 0.0025M in C$_2$H$_5$OH

CuCl$_2$ . 2H$_2$O = 0.0025M

Wavelength used: ○ 440 nm.

△ 570 nm.

Fig. 1

- 199 -
Fig. 2

**JOB'S METHOD FOR COPPER BIS 2-HYDROXY-5-METHYLPROPIONONEHYDRAZONE**

<table>
<thead>
<tr>
<th>Copper solution taken ml.</th>
<th>Reagent solution ml.</th>
<th>Percentage Transmission</th>
<th>Optical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>440 nm.</td>
<td>570 nm.</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>80.0</td>
<td>91.0</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>67.0</td>
<td>87.0</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>55.0</td>
<td>80.0</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>58.0</td>
<td>81.0</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>62.5</td>
<td>84.0</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>71.0</td>
<td>87.0</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>75.0</td>
<td>90.0</td>
</tr>
</tbody>
</table>

Reagent = 0.0025M in C$_2$H$_5$OH
CuCl$_2$.2H$_2$O = 0.0025 M

Wavelength used: ◇ 440 nm
△ 570 nm
JOB'S METHOD FOR
NICKEL BIS-2-HYDROXY-5-METHYLACETOPHENONEHYDRAZONE

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>85.5</td>
<td>95.0</td>
<td>0.070</td>
<td>0.025</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>78.0</td>
<td>92.0</td>
<td>0.110</td>
<td>0.035</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>75.5</td>
<td>90.0</td>
<td>0.125</td>
<td>0.045</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>76.0</td>
<td>91.0</td>
<td>0.120</td>
<td>0.040</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>85.0</td>
<td>93.5</td>
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<td>0.075</td>
<td>0.030</td>
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<td>89.5</td>
<td>95.5</td>
<td>0.050</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Reagent: 0.0025M in C$_2$H$_5$OH
NiCl$_2$ . 6H$_2$O = 0.0025M

Wavelength used: ○ 440 nm.
△ 570 nm.
Fig. 4

JOB'S METHOD FOR
NICKEL BIS-2-HYDROXY-5-METHYLPROPIOPHENONEHYDRAZONE

<table>
<thead>
<tr>
<th>Nickel solution taken ml.</th>
<th>Reagent solution ml.</th>
<th>Percentage Transmission</th>
<th>Optical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>440 nm.</td>
<td>570 nm.</td>
<td>440 nm.</td>
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<tr>
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<td>84.0</td>
<td>94.0</td>
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<td>2</td>
<td>8</td>
<td>76.0</td>
<td>92.0</td>
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<tr>
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<td>73.0</td>
<td>90.0</td>
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<td>74.0</td>
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<td>92.0</td>
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</tr>
<tr>
<td>7</td>
<td>3</td>
<td>87.5</td>
<td>95.0</td>
</tr>
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</table>

Reagent = 0.0025M in C$_2$H$_5$OH

NiCl$_2$·6H$_2$O = 0.0025M

Wavelength used: ○ 440 nm
△ 570 nm
JOB'S METHOD FOR COBALTIC BIS-2-HYDROXY-5-METHYLACETOPHENONEHYDRAZONE

<table>
<thead>
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Reagent = 0.0025M in C$_2$H$_5$OH

CoCl$_2$·6H$_2$O = 0.0025M

Wavelength used: ⊗ 440 nm

△ 570 nm
JOB'S METHOD FOR
COBALTOUS BIS 2-HYDROXY-5-METHYLPROPIOPHENONEHYDRAZONE

<table>
<thead>
<tr>
<th>Cobalt solution ml.</th>
<th>Reagent solution ml.</th>
<th>Percentage Transmission 440 nm</th>
<th>Optical Density 440 nm</th>
<th>Percentage Transmission 570 nm</th>
<th>Optical Density 570 nm</th>
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</table>

Reagent = 0.0025M in C$_2$H$_5$OH
CoCl$_2$ . 6H$_2$O = 0.0025M

Wavelength used: 440 nm

Optical density vs. Cobalt solution ml.

Optical density vs. Reagent ml.
JOBS'S METHOD FOR FERROUS 2-HYDROXY-5-METHYLACETOPHENONEHYDRAZONE

<table>
<thead>
<tr>
<th>Ferrous solution taken ml.</th>
<th>Reagent solution ml.</th>
<th>Percentage Transmission 440 nm</th>
<th>570 nm</th>
<th>Optical Density 440 nm</th>
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<td>0.0100</td>
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<td>89.0</td>
<td>98.5</td>
<td>0.0450</td>
<td>0.0075</td>
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<td>0.0500</td>
<td>0.0125</td>
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<td>90.0</td>
<td>97.5</td>
<td>0.0550</td>
<td>0.0125</td>
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<td>92.5</td>
<td>98.0</td>
<td>0.0450</td>
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</table>

Reagent = 0.0025M in C₂H₅OH
FeSO₄(NH₄)₂SO₄.H₂O = 0.0025M

Wavelength used: ○ 440 nm
△ 570 nm
## JOB'S METHOD FOR FERROUS 2-HYDROXY-5-METHYLPROPIOPHENONEHYDRAZONE

<table>
<thead>
<tr>
<th>Ferrous solution taken ml.</th>
<th>Reagent solution ml.</th>
<th>Percentage Transmission</th>
<th>Optical Density</th>
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</tr>
<tr>
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<td>92.0</td>
<td>98.0</td>
</tr>
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</table>

Reagent = 0.0025M in C₂H₅OH

FeSO₄·(NH₄)₂SO₄·6H₂O = 0.0025M

Wavelength used: I 440 nm

II 570 nm

---

**Fig. 8**

**Optical density vs. Reagent solution**

- Reagent = 0.0025M in C₂H₅OH
- FeSO₄·(NH₄)₂SO₄·6H₂O = 0.0025M
- Wavelength used: I 440 nm
- II 570 nm
JOB'S METHOD FOR FERRIC 2-HYDROXY-5-METHYLACETOPHENONEHYDRAZONE

<table>
<thead>
<tr>
<th>Ferric solution taken ml.</th>
<th>Reagent solution ml.</th>
<th>Percentage Transmission</th>
<th>Optical Density</th>
</tr>
</thead>
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<td>440 nm</td>
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</tr>
<tr>
<td>7</td>
<td>3</td>
<td>95.0</td>
<td>99.0</td>
</tr>
</tbody>
</table>

Reagent = 0.0025M in C\textsubscript{2}H\textsubscript{5}OH

Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} \cdot 24H\textsubscript{2}O = 0.0025M

Wavelength used: ⭕ 440 nm
△ 570 nm
Fig. 10

JOB'S METHOD FOR
FERRIC 2-HYDROXY-5-METHYLPROPIOPHENONEHYDRAZONE

<table>
<thead>
<tr>
<th>Ferric solution taken ml.</th>
<th>Reagent solution ml.</th>
<th>Percentage Transmission</th>
<th>Optical Density</th>
</tr>
</thead>
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<td></td>
<td></td>
<td>440 nm</td>
<td>570 nm</td>
</tr>
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<td>1</td>
<td>9</td>
<td>94.0</td>
<td>97.5</td>
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<td>89.0</td>
<td>95.0</td>
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<td>4</td>
<td>91.0</td>
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<tr>
<td>7</td>
<td>3</td>
<td>94.0</td>
<td>97.5</td>
</tr>
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</table>

Reagent = 0.0025M in C₂H₅OH
Fe₂[SO₄]₃[NH₄]₂SO₄·24H₂O=0.0025M

Wavelength used: ○ 440 nm
△ 570 nm
D. ABSORPTION SPECTRA

Instrumental analysis plays an important role in structural determination of complex compounds. Spectral data of I.R., N.M.R., electronic and mass spectra are used to elucidate the structure of large number of molecules supported with or without other information.\(^{(25)}\)

The light absorption occurs due to number of factors viz.\(^{(25)}\)

(i) the absorption arising from an electronic transition in a conjugated system in which a metal may or may not have any influence,

(ii) the absorption resulting from electronic (d-d) transition in the metal ion itself and

(iii) due to charge transfer LMCT band i.e. ligand to metal ion charge transfer.

(iv) Combination and overtone vibrations of the ligands\(^{(26)}\)

(v) Intervalence charge transfer transitions.\(^{(27)}\)
The first factor which is due to the conjugate system in the ligand, is very strong and is known as 'K' type absorption.

It has been investigated in several cases (28-30) that the absorption bands characteristic of a metal ion alone are usually relatively weak and they result from the d-d transitions which are Laporte forbidden. This transition corresponds to an electron shift in the unfilled 'd' orbitals of the transition metals and may be observed in a free metal ion as well as in a metal chelate. They are frequently intensified by co-ordination of the metal ion. Calvin and co-workers (29-30) observed absorption in the visible region due to the Laporte forbidden transition and also 'K' type absorption due to LMCT bands, e.g., bands in the case of Cu$^{+2}$ and its chelates being in the ultra-violet region.

The intensity of the absorption characteristic of Cu$^{+2}$ ion is much weaker than that of the 'K' type of bands. Calvin and co-workers (29-30) concluded from the experi-
mental data that the influence of metal ions on the characteristic absorption is much weaker compared to that of the ligand which has a large conjugated system.

In the light of Frank Condon principle, during electron transition the atom in a molecule does not change the relative position. The charge transfer transition takes place by absorption of a Photon due to electron transition from ligand to metal ion. The absorption bands due to charge transfer transition are usually intense. Generally such bands are at higher frequency (mostly in the u.v. region) compared to that of d-d transition spectra in the visible region.

The d-d transition is subject to the following selection rules.

(i) The d-d transitions are spin or multiplicity forbidden.

(ii) Those transitions (in which the symmetry of the orbital does not change) are Laporte forbidden.

The d-d transitions in the complexes of transition metal cations are symmetry forbidden.
because these d-orbitals have Centre of Symmetry and transition of electron from lower energy d-orbital to the higher energy d-orbital is Laporte forbidden. However there is some distortion in the orbital symmetry due to ligand field or due to solvent effect. Hence the partial hybridization of d and p orbitals takes place in the excited state. Consequently, weak absorption is observed.

Crystal-field calculations cannot give the precise energies or even the ordering of these levels (31-35) i.e. they cannot specifically determine whether the $dz^2$ orbital lies above or below the $d_{xy}$, $d_{xz}$ or $d_{yz}$ levels in a square co-planer stereochemistry, but crystal-field calculations can specify which of the five d-orbitals has the highest energy and which, therefore, will contain the odd electron of the $d^9$ configuration in case of Cu$^{+2}$.

The vast majority of copper(II) complexes give rise to orbitally degenerate ground states (36) involving a static form of distortion i.e. square co-planer. The majority also involve a $d_{x^2 - y^2}$ ground state, but
a number involve either a $d_{z^2}$ or $d_{xy}$ ground state.

\[ dx^2 - y^2 \]

\[ d_{z^2} \]
\[ d_{x^2 - y^2} \]

\[ d_{xy} \]

\[ d_{xy} \]
\[ d_{xz}, d_{yz} \]

\[ d_{xz}, d_{yz} \]
\[ d_{z^2} \]

Square co-planner
D$_{4h}$

The electronic structure of nickel (II) complexes has been investigated using optical spectroscopic and magnetic susceptibility and N.M.R. techniques.\(^{(37-41)}\)
Nickel (II) is a 3d$^8$ ion from this configuration the Russell-Saunders terms $^3P$, $^3P^G$, $^1D$, and $^1S$ arise.

In a regular square planner environment ($D_{4h}$ symmetry), three spin allowed transitions corresponding to $^1A_{1g} \rightarrow ^1B_{2g}$, $^1A_{1g} \rightarrow ^1E_g$ and $^1A_{1g} \rightarrow ^1B_{1g}$ are expected with low intensity due to the presence of the inversion centre. Generally, the d-d spectra are not very well resolved and are obscured by charge transfer transitions; much ambiguity still remains in the assignment of the electronic transitions which are very sensitive to low symmetry effects and interactions. On passing to low symmetry chromophores the $E_g$ state is split and two transitions can in principle be observed.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^1B_{2g}(E_{M})$</th>
<th>$^1E_g(E_{M})$</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
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<td>11600 sh</td>
<td>-</td>
<td>42</td>
</tr>
<tr>
<td>Ni(ptt)</td>
<td>13800(225)</td>
<td>17400(2300)</td>
<td>42</td>
</tr>
<tr>
<td>Ni(O Et:sacsac)$_2$</td>
<td>14700(101)</td>
<td>17500(385)</td>
<td>43</td>
</tr>
<tr>
<td>Ni(Sacsac)$_2$</td>
<td>14890(330)</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
bdt = ethylene - 1, 2 dithiolato  
ptt = propene - 3 - thione 1-thiolato  
OEtsassac = O-ethyl thioacetate  
Sacsac = dithioacetylacetonato  
taa = monothioacetylacetonato

In Ni(taa) absorption maxima at 19000-25000 cm\(^{-1}\) have been attributed to charge transfer transition\(^{(45)}\).

The tetracyanonickelate(II) ion is the most extensively studied square planar complex of nickel(II). The electronic spectrum is characterized by d-d bands at 31000-32000 cm\(^{-1}\) and charge transfer bands at 33000-37000 cm\(^{-1}\).

In the present work, the absorption spectra of said ligands and their metal chelates were recorded in U.V. and I.R. region. The NMR spectra are recorded as well.

Ultra-Violet Spectra:

2-hydroxy, 5-methylacetophenonhydrazone  
and 2-hydroxy-5-methylpropiophenonehydrazone  
were dissolved in dichloromethane and their u.v. absorption spectra were recorded using Carey-2000 U.V. -visible spectrophotometer.  
Similarly the u.v. spectra of the chelates
of Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Fe\(^{2+}\) and Fe\(^{3+}\) dissolved in dichloromethane were also recorded. (Fig. 11 to 22).

Absorption spectra of ligands in ultra-violet region shows three absorption peaks at 374-364 nm, 315-325 nm and 275-265 nm. The absorption curves of copper chelates show weak absorption peaks at 265, 290. The nickel complexes show absorption bands at 260 nm and 332 nm. However the absorption spectra of chelates of cobalt, ferrous and ferric show the peaks at 290-300 nm, 328-332 nm and 380-388 nm but does not give any clearcut idea.

**Infra-red Spectra:**

The infra-red spectrum provides a rich array of absorption bands in contrast to (compared to) only few absorption bands observed in the u.v. and visible region for most organic compounds. Although, all the bands in the I.R. spectrum can not be accurately assigned but those that can, provide rich informations about the structure of the molecules.
Interpretation of I.R. spectrum is not a simple matter. Bands may be obscured by the superimposition of other bands and overtones may appear at just twice the frequency of fundamental bands. The absorption band of a particular group may be shifted by various structural features - conjugation, electron withdrawal by neighbouring substituent, angle strain, hydrogen bonding etc.

If strong intramolecular hydrogen bonding occurs, for example, to a carbonyl group, then a relatively sharp band is found at about 3200 cm\(^{-1}\). If, on the other hand, hydrogen bonding is inhibited by the presence of large group in the ortho position\(^{(46-48)}\), the absorption occurs in the region 3650-3600 cm\(^{-1}\).

O-Phenols usually have a band at 1255-1240 cm\(^{-1}\) and addition a band at 1320 cm\(^{-1}\), due to C-O stretching and O-H stretching band between 3200-3600 cm\(^{-1}\). However the N-H stretching vibration of the group C=N-H occurs in the region 3400-3300 cm\(^{-1}\). \(^{(49-51)}\)
For oximes and iminies \((52-55)\) the \(C=N\) stretching vibration occurs in the region \(1690-1620\ \text{cm}^{-1}\).

Conjugated cyclic systems containing \(C=N\) have a band of variable intensity due to the stretching vibration in the region \(1660-1480\ \text{cm}^{-1}\).

A band which is weak, except for conjugated compounds is observed at \(1685-1650\ \text{cm}^{-1}\) due to the \(C = N\) stretching vibration, the frequency of the band being increased in ring strained situation.\((56)\)

Phenols show a strong, broad band due to \(C - O\) stretching at about \(1230\ \text{cm}^{-1}\).\((57)\)

The \(C-O\) stretching vibration for \(P\)-mono substituted phenols \((58)\) i.e. the strongest band in the region \(1300-1200\ \text{cm}^{-1}\), increase in frequency with electron withdrawing ability of the substituent.

Amides of the type \(-CO - NH-NH_2\) \((59)\) have a number of medium intensity bands in the region \(3350-3180\ \text{cm}^{-1}\), due to the \(NH\) and
NH₂ streching vibrations. A medium intensity band due to the (band) deformation of the NH₂ group occurs at 1635-1600 cm⁻¹.

Interactions between ring C = C and C = N streching vibrations result in two strong medium intensity absorptions which occur at 1615-1575 and 1520-1465 cm⁻¹. (60)

Infrared spectra of ligands and their metal chelates were recorded using Prkin-Elmer-1310 infrared spectrophotometer. Samples were analysed in mineral oil mull, on sodium chloride cells. (Fig. 23 to 34).

Matching of the I.R. spectra of the ligands with that of the metal chelates, provides useful confirmation for formation of M-C bands.

The presence of a broad intense band between 3600-3200 cm⁻¹ in spectra of 2-hydroxy-5-methylacetophenonehydrazone (Fig. 23) and 2-hydroxy-5-methylpropiophenonehydrazone (Fig. 29) indicates the presence of O-H group showing H-...
bonding but the absence of this absorption band in the spectrum of all the chelates suggest that it is involved in the chelate formation giving M-O bond with removal of hydrogen of phenolic 0-H group and other linkage is through nitrogen atom of N-NH$_2$ group giving M-N bond and hence the I.R. absorption data supports the following structure of the chelate.

\[ \text{Chemical Structure} \]

(A)

The conclusion drawn from the I.R. spectra are given in tabular form and supports the above structural details. It gives C=C, C-C, N-H, C=N stretching bands.
I.R. Spectra of 2-hydroxy-5-methylacetophenone-hydrazone [Fig. 23]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Frequencies</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3600-3200 cm(^{-1})</td>
<td>broad band due to O-H stretching mode (shows intramolecular H-bonding)</td>
</tr>
<tr>
<td>B</td>
<td>3380 cm(^{-1})</td>
<td>sharp band due to N-H stretching mode.</td>
</tr>
<tr>
<td>C</td>
<td>2880 cm(^{-1})</td>
<td>It is due to Aliphatic C-H stretching mode which is superimposed on N-H stretching mode.</td>
</tr>
<tr>
<td>D</td>
<td>1640 cm(^{-1}) &amp; 1580 cm(^{-1})</td>
<td>It is due to C-N stretching mode which is superimposed on N-H stretching mode.</td>
</tr>
<tr>
<td>E</td>
<td>1250 cm(^{-1}) &amp; 1050 cm(^{-1})</td>
<td>weak bands due to C=O stretching mode.</td>
</tr>
</tbody>
</table>
### I.R. Spectra of Copperbis-2-hydroxy-5-methylaceto-phenonehydrazone [Fig. 24]

<table>
<thead>
<tr>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>D</td>
</tr>
<tr>
<td>E</td>
</tr>
<tr>
<td>F</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Frequencies</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600-3200 cm$^{-1}$</td>
<td>No broad band between 3600-3200 cm$^{-1}$ shows that H of O-H group is involved in chelate formation with metal.</td>
</tr>
<tr>
<td>3350 cm$^{-1}$</td>
<td>Sharp band due to N-H stretching mode</td>
</tr>
<tr>
<td>2880 cm$^{-1}$</td>
<td>It is due to Aliphatic C-H stretching mode which superimposed on N-H stretching mode.</td>
</tr>
<tr>
<td>1585 cm$^{-1}$ &amp; 1550 cm$^{-1}$</td>
<td>It is due to C=N stretching mode which superimposed on N-H bending (compared to that of ligand slightly shifted)</td>
</tr>
<tr>
<td>950 cm$^{-1}$</td>
<td>It is due to C-O stretching mode.</td>
</tr>
<tr>
<td>950 cm$^{-1}$</td>
<td>It is due to N-H stretching mode.</td>
</tr>
<tr>
<td>840 cm$^{-1}$</td>
<td>It is due to N-H stretching mode.</td>
</tr>
</tbody>
</table>
I.R. Spectra of Nickel-bis-2-hydroxy-5-methylaceto-phenonehydrazone [Fig. 25]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Frequencies</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>No broad band (3600 - 3200 \text{ cm}^{-1})</td>
<td>This shows that (H) of O-H group is involved in chelate formation with metal.</td>
</tr>
<tr>
<td>B</td>
<td>3350 \text{ cm}^{-1}</td>
<td>Sharp band due to N-H stretching mode.</td>
</tr>
<tr>
<td>C</td>
<td>2880 \text{ cm}^{-1}</td>
<td>It is due to Aliphatic C-H stretching mode which is superimposed on N-H stretching mode.</td>
</tr>
<tr>
<td>D</td>
<td>1620 \text{ cm}^{-1} and 1570 \text{ cm}^{-1}</td>
<td>It is due to C=N stretching mode which is superimposed on N-H bending (compared to that of ligand slightly shifted).</td>
</tr>
<tr>
<td>E</td>
<td>1300 \text{ cm}^{-1} and 1250 \text{ cm}^{-1} and 930 \text{ cm}^{-1}</td>
<td>These may be due to C-O stretching mode.</td>
</tr>
<tr>
<td>F</td>
<td>840 \text{ cm}^{-1}</td>
<td>It is due to N-H stretching mode.</td>
</tr>
</tbody>
</table>
I.R. Spectra of Cobaltbis-2-hydroxy-5-methylaceto-phenonehydrazone [Fig. 26]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Frequencies</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>No broad band between 3600-3200 cm(^{-1})</td>
<td>This shows that 'H' of O-H group is involved in chelate formation with metal.</td>
</tr>
<tr>
<td>B</td>
<td>2880 cm(^{-1})</td>
<td>It is due to Aliphatic C-H stretching mode which is superimposed on N-H stretching mode.</td>
</tr>
<tr>
<td>C</td>
<td>1580 cm(^{-1})</td>
<td>It is due to C=N stretching mode, which is superimposed on N-H bending (compared to that of ligand slightly shifted).</td>
</tr>
<tr>
<td>D</td>
<td>1300 cm(^{-1})</td>
<td>These may be due to C-O stretching mode.</td>
</tr>
<tr>
<td>E</td>
<td>840 cm(^{-1})</td>
<td>It is due to N-H stretching mode.</td>
</tr>
</tbody>
</table>
I.R. Spectra of Ferrous-2-hydroxy-5-methylaceto-phenonehydrazone [Fig. 27]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Frequencies</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>No broad band between 3600 - 3200 cm⁻¹</td>
<td>This shows that H of O-H group is involved in chelate formation with metal</td>
</tr>
<tr>
<td>B</td>
<td>2880 cm⁻¹</td>
<td>It is due to Aliphatic C-H stretching mode which is superimposed on N-H stretching mode.</td>
</tr>
<tr>
<td>C</td>
<td>1580 cm⁻¹</td>
<td>It is due to C=N stretching mode which is superimposed on N-H bending (compared to that of ligand slightly shifted).</td>
</tr>
<tr>
<td>D</td>
<td>1300 cm⁻¹</td>
<td>These may be due to C-O stretching mode.</td>
</tr>
<tr>
<td></td>
<td>1250 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>840 cm⁻¹</td>
<td>It is due to N-H stretching mode.</td>
</tr>
</tbody>
</table>
I.R. Spectra of Ferric-2-hydroxy-5-methylaceto-phenonshydrazone [Fig. 28]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Frequencies</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>No broad band in chelate formation with metal.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3600-3200 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2880 cm⁻¹</td>
<td>It is due to Aliphatic C-H stretching mode which is superimposed on N-H stretching mode.</td>
</tr>
<tr>
<td>C</td>
<td>1620 cm⁻¹ &amp; 1570 cm⁻¹</td>
<td>It is due to C=N stretching mode which is superimposed on N-H bending (compared to that of ligand slightly shifted).</td>
</tr>
<tr>
<td>D</td>
<td>1300 cm⁻¹, 1250 cm⁻¹, 880 cm⁻¹</td>
<td>They may be due to C-O stretching mode.</td>
</tr>
<tr>
<td>E</td>
<td>840 cm⁻¹</td>
<td>It is due to N-H stretching mode.</td>
</tr>
</tbody>
</table>

...227
I.R. Spectra of 2-hydroxy-5-methylpropiophenone-hydrazone [Fig. 29]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Frequencies</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3600 - 3200 cm(^{-1})</td>
<td>Broad band due to O-H stretching mode (shows intramolecular H-bending).</td>
</tr>
<tr>
<td>B</td>
<td>2880 cm(^{-1})</td>
<td>It is due to Aliphatic C-H stretching mode which is superimposed on N-H stretching mode.</td>
</tr>
<tr>
<td>C</td>
<td>1630 cm(^{-1})</td>
<td>It is due to C=N stretching mode which is superimposed on N-H bending mode.</td>
</tr>
<tr>
<td>D</td>
<td>1300 cm(^{-1}) and 1020 cm(^{-1})</td>
<td>Weak bands due to C-O stretching mode.</td>
</tr>
</tbody>
</table>
I.R. Spectra of Copper-bis-2-hydroxy-5-methylpropio-phenonehydrazone [Fig. 30]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Frequencies</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>No broad band between 3600-3200 cm⁻¹</td>
<td>This shows that H of O-H group is involved in chelate formation with metal.</td>
</tr>
<tr>
<td>B</td>
<td>2880 cm⁻¹</td>
<td>It is due to C-H stretching mode which is superimposed on N-H stretching mode.</td>
</tr>
<tr>
<td>C</td>
<td>1570 cm⁻¹</td>
<td>It is due to C=N stretching mode which superimposed on N-H bending (compared to that of ligand the band is slightly shifted).</td>
</tr>
<tr>
<td>D</td>
<td>1350 cm⁻¹</td>
<td>These may be due to C=O stretching mode.</td>
</tr>
<tr>
<td></td>
<td>1300 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1250 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1070 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>830 cm⁻¹</td>
<td>It is due to N-H stretching mode.</td>
</tr>
</tbody>
</table>
I.R. Spectra of Nickel-bis-2-hydroxy-5-methylpropio-phenonehydrazone [Fig. 31]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Frequencies</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>No broad band between 3600-3200 cm(^{-1})</td>
<td>This shows that 'H' of O-H group is involved in chelate formation with metal.</td>
</tr>
<tr>
<td>B</td>
<td>2880 cm(^{-1})</td>
<td>It is due to C-H stretching mode which is superimposed on N-H stretching mode.</td>
</tr>
<tr>
<td>C</td>
<td>1650 cm(^{-1})</td>
<td>It is due to C=N stretching mode which is superimposed on N-H bending (compared to that of ligand the band is slightly shifted).</td>
</tr>
<tr>
<td></td>
<td>1570 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1350 cm(^{-1})</td>
<td>These may be due to C-O stretching mode.</td>
</tr>
<tr>
<td></td>
<td>1300 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1250 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>830 cm(^{-1})</td>
<td>It is due to N-H stretching mode.</td>
</tr>
</tbody>
</table>
I.R. Spectra of Cobalt-bis-2-hydroxy-5-methylpropio-phenonehydrazone [Fig. 32]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Frequencies</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>No broad band</td>
<td>This shows that H of 0-H group is involved in chelate formation with metal. 3600-3200 cm⁻¹</td>
</tr>
<tr>
<td>B</td>
<td>2880 cm⁻¹</td>
<td>It is due to C-H stretching mode which is superimposed on N-H bending mode.</td>
</tr>
<tr>
<td>C</td>
<td>1570 cm⁻¹</td>
<td>It is due to C=N stretching mode which is superimposed on N-H bending (compared to that of ligand slightly shifted).</td>
</tr>
<tr>
<td>D</td>
<td>1300 cm⁻¹</td>
<td>They may be due to C-O stretching mode. 1250 cm⁻¹ 1225 cm⁻¹ 1040 cm⁻¹</td>
</tr>
<tr>
<td>E</td>
<td>840 cm⁻¹</td>
<td>It is due to N-H stretching mode.</td>
</tr>
</tbody>
</table>
### I.R. spectra of ferrous-2-hydroxy-5-methylpropio-phenonehydrazone [Fig. 33]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Frequencies</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>No broad band between 3600-3200 cm⁻¹</td>
<td>This shows that H' of O-H group is involved in chelate formation with metal.</td>
</tr>
<tr>
<td>B</td>
<td>2880 cm⁻¹</td>
<td>It is due to C-H stretching mode which is superimposed on N-H bending mode.</td>
</tr>
<tr>
<td>C</td>
<td>1650 cm⁻¹</td>
<td>It is due to C=N stretching mode which is superimposed on N-H bending (compared to that of ligand slightly shifted).</td>
</tr>
<tr>
<td>D</td>
<td>1300 cm⁻¹, 1250 cm⁻¹, 1040 cm⁻¹</td>
<td>They may be due to C-O stretching mode.</td>
</tr>
<tr>
<td>E</td>
<td>805 cm⁻¹</td>
<td>It is due to N-H stretching mode.</td>
</tr>
</tbody>
</table>
I.R. Spectra of Ferric-2-hydroxy-5-methylpropio-phenonehydrazone [Fig. 34]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Frequencies</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>No broad band 3600-3200 cm(^{-1})</td>
<td>This shows that H of O-H group is involved in chelate formation with metal.</td>
</tr>
<tr>
<td>B</td>
<td>2880 cm(^{-1})</td>
<td>It is due to C-H stretching mode which superimposed on N-H bending mode.</td>
</tr>
<tr>
<td>C</td>
<td>1640 cm(^{-1})</td>
<td>It is due to C=N stretching mode which superimposed on N-H bending (compared to that of ligand slightly shifted)</td>
</tr>
<tr>
<td>D</td>
<td>1300 cm(^{-1}) 1160 cm(^{-1}) 1040 cm(^{-1})</td>
<td>They may be due to C-O stretching mode.</td>
</tr>
</tbody>
</table>
The majority of investigations in the NMR of coordination compounds have utilized proton NMR. Due to the relative unimportance of the paramagnetic terms in the shielding of protons, proton spectra differ from virtually all other NMR spectra. Most proton resonances are found in a region of 10 ppm of the magnetic field. The narrow span of proton resonances, however, is generally not a serious problem in distinguishing protons which are in different magnetic environments. On a properly tuned 100 MHz spectrometer, proton resonances will rarely be broader than 0.5 Hz, while the entire span of 10 ppm represents 1000 Hz.

If the chemical shifts among these protons are less than about seven times their coupling constants to one another, higher order spectra results, the resonances of which can be difficult to analyze and are sometimes unresolvable one from another. Thus the ethylenic proton resonances of a coordinated ethylenediamine will often appear as a single
broad resonance even though the individual protons
may be magnetically nonequivalent.

A related situation is encountered in the
tris-salicylaldimino Co(III) and tris-pyrrole-2-
alldimino Co(III) complexes\(^{(61)}\).

![Chemical Structures](image)

In these cases the steric disposition of the
nitrogen substituents in the cis forms destabilizes
them to an extent such that they cannot be detected
in the proton NMR spectra and are probably absent
altogether. The trans isomers are unambiguously
identified by the three equally intense signals
of the \(N\-CH_3\) group in (B) and the \(H - C = N\) group
in (C). The secondary splittings of the methyl signals
in (B) are due to spin coupling with the azomethine
protons. This result illustrates the point that
the separate chemical shifts of non-equivalent chelate ring substituents may be beyond the limits of resolution. (62)

In a spectra of the bis (N, N' - diethylamino- troponeimino) Ni(II) complex the resonances are so widely separated by the interaction of the unpaired electrons with the protons that the spectrum is of first order simplicity. Closer examination of the individual resonances show that the line widths are still so narrow that spin-spin coupling can be detected, a point which makes all resonances readily assignable. Even when the ethyl groups are replaced by β-naphthyl groups first order spectra observed, in sharp contrast to the spectrum of the free ligand. (63)
In principle, measurement of the nuclear magnetic resonance of paramagnetic molecules allows measurement of the delocalized spin density over the ligand and gives information on the MO nature of the ground state. (64)

Nickel (II) complexes have been particularly studied by this technique because: (i) the electron relaxation time and/or the characteristic exchange time are favourable, (ii) in most cases, especially in octahedral complexes, the pseudocontact shift, which originates from magnetic anisotropy effects,
can be neglected in comparison to the Fermi Contact Shift due to the coupling of the nuclear spin with the unpaired spin density on the nucleus (65-70) while no theoretical approach has been found to be valid to account completely for the spin delocalization in nickel (II) complexes. Several trends have, however, been justified within a valence bond formalism.

Proton NMR spectra of Co(III) complexes of ethylenediamine and (-) propylenediamine in $D_2O - D_2SO_4$ solution at $100 \text{ MHz}$ show NH signals at $5.22\delta$ to $5.52\delta$ (71-72).

*N-ethylbenzylamine give rise* absorption band of NH at $1.1 \text{ ppm}$ (79).

*P-Phenetidine (P-Ethoxyaniline) give rise* absorption band of NH$_2$ at $3.2 \text{ ppm}$ (73).

*p-Toluidine give rise* absorption band of NH$_2$ at $3.3 \text{ ppm}$ (73).

*β - Phenylethylamine give rise* absorption band of NH$_2$ at $1.0 \text{ ppm}$ (73).

*α - Phenylethylamine give rise* absorption band of NH$_2$ at $1.4 \text{ ppm}$ (73).
A carbonyl group in the ortho position to -OH group shifts the phenolic proton absorption downfield to the range of about 10 to 12 $\delta$ because of intramolecular hydrogen bonding. Thus O-hydroxy acetophenone shows a peak at about 12.05 $\delta$ almost completely invariant with concentration.(74)

It is rarely possible to deduce a structural formula solely from the nuclear magnetic resonance spectrum of a compound. The more important factors necessary for the exact interpretation of a spectrum are line positions, intensities and precise nature of spin-spin multiplets.

In the present work, the H-NMR spectra of ligands and their chelates with Cu(II), Ni(II) and Co(II) were taken on VARIAN-XL - 200 MHz NMR. The ligands and the metal-chelates were dissolved in CDCl$_3$ or CDCl$_3$+1% DMSO-d$_6$ and TMS was used as internal standard. (Fig. 35-42)

(a) NMR Spectra of Copper-bis-2-hydroxy-5-methyl-acetophenonehydrazone (Fig. 35)

It shows a signal at 7.4 $\delta$ due to ring protons. A signal at 2.65 $\delta$ is due to two methyl groups which are merged. Due to poor solubility of this chelate, other signals may be due to noise.

...239
(b) **NMR Spectra of Nickel-bis-2-hydroxy-5-methyl-acetophenonehydrazone. (Fig. 36)**

It shows signals around 7.3 \( \delta \) due to ring protons. Two methyl groups are merged giving signals between 2.2 \( \delta \) and 2.5 \( \delta \). A signal of \( \text{NH}_2 \) group may be superimposed with the \( -\text{CH}_3 \) signals.

(c) **NMR Spectra of Cobalt-bis-2-hydroxy-5-methyl-acetophenonehydrazone. (Fig. 37)**

It shows a signals around 7.3 \( \delta \) due to ring protons. Two methyl groups are giving signals around 2.3 \( \delta \) and 2.6 \( \delta \). A signal at 1.6 \( \delta \) may be for \( \text{NH}_2 \) group.

(d) **NMR Spectra of Copper-bis-2-hydroxy-5-methyl-propiophenonehydrazone. (Fig. 38)**

It shows signals around 7.3 \( \delta \) due to ring protons. A signal at 2.3 \( \delta \) is due to (aromatic) methyl group. The signals around 1.3 \( \delta \) and 1.8 \( \delta \) are due to \( -\text{CH}_3 \) and \( -\text{CH}_2 \) of ethyl group. A signal around 3.3 \( \delta \) may be due to \( -\text{NH}_2 \) group.
(e) **NMR Spectra of Nickel-bis-2-hydroxy-5-methylpropiophenonehydrazone. (Fig. 39)**

Due to poor solubility of this chelate, signals shows poor resolution. We get a signal for ring protons around 7.4 \( \delta \) and signals of aromatic methyl group and ethyl group are merged at 2.6 \( \delta \).

(f) **NMR Spectra of Cobalt-bis-2-hydroxy-5-methylpropiophenonehydrazone. (Fig. 40)**

It shows signals around 7.3 \( \delta \) due to ring protons. A signal at 2.7 \( \delta \) is due to (aromatic) methyl group. The signals at 1.3 \( \delta \) and 2.5 \( \delta \) are due to \(-CH_2\) and \(-CH_3\) group of ethyl group respectively. A signal at 3.3 \( \delta \) may be due to \(-NH_2\) group.

(g) **NMR Spectra of 2-hydroxy-5-methylacetophenonehydrazone. (Fig. 41)**

It shows signals for ring protons around 7.0 \( \delta \) and two methyl groups around 1.3 \( \delta \) and 2.3 \( \delta \). It shows a signal for \( NH_2 \) around 3.7 \( \delta \). A signal of 1H at 12.5 \( \delta \) may be due to OH group.
NMR spectra of 2-hydroxy-5-methylpropiophenone-hydrazone. (Fig. 42)

It shows signal for ring protons around 7.2 δ. A signal around 2.3 δ is due to (aromatic) methyl group. The signals around 1.3 δ and 1.6 δ are due to -CH₃ and -CH₂ of ethyl group. A signal around 3.1 δ may be due to -NH₂ group. A signal of 1H at 13.2 δ may be due to -OH group.

NMR spectra give supporting evidence for the structure of the chelate (Structure A - Page: 220).

Although high frequency of 200 MHz used increases the sensitivity but due to paramagnetic nature of the complexes, pseudocontact interactions, steric disposition of the Nitrogen-substituents and possible existence of equilibrium between planar and tetrahedral structures in solution, make detail analysis of spectra rather not very conclusive.
Spectra of 2-hydroxy 5-methyl acetoephone hydrazone in dichloromethane

BASELINE SCAN 1

SCAN RATE (NM/SEC): 2.0
SPECTRAL BAND WIDTH (NM): 1.00
EFFECTIVE PERIOD (SEC): 0.5
Fig. 12

Spectra of

Copper bis 2-hydroxy 5-methyl acetophenone hydrazone

in dichloromethane

BASELINE SCAN 1

SCAN RATE (NM/SEC): 2.0
SPECTRAL BAND WIDTH (NM): 1.00
EFFECTIVE PERIOD (SEC): 0.5
Fig. 13

Spectra of

Nickel bis 2-hydroxy 5-methyl acetophenone hydrazone

in dichloromethane

BASELINE SCAN 1

SCAN RATE (NM/SEC): 2.0
SPECTRAL BAND WIDTH (NM): 1.00
EFFECTIVE PERIOD (SEC): 0.5
Fig. 14

Spectra of

Cobalt bis 2-hydroxy 5-methyl acetophenone hydrazone

in dichloromethane

BASELINE SCAN 1

SCAN RATE (NM/SEC): 2.0
SPECTRAL BAND WIDTH (NM): 1.00
EFFECTIVE PERIOD (SEC): 0.5

WAVELENGTH (nm)
Fig. 15

Spectra of

Ferrous 2-hydroxy 5-methyl acetophenone hydrazone

in dichloromethane

Baseline scan

Scan rate (NM/SEC): 2.0
Spectral band width (NM): 1.00
Effective period (SEC): 0.5

WAVELENGTH (nm)
Fig. 16

Spectra of

Ferric 2-hydroxy 5-methyl acetophenone hydrazone

in dichloromethane

BASELINE SCAN 1

SCAN RATE (NM/SEC): 2.0
SPECTRAL BAND WIDTH (NM): 1.00
EFFECTIVE PERIOD (SEC): 0.5
Spectra of

2-hydroxy 5-methyl propiophenone hydrazone

in dichloromethane

BASELINE SCAN 1

SCAN RATE (NM/SEC): 2.0
SPECTRAL BAND WIDTH (NM): 1.00
EFFECTIVE PERIOD (SEC): 0.5

220.0 276.0 332.0 388.0 444.0 500.0
WAVELENGTH (nm)
Spectra of

Copper bis 2-hydroxy 5-methyl propiophenone hydrazone

in dichloromethane

Fig. 18

Baseline Scan 1

Scan Rate (NM/SEC): 2.0
Spectral Band Width (NM): 1.00
Effective Period (SEC): 0.5

Wavelength (nm)
Fig. 19

Spectra of

Nickel bis 2-hydroxy 5-methyl propiophenone hydrazone

in dichloromethane

BASELINE SCAN 1

SCAN RATE (NM/SEC): 2.0
SPECTRAL BAND WIDTH (NM): 1.00
EFFECTIVE PERIOD (SEC): 0.5
Fig. 20

Spectra of

Cobalt bis 2-hydroxy 5-methyl propiophenone hydrazone

in dichloromethane

Baseline Scan 1

Scan Rate (nm/sec): 2.0
Spectral Band Width (nm): 1.00
Effective Period (sec): 0.5

Wavelength (nm)

220.0 276.0 332.0 388.0 444.0 500.0
Fig. 21

Spectra of
Ferrous 2-hydroxy 5-methyl propiophenone hydrazone
in dichloromethane

BASELINE SCAN 1

SCAN RATE (NM/SEC): 2.0
SPECTRAL BAND WIDTH (NM): 1.00
EFFECTIVE PERIOD (SEC): 0.5
Spectra of Ferric 2-hydroxy 5-methyl propiophenone hydrazone in dichloromethane

Baseline Scan 1

Scan Rate (NM/SEC): 2.0
Spectral Band Width (NM): 1.00
Effective Period (SEC): 0.5

220.0 255.0 278.0 332.0 388.0 444.0 500.0
Wavelength (nm)
I.R. Spectra of
2-hydroxy 5-methyl acetophenone hydrazone

Fig: 23
Infrared Spectra of
Copper bis 2-hydroxy 5-methyl acetophenone hydrazones

Figs 24
L.R. Spectra of

Cobalt bis 2-hydroxy 5-methyl acetoephone hydrazone.
The spectra of ferric 2-hydroxy 5-methyl acetophenone hydrazone is depicted in the figure. The graph shows various absorption bands labeled A, B, C, D, and E, indicating specific vibrational modes of the compound. The wavenumber range is from 4,000 to 1,700 cm⁻¹.
I.R. Spectra of Copper bis 2-hydroxy 5-methyl propiophenone hydrazone.
Figure 31

**I. R. Spectra of**

**Nickel bis 2-hydroxy 5-methyl propiophenone hydrazone**
I.R. Spectra of

Cobalt bis 2-hydroxy 5-methyl propiophenone hydrazone

FIG: 32

TRANSMISSION (%)
Fig: 34

I.r. Spectra of Ferric 2-hydroxy 5-methyl propiophenone hydrazone.
Fig. 35
NMR Spectra

\[
\text{H}_3\text{C} - \text{O} - \text{M}^{1/2} - \text{C} = \text{N} - \text{NH}_2 - \text{CH}_3
\]
Fig: 36
NMR Spectra

\[
\begin{align*}
 & \text{H}_3\text{C} \\
 & \text{C} = \text{N} \cdot \text{NH}_2
\end{align*}
\]

\[
\text{O} \quad \text{M/2} \quad \text{CH}_3
\]

M = N

+2

8.4 15.8 167.5

12 18 24 30 36 42 48 54 60
Fig: 37
NMR Spectra

\[
\begin{aligned}
&\text{H}_3\text{C} &\text{C} = \text{N} &\text{NH}_2 \\
&\text{CH}_3 \\
&\text{M} = \text{Co}^{+2}
\end{aligned}
\]
Fig. 38
NMR Spectra

$M = C_{H_2}^+$

$\text{C}_2\text{H}_5$

$\text{C} = \text{N}_2\text{H}_2$

$\text{H}_3\text{C}$
Fig. 39

NMR Spectra

\[
\begin{align*}
\text{H}_3\text{C} & \text{O}\text{M/2} \\
\text{C} = \text{N} & \text{NH}_2 \\
\text{C}_2\text{H}_5 &
\end{align*}
\]

\[M = \text{Ni}^{2+}\]
Magnetic Susceptibility:

The use of magnetic properties as a potent tool for the determination of structures of transition metal complexes, has increased to a considerable extent in the past few years. The study of magnetic property has been found useful in the investigation of the structure of complex compounds. Both the spin and the orbital motion of an electron are sources of magnetic moment. The total magnetic moment of a material is then made up of two components, one due to the electron spin and the other due to the orbital motion of unpaired electrons. In such cases, the spin contribution becomes important, and the orbital contribution being small enough is neglected. Hence the greater portion of the orbital contribution gets cancelled by the interaction of these materials with other ions in solution or in the crystalline state. The most common examples are the ions of the transition group elements. The magnetic moment is given by the following relation.
B. M. = \( \frac{e \hbar}{4 \pi mc} \)

where, \( \hbar = \) Plank's Constant
\( e = \) electronic charge
\( m = \) mass of electron
\( c = \) velocity of light

\( B. M. = \) Bohr magneton
\( = 9.27 \times 10^{-21} \quad \text{erg/gauss} \)

Now, the magnetic moment is related to the molar susceptibility \( (X_M) \) by the Langevin expression:

\[
X_M = \frac{N e \mu B^2}{3KT}
\]

where, \( N = \) Avogadro's number
\( K = \) Boltzman Constant
\( T = \) Absolute temperature
\( B = \) Magnetic Induction.

For most cases, permanent moment is given by the expression:

\[
\mu B = \left( 4S(S+1) + L(L+1) \right)^{3/2}
\]

Where, \( S = \) the resultant spin angular momentum
\( L = \) the resultant orbital angular momentum.
For those cases where the orbital contribution is small and can be neglected, the moment then becomes:

\[ \mathcal{U}_B = \left( 4S(S+1) \right)^{1/2} \]

The number of unpaired electrons \( n \) = 2S.

Thus the magnetic moment may be related directly to the number of unpaired electrons by the expression:

\[ \mathcal{U}_B = \left( n(n+2) \right)^{1/2} \]

The measurement of molar susceptibility \( \chi_M \), of molecules of transition metal is of great importance in arriving at conclusions pertaining the number of unpaired electrons and the structure of chelates. Calvin et al. (75) correlated the values of \( \chi_M \) (in emu) with number of unpaired electrons and showed that

\[ \chi_M \propto n(n+2) \]

Where \( n \) = number of unpaired electrons.

In the light of this, they established the structures of several bis salicylaldimines chelates of Cu\(^{+2}\), Ni\(^{+2}\) and Co\(^{+2}\). This was also supported by X-ray analysis. Mellor and Craig (76) pointed out...
that the chelates of the type given below are cova-
lent or ionic.

\[
\begin{array}{c}
\text{N} \\
\text{M} \\
\text{O} \\
\text{O}
\end{array}
\]

\[=N\text{M}\text{O}\]

\[\text{N}^{-}\]

\[\text{e.g. Co}^{2+} \text{ chelates of above type are reported to be paramagnetic having tetrahedral structure}^{(77-80)}.\]
\[\text{Ni}^{2+} \text{ chelate of the above type are found to be diamagnetic. There are no unpaired electron and hence possess square planar structure indicating } \text{dsp}^2 \text{ hybridization state of the metal}^{(75, 79, 80)}. \text{ The above generalisation was confirmed by x-ray analysis of Nickel-bis-Salicylaldoximes as well as other chelates of Ni}^{2+}. \text{ (75,81,82,83)}\]

The study of divalent copper is of great interest since Cu\(^{2+}\) ion contains one more electron than that in Ni\(^{2+}\). Although the electronic configuration of Cu\(^{2+}\) suggests that SP\(^3\) hybridization must result, Pauling\(^{84}\) pointed out that placing the unpaired electron in a 4P orbital requires no loss of energy.
and this might result in the stronger $\text{dsp}^2$ hybridization. Obviously magnetic data would be of little value in this case. However, the x-ray studies indicate\(^{(81)}\) that $\text{Cu}^{+2}$ complexes are not planar. In an arrangement where 'd' orbital is not available tetra-hedral complex formation occurs.

<table>
<thead>
<tr>
<th>Cu$^{+2}$ configuration</th>
<th>3d</th>
<th>4s</th>
<th>4p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal</td>
<td>1↑</td>
<td>1↑</td>
<td>1↑</td>
</tr>
<tr>
<td>Square planar $\text{dsp}^2$</td>
<td>1↑</td>
<td>1↑</td>
<td>1↑</td>
</tr>
<tr>
<td>Tetrahedral $\text{sp}^3$</td>
<td>1↑</td>
<td>1↑</td>
<td>1↑</td>
</tr>
</tbody>
</table>

Ray and Sen\(^{(85)}\) showed that penetration complexes have an unpaired electron in lower lying orbital and hence have a lower magnetic moment and proposed a square planar structure having $\text{dsp}^2$ hybridization for such chelates. The square planar structure of $\text{Cu}^{+2}$ chelates of the above type is also supported by the study of Cotton effect\(^{(86)}\). Kato, Jonassen and Fanning \(^{(87)}\) reviewed $\text{Cu}^{+2}$ complexes with 'sub-
normal magnetic moments and attributed this to a
dimeric structure with Cu-Cu linkage which gives
an absorption band at 375 nm \((88, 89)\).

Molar Susceptibility \(\chi_M\) can be measured by
Gouy's method. This method involves the use of cylin­

mical specimen of the material in a region of non-
uniform field. The force acting on the rod in air
after necessary correction is given by the expression:

\[
F = \frac{1}{4}A(K_1 - K_2)(H^2 - H_0^2) + \mathcal{G}
\]

Where
- \(A\) = Cross-section area of the specimen
- \(H\) = Magnetic field
- \(H_0\) = Field in the region out of the influence
  of magnet
- \(K_1\) = Volume susceptibility of the specimen
- \(K_2\) = Volume susceptibility of air
- \(\mathcal{G}\) = Tube correction (constant of the tube)

In practice \(H_0\) is very small or zero. Therefore
\(A(H^2 - H_0^2)\) is constant for a given set and hence
can be expressed as:

\[
\ldots 280
\]
where, \( \varphi \) = constant for the displaced air

\[ \varphi = 0.029 \times 10^{-6} \times \text{specimen volume} \]

\( \beta \) = Tube calibration constant if \( H \) is constant

\( W \) = Weight of substance

\( F \) = Difference in weight of substance on application of magnetic field i.e. observed force

\( P \) = Difference in weight of empty tube on application of magnetic field.

The magnetic susceptibility of the chelates was measured using the above relation at a constant temperature.

Magnetic balance is frequently calibrated with the aid of substances of known susceptibility. The Gouy balance is often calibrated with water, provided the substance under investigation has low susceptibility. The magnetic susceptibility of water at 20°C may be assumed to \(-0.720 \times 10^{-6}\) unit per gram, but water should be free from dissolved air.
The calibration of the Gouy balance has been investigated by Angus \(^{(90,91)}\) who pointed out that the water, as a calibrating agent, had some deficiencies and therefore he recommended Benzene as calibrating agent. However, it has been pointed out \(^{(92)}\) that oxygen is fairly soluble in Benzene. A carefully prepared solution of nickel chloride is useful as a calibrating agent. This solution has been investigated by Brant \(^{(93)}\); by Carbera, Moles and Guzman \(^{(94)}\); Weiss and Bruins \(^{(95)}\) and by Nettleton and Sugden. \(^{(96)}\)

In the present work, de-ionised distilled water and mercury tetrathiocyanato-cobaltate were used for calibration.

In the broad outline of the crystal field theory, the energy levels of 'd' orbitals of transition metal ions undergo splitting in an octahedral or tetrahedral field. The octahedral splitting undergoes further deviation leading to a square planar structure according to Jahn-Tellor theorem which says that if a non-linear molecule has a degenerate state, then there is at least one vibrational coordinate along which a distortion can occur so as to remove the degeneracy.
The electron of 'd' orbitals of metal ions can be assigned configuration in the light of energy sequence and Hund's rule. Such configurations help to predict only spin values of paramagnetic moment. Obviously the observed values deviate due to several other factors. In case of $\text{HL}_4$ complex of $\text{Ni}^{2+}$ there can be a tetrahedral or a square planar structure. The former has two unpaired electrons resulting in $\mu_{\text{eff}} = 2.83$ B.M. while the latter has no unpaired electron hence it is a diamagnetic in nature.
Experimental

The chelates of (1) 2-hydroxy-5-methylaceto phenonehydrazone and (2) 2-hydroxy-5-methylpropio phenonehydrazone with Cu$^{+2}$, Ni$^{+2}$, Co$^{+2}$, Fe$^{+2}$ and Fe$^{+3}$ were crystallised from chloroform and dried at 100°-110°C.

The Gouy tube was thoroughly cleaned with cromic acid, washed and rinsed several times with distilled water and then with acetone. The tube was then dried in an air-oven maintained at about 100°-110°C.

The specimen tube was suspended carefully on the hook between poles of a magnet so that each end was maintained in a region of uniform field. In order to fix the height of the specimen column at which the field is nearly zero, the specimen tube was filled with a mercury tetrathio cyanato cobaltate to different heights and the magnitudes of the force in the magnetic field were measured at these heights. The height beyond which there was no change in the magnetitude of
the force acting on the mercury tetrathiocyanato cobaltate was fixed as the height of the specimen column. A circular mark was etched to indicate the height. The tube was then accurately weighed without and with magnetic field. This procedure was repeated and the mean value of such readings was obtained. The difference between the two weights: (i) with the magnetic field and (ii) without the magnetic field gave a measure of the force on the tube in the presence of the magnetic field. The tube was then removed from the suspension and filled with the specimen under investigation upto the mark. The tube was then resuspended and the electromagnetic box was closed. The readings were taken in the same manner as for the empty tube. Five such readings were taken. The tube was then cleaned and dried. Measurements on the same specimen were made with different packings.

In this investigation values of magnetic susceptibilities have been determined with the help of a standard substance. The choice of the standard substance was made after carefully examining the substance used by different workers for calibration. The standard substances used were water and mercury tetrathiocyanate cobaltate.
It has been shown earlier that the susceptibility per unit mass $x$ is given by:

$$x = \frac{\infty + \beta F'}{W}$$

where $\infty$ = constant for displaced air

$\beta$ = tube calibration constant

$W$ = weight of substance

$F' = F + p$ (where $F$ = observed force)

Determination of $\infty$ and $\beta$:

$\infty$ is the product of volume susceptibility of air and the volume occupied by the specimen.

It has been determined by Angus and Tilston.\[97\]

Accordingly,

$$\infty = 0.029 \times 10^{-6} \times \text{specimen volume}$$

$$= 0.029 \times 10^{-6} \times 0.4662$$

$$= 0.0135 \times 10^{-6}$$

$\beta$ is given by the expression:

$$\beta = \frac{2}{l} \frac{1}{(l_2^2 + l_1^2)}$$
It required determination of 'l', the length of the specimen column. \( H_1 \) and \( H_2 \) are the respective field strengths at the two ends of the specimen tube. It is difficult to determine these quantities with a great accuracy. Hence in practice to overcome this shortcoming is determined by using a standard substance of known magnetic susceptibility, i.e., mercury tetrathiocyanate cobaltate.

The gram susceptibility of mercury tetrathiocyanate cobaltate was found by using the following equation:

\[
x = \frac{\beta \, dw + \infty}{w}
\]

\[
\beta = \frac{x \cdot w - \infty}{dW}
\]

where \( w = \) weight of mercury tetrathiocyanate cobaltate in gm = 0.6962 gm.

\[
dW = \delta w - \delta \text{(in mg.)} = 9.1 \text{ mg. (4 amp.)}
\]

\[
= 17.3 \text{ mg. (6 amp.)}
\]

...287
\( \delta w \) = weight in difference of mercury tetra-thiocyanate cobaltate on application of magnetic field

\[ \alpha_C = 0.0067 \text{ gm. (4 amp)} \]

\[ \alpha_C = 0.0134 \text{ gm. (6 amp)} \]

\( \delta \) = weight in difference of empty tube on application of magnetic field

\[ \alpha_C = -0.0024 \text{ gm. (4 amp)} \]

\[ \alpha_C = -0.0039 \text{ gm. (6 amp)} \]

\( \chi \) = the gram susceptibility of mercury tetra-thiocyanate cobaltate at room temperature (30°C).

\[ \chi = 15.94 \times 10^{-6} \text{ emu.} \]

\( \beta \) was calculated and was found 1.2180 x 10^{-6} at 4 amp. and 0.6407 x 10^{-6} at 6 ampere.

From the stand-point of the magnetic susceptibilities, the present work envisages the investigation of the structure of chelates of Cu^{+2}, Ni^{+2}, Co^{+2}, Fe^{+2} and Fe^{+3} formed with ligands (i) 2-hydroxy-5-methylacetophenonehydrazone and (ii) 2-hydroxy-5-methylpropiophenonehydrazone.
1. (a) Cu$^{+2}$ chelate with 2-hydroxy-5-methylacetophenonehydrazone gave molar susceptibility, $X_M = 1879 \times 10^{-6}$ emu at 4 ampere current and $1291 \times 10^{-6}$ emu at 6 ampere current and the paramagnetic moment calculated were found to be 2.14 B.M. and 1.78 B.M. respectively.

(b) Similarly Cu$^{+2}$-chelate with 2-hydroxy-5-methylepropiophenonehydrazone gave molar susceptibility, $X_M = 1968 \times 10^{-6}$ emu at 4 ampere current and $1378 \times 10^{-6}$ emu at 6 ampere current and the paramagnetic moment calculated were found to be 2.14 B.M. and 1.84 B.M. respectively.

Cu$^{+2}$ gives ML$_4$ complexes which can be tetrahedral or square-planer. In either case the d$^9$ electron configuration in splitted energy level will have one unpaired electron. Hence only spin value of $\mu_{\text{eff}} = 1.73$ B.M. is not conclusive regarding its structure. The deviation from expected value of 1.73 B.M. may be due to orbital contribution. Distorted tetragonal structure may be assigned to the Cu$^{+2}$-chelate.
2. The chelates of $\text{Ni}^{2+}$ investigated were found to be diamagnetic leading to the conclusion that they have square planner structure.

3. (a) $\text{Co}^{2+}$-chelate with 2-hydroxy-5-methylacetophenonehydrazone gave molar susceptibility, $X_M = 1861 \times 10^{-6}$ emu at 4 ampere current and $1476 \times 10^{-6}$ emu at 6 ampere current and the paramagnetic moment calculated were found to be 2.13 B.M. and 1.99 B.M. respectively.

(b) In the same way $\text{Co}^{2+}$-chelate with 2-hydroxy 5-methylpropiophenonehydrazone gave molar susceptibility $X_M = 2008 \times 10^{-6}$ emu at 4 ampere current and $1565 \times 10^{-6}$ emu at 6 ampere current and the paramagnetic moment calculated were found to be 2.22 B.M. and 1.96 B.M. respectively.

These values show that they are low spin complex with one unpaired electron.

4. (a) $\text{Fe}^{2+}$-chelate with 2-hydroxy-5-methylacetophenonehydrazone gave molar susceptibility $X_M = 13628 \times 10^{-6}$ emu at 4 ampere current and $9893 \times 10^{-6}$ emu at 6 ampere current and
the paramagnetic moment calculated were found to be 5.77 B.M. and 4.92 B.M. respectively.

(b) Fe$^{+2}$-chelate with 2-hydroxy-5-methylpropiophenonehydrazone gave molar susceptibility $X_M = 14217 \times 10^{-6}$ emu at 4 ampere current and $10515 \times 10^{-6}$ emu at 6 ampere current and the paramagnetic moment calculated were found to be 5.89 B.M. and 5.07 B.M. respectively.

Fe$^{+2}$-chelates were found to be paramagnetic.

5. (a) Fe$^{+3}$-Chelates with 2-hydroxy-5-methylacetophenonehydrazone gave molar susceptibility, $X_M = 26044 \times 10^{-6}$ emu at 4 ampere current and $22706 \times 10^{-6}$ emu at 6 ampere current and the paramagnetic moment calculated were found to be 7.98 B.M. and 7.45 B.M. respectively.

(b) Fe$^{+3}$-chelate with 2-hydroxy-5-methylpropiophenonehydrazone gave molar susceptibility $X_M = 27066 \times 10^{-6}$ emu at 4 ampere current and $23554 \times 10^{-6}$ emu at 6 ampere current and the paramagnetic moment calculated were found to be 8.12 B.M. and 7.59 B.M. respectively.

Fe$^{+3}$-chelates were found to be paramagnetic.
In nutshell, the above observations with respective conclusions are tabulated below.

Table -
Magnetic Susceptibilities of metal chelates

<table>
<thead>
<tr>
<th>No.</th>
<th>Metal Chelates</th>
<th>X x 10^{-6} in emu</th>
<th>X_M x 10^{-6} in B.M.</th>
<th>Magnetic Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Copper-bis-2-hydroxy-5-methylacetophenone-hydrazone</td>
<td>4.8237</td>
<td>1879</td>
<td>2.14 Paramagnetic</td>
</tr>
<tr>
<td>2</td>
<td>Copper-bis-2-hydroxy-5-methylpropiophenone-hydrazone</td>
<td>4.4732</td>
<td>1868</td>
<td>2.14 Paramagnetic</td>
</tr>
<tr>
<td>3</td>
<td>Nickel-bis-2-hydroxy-5-methylacetophenone-hydrazone</td>
<td></td>
<td></td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>4</td>
<td>Nickel-bis-2-hydroxy-5-methylpropiophenone-hydrazone</td>
<td></td>
<td></td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>5</td>
<td>Cobalt-bis-2-hydroxy-5-methylacetophenone-hydrazone</td>
<td>4.8363</td>
<td>1862</td>
<td>2.13 Paramagnetic</td>
</tr>
<tr>
<td>6</td>
<td>Cobalt-bis-2-hydroxy-5-methylpropiophenone-hydrazone</td>
<td>4.8633</td>
<td>2008</td>
<td>2.22 Paramagnetic</td>
</tr>
<tr>
<td>7</td>
<td>Ferrous-2-hydroxy-5-methylacetophenone-hydrazone</td>
<td>62.229</td>
<td>13628</td>
<td>5.77 Paramagnetic</td>
</tr>
<tr>
<td>No</td>
<td>Metal Chelates</td>
<td>$X \times 10^{-6}$</td>
<td>$X_M \times 10^{-6}$</td>
<td>$\mu_{\text{eff}}$</td>
</tr>
<tr>
<td>----</td>
<td>---------------------------------------------------</td>
<td>---------------------</td>
<td>----------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>8</td>
<td>Ferrous-2-hydroxy-5-methylpropiophenonehydrazone.</td>
<td>61.019</td>
<td>14217</td>
<td>5.89</td>
</tr>
<tr>
<td>9</td>
<td>Ferric-2-hydroxy-5-methylacetophenonehydrazone.</td>
<td>118.9216</td>
<td>26044</td>
<td>7.98</td>
</tr>
<tr>
<td>10</td>
<td>Ferric-2-hydroxy-5-methylpropiophenonehydrazone.</td>
<td>116.1619</td>
<td>27066</td>
<td>8.13</td>
</tr>
</tbody>
</table>

...293
Table -

**Magnetic Susceptibilities of metal chelates**

Current 6 ampere

Absolute temperature 303°K

<table>
<thead>
<tr>
<th>No.</th>
<th>Metal Chelates</th>
<th>$X \times 10^{-6}$</th>
<th>$\chi_m \times 10^{-6}$</th>
<th>$\mu_{\text{eff}}$</th>
<th>Magnetic Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Copper-bis-2-hydroxy-5-methylacetophenone-hydrazone</td>
<td>3.3154</td>
<td>1291.4</td>
<td>1.78</td>
<td>Para magnetic</td>
</tr>
<tr>
<td>2.</td>
<td>Copper-bis-2-hydroxy-5-methylpropiophenone-hydrazone</td>
<td>3.3014</td>
<td>1378.3</td>
<td>1.84</td>
<td>Para magnetic</td>
</tr>
<tr>
<td>3.</td>
<td>Nickel-bis-2-hydroxy-5-methylacetophenone-hydrazone</td>
<td></td>
<td></td>
<td></td>
<td>Dia magnetic</td>
</tr>
<tr>
<td>4.</td>
<td>Nickel-bis-2-hydroxy-5-methylpropiophenone-hydrazone</td>
<td></td>
<td></td>
<td></td>
<td>Dia magnetic</td>
</tr>
<tr>
<td>5.</td>
<td>Cobalt-bis-2-hydroxy-5-methylacetophenone-hydrazone</td>
<td>3.8350</td>
<td>1475.9</td>
<td>1.99</td>
<td>Para magnetic</td>
</tr>
<tr>
<td>6.</td>
<td>Cobalt-bis-2-hydroxy-5-methylpropiophenone-hydrazone</td>
<td>3.750</td>
<td>1564.9</td>
<td>1.96</td>
<td>Para magnetic</td>
</tr>
<tr>
<td>No.</td>
<td>Metal Chelates</td>
<td>$X \times 10^{-6}$</td>
<td>$X_H \times 10^{-6}$</td>
<td>$\mu_{\text{eff}}$</td>
<td>Magnetic Type</td>
</tr>
<tr>
<td>-----</td>
<td>------------------------------------</td>
<td>--------------------</td>
<td>----------------------</td>
<td>---------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>7</td>
<td>Ferrous-2-hydroxy-5-methylacetophenone-hydrazone</td>
<td>45.1724</td>
<td>9892.8</td>
<td>4.92</td>
<td>Para magnetic</td>
</tr>
<tr>
<td>8</td>
<td>Ferrous-2-hydroxy-5-methylpropiophenone-hydrazone</td>
<td>45.1274</td>
<td>10514.7</td>
<td>5.07</td>
<td>Para magnetic</td>
</tr>
<tr>
<td>9</td>
<td>Ferris-2-hydroxy-5-methylacetophenone-hydrazone</td>
<td>103.6819</td>
<td>22706.3</td>
<td>7.45</td>
<td>Para magnetic</td>
</tr>
<tr>
<td>10</td>
<td>Ferric-2-hydroxy-5-methylpropiophenone-hydrazone</td>
<td>101.6910</td>
<td>23554.2</td>
<td>7.59</td>
<td>Para magnetic</td>
</tr>
</tbody>
</table>
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...301


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