Introduction
CHAPTER 3

INTRODUCTION

Oxazepam\(^{(1)}\) (serepax), an antianxiety agent is a 1,4-benzodiazepine with the chemical name 7-chloro-1,3-dihydroxy 5-phenyl-\(2H\)-1,4 benzodiazepine-2-one. Its structural formula is given below.

\[
\begin{align*}
\text{Cl} & \quad \text{N} & \quad \text{O} & \quad \text{H} \\
\text{Cl} & \quad \text{N} & \quad \text{O} & \quad \text{H}
\end{align*}
\]

This compound was synthesized by several workers.\(^{(2,3,4)}\) Oxazepam is used as central nerves sensitizer drug under the name "serepax".

Its crystal and molecular structure has been reported by Gilli et al.\(^{(5)}\) Its metabolic studies has been reported by sisevwine et al.\(^{(6)}\) Its Toxicity data has been given by Goldenthal.\(^{(7)}\)

It is readily absorbed when given orally. Peak concentrations in plasma occur approximately 2-3 hours following administration of 30 mg. The half life of this compound in human plasma ranges from 4 to 15 hours.
Oxazepam exerts prompt action in a variety of disorders associated with anxiety, tension, agitation and irritability, and with anxiety associated with depression. Benzodiazepines appear to work through several mechanisms. Benzodiazepines presumably exert their effect by binding to specific receptors sites within the central nervous system either by potentiating the effects of synaptic or presynaptic inhibition mediated by gamma-aminobutyric acid or by directly affect- ing the action potential generating mechanism.

Oxazepam is indicated for the management of anxiety disorders. Anxiety associated with depression in also responsive to Serepax therapy. It is useful in the management of anxiety, tension, agitation and irritability in older patients. This drugs which has to be used with precautions with doctors constant observations.

As with other benzodiazepines, periodic blood counts and liver - function tests are recommended for patients in long term therapy. There can be a drop in blood pressure which might lead to cardiac complications.

Properties:

Oxazepam (7-chloro-3-hydroxy1 5-phenyl-1,3 dihydro-2H-1,4 - benzodiazepine - 2 - one(1) has the following properties.
(1) **Molecular Formula:** $C_{15}H_{11}ClN_2O_2$

(2) **Molecular wt:** 286.74 gm.

(3) **Percentage composition:**
- $C = 62.83\%$
- $H = 3.87\%$
- $Cl = 12.37\%$
- $N = 9.77\%$
- $O = 11.16\%$

(4) **Melting point:** 205°C - 206°C.

(5) It is a creamy-white to paleyellow powder.

(6) It is practically odourless.

(7) Its crystals obtained from alcohol.

(8) It is slightly soluble in alcohol, chloroform, dioxane but practically insoluble in water.

(9) It has a bitter taste.
Present Work
PRESENT WORK

With the view of search for compounds of better chelating and pharmacological properties, an attempt has been made to prepare 7-chloro-1,3-dihydroxy-5-phenyl-2H-1,4-benzodiazepine-2-one hydrazone from oxazepam and their metal complexes; as the hydrazones and metal chelates are known to exhibit high stability. Structural formula of this chelating agent is given below.

\[
\text{Structural formula of the chelating agent.}
\]

This chapter describes the synthesis of 7-chloro-1,3 dihydroxy-5 phenyl-2H-1,4-benzodiazepine-2-one hydrazone and its application as a chelating agent for the metal ions like Cu\(^{+2}\), Ni\(^{+2}\), Co\(^{+2}\), Fe\(^{+2}\) and Fe\(^{+3}\).

The composition of the structure of the chelates thus prepared has been determined on the basis of:

(A) Molecular weight determination by Rast method.
(B) Job's continuous variation method.
(C) Results of Magnetic properties.
Experimental
SYNTHESIS OF 7-CHLORO-3-HYDROXY -5- PHENYL - 1,3 DIHYDRO-2H-1,4 - BENZODIAZEPINE - 2-ONE HYDRAZONE.

Ethanoic solution of 7-chloro - 3- hydroxy -5-phenyl - 1,3 dihydro -2H-1,4-Benzodiazepine-2-one (5.0 g), hydrazine hydrate (2.1g) and potassium hydroxide (5 ml, 40%, solution) were mixed and refluxed on water bath at 100°C for one hour. It was kept aside overnight and then neutralised with dilute HCl using methyl orange as an indicator. The solid 7-chloro-3-hydroxy -5- phenyl -1,3 dihydro -2H-1,4-Benzodiazepine-2-one hydrazone that separated was collected and crystallized from absolute alcohol as offwhite pallet shape crystals yield : 89%; M.P: 218°C.

CHELATION OF METAL IONS (Cu²⁺, Ni²⁺, Co²⁺, Fe²⁺ and Fe³⁺) USING 7-CHLORO-3-HYDROXY -5-PHENYL 1,3-DIHYDRO - 2H-1,4 BENZODIAZEPINE - 2-ONE HYDRAZONE AS A CHELATING AGENT.

(1) Reaction with copper (II) ion:

1% ethanoic solution of 7-chloro-3-hydroxy -5-phenyl 1,3 dihydro-2H-1,4 Benzodiazepine -2-one hydrazone was added dropwise to a warm solution of copper chloride. Maintaining the pH of the mixture during the reaction between 7.8 to 8.0, Green coloured precipitates were formed. Precipitates thus obtained were washed with warm ethanol. The precipitates are soluble in carbon tetrachloride, chloroform, dimethyl formamide (DMF) and benzene solvents.
Thus Bis (7-chloro-3-hydroxy-, 5-phenyl, -1,3 dihydro-2H - 1,4 Benzodiazepine -2- one hydrazonato ) copper (II) chelate is formed.

(2) Reaction with Nickel (II) ion :

1% ethanolic solution of 7-chloro-3-hydroxy-5-phenyl 1,3 dihydro 2H-1,4 Benzodiazepine -2- one hydrazone was added dropwise to a warm solution of nickel chloride. Maintaining the pH of the mixture at pH 7.8 to 8.0 during the reaction, dark pink coloured precipitates were obtained. These precipitates were washed with warm ethanol. The precipitates are soluble in chloroform, carbon tetrachloride, dimethyl formamide (DMF) and benzene. Thus Bis (7-chloro-, 3-hydroxy; 5-phenyl, 1,3 - dihydro -2H 1,4 - Benzodiazepine -2- one hydrazonato) Nickel (II) chelate is formed.

(3) Reaction with cobalt (II) ion :

1% ethanolic solution of 7-chloro 3-hydroxy -5-phenyl 1,3 dihydro 2H-1,4 Benzodiazepine -2- one hydrazone was added dropwise to a warm cobalt chloride solution. Maintaining the pH of the mixture at pH 7.0 to 8.0 during the reaction Grey coloured precipitates were formed. Precipitates thus obtained were washed with warm ethanol. The precipitates are
soluble in organic solvents like carbon tetrachloride, chloroform, dimethyl formamide and benzene solvents. By this way Bis (7-Chloro, 3-hydroxy, 5 phenyl, 1,3 - dihydro -2H -1,4 - Benzodiazepine -2- one hydrazonato ) cobalt (II) chelate is formed.

(4) Reaction with Ferrous ions:

1% ethanolic solution 7-chloro, -3-hydroxy, -5- phenyl 1,3-dihydro -2H -1,4 -Benzodiazepine -2- one hydrazone was added dropwise to a warm solution of ferrous ammonium sulphate. Maintaining the pH of the mixture at 6.8 to 7.0 during the reaction. Light brown coloured precipitates were formed. Precipitate thus obtained were washed with warm ethanol. The precipitates are soluble in chloroform, carbon tetrachloride benzene and dimethyl formamide solvents. Thus (7-chloro-3-hydroxy -5- phenyl - 1,3 - dihydro -2H -1,4 - Benzodiazepine -2- one hydrazonato ) iron (II) chelate is formed.

(5) Reaction with Ferric ion:

1% ethanolic solution of 7-chloro-3- hydroxy -5- phenyl 1,3 dihydro -2H - 1,4 - Benzodiazepine -2- one hydrazone was added dropwise to a warm ferric
alum solution. Maintaining the pH of the mixture 6.8 to 7.0 during the reaction. Reddish brown coloured precipitates were formed. Precipitates thus obtained were washed with warm ethanol. The precipitates are soluble in benzene, chloroform carbon tetrachloride and dimethyl formamide solvents. Thus (7 - chloro -3- hydroxy -5- phenyl -1,3 -dihydro -2H - 1,4 - Benzodiazepine -2- one - hydrazonato ) iron (III) chelate is formed.
Table - 1

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of the metal chelates</th>
<th>Mixed melting point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Bis (7-chloro-3-hydroxy-5-phenyl-1,3 dihydro-2H-1,4 Benzodiazepine-2-one hydrazonato) copper (II).</td>
<td>222</td>
</tr>
<tr>
<td>(2)</td>
<td>Bis (7-chloro-3-hydroxy-5-phenyl-1,3 dihydro-2H-1,4 Benzodiazepine-2-one hydrazonato) Nickel (II)</td>
<td>225</td>
</tr>
<tr>
<td>(3)</td>
<td>Bis (7-chloro-3-hydroxy-5-phenyl-1,3 dihydro-2H-1,4-Benzodiazepine-2-one hydrazonato) cobalt (II).</td>
<td>223</td>
</tr>
<tr>
<td>(4)</td>
<td>(7-chloro-3-hydroxy-5-phenyl-1,3 dihydro-2H-1,4-Benzodiazepine-2-one hydrazonato) Iron (II)</td>
<td>219</td>
</tr>
<tr>
<td>(5)</td>
<td>(7-chloro-3-hydroxy-5-phenyl-1,3 dihydro-2H-1,4-Benzodiazepine-2-one hydrazonato) Iron (III).</td>
<td>218</td>
</tr>
</tbody>
</table>
Molecular weights determination of chelates by Rast's method:

The molecular weights of the chelates formed with the different metal ions were determined by Rast's method using pure camphor. The results are recorded in the following table.

(1) weight of complex taken = 0.2 gram
(2) weight of camphor taken = 0.2 gram
(3) $K_f$ of camphor = 39.68 $°\text{C/lit.}$

<table>
<thead>
<tr>
<th>No. of compounds</th>
<th>Chelates Molecular formula</th>
<th>Depression in Molecular weights</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Theoretical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TC</td>
</tr>
<tr>
<td>1.</td>
<td>$\text{Cu} (\text{C}<em>1\text{H}<em>1\text{O}</em>\text{Cl}</em>\text{N}_2\text{O}_2)_2$</td>
<td>5.77</td>
</tr>
<tr>
<td>2.</td>
<td>$\text{Ni} (\text{C}<em>1\text{H}<em>1\text{O}</em>\text{Cl}</em>\text{N}_2\text{O}_2)_2$</td>
<td>5.81</td>
</tr>
<tr>
<td>3.</td>
<td>$\text{Co} (\text{C}<em>1\text{H}<em>1\text{O}</em>\text{Cl}</em>\text{N}_2\text{O}_2)_2$</td>
<td>5.81</td>
</tr>
<tr>
<td>4.</td>
<td>$\text{Fe} (\text{C}<em>1\text{H}<em>1\text{O}</em>\text{Cl}</em>\text{N}_2\text{O}_2)$</td>
<td>10.9</td>
</tr>
</tbody>
</table>

The above stated results are in good agreement with the composition of chelates.
Job's method of Continuous Variation can be applied for confirming metal : ligand ratio.

In a chemical reaction of the type -

\[ M + n \cdot A = MA_n \]

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

Now \[ M + n \cdot A = MA_n \] ......(i)

Therefore, \[ \frac{(MA_n)}{(M)^n (A)^n} = \text{Const.} \] ......(ii)

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

It can be shown that when concentration of chelate \( (MA_n) \) is maximum,

\[ \frac{d(MA_n)}{d(M)} = 0 \] ......(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 'ligand 'A' is mixed with a solution of metal ion 'M' so that the total molar concentration of the ligand plus that of metal ion is maintained constant.

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

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

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

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.

\[D = l \left( E_1(M) + E_2(A) + E_3(MA_n) \right) \ldots \ldots \text{(viii)}\]

Where 'l' is the length of the lightpath through the solution and \(E_1, E_2, E_3\) are respective molar extinction co-efficients of 'M', 'A' and 'MA_n' respectively.

\[Y = l \left( E_1(M) + E_2(A) + E_3(MA) - l(E_1M_t + E_2A_t) \right) \ldots \ldots \text{(ix)}\]

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 (1) is 1 cm. the function 'Y' is defined by the relationship.

$$Y = E_1(M) + E_3(MA_n) - (E_1M_t)$$

Differentiating the equation (x) with respect to $(A_t)$ gives

$$\frac{dy}{d(A_t)} = \frac{d(M)}{d(A_t)} - \frac{d(M_t)}{d(A_t)} + E_3 \frac{d(MA_n)}{d(A_t)}$$

now according to equation (v)

$$(M) = (M_t) - (MA_n)$$

differentiating with respect to $A_t$

$$\frac{d(M)}{d(A_t)} = \frac{d(M_t)}{d(A_t)} - \frac{d(MA_n)}{d(A_t)}$$

Putting this value in equation (xi)

$$\frac{dy}{d(A_t)} = E_3 \frac{d(MA_n)}{d(A_t)} - E_1 \frac{d(MA_n)}{d(A_t)}$$

$$\frac{dy}{d(A_t)} = (E_3 - E_1) \frac{d(MA_n)}{d(A_t)}$$

...(xiii)
Equation (xiii) represents the base for the Job's method of continuous variation.

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 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\(^{(8)}\) 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\(^{(9)}\), Turner and Anderson\(^{(10)}\), Yoe and Harvey\(^{(11)}\), Moss and Mellon\(^{(12)}\) employed this method for iron and kojic acid. Pandya\(^{(13)}\) and Amin\(^{(14)}\) used this method to determine the composition of \(-\text{O}-\text{hydroxy ketoxime}\) chelates with Cu\(^{+2}\), Ni\(^{+2}\) and 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 CHCl₃ and the optical density of the chloroform extract was measured. The results showed that in the case of Cu⁺², Ni⁺² and Co⁺², there was maximum when the metal : ligand ratio was 1:2.

The above results indicate that the chelates of these ligands with Cu⁺², Ni⁺², and Co⁺² should have the following structure.
Feigl and Bondi\(^{15}\), Wardlaw and Webster\(^{16}\) have reported that at a higher pH salicylaldoxime give 1:1 chelate with Cu\(^{+2}\).

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\(^{17}\). In the present work, 0.002 M solutions of all the metal salts were prepared and 0.002 M 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 7.8 for Cu\(^{+2}\), pH=7.9 for Ni\(^{+2}\), pH = 8.0 for Co\(^{+2}\), pH = 6.9 for Fe\(^{+2}\) and pH = 7.0 for Fe\(^{+3}\). The precipitated complex in each case was extracted by adding 15 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 340 mm. etc 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 - 5)
BIS(7-CHLORO 3-HYDROXY 5-PHENYL-1,3 DIHYDRO-2H-1,4 BENZODIAZEPINE -2-ONE, HYDRAZONATO) COPPER(II)

Reagent:
7-Chloro 3-hydroxy 5-phenyl-1,3 dihydro
-2H-1,4-Benzodiazepine-2-one hydrazone.

<table>
<thead>
<tr>
<th>Cu²⁺ Solution, Taken</th>
<th>Reagent Soln.</th>
<th>Optical Density</th>
<th>λ=340nm; λ=570nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ml.</td>
<td>ml.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>0.149</td>
<td>0.058</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.314</td>
<td>0.111</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.460</td>
<td>0.150</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0.524</td>
<td>0.174</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.423</td>
<td>0.141</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0.344</td>
<td>0.118</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.275</td>
<td>0.091</td>
</tr>
</tbody>
</table>

Reagent: 0.002 M in ethanol
CuCl₂·2H₂O: 0.002 M

Fig. 1
BIS (7-CHLORO 3-HYDROXY 5-PHENYL-1,3 DIHYDRO-2H-1,4 BENZODIAZEPINE -2-ONE, HYDRAZONATO) NICKEL(II)

Reagent:
7-Chloro 3-hydroxy 5-phenyl-1,3 dihydro -2H-1,4-Benzodiaze-2-one hydrazone.

<table>
<thead>
<tr>
<th>Ni²⁺ Solution Taken</th>
<th>Reagent Soln.</th>
<th>Optical Density λ=320nm</th>
<th>Optical Density λ=400nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ml</td>
<td>9 ml</td>
<td>0.052</td>
<td>0.018</td>
</tr>
<tr>
<td>2 ml</td>
<td>8 ml</td>
<td>0.101</td>
<td>0.037</td>
</tr>
<tr>
<td>3 ml</td>
<td>7 ml</td>
<td>0.138</td>
<td>0.056</td>
</tr>
<tr>
<td>4 ml</td>
<td>6 ml</td>
<td>0.146</td>
<td>0.053</td>
</tr>
<tr>
<td>5 ml</td>
<td>5 ml</td>
<td>0.122</td>
<td>0.044</td>
</tr>
<tr>
<td>6 ml</td>
<td>4 ml</td>
<td>0.096</td>
<td>0.034</td>
</tr>
<tr>
<td>7 ml</td>
<td>3 ml</td>
<td>0.071</td>
<td>0.024</td>
</tr>
</tbody>
</table>

Reagent: 0.002 M in ethanol NiCl₂·6H₂O; 0.002 M.

Fig - 2
JOB'S METHOD
FOR
BIS(7-CHLORO 3-HYDROXY 5-PHENYL-1,3 DIHYDRO-2H-1,4 BENZODIAZEPINE-2-ONE, HYDRAZONATO) COBALT(II)

Reagent:
7-Chloro 3-hydroxy 5-Phenyl-1,3 dihydro-2H-1,4-Benzodiazepine-2-one hydrazone.

<table>
<thead>
<tr>
<th>Co Solution Taken (ml)</th>
<th>Reagent Soln. (ml)</th>
<th>Optical Density (λ=340nm)</th>
<th>Optical Density (λ=570nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>0.172</td>
<td>0.072</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.360</td>
<td>0.136</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.510</td>
<td>0.183</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0.487</td>
<td>0.172</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.390</td>
<td>0.160</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0.317</td>
<td>0.123</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.240</td>
<td>0.093</td>
</tr>
</tbody>
</table>

Reagent: 0.002 M in ethanol
CoCl₂ 6H₂O: 0.002 M

Graph: O = λ = 340 nm
□ = λ = 570 nm

Fig. 3
JOB'S METHOD FOR
(v-Chloro 3-hydroxy 5-phenyl-1,3 dihydro-2H-1,4 benzodiazepine-2-one hydrazonato) iron(II)

Reagent:
7-Chloro 3-hydroxy 5-phenyl-1,3 dihydro-2H-1,4 benzodiazepine-2-one hydrazone.

<table>
<thead>
<tr>
<th>Fe²⁺ Solution Taken</th>
<th>Reagent Soln.</th>
<th>Optical Density λ=340nm</th>
<th>Optical Density λ=370nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>0.017</td>
<td>0.008</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.030</td>
<td>0.012</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.042</td>
<td>0.014</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0.054</td>
<td>0.019</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.067</td>
<td>0.023</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0.057</td>
<td>0.019</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.041</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Reagent: 0.002 M in ethanol
10.002 M FeSO₄(NH₄)₂SO₄·6H₂O

θ = λ = 340nm
θ = λ = 370nm

Fig-4
JOB'S METHOD
FOR
(7-CHLORO 5-HYDROXY 5-PHENYL-1,3 DIHYDRO-2H-1,4 BENZODIAZEPINE
-2-ONE, HYDRAZONATO) IRON(III)

Reagent:
7-Chloro 3-hydroxy 5-Phenyl-1,3 dihydro
-2H-1,4-Benzodiazepine-2-one hydrazone.

<table>
<thead>
<tr>
<th>Fe³⁺ Solution Taken</th>
<th>Reagent Soln</th>
<th>Optical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>ml</td>
<td>ml</td>
<td>λ=340 nm</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>0.009</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.013</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.021</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0.021</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.044</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0.035</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Reagent: 0.002 M in ethanol
Ferric alun: 0.002 M

Fig: 5
The use of magnetic properties as a potent tool for the determination of structures of d-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.

\[
\text{B. M.} = \frac{eh}{4 \pi mc}
\]

where,  
- \( h = \) Plank's Constant  
- \( e = \) electronic charge  
- \( m = \) mass of electron  
- \( c = \) velocity of light  
- \( \text{B. M.} = \) Bohr magneton  
- \( \text{B. M.} = 9.27 \times 10^{-21} \) erg/gauss
Now, the magnetic moment is related to the molar susceptibility \( (\chi_M) \) by the Langevin expression:

\[
\chi_M = \frac{NAM^2}{3KT}
\]

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

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

\[
\mathcal{H}_B = \left[ 4S(S+1) + L(L+1) \right]^{\frac{1}{2}}
\]

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:

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

The number of unpaired electrons \((n) = 2S.\) Thus the magnetic moment may be related directly to the number of unpaired electrons by the expression:

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

The measurement of molar susceptibility \( \chi_M \) of molecules of transition metal is of great importance in arriving at conclusion pertaining the number of unpaired electrons and the structure of chelates. Calvin et al. \( ^{18} \). 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 \( \text{Cu}^{+2} \), \( \text{Ni}^{+2} \), and \( \text{Co}^{+2} \). This was also supported by X-ray analysis. Mellor and Craig\(^{19}\) pointed out that the chelates of the type given below are covalent or ionic.

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

e.g. \( \text{Co}^{+2} \) chelates of above type are reported to be paramagnetic having tetrahedral structure\(^{20-23}\). \( \text{Ni}^{+2} \) chelate of the above type are found to be diamagnetic. There are no unpaired electron and hence possess square planar structure indicating \( \text{dsp}^2 \) hybridization state of the metal\(^{18,22,23}\). The above generalisation was confirmed by X-ray analysis of Nickel-bis-Salicylaldoximes as well as other chelates of \( \text{Ni}^{+2} \)\(^{18,24,25,26}\).

The study of divalent copper is of great interest since \( \text{Cu}^{+2} \) ion contains one more electron than that in \( \text{Ni}^{+2} \). Although the electronic configuration of \( \text{Cu}^{+2} \) suggests that \( \text{SP}^3 \) hybridization must result. Pauling\(^{27}\) pointed out that placing the unpaired electron in a \( 4\text{P} \) 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 that Cu\(^{2+}\) complexes are not planer. 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>
</table>
| Ideal                     | \[\begin{array}{c}
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\end{array}\] | \[\begin{array}{c}
\Box \\
\Box \\
\Box \\
\Box \\
\end{array}\] | \[\begin{array}{c}
\Box \\
\Box \\
\Box \\
\Box \\
\end{array}\] |
| Square planar dsp\(^2\) | \[\begin{array}{c}
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\end{array}\] | \[\begin{array}{c}
\Box \\
\uparrow \\
\Box \\
\Box \\
\end{array}\] | \[\begin{array}{c}
\Box \\
\Box \\
\Box \\
\Box \\
\end{array}\] |
| Tetrahedral sp\(^3\)     | \[\begin{array}{c}
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\end{array}\] | \[\begin{array}{c}
\Box \\
\Box \\
\Box \\
\Box \\
\end{array}\] | \[\begin{array}{c}
\Box \\
\Box \\
\Box \\
\Box \\
\end{array}\] |

Ray and Sen\(^{28}\) 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 dsp\(^2\) hybridization for such chelates. The square planar structure of Cu\(^{2+}\) chelates of the above type is also supported, by the study of cotton effect\(^{29}\). Kato, Jonassen and Eanning\(^{30}\) reviewed Cu\(^{2+}\) complexes with subnormal magnetic \(\epsilon\) moments and attributed this to a dimeric structure with Cu-Cu linkage which gives an absorption band at 375 nm\(^{31,32}\).

Molar Susceptibility \(X_M\) can be measured by Gouy's method. 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:
\[ F = \frac{1}{2} A(K_1 - K_2) \left( H^2 - H_0^2 \right) + \psi \]

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
- \( \psi \) = 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:

\[ X = \beta \frac{F'}{W} + \omega \]

Where,

- \( \omega \) = constant for the displaced air
- \( \beta \) = Tube calibration constant if \( H \) is constant
- \( W \) = Weight of substance
- \( F' = F + P \)

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 substance 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\(^{(33,34)}\) 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\(^{(35)}\) out 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\(^{(36)}\), by Carbera, Moles and Guzman\(^{(37)}\), Weiss and Bruins\(^{(38)}\) and by Nettleton and Sugden.\(^{(39)}\)

In the present work, distilled-water which is free from dissolved air was 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-Teller theorem which says that if a non-linear molecule has a degenerate state, then there is at least one vibrational co-ordinate along which a distortion can occur so as to remove the degeneracy.
The chelates of 7-chloro-3-hydroxy-5-phenyl-1,3-dihydro-2H-1,4-benzodiazepine hydrazone with Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Fe$^{2+}$ and Fe$^{3+}$ were crystallised from chloroform and dried at 100 - 110°C.

Standard "selecta Sartorius" single pan, semi-micro balance was used. This is air-damped and has a sensitivity of 0.01 mg. Schematic diagram of selecta sartorius balance is given a page-150.

The Gouy tube was throughly cleaned with chromic 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, used in this work, was made from hand pyrex glass tubing about 1 m.m. in thickness and having a uniform bore of about 0.5 cm. The length of the tube was about 10 cms, and it was provided with a ground glass stopper. A mark was etched on the outside of the tube at about 7.5 cms, from the bottom. All the substances measured were packed or filled to this mark. The tube was vertically suspended by means of a suitable glass coller whose horizontal arms rested on the y-shaped phosphor bronze suspension in such a way that the lower and of the tube hung symmetrically in the centre of the pole gap.
Schematic diagram of Sartorius balance
The specimen tube was suspended carefully on the hook between poles of a magnet so that each and 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 distilled water free from dissolved air 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 magnetitute of the force acting on the distilled water free from dissolved air was fixed at 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 reading was obtained. The difference between the two weights: (i) with the magnetic field and (ii) without 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 up to the mark. The tube was then resuspended and the electro-magnetic box was closed. The reading 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 substance used was a distilled water free dissolved air.

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

$$X = \frac{\alpha + \beta F'}{W}$$

but

$$\alpha = K\cdot V.$$  

Where,

- $K = \text{Volume susceptibility of air}$
  
  $$= 0.029 \times 10^{-6}$$

- $V = \text{Volume of water}$
- $\beta = \text{tube calibration constant}$
- $W = \text{Weight of substance}$
- $F' = \text{Apparent change in weight.}$

I.e. force exerted on the specimen by the field.

$\alpha$ is the product of volume susceptibility of air and the volume occupied by the specimen. It has been determined by Angus and Tilstone. (40)
DETERMINATION OF MAGNETIC MOMENT OF COMPOUND: (e.g. COPPER COMPLEX).

(I) CALIBRATION OF GOUY TUBE (FIELD = 4 amp.)

(i) Weight of the empty tube without magnetic field.
   \[ a = 11.6759 \text{ gm.} \]

(ii) Weight of the empty tube with magnetic field.
    \[ b = 11.6746 \text{ gm.} \]

(iii) Apparent change in weight (6-a)
    \[ c = -0.0013 \text{ gm.} \]

(iv) Weight of the tube + H₂O = d = 12.1806 gm.

(v) Weight of the H₂O = Volume of H₂O = (d-a) =
    \[ V = 0.5047 \text{ gm.} \]

(vi) Weight of the tube + Calibrant without magnetic field
    \[ e = 12.1806 \text{ gm.} \]

(vii) Weight of the tube + calibrant magnetic field.
    \[ F = 12.1782 \text{ gm.} \]

(viii) Weight of the calibrant (e-a) =
    \[ W = 0.5047 \text{ gm.} \]

(ix) Apparent change in weight (F-e) =
    \[ dF = -0.0024 \text{ gm.} \]

(x) Apparent change in weight with diamagnetic correction
    \[ (F-e) - (-c) = F' = -0.0037 \text{ gm.} \]
Tube constant $B$ can be determined from the following equation.

$$B = \frac{X \cdot W - K \cdot V}{P}$$

Where $X =$ Magnetic susceptibility of the calibrant (distilled water free from dissolved air)  
= $-0.72 \times 10^{-6}$

$W =$ Weight of the calibrant = 0.5047 gm.

$K =$ Volume susceptibility of air  
= $0.029 \times 10^{-6}$.

$V =$ Volume of water  
= 0.5047 gm.

$F' =$ Apparent change in Wt.  
= $-0.0037$ gm.

Now,  
$$B = \frac{XW - KV}{P'}$$

$$= \frac{[(-0.72 \times 10^{-6}) \cdot 0.5047] - [(0.029 \times 10^{-6}) \cdot 0.5047]}{-0.0037}$$

$$= 102.16 \times 10^{-6}, \text{ at } 4 \text{ amp.}$$

(II) **CALCULATION OF $H_{eff}$ OF A GIVEN COMPOUND.**

( FIELD = 4 AMP.)

xi) Weight of the tube + compound without magnetic field  
$g =$ 12.4486 gm.

xii) Weight of the tube + compound with magnetic field  
$h =$ 12.4632 gm.
xiii) Weight of the compound \((g-a) = W = 0.7727\) gm.

xiv) Apparent change in weight \((h-g) = \Delta F = 0.0146\) gm.

xv) Apparent change in weight with diamagnetic correction

\[ (h-g) - (-c) = F' = 0.0133 \text{ gm.} \]

Magnetic susceptibility of the compound can be determined from the following equation.

\[
X = \frac{KV + \beta F'}{W}
\]

Where, 
- \(W\) = Weight of the compound
  \[ = 0.7727 \text{ gm.} \]
- \(F'\) = Apparent change in weight
  \[ = 0.0133 \text{ gm.} \]
- \(\beta\) = Tube constant
  \[ = 102.16 \times 10^{-6} \]

Now,

\[
X = \frac{KV + \beta F'}{W} = \frac{[(0.029 \times 10^{-6}) (0.5047)] + [(102.16 \times 10^{-6}) (0.0133)]}{0.7727}
\]

\[ = 1.773 \times 10^{-6} \text{ emu.} \]
\[ X_m = X \times \text{Mol. wt of compound}. \]
\[ = 1.773 \times 10^{-6} \times 663.02 \text{ gm. (for copper complex)} \]
\[ = 1175.53 \times 10^{-6} \text{ emu.} \]

\[ \mu_{\text{eff}} = 2.83 \sqrt{X_m \times T} \quad \text{(where } T = 300^\circ \text{K)} \]
\[ = 2.83 \sqrt{(1175.53 \times 10^{-6}) \times 300}. \]
\[ = 1.68 \text{ B.M.} \]

(I) CALIBRATION OF GOUY TUBE: (FIELD = 6 amp.)

i) Weight of the empty tube without magnetic field
   \[ a = 11.6759 \text{ gram.} \]

ii) Weight of the empty tube with magnetic field
    \[ b = 11.6737 \text{ gram.} \]

iii) Apparent change in weight \( (b-a) = c = -0.0022 \text{ gm.} \)

iv) Weight of the tube + H\(_2\)O = \( d = 12.1806 \text{ gm.} \)

v) Weight of the H\(_2\)O = volume of H\(_2\)O = \( d-a \)
   \[ V = 0.5047 \text{ gm.} \]

vi) Weight of the tube + calibrant without magnetic field
    \[ e = 12.1806 \text{ gm.} \]

vii) Weight of the tube + calibrant magnetic field,
     \[ F = 12.1756 \text{ gm.} \]

viii) Weight of the calibrant \( (e-a) = W = 0.5047 \text{ gm.} \)

ix) Apparent change in weight \( (F-e) = \Delta F = -0.0050 \text{ gm.} \)
x) Apparent change in weight with diamagnetic correction

= (F - e) - (-c) = F = -0.0072 gm.

The constant $\beta$ can be determined from the following equation.

\[
\beta = \frac{XW - KV}{F'}
\]

Where, $X =$ Magnetic susceptibility of the calibrant
= (distilled water free from dissolved air)
= -0.72 x 10^{-6}

$W =$ Weight of the calibrant
= 0.5047 gm.

$K =$ Volume susceptibility of air
= 0.029 x 10^{-6}

$V =$ Volume of the water
= 0.5047 gm.

$F'$ = Apparent change in weight
= -0.0037 gm.

Now,

\[
\beta = \frac{XW - KV}{F'}
= \frac{[-0.72 \times 10^{-6} \times 0.5047] - [0.029 \times 10^{-6} \times 0.5047]}{-0.0072}
= 52.5 \times 10^{-6} \text{ emu.}
\]
(II) CALCULATION OF $\mu_{\text{eff.}}$ OF A GIVEN COMPOUND:

(FIELD = 6 AMP.)

xi) Weight of the tube + compound without magnetic field
   \[ g = 12.1058 \text{ gm.} \]

xii) Weight of the tube + compound with magnetic field
    \[ h = 12.1275 \text{ gm.} \]

xiii) Weight of the compound \(= (g-a) = W = 0.4299 \text{ gm.} \)

xiv) Apparent change in weight \(= h-g = dF = 0.0217 \text{ gm.} \)

xv) Apparent change in weight with diamagnetic correction
    \[ = (h-g) - (-c) = F' = 0.0195 \text{ gm.} \]

Magnetic susceptibility of the compound can be determined from
the following equation.

\[
X = \frac{KV + PF'}{W} \quad \text{(g units)}
\]

Where, \(W = \) Weight of the compound
    \[ = 0.7727 \text{ gm.} \]
\(F' = \) Apparent change in weight
    \[ = 0.0195 \text{ gm.} \]
\(P = \) Tube constant
    \[ = 52.5 \times 10^{-6} \]

Now, \(X = \frac{KV + PF'}{W} \)
\[
\begin{align*}
\frac{[(0.029 \times 10^{-6}) (0.5047)] + [(52.5 \times 10^{-6}) (0.0195)]}{0.7727} &= 1.344 \times 10^{-6} \text{ emu at 6 amp.} \\
X_m &= X \times \text{Molecular weight of compound} \\
&= 1.344 \times 10^{-6} \times 663.02 \text{ gm. (for copper complex)} \\
&= 891.10 \times 10^{-6} \text{ emu} \\
U_{\text{eff.}} &= 2.83 \sqrt{X_m \times T} \\
&= 2.83 \sqrt{(891.10 \times 10^{-6}) \times 300} \\
&= 1.46 \text{ B.M.}
\end{align*}
\]

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 ligand 2- (2'-hydroxy-5'-methylacetophenonehydrazone) -4,6 - S- triazine. In nut-shell, the magnetic susceptibility observations are tabulated in the following tables.
Table 2

Magnetic susceptibility of metal chelates

Current: 4 amperes, Absolute temperature: 303° K

<table>
<thead>
<tr>
<th>No.</th>
<th>Metal chelates</th>
<th>$X \times 10^{-6}$</th>
<th>$X_m \times 10^{-6}$</th>
<th>$\mu_{\text{eff.}}$</th>
<th>Magnetic property</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Bis (7-chloro-3-hydroxy-5-phenyl-1, 3 dihydro-2H-1,4 benzodiazepine-2-one hydrazonato) copper(II)</td>
<td>1.773</td>
<td>1174.69</td>
<td>1.68</td>
<td>Para- magnetic</td>
</tr>
<tr>
<td>2.</td>
<td>Bis(7-chloro-3-hydroxy-5-phenyl-1,3 dihydro-2H-1,4 benzodiazepine-2-one hydrazonato) Nickel (II)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Diagonal magnetic</td>
</tr>
<tr>
<td>3.</td>
<td>Bis (7-chloro-3-hydroxy-5-phenyl-1, 3 dihydro-2H-1,4 benzodiazepine-2-one hydrazonato) cobalt (II)</td>
<td>2.6526</td>
<td>1745.27</td>
<td>2.048</td>
<td>Para- Magnetic</td>
</tr>
<tr>
<td>4.</td>
<td>(7-chloro-3-hydroxy-5-phenyl-1,3 dihydro-2H-1,4 benzodiazepine-2-one hydrazonato) Iron (II)</td>
<td>29.61</td>
<td>10522.34</td>
<td>5.028</td>
<td>Para- Magnetic</td>
</tr>
<tr>
<td>5.</td>
<td>(7-chloro-3-hydroxy-5-phenyl-1, 3 dihydro-2H-1,4 benzodiazepine-2-one hydrazonato) Iron (III)</td>
<td>46.52</td>
<td>16531.16</td>
<td>6.300</td>
<td>Para- magnetic</td>
</tr>
</tbody>
</table>
Table: 3

Magnetic susceptibility of metal chelates

<table>
<thead>
<tr>
<th>No.</th>
<th>Metal chelates</th>
<th>$X \times 10^{-6}$ in emu</th>
<th>$X_m \times 10^{-6}$ in emu</th>
<th>$\mu_{\text{eff.}}$ in B. M.</th>
<th>Magnetic Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Bis (7-chloro-3-hydroxy-5-phenyl-1,3 dihydro-2H-1,4-Benzodiazepine 2-one hydrozonato) copper (II)</td>
<td>1.344</td>
<td>890.35</td>
<td>1.46</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>2.</td>
<td>Bis (7-chloro-3-hydroxy-5-phenyl-1,3 dihydro-2H-1,4-Benzodiazepine 2-one hydrazonato) Nickel (II)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>3.</td>
<td>Bis (7,chloro-3-hydroxy-5-phenyl-1,3 dihydro-2H-1,4-Benzodiazepine 2-one hydrazepato) cobalt (II)</td>
<td>1.7562</td>
<td>1155.49</td>
<td>1.67</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>4.</td>
<td>(7-chloro-3-hydroxy-5-phenyl-1,3-dihydro-2H-1,4-Benzodiazepine-2-one-hydrazonato) Iron(II)</td>
<td>22.259</td>
<td>7909.62</td>
<td>4.36</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>5.</td>
<td>(7-chloro-3-hydroxy-5-phenyl-1,3 dihydro-2H-1,3 Benzodiazepine-2-one hydrozonato) Iron(III)</td>
<td>30.18</td>
<td>10726.43</td>
<td>5.076</td>
<td>Paramagnetic</td>
</tr>
</tbody>
</table>
SUMMARY

7-chloro-3-hydroxy-5-phenyl-1,3-dihydro-2H-1,4 benzodiazepine-2-one hydrazene synthesised. It was used in the complex formation with several metal ions.

The metal ligend was prepared by using 7-chloro-3-hydroxy-5-phenyl-1,3-dihydro-2H-1,4-benzodiazepine-2-one hydrazone as a chelating reagent and was studied its corresponding metal chelates with Cu$^{+2}$, Ni$^{+2}$, Co$^{+2}$, Fe$^{+2}$ and Fe$^{+3}$. The said ligend was prepared and purified by usual methods.

pH measurements were made on systronics pH-meter. The pH was adjusted using the buffer solution prepared from sodium acetate, acetic acid, ammonium hydroxide as reported by Bates; Determination of pH, John wiley and sons, 1979.

The molecular weights of the chelates were determined by Rast's method using pure comphor. The results are in good agreement with the composition of the chelates.

The metal chelates of 7-chloro 3-hydroxy-5-phenyl-1,3-dihydro-2H-1,4-benzodiazepine-2-one hydrazone with Cu$^{+2}$, Ni$^{+2}$, Co$^{+2}$, Fe$^{+2}$ and Fe$^{+3}$ are coloured and soluble in organic solvents. Metal chelates manifest remarkable stability; probably due to formation of five membered heterocyclic ring.

The metal ions Cu$^{+2}$, Ni$^{+2}$ and Co$^{+2}$ have co-ordination number four and the said ligends are bidentate; here evidently $ML_2$ type of chelates are formed.
Job's method of continuous variation could be made applicable and this study revealed that the chelates of Cu\(^{2+}\), Ni\(^{2+}\) and Co\(^{2+}\) are formed with metal-ligand ratio 1:2 while for Fe\(^{2+}\) and Fe\(^{3+}\) the metal-ligand ratio is 1:1.

The observed molecular weight by Rast method is in the confirmation of the metal-ligand ratio 1:2 for Cu\(^{2+}\), Ni\(^{2+}\), and Co\(^{2+}\) but it is 1:1 in the case of Fe\(^{2+}\) and Fe\(^{3+}\) chelates.

The chelates described here are also investigated for their magnetic susceptibility. The metal chelates of Cu\(^{2+}\), Co\(^{2+}\), Fe\(^{2+}\) and Fe\(^{3+}\) are paramagnetic and the metal chelate of Ni\(^{2+}\) is diamagnetic.
The result supports the square planar structure of Ni\(^{+2}\) metal chelate, Co\(^{+2}\) chelate is a low spin complex while Fe\(^{+2}\) and Fe\(^{+3}\) complexes are of high spin.

The data on the magnetic moment indicate distorted octahedral, square planar, low spin tetrahedral and octahedral geometry for the copper (II), Nickel (II), cabalt (II), Iron (II) and iron (III) complexes respectively.\(^{(41)}\)

Results of Infra-Red spectra for reagent and metal chelates are given in chapter - 4.
References
REFERENCES


(2) Bell, childress,
    J. Org. chem. 27, 1691 (1962)

(3) E. Reeder and L. sternbiach
    U.S. Pat. 3, 109, 843 (1963)

(4) E. Reeder et. al.
    Belg. pat. 629, 227 (1967)
    eiden. U.S. Pat. 3, 340, 253 (1967)

(5) G. Gilli et. al.
    Acta crystalloigrr. B 34, 2826 (1978)

(6) Sisenwine et. al.
    Aggneimittel - Forsch 22, 682 (1972)

(7) E. I. Golienthai,
    18, 185, (1971).
(8) P. Job,
Ann. chim 97, 11 (6), (1936)

(9) R.T. Foley and R.C. Anderson,
J. Am. Chem. Soc. 1195, 70, (1948)
909, 71, (1949)

(10) S.E. Turner and R.C. Anderson,

(11) J. H. Yoe and A.E. Harvey,
J. Am. Chem. Soc. 648, 70, (1948)

(12) M. L. Moss and M.G. Mellon,
Ind. Eng. ( Chem. Anal, 612, 13, (1941)

(13) P. K. Pandya,

(14) K. C. Amin,

(15) F. Feigl and A. Bondi,
Ber. 2819, 64, (1931)

(16) E.G. Cox, W. Wardlaw and K.C. Webster,

(17) Reddy, Kadarmandigi and Murthy,
Ind. Acad. Sci. 159, 59, (1964)

(18) M. Calvin,

(19) D. P. Mellor and D.P. Craig,
(20) D. P. Mellor,

(21) G. N. Tyson and S.C. Adams,
 J. Am. Chem. Soc. 1228, 62, (1940)

(22) J. W. Wiley, G. N. Tyson and J. S. Steller,
 J. Am. Chem. Soc. 963, 64, (1942)

(23) N. K. Dutt,
 J. Ind. Chem. Soc. 572, 14, (1937)

(24) E.G. Cox and K.C. Webster,

(25) E. G. Cox, W. Wardlaw and K.C. Webster,

(26) E.G. Cox, E. Sharratt, W. Wardlaw and K.C. Webster,

(27) D. Pauling,
 "The nature of the chemical bonding"
 2nd Ed., Ch. II, C.U. Press, Ithaca (1940)

(28) P. Ray and D.H. Sen,

(29) P. Pfeiffer, Th. Wesse, H. Pfiztnar and H. Thielert,
 J. Prakt Chem. 261, 150, (1948)

(30) M. Kato, H.B. Jonassen and J.C. Fanning,
 Chem. Rav. 103, 64, (1964)
(31) R. Tsuchida and S. Yamada,
    Nature 1171, 176, (1955)

(32) S. Yamada, H. Kanamura and H. Tsuchida,

(33) W. R. Angus and W.K. Hill,
    Trans, Faraday Soc. 185, 40, (1943)

(34) W.R. Angus and D.V. Tilsten,
    Trans, Faraday Soc. 235, 43, (1946)

(35) B.C. Eggleston, D.F. Evans and R.E. Richards,

(36) L. Brant,
    Phys, Rev. 678, 17, (1921)

(37) B. Cabrera, E. Moles and J. Guzman,
    Arch, Sci. Phys. nat. 324, 37, (1914)

(38) P. Weiss and E.D. Bruins,
    Proc. Acad. Sci., Amsterdam, 346, 18, (1915)

    (London ) 313, A 173 (1937)

(40) W. R. Angus and D. V. Tilsten
    Trans, Faraday Soc. 221, 43, (1947)

(41) A. F. Wells,
    Structural Inorganic chemistry ELBS, orferd