The present study was aimed to prepare Ligand 3– Phenyl Pyrazole I–Carboxylo Hydroxamic Acid (HPPC = LH) and its complex with Cobalt(II) and derivation of structural formula of Cobalt (II) complex. Elemental analysis, magnetic moment determination, U.V. and Infrared Spectral studies of Cobalt (II) complex have been used to elucidate the structure.

Structural features of cobalt(II) complexes of ligand 3 – phenyl pyrazole I – carboxylo hydroxamic acid
KUMARI ASHA

Correspondence to:
KUMARI ASHA
Department of Chemistry,
M.S. College,
BHAGALPUR (I) INDIA

ABSTRACT
The present study was aimed to prepare Ligand 3– Phenyl Pyrazole I–Carboxylo Hydroxamic Acid (HPPC = LH) and its complex with Cobalt(II) and derivation of structural formula of Cobalt (II) complex. Elemental analysis, magnetic moment determination, U.V. and Infrared Spectral studies of Cobalt (II) complex have been used to elucidate the structure.

Key words: Ligand, Cobalt (II) Complex, Solvent, 3 Phenyl Pyrazole I – Carboxylo Hydroxamic Acid, Cobalt Bromide, Cobalt Formate

Various studies have been reported with regard to complexing behaviour of O, N, S, donor ligands and chelating molecules containing these atoms e.g. O/N, N/S, NS0 etc. Such co-ordination compounds are being used in chemotherapy. The use of metal chelates in Cancer treatment is the earnest craze of the age.

A large scope of work still remains in this field. With a view to add some novel complexes, a number of chelates of some Hydroxamic Acid i.e. 3 – Phenyl Pyrazole I – Carboxylo Hydroxamic Acid with metal Ion Cobalt (II) have been prepared.

The complexes of Co(II), Ni(II), Cu(II), and Zn(II) with 4 – salicyaldimine 3 – Mercupto 5- phenyl – 1, 2, 3 triazole (SMPT H) have been reported by Mishra et al.(1)

The complexes of 4 – Amino 3, 5 dimethyl 1, 2, 4 triazole have been prepared by J. Singh and N.K. Singh (2) of the type [M (ADMT) Cl]

M = Co, Ni
ADMT = 4 – Amino 3, 5 dimethyl 1, 2, 4 triazole.

Magnetic moment and electric spectra suggested tetrahedral geometry for [Co (ADMT) Cl]

MATERIALS AND METHODS
Ligand (HPPC = LH) was prepared in laboratory using Hydroxyl Amine Hydrochloride in Methanol, KOH in Methanol, Ethyl 3 – Phenyl Pyrazole I- Carboxylate by the method reported by Blatt.

Cobalt(II) complex was prepared using Cobalt Bromide / Formate Analar – grade of B.D.H. F. Merk. The mole formula of the complex was determined on the basis of Elemental analysis. Magnetic moment determination was used to predict the geometry of complex. Geometry of complex was supported by u.v. spectral analysis whereas Infrared Spectral studies were used to determine the co-ordination site of ligand to metal Ion Co(II).

Elemental analysis was done manually by standard methods of analysis. Magnetic and Spectra analysis was done with the help of Advanced Laboratories on personal request.

RESULTS AND DISCUSSION
The results obtained from the present investigation are below:

Preparation of ligand:
Preparation of 3 – Phenyl Pyrazole I – Carboxylo Hydroxamic Acid (HPPC = LH)
The ligand was prepared by the method reported by Blatt. 1 mole of KOH(56.1g) dissolved in 10 ml. of Methanol was added to a solution of 0.67 mole of Hydroxyl Amine Hydrochloride (46.7g) in 240ml of Methanol. Both solution were mixed together keeping the temperature range at 30°–50°C. The mixture was left in ice bath for five minutes ensuring the complete precipitation of KCl. Then 0.35 mole of Ethyl - 3 Phenyl Pyrazole - I – Carboxylate was added in portion with constant shaking and after addition the solution was filtered immediately through suction. The residue in funnel was washed with a little methanol. The filtrate was kept in Erlenmeyer Flask for 36 hrs. Crystal of Potassium salt of 3 – Phenyl Pyrazole I – Carboxyl Hydroxamic Acid was filtered, washed with little absolute Alcohol and dried in air.

About half of the yield was mixed with 80ml. 1.25 N Acetic Acid and stirred while heating until a clear solution was obtained. The solution was allowed to cool at room temperature and finally chilled in ice bath. Brown crystal
of 3 – Phenyl Pyrazole - I – Carboxyl Hydroxamic Acid was prepared.

Preparation of metal complex :
[Co PPc Br(H₂O)₂] 2H₂O / [Co.PPc.HCOO (H₂O)₂ ] .2H₂O

Aqueous ethanolic cobalt bromide /formate solution was treated with ligand solution in Ethanol in 1:2 ratio and was just made alkaline. The content was warmed on water bath for few hours and allowed to cool. Pink colour precipitate was separated which was filtered, washed several times with alcoholic water till free from sulphate ion and dried at 105° – 110°C.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>µeff (B.M.)</th>
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<tbody>
<tr>
<td>[Co.PPc.Br(H₂O)₂]2H₂O</td>
<td>2.08</td>
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<tr>
<td>[Co.PPc.HCOO(H₂O)₂].2H₂O</td>
<td>2.12</td>
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</table>

Magnetic moment :
Magnetic Moment of cobalt(II) complexes was determined at 304°K.
The µeff value of cobalt complexes lies in between high spin octahedral and low spin octahedral or planar cobalt(II) complexes.

U.V. spectral studies of metal complex:
Absorption spectra of cobalt(II) complexes by U.V.
spectral studies was investigated as below:
The value suggested that cobalt(II) complexes have high or low spin octahedral structure.

Infrared spectral studies of cobalt(II) complex:
Studies on I.R. spectra help in deciding the site of linkage of ligand to metal Ion Co(II).
The absorption band at 3265/3270cm⁻¹ owing to N-H stretching vibration in the I.R. spectrum of the ligand disappear in I.R. spectrum of metal complexes. This indicates the involvement of NH group in enolisation of the ligand during complex formation. Further the carbonyl frequency observed in the ligand spectra disappear in the spectra of complexes which indicates that carbonyl group of –Co, NH and –OH group enolises during complex formation. This indicates that oxygen atom of the carbonyl group is involved in co-ordination to the metal Ion in the metal complexes. The appearance of a new bond near 640cm⁻¹ assignable to M-O supports the co-ordination of C=O.

Proposed structure of complexes :

On Elemental Analysis, following results were obtained

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<tr>
<th>Complexes</th>
<th>Cal</th>
<th>Found</th>
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<tbody>
<tr>
<td>[Co.PPc.Br(H₂O)₂]2H₂O</td>
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<td>14.25</td>
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<tr>
<td>% C</td>
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<tr>
<td>% H</td>
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<tr>
<td>% N</td>
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<tr>
<td>% Br</td>
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<table>
<thead>
<tr>
<th>Complexes</th>
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<tbody>
<tr>
<td>[Co.PPc.HCOO(H₂O)₂].2H₂O</td>
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<td>15.57</td>
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<tr>
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<tr>
<td>% N</td>
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<td>11.13</td>
</tr>
<tr>
<td>% Br</td>
<td></td>
<td>-</td>
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</table>

In general amide II and ν (N-O) bonds were recorded to have shifted to lower frequency in complexes.
Amide II band is mainly due to $\nu$(N-H) and $\nu$(C≡N). As has already been indicated there is no (N-H) in complexes of Hydroxamic Acid unless Alkyl or Aryl system posseses it. The retention of the amide band in spectra of complexes, at low frequency is due to the presence of –C – N in complexes. Shifting of (N-O) band to lower energy indicates the involvement of this oxygen atom in the co-ordination.

The other bands which appear in the lower i.e. 450-430, 310-300, 245-230 and 210-200cm$^{-1}$ are assigned due to M-O, M-N, and M-Br, respectively. On the basis of foregoing observation the complexes are suggested the following general features:

REFERENCES