This part of the thesis deals with the investigation on the composition and the structure of the chelates. The chelating agents salicylaldoxime and resacetophenone oxime and several salicylaldiamines \((I)\) possess some reactive system and the corresponding chelates \((II)\) are assigned the structure, based on experimental and theoretical considerations \((1-9)\).

\[
\begin{array}{c}
\text{(I)} \\
\text{(II)}
\end{array}
\]

\[R = \text{H, CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5\]

\[R_1 = -\text{OH}, -\text{C}_6\text{H}_5, -\text{C}_6\text{H}_4(\text{P})\text{NO}_2, -\text{C}_6\text{H}_4(\text{P})\text{O}_2\text{H}, -\text{C}_6\text{H}_4(\text{P})\text{C}_6\text{H}_3\text{Na}
-\text{C}_6\text{H}_4(\text{P})\text{CH}_3, -\text{C}_6\text{H}_4(\text{P})\text{CH}_2\text{CH}_3\]

In the present case, the composition has been determined on the basis of (i) elemental composition and (ii) the results of Job's method of continuous variation.
(i) Elemental Composition:

Several methods are adopted for determining the percentage of elements in a given chelate. The percentage of metals has been determined by weighing the oxide of the metal obtained on ignition of a known weight of the chelate(10-14).

The chelates prepared from (i) 2-hydroxy-4-chloro-5-methylacetophenone oxime and (ii) 2-hydroxy-4-chloro-5-methylpropiophenone oxime with Cu$^{2+}$, Ni$^{2+}$ and Fe$^{2+}$ were ignited and their complete oxidation was ensured by adding a drop of nitric acid to the residue and reheating. The resulting oxide was weighed and the percentage calculated. The chelates of palladium were also ignited in air and then resulting oxide was weighed and the percentage calculated.

In the case of Co$^{2+}$ chelates the residue after ignition was dissolved in hydrochloric acid and then cobalt was determined as cobalt anthranilate. The metal chelates were also quantitatively analysed for carbon and hydrogen by combustion. Nitrogen content was determined by the Kjeldahl’s method. The results are tabulated below:
<table>
<thead>
<tr>
<th>Compound</th>
<th>Carbon percent</th>
<th>Hydrogen percent</th>
<th>Nitrogen percent</th>
<th>Metal percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>7$H$</em>{10}$O$_2$NCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>54.13</td>
<td>5.01</td>
<td>7.01</td>
<td></td>
</tr>
<tr>
<td>Obtained</td>
<td>54.16</td>
<td>5.03</td>
<td>6.80</td>
<td></td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{12}$O$_2$NCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>56.20</td>
<td>5.62</td>
<td>6.55</td>
<td></td>
</tr>
<tr>
<td>Obtained</td>
<td>55.22</td>
<td>5.46</td>
<td>6.32</td>
<td></td>
</tr>
<tr>
<td>Cu(C$_7$H$_9$O$_2$NCl)$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>46.90</td>
<td>3.9</td>
<td>6.0</td>
<td>13.78</td>
</tr>
<tr>
<td>Obtained</td>
<td>46.95</td>
<td>3.2</td>
<td>6.6</td>
<td>13.50</td>
</tr>
<tr>
<td>Cu(C$<em>{10}$H$</em>{11}$O$_2$NCl)$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>49.1</td>
<td>4.5</td>
<td>5.7</td>
<td>13.01</td>
</tr>
<tr>
<td>Obtained</td>
<td>48.9</td>
<td>4.7</td>
<td>5.3</td>
<td>12.93</td>
</tr>
<tr>
<td>Ni(C$_7$H$_9$O$_2$NCl)$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>49.3</td>
<td>3.9</td>
<td>6.1</td>
<td>12.88</td>
</tr>
<tr>
<td>Obtained</td>
<td>47.0</td>
<td>3.2</td>
<td>6.8</td>
<td>12.94</td>
</tr>
<tr>
<td>Ni(C$<em>{10}$H$</em>{11}$O$_2$NCl)$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>49.6</td>
<td>4.5</td>
<td>5.7</td>
<td>12.14</td>
</tr>
<tr>
<td>Obtained</td>
<td>49.7</td>
<td>4.1</td>
<td>5.9</td>
<td>12.22</td>
</tr>
<tr>
<td>Co(C$_7$H$_9$O$_2$NCl)$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>47.34</td>
<td>3.9</td>
<td>6.1</td>
<td>12.93</td>
</tr>
<tr>
<td>Obtained</td>
<td>47.30</td>
<td>3.11</td>
<td>5.9</td>
<td>13.01</td>
</tr>
<tr>
<td>Co(C$<em>{10}$H$</em>{11}$O$_2$NCl)$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>49.6</td>
<td>4.5</td>
<td>5.7</td>
<td>12.18</td>
</tr>
<tr>
<td>Obtained</td>
<td>49.3</td>
<td>4.7</td>
<td>5.3</td>
<td>12.04</td>
</tr>
<tr>
<td>Fe(C$_7$H$_9$O$_2$NCl)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>42.47</td>
<td>3.5</td>
<td>5.5</td>
<td>21.97</td>
</tr>
<tr>
<td>Obtained</td>
<td>42.53</td>
<td>3.1</td>
<td>5.9</td>
<td>22.08</td>
</tr>
</tbody>
</table>
The results show that in the case of Cu\textsuperscript{+2}, Ni\textsuperscript{+2}, Pd\textsuperscript{+2} and Co\textsuperscript{+2} chelates correspond to the formula in which the metal-ligand ratio is 1:2 and for Fe\textsuperscript{+2} the metal-ligand ratio is 1:1.

(II) Job's Method of Continuous Variation:

The metal chelates ratio was also established by colorimetric method as the chelates obey Beer's law (Ref. Part I). In a reaction of the type:

\[ M + nA \xrightarrow{\text{K}} M\text{A}_n \]

in which the complex \( M\text{A}_n \) is formed from the ions \( M \) and \( A \). Solutions of \( M \) and \( A \) of the same concentration are mixed in varying proportions:

\[ M + nA \xrightarrow{\text{K}} M\text{A}_n \]

(1)

\[ K = \frac{[M\text{A}_n]}{[M][A]^n} \]

(2)
where 'K' represents activities (molar concentrations).

If we impose the restriction

\[(M) + (A) = C.\]

where 'C' is a constant, it can be shown that when concentration \[MA_n\] is maximum,

\[
\frac{(A)}{(n)} = n
\]  

or

\[
\frac{d(MAn)}{d(n)} = 0
\]

In other words, for a constant total concentration of a metal and chelating agent, the concentration of the chelate is the greatest, when a metal and a chelating agent are brought together in the same ratio in which they exist in the chelates. This can be evaluated in terms of optical density and the extinction coefficient. If a solution of a ligand 'A' is mixed with a solution of a metal ion 'M', so that the total molar concentration of the ligand plus the metal is maintained constant, the following equation would hold:

\[
K = (Mt) - (MAn)
\]  

\[
(A) = (At) - n(MAn)
\]  

\[
(Mt) + (At) = \text{constant}
\]
where \((Mt)\) and \((At)\) are the total molarities of the species containing 'M' and 'A' respectively. The optical density of the solution 'D' at a given wavelength represents the total absorption of all the species in the solution:

\[
D = \mu \sum E_i(M) + E_2(A) + E_3(MA_n) \tag{8}
\]

where \(\mu\) is the length of the light path through the solution and \(E_1, E_2\) and \(E_3\) are the respective extinction coefficients of \(K, A\) and \(MA_n\). Let us now introduce a function \(\mathcal{Y}\), which represents the difference in the optical density 'D' of equation (9) and the corresponding optical density that would have resulted if no reaction occurred when the solutions of \(K\) and \(A\) were mixed.

\[
\mathcal{Y} = \mu \left[ E_1(M) + E_2(A) + E_3(MA_n) \right] - \mu (E_1Mt + E_2At) \tag{9a}
\]

where the chelating ligand is optically transparent, equation (9) may be simplified by assuming \(E_2 = 0\). If the cell path is 1 cm, the function \(\mathcal{Y}\) is defined by the relationship.

\[
\mathcal{Y} = E_1(M) + E_3(MA_n) - E_1Mt \tag{10}
\]

Differentiation of the equation (10) with respect to \(At\) and combination with the differentiated form of equation (9) gives

\[
\frac{d\mathcal{Y}}{dAt} = (E_3 - E_1) \frac{d(M/n)}{dAt} \tag{11}
\]
Equation (11) represents the base for the Job's method of continuous variation. It shows that

\[ \frac{dy}{dx} = 0 \]

If the chelate is the only coloured substance present, the optical density of the solution is proportional to the concentration of the chelate, hence a graph of optical density against molar concentration of the metal and the ligand would give a curve with the maximum at the composition corresponding to the formula of the chelate. If the substances are present which absorb light in the same region as does the chelate, it is necessary to make an allowance for the same. Job (15) 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 UO\(_2\)\(^{2+}\) chelates with several salicylic acid derivatives. Foley and Anderson (16), Turner and Anderson (17), Yoo and Harvey (18), Ross and Mellon (19) employed this method for iron and Kojic acid. Pandya (9) used this method to determine the composition of orthohydroxyketoxime chelates with Cu\(^{2+}\), Ni\(^{2+}\) and Co\(^{3+}\).

In the present work this method has been adopted as follows. The solution of the same molar strength of the metal ions and the ligands were prepared. The solutions of the metal ions and
the ligands were mixed in the molar ratio of 9:1, 8:2, ..., 1:9 buffered to the required pH. The chelate formed was extracted with chloroform and diluted to the same volume and the optical density of the solution measured. The measurements were carried out using a "Erma Japan Photoelectric Colorimeter." The results and the graphs are given in the experimental. The results show that in the case of Cu$^{+2}$, Ni$^{+2}$ and Co$^{+2}$ there is a maxima when the metal ligand molar ratio is 1:2.

The above results indicate that the chelates of these ligands with Cu$^{+2}$, Ni$^{+2}$, Co$^{+2}$, Fe$^{+2}$ and Pd$^{+2}$ should have the following structure.

![Chemical structure diagram]

\[ R = \text{CH}_3, \text{C}_2\text{H}_5 \]

\[ H = \text{Cu}^{+2}, \text{Ni}^{+2}, \text{Co}^{+2}, \text{Pd}^{+2} \]

The results show in all the cases there is a maxima when the metal ligands ratio is 1:1. The above results indicate that the chelates of these ligands with Fe$^{+2}$ would have the following structure:
Flegl and Bondi (20) and Cox, Wardlaw and Webster have reported that at a higher pH salicylaldoxime gives 1:1 chelate with Cu$^{2+}$. This is probably due to the predominance of the structures (II) and (III).

$R = -\text{CH}_3, -\text{C}_2\text{H}_5$

(I)  (II)  (III)

(IV)
The reagents under investigation form complexes with Fe\(^{+2}\)

at a lower pH having metal-ligand ratio 1:1 based on structure(IV).

EXAMINATION OF ABSORPTION SPECTRA:

For a metal chelate, two types of light absorption occur
in the visible and ultra-violet regions (i) the absorption
arising from an electronic transition in a conjugated system
in which a metal may or may not have taken part and (ii) the
absorption resulting from electronic transition in the metal
ion itself. The former which is due to the ligand, is very
strong and is known as 'K' type absorption. It has been investi­
gated in several cases (22-24). The absorption bands characteris­
tic of a metal ion alone are usually relatively weak and they
result from the so-called forbidden transition in the electron
shells of the metal itself. This transition corresponds to an
electron shift in the unfilled 'd' orbitals of the transition
metals may be observed in a free metal ion as well as in a
metal chelate, although they are frequently intensified by
coordination of the metal ion. Calvin and co-workers(23,24)
observed absorption in the visible region due to the forbidden
transition and also 'K' type absorption bands characteristics of
the ligand in the ultra-violet region as for example Cu\(^{+2}\) ethyl
acetoacetate and other substituted \(\beta\)-diketochelates. The intensity
of the absorption characteristic of Cu\(^{+2}\) ion is much weaker than
that of the "K" type of bands; Calvin and coworkers (23, 24) concluded from the experimental data that the influence of a metal ion on the characteristic absorption is much weaker than the ligand which has a large conjugated system.

The chelates of 2-hydroxy-4-chloro-5-methylacetophenone oxime and 2-hydroxy-4-chloro-5-methylpropiophenone oxime with Cu$^{+2}$, Ni$^{+2}$, Co$^{+2}$, Fe$^{+2}$ and Pd$^{+2}$ have been purified and the absorption of the chelates has been determined in the visible and infra-red regions. The results and the graphs are given in the experimental.

The transition metal cations are characterised by their absorption in the visible and near U.V. range of spectra and position of absorption band considerably changes according to stericchemical forms and ligand strength with the same solvent. In case of complexes in nonpolar solvents the origin of the absorption band may be due to electron transition from lower to higher \(d\) orbitals or may be due to charge transfer. In the light of Frank-Condon principles 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 which the electron is transferred from ligand to metal. The absorption bands due to charge transfer transition are intense. Generally such bands are at higher frequency compared to \(d\)-\(d\) transition spectra. In case of \(d\)-\(d\) transition the selection rule may be obeyed:
(i) The transitions, in which the number of unpaired electron changes in going from ground to excited state, are spin or multiplicity-forbidden. (ii) Those transitions, in which the symmetry of the orbital does not change, are forbidden.

The d-d transition in the complexes of transition metal cations is forbidden, because these orbitals have centre of symmetry and it does not change on transition of electron from lower to the higher level. However, there is some distortion in the orbital symmetry due to ligand field or due to solvent effect. Hence, the partial hybridisation of d and p orbitals takes place in the excited state. As a result, weak absorption is observed in many cases.

$\text{ML}_6$ complex of $\text{Ni}^{2+}$ exhibits a simple spectrum involving 3 spin allowed transitions in the range of 7000-13000, 11000-20000, and 19000-27000 cm$^{-1}$. In addition, two spin forbidden bands are also observed. $\text{ML}_4$ square planar complexes of $\text{Ni}^{2+}$ gives strong absorption bands between 15000-25000 and 23000-30000 cm$^{-1}$. On the other hand $\text{ML}_4$ tetrahedral complex of $\text{Ni}^{2+}$ gives one less intense band nearly at 16000 cm$^{-1}$ (25-29).

The absorption spectra of 2-hydroxy-4-chloro-5-methyl acetophenone oxime and 2-hydroxy-4-chloro-5-methylpropiophenone oxime with $\text{Ni}^{2+}$ gives no absorption below 10000 cm$^{-1}$; this is characteristic of square planar complex (30). The absorption bands in the range 15000 - 25000 cm$^{-1}$ and 23000-30000 cm$^{-1}$, are however, weak in consonance with the square planar structure.
of these complexes. Cu$^{+2}$ is a$^9$ cation which gives an absorption band nearly at $16000 \text{ Cm}^{-1}$ with a broad tail in infra-red region in ML$_4$ complexes. The nature of the absorption bands generally depends on the extent of axial metal ligand interaction. The complexes of 2-hydroxy-4-chloro-5-methylacetophenone oxime, and 2-hydroxy-4-chloro-5-methylpropiophenone oxime with Cu$^{+2}$ give one absorption band in the range 600-650 nm which is characteristic for ML$_4$ square planar complexes.

**INFRARED SPECTRA:**

In contrast to the relatively few absorption peaks observed in the ultraviolet region for most organic compounds and complexes, the infrared spectrum provides a rich array of absorption bands. Many of the absorption bands can not be assigned accurately; those that can, however, provide a wealth of structural information about a molecule.

Comparison of the IR spectra of the ligands with that of complexes can provide very useful information regarding the nature of the bond in complexes. In the metal ketoxime complexes, the metal ion is bound between oximino group and o-hydroxy group. The exact linking is ascertain by above comparison.

Singh and Gupta(31) reported that the IR spectrum of 2-4-dihydroxyvalerophenone oxime shows the bands in the OH stretch region assigned to three different types of hydroxyl
groups present in the ligand. The band at 3500 cm⁻¹ remains unaffected in the complex, hence it may be due to the 4-hydroxy group. The position of second band at 3380 cm⁻¹ which is disappeared in the spectra of complexes and it may be due to an intramolecularly hydrogen bonded OH, a clear possibility in the case of 2-hydroxy group. The third band observed at 3280 cm⁻¹ remains unaffected on coordination and it may be due to the oximino hydroxyl group, through nitrogen (and not hydroxy group) is indicated by lowering of the C = N band from 1650 cm⁻¹ in the ligand to 1600 cm⁻¹ in the complexes. This is also supported by a slight down-ward shift (32,33) of N-O of (ligand 990 cm⁻¹, complexes 970 cm⁻¹). In case of palladium chelate with same ligand, Singh and Gupta (31) have observed new bands in the spectra of complex at 580 cm⁻¹ which they assigned to metal nitrogen and metal oxygen stretching modes respectively (34,35).

In case of the IR spectra of 2-hydroxy-4-chloro-5-
methylacetoephone oxime and 2-hydroxy-4-chloro-5-methylpropio-
phenone oxime two bands in the OH stretch region assigned to
two different types of hydroxyl groups present in the ligands.
The first band observed at 3390 cm⁻¹ - 3380 cm⁻¹ is disappeared
in the complexes of Cu⁺² , Ni⁺² , Co⁺² , Fe⁺² and Pd⁺² which
may be due to intramolecularly hydrogen bonded OH group i.e.
2-hydroxy group. The second band at 2960 cm⁻¹ - 2908 cm⁻¹
remains unaffected in the complexes is assigned to oximino
The coordination of oximino group through nitrogen and not through hydroxyl group is indicated by lowering of the C = N band from 1615 cm⁻¹ - 1605 cm⁻¹ in the ligands to 1600 cm⁻¹ - 1590 cm⁻¹ in the complexes. This is supported by a slight downward shift of N-Oκ (Ligands 922 cm⁻¹ - 910 cm⁻¹, complexes 950 cm⁻¹ - 910 cm⁻¹) see Fig. No. 33 to 44.

On the basis of above data following structure may be assigned to the complex.

\[ R = \text{-CH}_3, \text{-C}_2\text{H}_5 \]

**Infrared absorption frequencies (cm⁻¹) of oximes and metal oxime complexes:**
<table>
<thead>
<tr>
<th></th>
<th>2-OH group</th>
<th>-OH of oximino group</th>
<th>C = N stretching</th>
<th>( \gamma ) Ho</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-hydroxy-4-chloro-5-methylaceto phenone oxine</td>
<td>3390</td>
<td>2950</td>
<td>1615</td>
<td>922</td>
</tr>
<tr>
<td>Cu-complex</td>
<td>disappeared</td>
<td>2920</td>
<td>1595</td>
<td>945</td>
</tr>
<tr>
<td>Ni-complex</td>
<td>disappeared</td>
<td>2900</td>
<td>1600</td>
<td>950</td>
</tr>
<tr>
<td>Co-complex</td>
<td>disappeared</td>
<td>2908</td>
<td>1590</td>
<td>925</td>
</tr>
<tr>
<td>Fe-complex</td>
<td>disappeared</td>
<td>2910</td>
<td>1590</td>
<td>925</td>
</tr>
<tr>
<td>Pd-complex</td>
<td>disappeared</td>
<td>2910</td>
<td>1595</td>
<td>950</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>2-OH group</th>
<th>-OH of oximino group</th>
<th>C = N stretching</th>
<th>( \gamma ) Ho</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-hydroxy-4-chloro-5-methyl propiophenone oxine</td>
<td>3380</td>
<td>2960</td>
<td>1605</td>
<td>910</td>
</tr>
<tr>
<td>Cu-complex</td>
<td>disappeared</td>
<td>2910</td>
<td>1590</td>
<td>915</td>
</tr>
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<td>Ni-complex</td>
<td>disappeared</td>
<td>1960</td>
<td>1595</td>
<td>918</td>
</tr>
<tr>
<td>Co-complex</td>
<td>disappeared</td>
<td>2910</td>
<td>1595</td>
<td>915</td>
</tr>
<tr>
<td>Fe-complex</td>
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<td>2900</td>
<td>1595</td>
<td>910</td>
</tr>
<tr>
<td>Pd-complex</td>
<td>disappeared</td>
<td>2910</td>
<td>1590</td>
<td>910</td>
</tr>
</tbody>
</table>

**Magnetic Susceptibility:**

All materials exhibit some degree of polarisation on orientation when placed in a magnetic field. Magnetic field may have three kinds of interaction with chemical substances.

1. **Diamagnetic polarisation**: It is produced in all substances
due to an accelerating effect of a field on electrons and produces a very weak induced field opposite to the applied.

(ii) **Paramagnetic polarisation**: It is produced in some substance by an interaction of an applied field with the permanent dipole in an atom or molecule. Hence atoms or molecules tend to line up in such a manner that their own magnetic field reinforces the applied field. A paramagnetic polarisation is much greater than a diamagnetic polarisation.

(iii) **Ferromagnetic polarisation**: In a few instances, the fields within materials are increased tremendously (perhaps a millionfold or more). Substances exhibiting this behaviour are ferromagnetic and are comparatively rare.

The paramagnetic field has been found useful in the investigation of chemical bonds and the structure of the molecules. The most important source of this effect is the magnetic moment which is associated with the spin of electron. It has been pointed out that 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 of two components, the so-called spin and angular contributions. These contributions are due to the presence of unpaired electrons, but in many instances these unpaired electrons are in effect the outermost ones in the species under consideration and are not screened by other electrons. In such cases, the spin contribution becomes important, and the orbital contribution may be neglected. This
amounts to be a cancellation of the greater portion of the orbital contribution by the interaction of these materials with other ions in solution or in the crystalline state. The most common examples embrace ions of the transition group elements.

\[ B.M. = \frac{\epsilon \hbar}{4 \pi mc} \]

where

- \( \hbar = \text{Planck's constant} \)
- \( \epsilon = \text{electronic charge} \)
- \( m = \text{mass of electron} \)
- \( c = \text{the velocity of light} \)

\[ B.M. = \text{Bohr magneton} = 9.27 \times 10^{-21} \text{ erg/gauss}. \]

The magnetic moment is related to the molar susceptibility by the Langevin expression:

\[ M = \frac{N \mu_B^2}{3K T} \]

where

- \( N = \text{Avogadro's number} \)
- \( K = \text{Boltzmann constant} \)
- \( T = \text{Absolute temperature} \)

For many cases, permanent moment is given by the expression

\[ \mu_B = (4\pi \left( S + \frac{1}{2} \right) + L(L + 1) )^{1/2} \]

where

- \( S = \text{the resultant spin angular momentum} \)
- \( L = \text{the resultant orbital angular momentum} \)

For these cases where the orbital contribution is small and
can be neglected, the moment then becomes

$$\mu \Theta = \sqrt{4S(S + 1)} \frac{7}{2}$$

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

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

$$\mu \Theta = \sqrt{n(n + 2)} \frac{7}{2}$$

The measurement of \( \chi M \) of complexes of transition metal is of great importance in arriving at the number of unpaired electrons and the structure of chelates. Calvin and co-workers (36) pointed out that \( \chi M \) at 25°C for one unpaired electron is of the order \( 1260 \times 10^{-6} \) emu, for two unpaired electrons \( 3350 \times 10^{-6} \) emu and so on to values of \( 6290 \times 10^{-6} \), \( 10060 \times 10^{-6} \) and \( 14670 \times 10^{-6} \) emu for three, four and five unpaired electrons respectively. In the light of this they established the structures of several \( \text{Cu}^{+2} \), \( \text{Ni}^{+2} \) and \( \text{Co}^{+2} \) chelates of salicylalcoholxime which were also supported by x-ray analyses. Mellor and Craig (37) have pointed out that the chelates of the type below are covalent or ionic.


CO\(^{2+}\) chelates of above type are reported to be paramagnetic and hence tetrahedral or ionic octahedral (36-41). Ni\(^{2+}\) and Pd\(^{2+}\) chelates of the above type have been found to be diamagnetic having no unpaired electron and hence possess square planar structures indicating dsp\(^2\) hybridisation in metal valence bond (36, 40, 41). The above generalisation was confirmed by X-ray analyses of the bisalicylaldoximes and other such chelating agents of Ni\(^{2+}\) and Pd\(^{2+}\) and hence their trans-planar structures (36, 42-44).

The situation with dipositive copper is interest since Cu\(^{2+}\) ion contains one more electron than Ni\(^{2+}\). Although the electronic configuration of Cu\(^{2+}\), suggests that sp\(^3\) bonding must result, Pauling (45) pointed out that placing the unpaired electron in a 4p orbital requires no loss in energy. Hence the stronger dsp\(^2\) bonding might result. Obviously magnetic data would be of no value in this case. X-ray studies do indicate (42) however, that Cu\(^{2+}\) complexes are planar in arrangement. Where no ‘d’ orbitals are available, tetrahedral complex will result.

<table>
<thead>
<tr>
<th>II</th>
<th>Cu configuration</th>
<th>3d</th>
<th>4s</th>
<th>4p</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ionic</td>
<td>4↑↑↑↑↑↑↑↑↑↑↑</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Square planar dsp(^2)</td>
<td>4↑↑↑↑↑↑↑↑↑↑↑</td>
<td>1↑</td>
<td>1↑↑↑↑↑↑↑↑↑↑↑</td>
</tr>
<tr>
<td></td>
<td>Tetrahedral sp(^3)</td>
<td>4↑↑↑↑↑↑↑↑↑↑↑</td>
<td>1↑</td>
<td>1↑↑↑↑↑↑↑↑↑↑↑</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>II</th>
<th>Cu configuration</th>
<th>3d</th>
<th>4s</th>
<th>4p</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ionic</td>
<td>4↑↑↑↑↑↑↑↑↑↑↑</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Square planar dsp(^2)</td>
<td>4↑↑↑↑↑↑↑↑↑↑↑</td>
<td>1↑</td>
<td>1↑↑↑↑↑↑↑↑↑↑↑</td>
</tr>
<tr>
<td></td>
<td>Tetrahedral sp(^3)</td>
<td>4↑↑↑↑↑↑↑↑↑↑↑</td>
<td>1↑</td>
<td>1↑↑↑↑↑↑↑↑↑↑↑</td>
</tr>
</tbody>
</table>
Hay and Sen\(^{(46)}\) pointed out that penetration complexes have an unpaired electron in a lower lying orbital and hence have a lower magnetic moment (1.72 to 1.82 B.M.) and proposed a square planar covalent (\(\text{dsp}^2\) hybridisation) structure for such chelates. The square planar structure of \(\text{Cu}^{4+}\) chelates of the above type is also supported by a study of Cotton effect\(^{(47)}\). Kato, Jonassen and Fanning\(^{(48)}\) reviewed \(\text{Cu}^{4+}\) complexes with subnormal magnetic moments and attributed this to a dimeric structure with Cu-Cu bond and also related to Cu-Cu linkage to absorption bonds at 375 nm\(^{(49,50)}\).

\(\chi_M\) can be measured by the Faraday or Gouy's method, the latter being used by many workers to determine \(\chi_M\). This method involves the use of cylindrical specimen of the material in a region of nonuniform field. The force acting on the rod in air after necessary correction is given by the expression.

\[
F = \frac{1}{2} A (K_1 - K_2) \left( H^2 - H_0^2 \right) + \bar{F}
\]

A = Cross-sectional area of the specimen

\(H\) = Magnetic field

\(H_0\) = Field in region out of the influence of magnet

\(K_1\) = Volume susceptibility of the specimen

\(K_2\) = Volume susceptibility of the air

\(\bar{F}\) = 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
\[
\gamma C_10^{-6} = \frac{\beta F'}{W} + \frac{\infty}{W} \text{ emu.}
\]

\( F' = F + P \)

\( \infty = \text{constant for the displaced air} \)

\( = 0.029 \times 10^{-6} \times \text{specimen volume} \)

\( \beta = \text{tube calibration constant if } H \text{ is constant.} \)

\( W = \text{weight of substance} \)

\( F = \text{difference in weight of substance on application of magnetic field} \)

\( = \text{observed force} \)

\( P = \text{difference in weight of empty tube on application of magnetic field.} \)

The magnetic susceptibility of the chelates described in this thesis is measured using the above relation at a constant temperature. Deionised distilled water and mercury tetra-thiocyanato-cobaltate were used for calibration of the Gouy's tube. The results are tabulated in the experimental on pages 226 and 227.

In the broad outline of the Crystal field theory, the energy level of 'd' orbitals of transition metal ions undergoes splitting depending on the octahedral or tetrahedral orientation of ligands. The octahedral splitting undergoes the deviation due to the distortion as described by John Tellor and leads to square planar structure, particularly when the ligands on 'Z' axis are eliminated.
The electron present in 'd' orbitals of a given metal ion can be assigned configuration in the light of energy sequence and Hund's rule. Such a configuration helps to predict spin only value of paramagnetic moment. Obviously, the observed value deviates due to several other factors (vide infra). In case of ML₄⁺ complex of Ni²⁺, there can be a tetrahedral or square planar structure. The former will have two unpaired

\[ dx^2 - y^2 \]

\[ dx^2 + dy^2 \]

\[ dx'y' - dy' \]

\[ dx'y' + dy' \]

TETRAHEDRAL OCTAHEDRAL TETRAHEDRAL OCTAHEDRAL SQUARE PLANAR
electrons resulting in $\mu_{\text{eff}} \approx 2.83$ B.M. The latter will have no unpaired electron imparting diamagnetic nature. The chelates of Ni$^{2+}$ investigated in the present work have been found to be diamagnetic leading to the conclusion that they have square planar structure.

Cu$^{2+}$ cation gives ML$_4$ complexes which can be tetrahedral or square planar. In either case the configuration of $d^9$ electron in split level will have one unpaired electron leading to spin only value of $\mu_{\text{eff}} \approx 1.73$ B.M., hence precise conclusion for ML$_4$ chelates of Cu$^{2+}$ from magnetic data is not clear. The chelates of Cu$^{2+}$ with 2-hydroxy-4-chloro-5-methylacetophenone oxime and 2-hydroxy-4-chloro-5-methylpropiophenone oxime are paramagnetic having molar susceptibility ranging from $2926 \times 10^{-6}$ e.m.u. to $3025 \times 10^{-6}$ e.m.u. which give effective paramagnetic moment 1.83 to 1.99 at 4.0 amp. Current and molar susceptibility ranging from $2921 \times 10^{-6}$ e.m.u. to $3046 \times 10^{-6}$ e.m.u. give effective magnetic moment 1.80 to 1.91 B.M. at 6.0 amp. current.

Fe$^{2+}$ gives 1:1 neutral complex; $\mu_{\text{eff}}$ for 2-hydroxy-4-chloro-5-methylacetophenone oxime is 3.24 and that for 2-hydroxy-4-chloro-5-methylpropiophenone oxime is 3.06. The values are much higher than spin only value for two unpaired electrons. Figgis(52) explained the deviation of effective magnetic moment from the spin only value by spin orbital coupling which can mix in some of the higher levels having the same value as the ground state.
This gives the following generalisation in which $\lambda$ is the spin orbit coupling constant, which is negative for these cations with more than a half filled 3rd shell.

$$\mu = \mu_0 (1 - \frac{1}{\Delta})$$

where $\mu_0$ is the spin only moment.

$\Delta$ is a constant which depends upon spectroscopic ground state and with number of $d$ electrons; $\Delta (= 10 D)$ is the separation between the ground energy level and the level being mixed with, and $\lambda$ is the spin-orbit coupling constant.

Since both $\Delta$ and $\lambda$ are positive quantities, the observed moment will be greater when $\lambda$ is negative. This could explain higher values of $\mu$ spin free from $Fe^{+2}$. In these complexes out of four unpaired electrons of $Fe^{+2}$ free ion (two) might have been used for nearly covalent bonding with oxygen and nitrogen atoms one each of ligands. The remaining two unpaired electrons contribute to the magnetic properties. Even in these complexes the increasing field strength by increasing the current from 4 amp to 5 amp, there is a decline in magnetic susceptibility. As in case of copper these complexes show decreasing magnetic susceptibility due to increase in ligand strength of 2-hydroxy-4-chloro-5-methylacetophenone oxime and 2-hydroxy-4-chloro-5-methylpropionophenone oxime.
ESTIMATION OF COPPER AS COPPER OXIDE FROM ITS CHELATES:

Copper-2-hydroxy-4-chloro-5-methylacetophenone oxime (0.250 gm) was ignited in a covered crucible. The ignited mass was then treated with a drop of concentrated nitric acid and then excess of acid was evaporated off by heating the crucible over a low flame. The temperature was gradually raised to a dull red heat to ensure complete conversion of copper oxide. It was cooled and weighed as copper oxide. The same procedure was followed for copper-2-hydroxy-4-chloro-5-methylpropiophenone oxime. The results are tabulated below:

<table>
<thead>
<tr>
<th>Chelate</th>
<th>Weight of chelate ignited in gm.</th>
<th>Weight of CuO obtained in gm.</th>
<th>Percentage of metal Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(C₂H₄O₂Cl)₂</td>
<td>0.250</td>
<td>0.0396</td>
<td>13.78</td>
<td>13.60</td>
</tr>
<tr>
<td>Cu(C₁₀H₁₁O₂Cl)₂</td>
<td>0.250</td>
<td>0.0378</td>
<td>13.01</td>
<td>12.93</td>
</tr>
</tbody>
</table>

ESTIMATION OF NICKEL AS NICKEL OXIDE FROM ITS CHELATES:

Nickel-2-hydroxy-4-chloro-5-methylacetophenone oxime (0.250 gm) was ignited and treated as in the case of copper. It was cooled and weighed as nickel oxide. The same procedure was
followed for nickel-2-hydroxy-4-chloro-5-methylpropiophenone oxime. The results are tabulated below:

<table>
<thead>
<tr>
<th>Chelate</th>
<th>Weight of chelate ignited in gm.</th>
<th>Weight of CuO obtained in gm.</th>
<th>Percentage of calculated metal</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(C₉H₉O₂Cl)₂</td>
<td>0.250</td>
<td>0.0411</td>
<td>12.88</td>
<td>12.94</td>
</tr>
<tr>
<td>Ni(C₁₀H₁₁O₂Cl)₂</td>
<td>0.250</td>
<td>0.0383</td>
<td>12.14</td>
<td>12.22</td>
</tr>
</tbody>
</table>

**ESTIMATION OF COBALT ANTHRAILATE FROM THE CHELATES:**

Cobalt 2-hydroxy-4-chloro-5-methylacetophenone oxime (0.250 gm) was ignited in a covered crucible. The ignited mass was then treated with a drop of concentrated nitric acid. The excess of the acid was evaporated off by heating the crucible in presence of sulphuric acid with a 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, warmed up to boiling, the pH was adjusted between 3.5 to 4.5 and treated with a solution of sodium anthranilate (3 per cent) and the boiling continued for five minutes. It was then allowed to stand for 10 minutes, filtered through a sintered glass crucible and washed with a solution of sodium anthranilate (0.15 percent) followed by alcohol and dried at 105° to 110°C till constant
weight (Vogel: "A Text Book of Quantitative Inorganic Analysis", Longmans, 1960). The same procedure was followed for cobalt-2-hydroxy-4-chloro-5-methylpropiophenone oxime. The results are tabulated below:

<table>
<thead>
<tr>
<th>Chelate</th>
<th>Weight of chelate ignited in gm.</th>
<th>Weight of coanthanilate obtained in gm.</th>
<th>Percentage of metal Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(C$_7$H$_3$O$_2$HCl)$_2$</td>
<td>0.250</td>
<td>0.0395</td>
<td>12.93</td>
<td>13.01</td>
</tr>
<tr>
<td>Co(C$_7$H$_5$O$_2$HCl)$_2$</td>
<td>0.250</td>
<td>0.0389</td>
<td>12.18</td>
<td>12.04</td>
</tr>
</tbody>
</table>

**ESTIMATION OF FERROUS AS FERRIC OXIDE FROM ITS CHELATES:**

Ferrous 2-hydroxy-4-chloro-5-methylacetophenone oxime (0.250 gm) was ignited in a covered crucible. A drop of concentrated nitric acid was evaporated off. The temperature was gradually raised to a dull red heat so that the conversion to ferric oxide was complete. It was cooled and weighed. The same procedure was followed for ferrous-2-hydroxy-4-chloro-5-methylpropiophenone oxime. The results are tabulated below:
### Estimation of Palladium as Palladium Metal from Its Chelates

Palladium-2-hydroxy-4-chloro-5-methylacetophenone oxime (0.200 gm) was wrapped in an extra layer of filter paper, carefully charged, the filter paper burned away. It was ignited strongly in air to decompose all oxides of palladium to jewelry metal. It was cooled and weighed as palladium metal. The same procedure was followed for palladium-2-hydroxy-4-chloro-5-methylpropophenone oxime. The results are tabulated below:

<table>
<thead>
<tr>
<th>Chelate</th>
<th>Weight of chelate ignited in gm.</th>
<th>Weight of ferric oxide obtained in gm.</th>
<th>Percentage of metal Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(C₉H₉O₂Cl)₂</td>
<td>0.250</td>
<td>0.1629</td>
<td>21.97</td>
<td>22.08</td>
</tr>
<tr>
<td>Fe(C₁₀H₁₁O₂Cl)</td>
<td>0.250</td>
<td>0.1483</td>
<td>20.82</td>
<td>20.74</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chelate</th>
<th>Weight of chelate ignited in gm.</th>
<th>Weight of metal obtained in gm.</th>
<th>Percentage of metal Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(C₉H₉O₂Cl)₂</td>
<td>0.200</td>
<td>0.0425</td>
<td>21.18</td>
<td>21.26</td>
</tr>
<tr>
<td>Pd(C₁₀H₁₁O₂Cl)₂</td>
<td>0.200</td>
<td>0.0434</td>
<td>20.06</td>
<td>20.22</td>
</tr>
</tbody>
</table>
COMPOSITION OF METAL OXIME CHELATES BY JOB'S METHOD:

The solutions of metal salts (0.005 M) were prepared and standardised as described earlier. The solutions of the reagents (0.005 M) were prepared in ethanol. The solutions of the metal salt and the reagent were mixed in various proportions as under:

1:9, 2:8, 8:2, 9:1

maintaining the pH 2.5 for Cu$^{2+}$, 4.5 for Ni$^{2+}$, 6.8 for Co$^{2+}$, 3.5 for Fe$^{2+}$ and 1.0 for Pd$^{2+}$. The requisite amount of ethanol and water were added to maintain the proportion of ethanol to 20 percent in the final dilution. The precipitated complex in each case was extracted into 25.0 ml chloroform. The chloroform layer was separated and water droplets were removed by centrifugation. The percentage transmission and the optical density were recorded using Shimadzu Japan photoelectric Colorimeter Model AE-11. The percentage transmission and the optical densities at various concentrations are tabulated (See Table XXVII to XXXVI) and curves plotted (See Figs. 11 to 20).
CuCl₂ solution: 0.005 M
Reagent solution: 0.005 M in ethanol
Final volume of chloroform extract: 25.0 ml
pH = 2.5 to 3.0
Wavelength: 650 nm
(See Fig. No. 11)

<table>
<thead>
<tr>
<th>CuCl₂ solution taken ul.</th>
<th>Reagent solution taken ul.</th>
<th>Percentage transmission</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>92.5</td>
<td>0.03</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>89.0</td>
<td>0.054</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>84.0</td>
<td>0.074</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>85.0</td>
<td>0.070</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>86.0</td>
<td>0.065</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>88.5</td>
<td>0.05</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>91.0</td>
<td>0.035</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>92.5</td>
<td>0.03</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>97.5</td>
<td>0.015</td>
</tr>
</tbody>
</table>
TABLE: XXVIII

**Copper-2-Hydroxy-4-Chloro-5-Methylphenyl Oxime**

CuCl₂ solution: 0.005 M
Reagent solution: 0.005 M in ethanol

Final volume of chloroform extract: 25.0 ml
pH = 2.5 to 3.0

Wavelength: 650 nm.

(See Fig. No. 12)

<table>
<thead>
<tr>
<th>CuCl₂ solution taken ml</th>
<th>Reagent solution taken ml</th>
<th>Percentage transmission</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>97.5</td>
<td>0.01</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>90.0</td>
<td>0.043</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>86.0</td>
<td>0.065</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>85.5</td>
<td>0.062</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>83.0</td>
<td>0.052</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>91.0</td>
<td>0.04</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>93.0</td>
<td>0.03</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>95.0</td>
<td>0.02</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>97.5</td>
<td>0.01</td>
</tr>
</tbody>
</table>
TABLE XXIX

NICKEL-2-HYDROXY-4-CHLORO-5-METHYLACETOACETONE OXIME

NiCl$_2$ solution : 0.005 M
Reagent solution : 0.005 M in ethanol
Final volume of chloroform extract : 25 ml.
$pH$ : 4.5
wavelength : 610 nm.
(See Fig. No. 13)

<table>
<thead>
<tr>
<th>NiCl$_2$ taken ml</th>
<th>Reagent solution taken ml</th>
<th>Percentage transmission</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>96.0</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>91.0</td>
<td>0.04</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>86.0</td>
<td>0.064</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>86.5</td>
<td>0.06</td>
</tr>
<tr>
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<td>5</td>
<td>89.0</td>
<td>0.05</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>91.0</td>
<td>0.041</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>93.2</td>
<td>0.028</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>95.0</td>
<td>0.020</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>98.0</td>
<td>0.008</td>
</tr>
</tbody>
</table>
TABLE : XXX

NICKEL-2-HYDROXY-4-CHLORO-5-METHYLPROPIONONE OXIME

NiCl₂ solution : 0.005 M  Reagent solution : 0.005 M in ethanol
Final volume of chloroform extract: 25 ml pH : 4.5
wavelength : 610 nm (See Fig. No. 14)

<table>
<thead>
<tr>
<th>NiCl₂ solution taken ml</th>
<th>Reagent solution taken ml</th>
<th>Percentage transmission</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>96.0</td>
<td>0.015</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>93.0</td>
<td>0.030</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>90.5</td>
<td>0.045</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>90.5</td>
<td>0.045</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>91.0</td>
<td>0.040</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>93.0</td>
<td>0.030</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>93.2</td>
<td>0.025</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>95.5</td>
<td>0.018</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>97.5</td>
<td>0.010</td>
</tr>
</tbody>
</table>
TABLE: XXXI

COBALT-2-HYDROXY-4-CHLORO-5-METHYL ACETONE OXIME

CoCl₂ solution: 0.005 M
Reagent solution: 0.005 M
Final volume of chloroform extract: 25 ml
Wavelength: 530 nm
pH: 6.9

<table>
<thead>
<tr>
<th>NiCl₂ solution taken ml.</th>
<th>Reagent solution taken ml.</th>
<th>Percentage transmission</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>75.9</td>
<td>0.119</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>61.4</td>
<td>0.190</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>41.8</td>
<td>0.377</td>
</tr>
<tr>
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<tr>
<td>8</td>
<td>2</td>
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</tr>
<tr>
<td>9</td>
<td>1</td>
<td>-</td>
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</tr>
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</table>

(See Fig. No. 15)
<table>
<thead>
<tr>
<th>CoCl₂ solution taken ml.</th>
<th>Reagent solution taken ml</th>
<th>Percentage transmission</th>
<th>Optical density</th>
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<tbody>
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</tr>
<tr>
<td>9</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ferrous solution taken ml.</td>
<td>Reagent solution taken ml.</td>
<td>Percentage transmission</td>
<td>Optical density</td>
</tr>
<tr>
<td>---------------------------</td>
<td>-----------------------------</td>
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</tr>
</tbody>
</table>

FeSO₄(NH₄)₂SO₄ Solution: 0.005M in ethanol, pH: 3.5 (See Fig. No. 17)
TABLE: XXXIV

FERROUS-2-HYDROXY-4-CHLORO-5-METHYLPHENOXIMINE OXIME

FeSO$_4$(NH$_4$)$_2$SO$_4$ : 0.005 M  
Reagent solution : 0.005 M in ethanol
Final volume of chloroform extract : 25 ml  
$\phi$H : 3.5  
wavelength : 530 nm  
(See Fig. No. 18)

<table>
<thead>
<tr>
<th>Ferrous solution taken ml.</th>
<th>Reagent solution taken ml</th>
<th>Percentage transmission</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>9</td>
<td>1</td>
<td>72.5</td>
<td>0.14</td>
</tr>
<tr>
<td>( \text{PdCl}_2 ) solution taken ml</td>
<td>Reagent solution taken ml</td>
<td>Percentage transmission</td>
<td>Optical density</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>--------------------------</td>
<td>-------------------------</td>
<td>----------------</td>
</tr>
<tr>
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<td>9</td>
<td>83.0</td>
<td>0.079</td>
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<tr>
<td>9</td>
<td>1</td>
<td>90.5</td>
<td>0.042</td>
</tr>
</tbody>
</table>
TABLE: XXXVI

PALLADIUM-2-HYDROXY-4-CHLORO-5-METHYLPONPHENORE OXIME

PdCl₂ solution: 0.005 M  
Reagent solution: 0.005 M in ethanol
Final volume of chloroform extract: 25 ml  
\( \text{pH} = 1.0 \)  
Wavelength: 420 nm  
(See Fig. No. 20)

<table>
<thead>
<tr>
<th>PdCl₂ solution taken ml.</th>
<th>Reagent solution taken ml.</th>
<th>Percentage transmission</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
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<td>9</td>
<td>1</td>
<td>89.5</td>
<td>0.047</td>
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</tbody>
</table>
FIG. NO. 11
JOB'S METHOD FOR
COPPER - 2 - HYDROXY - 4 - CHLORO - 5 - METHYL -
ACETOPHENONE OXIME.

$\text{CuCl}_2: 0.005 \text{ M}$

REAGENT: 0.005 M IN ETHANOL

WAVELENGTH USED 650 nm
FIG. NO. 12

JOB'S METHOD FOR
COPPER-2-HYDROXY-4-CHLORO-5-METHYL-
PROPIOPHENONE OXIME.

CuCl$_2$: 0.005 M
REGENT: 0.005 M IN ETHANOL
WAVELENGTH USED 650 nm
FIG. NO. 13

JOB'S METHOD FOR
NICKEL-2-HYDROXY-4-CHLORO-5-METHYL-
ACETOPHENONE OXIME.

NiCl₂: 0.005 M
REAGENT: 0.005 M IN ETHANOL
WAVELENGTH USED 610 nm.
FIG. NO. 14

JOB’S METHOD FOR
NICKEL-2-HYDROXY-4-CHLORO-5-METHYL-
PROPIOPHENONE OXIME.

NiCl₂: 0·005 M
REAGENT: 0·005 M IN ETHANOL
WAVELENGTH USED 610 nm.
FIG. NO. 15

JOB'S METHOD FOR
COBALT-2-HYDROXY-4-CHLORO-5-METHYL
ACETOPHENONE OXIME.

CoCl₂: 0.005 M
REAGENT: 0.005 M IN ETHANOL
WAVELENGTH USED 530 nm.
FIG. NO. 16

JOB'S METHOD FOR COBALT-2-HYDROXY-4-CHLORO-5-METHYL-PROPIOPHENONE OXIME.

CoCl$_2$ 0.005M
REAGENT: 0.005 M IN ETHANOL
WAVELENGTH USED 530 nm.

![Graph showing the optical density against varying concentrations of CoCl$_2$ and reagent.](image)
FIG. NO. 17

JOB’S METHOD FOR
FERROUS-2-HYDROXY-4-CHLORO-5-METHYL
ACETOPHENONE OXIME.

\[ \text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 : 0.005 \text{ M} \]

REAGENT: 0.005 M IN ETHANOL
WAVELENGTH USED 530 nm.
FIG. NO. 18

JOB'S METHOD FOR
FERROUS-2-HYDROXY-4-CHLORO-5-METHYL-
PROPIOPHENONE OXIME.

FeSO\(_4\) \(\cdot\) \(\text{NH}_4\)\(_2\)\(\text{SO}_4\) : 0.005 M
REAGENT: 0.005 M IN ETHANOL
WAVELENGTH USED 530 nm
FIG. NO. 19
JOB'S METHOD FOR
PALLADIUM -2-HYDROXY-4-CHLORO-5-METHYL-
ACETOPHENONE OXIME.

\[ \text{PdCl}_2: 0.005 \text{ M} \]
\[ \text{REAGENT: } 0.005 \text{M IN ETHANOL} \]

WAVELENGTH USED 420nm

OPTICAL DENSITY

0.24
0.20
0.16
0.12
0.08
0.04

0 1 2 3 4 5 6 7 8 9 ml PdCl₂

9 8 7 6 5 4 3 2 1 ml REAGENT
FIG. NO. 20

JOB'S METHOD FOR
PALLADIUM-2-HYDROXY-4-CHLORO-5-METHYL-
PROPIOPHENONE OXIME.

\[ \text{PdCl}_2: 0.005 \text{ M} \]
\[ \text{REAGENT: 0.005 M IN ETHANOL.} \]

WAVELENGTH USED 420 nm.
UV spectra:

A definite amount of purified ketoximes was dissolved in definite volume of double distilled chloroform and their absorptions were measured at different wavelengths (200 nm to 400 nm) using UV-visible Hitachi 200 Japan UV. Vis Spectrophotometer at Cadila Laboratories, Ahmedabad (See Fig. No. 21 and 22).

Visible spectra:

$3 \times 10^{-3}$ M solutions of metal chelates were prepared in double distilled chloroform and their absorptions were measured in the visible region (350 nm to 700 nm) using Hitachi - 200 Japan UV visible spectrophotometer at Cadila Laboratories, Ahmedabad (See Fig. No. 23 to 32).

Infrared spectra:

Infrared spectra of ketoximes and their metal chelates were recorded in KBr pellet using Perkin Elmer Model No. 377 at Cadila Laboratories, Ahmedabad. (See Fig. No. 33 to 44).
FIG. NO. 21

ABSORPTION SPECTRA
OF
2-HYDROXY-4-CHLORO-5-METHYL-
ACETOPHENONE OXIME

OPTICAL DENSITY

WAVELENGTH - nm
FIG. NO. 22

ABSORPTION SPECTRA
OF
2'-HYDROXY-4'-CHLORO-5'-METHYL-
PROPIOPHENONE OXIME.
FIG. NO. 23

ABSORPTION SPECTRA
OF
COPPER-2-HYDROXY-4-CHLORO-5-METHYL-
ACETOPHENONE OXIME

OPTICAL DENSITY

WAVELENGTH - nm
FIG. NO. 24

ABSORPTION SPECTRA
OF
COPPER-2-HYDROXY-4-CHLORO-5-METHYL-
PROPIOPHENONE OXIME.
FIG. NO. 25

ABSORPTION SPECTRA
OF
NICKEL-2-HYDROXY-4-CHLORO
-5-METHYL-ACETOPHENONE OXIME.
FIG. NO. 26
ABSORPTION SPECTRA
OF
NICKEL-2-HYDROXY-4-CHLORO
-5-METHYL-PROPIOPHENONE OXIME.
FIG. NO. 27

ABSORPTION SPECTRA OF
COBALT-2-HYDROXY-4-CHLORO
-5-METHYL-ACETOPHENONE OXIME.
FIG. NO. 28

ABSORPTION SPECTRA OF COBALT-2-HYDROXY-4-CHLORO-5-METHYL-PROPIOPHENONE OXIME.
Fig. No. 29
Absorption spectra of ferrous-2-hydroxy-4-chloro-5-methyl-acetophenone oxime.
FIG. NO. 30

ABSORPTION SPECTRA
OF
FERROUS-2-HYDROXY-4-CHLORO
-5-METHYL-PROPIOPHENONE OXIME.

OPTICAL DENSITY

WAVELENGTH - nm
FIG. NO. 31

ABSORPTION SPECTRA
OF
PALLADIUM-2-HYDROXY-4-CHLORO-5-METHYL-
ACETOPHENONE OXIME.
FIG. NO. 32

ABSORPTION SPECTRA OF

PALLADIUM-2-HYDOXY-4-CHLORO
-5-METHYL-PROPIOPHENONE OXIME.
INFRARED SPECTRA OF 2-HYDROXY-4-CHLORO-5-METHYLPROPIONONE OXIME.

FIG. NO. 34
INFRARED SPECTRA OF COPPER-2-HYDROXY-4-CHLORO-5-METHYLACETOPHENONE OXIME
INFRARED SPECTRA OF COPPER-2-HYDROXY-4-CHLORO-5-METHYLPROPYLPHENONE OXIME.

FIG. NO. 36

TRANSMITTANCE (%)

WAVENUMBER (CM⁻¹)
INFRARED SPECTRA OF NICKEL-2-HYDROXY-4-CHLORO-5-METHYLACETOPHENONE OXIME

FIG. NO. 37
INFRARED SPECTRA OF NICKEL-2-HYDROXY-4-CHLORO-5-METHYL PROPYLPHENONE OXIME

FIG. NO. 38
INFRARED SPECTRA OF COBALT -2-HYDROXY-4-CHLORO-5-METHYL ACETOPHENONE OXIME

Fig. No. 39
INFRARED SPECTRA OF COBALT - 2-HYDROXY-4-CHLORO-5-METHYL PROPIOPHENONE OXIME.

FIG. NO. 40

TRANSMITTANCE (%)

WAVE NUMBER (CM⁻¹)
INFRARED SPECTRA OF FERROUS-2-HYDROXY-4-CHLORO-5-METHYLACETOPHENONE OXIME.
INFRARED SPECTRA OF FERROUS-2-HYDROXY-4-CHLORO-5-METHYL PROPIOPHENONE OXIME.
INFRARED SPECTRA OF PALLADIUM -2-HYDROXY-4-CHLORO-5-METHYL ACETOPHENONE OXIME

![Graph showing infrared spectra](image-url)
INFRARED SPECTRA OF PALLADIUM-2-HYDROXY-4-CHLORO-5-METHYL PROPIONALDEHYDE OXIME

FIG. NO. 44

TRANSMITTANCE (%)
Magnetic Susceptibility:

The measurement of magnetic susceptibility:

The chelates of (i) 2-hydroxy-4-chloro-5-methylacetoacetone (ii) 2-hydroxy-4-chloro-5-methylpropionophenone oximes with Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+} and Pd^{2+} were crystallised from chloroform and dried at 100°-110°C.

The Gouy tube was thoroughly cleaned with chronic 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 on the thread between the poles of a magnet so that each end is maintained in a region of uniform field. The tube was then accurately weighed without and with magnetic field. This procedure was repeated and the mean value of five such readings was obtained. The difference between the two weights: (i) with the magnetic field switched on and (ii) with the magnetic field switched off 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 up to mark. The tube was then resuspended and the electromagnet box was closed. The readings were taken in the same manner as for the empty tube. Five such readings were taken in the same manner as for the empty tube. Five such
Measurements on the same specimen were made with five 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 substance used were water, benzene, nickel chloride and mercury tetrathiocyanato cobaltate.

It has been shown earlier that the susceptibility per unit mass $\chi$ is given by

$$\chi = \frac{\infty + BF'}{V}$$

where $\beta$ and $\infty$ are the constants for given apparatus.

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

$\infty$ is given by the product of volume susceptibility of air and the volume occupied by the specimen. The volume susceptibility of air is known with accuracy and the volume occupied by the specimen is found according to the method of Angus and Tilson (51). It consists in determining the weight of the pure liquid filled in the tube upto the mark at a known temperature and dividing it by the density of the liquid at that temperature. The liquids used for this purpose are conductivity water, pure benzene and pure hexane.
Thus \(\chi\) was found as under

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

\[
= 0.029 \times 10^{-6} \times 1.000
\]

\[
= 0.029 \times 10^{-6}
\]

'\(\beta\)' is given by the expression

\[
B = \frac{2l}{(H_1^2 - H_2^2)}
\]

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. In practice, therefore, '\(\beta\)' is determined by using a standard substance of known magnetic susceptibility. Mercury tetrathiocyanato cobaltate was used to determine the value of '\(\beta\)'.

The gram susceptibility of mercury tetrathiocyanato cobaltate was found by using the equation

\[
\int = \frac{B \cdot dw + \infty}{W}
\]

\[
= \chi W \frac{-\infty}{dw}
\]

where \(W\) = weight of mercury tetrathiocyanato cobaltate in gm.
\[ \Delta w = \delta w - \delta \text{ in mg} \]

\( \delta w \) = weight in difference of mercury tetrathiocyanato cobaltate on application of magnetic field.

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

\( \chi \) = The gram susceptibility of mercury tetrathiocyanato cobaltate at room temperature

\[ \chi = 16.04 \times 10^{-6} \text{ (at 28°C)} \]

\( \beta \) was calculated and was found \( 0.6316 \times 10^{-6} \) at 4 ampere and \( 0.3713 \times 10^{-6} \) at 6 ampere.

Height of the specimen column:

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 tetrathiocyanato 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 magnitude 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.
<table>
<thead>
<tr>
<th>Metal chalate</th>
<th>Absolute $\chi \times 10^{-6}$</th>
<th>$\chi \times 10^{-6}$</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="#">Copper-2-hydroxy-4-chloro-5-methyl acetophenone oxime</a></td>
<td>301</td>
<td>6.3556</td>
<td>2926.7538</td>
</tr>
<tr>
<td><a href="#">Copper-2-hydroxy-4-chloro-5-methyl propiophenone oxime</a></td>
<td>301</td>
<td>6.5710</td>
<td>3025.8990</td>
</tr>
<tr>
<td><a href="#">Nickel-2-hydroxy-4-chloro-5-methyl acetophenone oxime</a></td>
<td></td>
<td></td>
<td><a href="#">Diamagnetic</a></td>
</tr>
<tr>
<td><a href="#">Nickel-2-hydroxy-4-chloro-5-methyl propiophenone oxime</a></td>
<td></td>
<td></td>
<td><a href="#">Diamagnetic</a></td>
</tr>
<tr>
<td><a href="#">Cobalt-2-hydroxy-4-chloro-5-methyl acetophenone oxime</a></td>
<td>301</td>
<td>9.972</td>
<td>4546.54</td>
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<td>15.913</td>
<td>4046.55</td>
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<td><a href="#">Ferrous-2-hydroxy-4-chloro-5-methyl propiophenone oxime</a></td>
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<td>13.965</td>
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<tr>
<td><a href="#">Palladium-2-hydroxy-4-chloro-5-methyl acetophenone oxime</a></td>
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<td></td>
<td><a href="#">Diamagnetic</a></td>
</tr>
<tr>
<td><a href="#">Palladium-2-hydroxy-4-chloro-5-methyl propiophenone oxime</a></td>
<td></td>
<td></td>
<td><a href="#">Diamagnetic</a></td>
</tr>
<tr>
<td>Metal chelate</td>
<td>Absolute temp.</td>
<td>$\chi \times 10^{-6}$ in emu</td>
<td>$\chi \times 10^{-6}$ in emu</td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td>----------------</td>
<td>-------------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Copper-2-hydroxy-4-chloro-5-methyl acetophenone oxime</td>
<td>301</td>
<td>6.3439</td>
<td>2921.1665</td>
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<tr>
<td>Copper-2-hydroxy-4-chloro-5-methyl propiophenone oxime</td>
<td>301</td>
<td>6.6160</td>
<td>3046.6</td>
</tr>
<tr>
<td>Nickel-2-hydroxy-4-chloro-5-methyl acetophenone oxime</td>
<td></td>
<td></td>
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20. A. Feigl and A. Bondi, Ber., 64, 2819 (1931).