

Research Paper :

Studies on structural features of copper (II) complexes of ligand 3-phenylpyrazole I-carboxylo hydroxamic acid

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ABSTRACT

The present study was aimed to prepare Ligand 3-Phenylpyrazole I-Carboxylo Hydroxamic Acid (HPPC = LH) and its complex with Copper (II) and derivation of structural formula of Copper (II) complex on the basis of Elemental analysis, Magnetic moment determination, U.V. and Infrared Spectral studies of Copper (II) complex, structure are assigned

Key words : Ligand, Copper (II) complex, Solvent, 3 Phenyl pyrazole 1 – Carboxylo hydroxamic acid

Much more work has been reported related to complexing behaviour of O, N, S, donor ligands and chelating molecules containing these atoms e.g. O/N, N/S, NSO etc. Such co-ordination compounds are well being used in chemotherapy. Relation to 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 Copper(II) have been prepared.

Verma *et al.*¹⁷⁷ have reported the copper (II) complexes of 4 – amino 3 – Hydrazine 5 – Mercapto 1, 2, 4, triazole . The complex are characterized by various analytical and spectral data.

the method reported by Blatt.

Cu(II) complex was prepared using Cupric Bromide / Formate Analar – grade of B.D.H.E. Merk. The molecular 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 study was used to determine the co-ordination site of ligand to metal Ion copper(II).

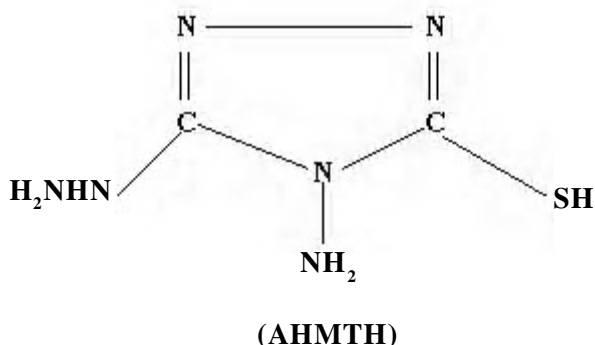
Elemental analysis will be done manually by standard methods of Analysis. Magnetic and Spectral analysis was done with the help of Advanced Laboratories on personal request (as was usually done)

RESULTS AND DISCUSSION

Preparation of ligand :

Preparation of 3 – Phenyl Pyrazole I – Carboxyl Hydroxamic Acid (HPPC = LH)

The legand was prepared by the method reported by Blatt. 1 mole of KOH(56.1gm) dissolved in 10 ml. of Methanol was added to a solution of 0.67 mole of Hydroxyl Amine Hydrochloride (46.7gm) in 240ml. of Methanol. Both solⁿ were mixed together keeping the temperature range at 30^o – 50^oC. The mixture was left in ice both for five minute 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 section. The filtrate was kept in Erlenmeyer Flask for 36 hrs. Crystal of Potassium salt of 3 – Phenyl Pyrazole I – Carboxyl Hydroxamic Acid was filtered,

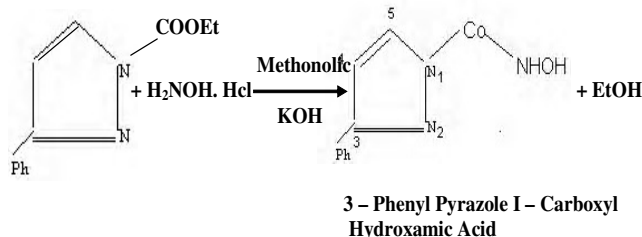


MATERIALS AND METHODS

Ligand (HPPC = LH) was prepared in laboratory using Hydroxyl Amino Hydrochloride in Methanol, KOH in Methanol, Ethyl 3 – Phenyl Pyrazole I- Carboxylate by

washed with little absolute Alcohol and dried in air.

About half of the yield was mixed with 80ml. 1.25N 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 complexes :

[Cu.PPC.Br(H₂O)₂].2H₂O/[Cu.PPC.HCOO(H₂O)₂].2H₂O

0.04 mole of Cupric Bromide/Formate was dissolved in 40ml of distilled water and added to an aqueous Ethanolic solution of the ligand (0.04 mole in 35 ml. water) slowly with constant stirring. Light green precipitate separated out which is filtered, washed with distilled water until free from chloride and dried at 115° – 120°C in air oven.

On elemental analysis, following results are obtained which is given by Table 1.

Magnetic moment :

Magnetic Moment of copper(II) complexes was

determined at 300K. The data are given by Table 2.

These value corresponds the value required for tetrahedral octahedral copper(II) complexes.

U.V. spectral studies of metal complex:

Absorption spectra of Cu(II) complexes by U.V. spectral studies was investigated as given in Table 3.

This value suggested that copper(II) complexes have distorted octahedral structure.

Infrared spectral studies of copper(II) complex :

Studies on I.R. spectra help in deciding the site of linkage of ligand to metal Ion Cu(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 enaliation of the legand 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 band near 640cm⁻¹ assignable to M-O supports the co-ordination of C=O.

The data of I.R. spectra of the ligand and metal complexes with reference to above mentioned three groups and (M – N) are given in the test Narayan et al. white discussing structure of complexes prepare from

Table 1 : Elemental analysis

[Cu.PPC.Br(H ₂ O) ₂].2H ₂ O Complex			[Cu.PPC.HCOO(H ₂ O) ₂].2H ₂ OComplex		
	Calculated	Found		Calculated	Found
%Cu	15.21	15.20	%Cu	16.60	16.61
%C	28.74	28.75	%C	34.50	34.52
%H	3.83	3.84	%H	4.44	4.43
%Br	19.14	19.16	%Br	-----	-----
%N	10.06	10.05	%N	10.98	10.99

Table 2 : Magnetic moment of copper (II) complex

Complexes	μ _{eff} (B.M.)
[Cu.PPC.Br(H ₂ O) ₂].2H ₂ O	2.11
[Cu.PPC.HCOO(H ₂ O) ₂].2H ₂ O	2.15

multi-substituted chalkoneoxime having this type of system adduced similar arguments.

In general amide II and ν(N-O) bonds were recorded to have shifted to lower frequency in complexes. Amide

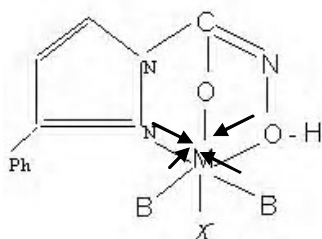
Table 3 : Absorption spectra of Cu (II) complexes

Complexes transition	[Cu.PPC.Br(H ₂ O) ₂].2H ₂ O	[Cu.PPC.HCOO(H ₂ O) ₂].2H ₂ O
Ligand absorption (nm)	225, 280	250, 270
C.T. Bands	360	375
d-d Transition	405	-----

Π band is mainly due to $\nu(\text{N-H})$ and $\nu(\text{C}=\text{N})$. As has already been indicated there is no (N-H) in complex of Hydroxamic Acid unless Alkyl or Aryl group possesses it. The retention of amide band in spectra of complexes, of course, at lower frequency is due to the presence of $-\text{C}=\text{N}$ in complexes. Shifting of (N-O) band to lower energy indicates the involvement of this oxygen atom in the coordination.

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

Proposed structure of complexes :



$X = \text{Br, HCOO}$

$B = \text{H}_2\text{O}$

$M = \text{Cu(II)}$

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