

## STUDIES ON CO-ORDINATION BEHAVIOUR OF THIOPYRUVIC HYDROXAMATO LIGAND(S) TOWARDS SOME METAL IONS.

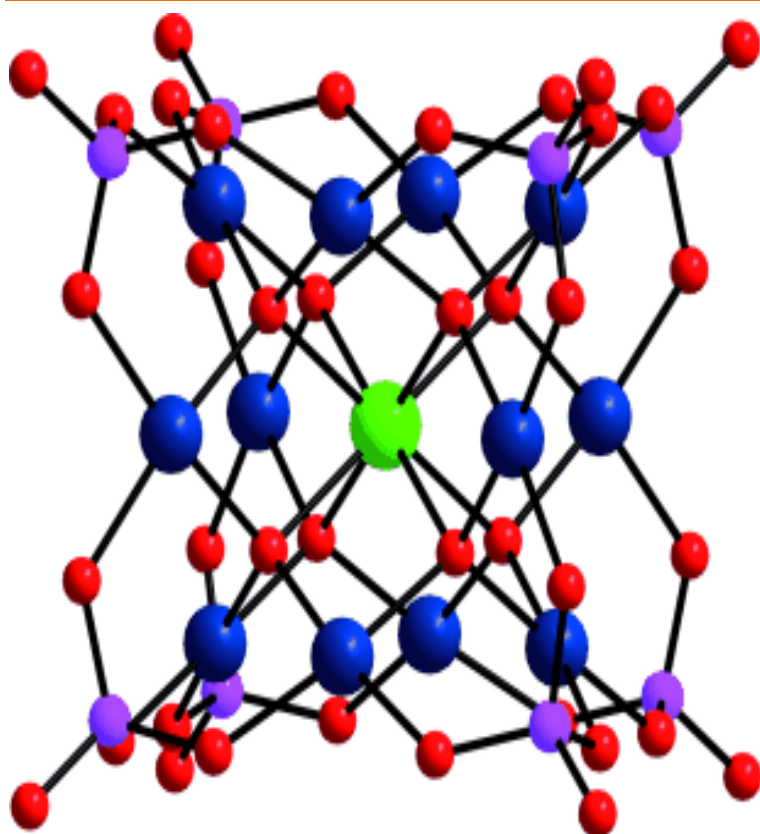


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### Authors Short Profile

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### Abstract :

This entitled “STUDIES ON COORDINATION BEHAVIOUR OF THIOPYRUVIC HYDROXAMATO LIGANDS(S) TOWARDS SOME METAL IONS” embodies the studies in coordination compounds of 2-amino ; 3 dichloro-Phenyl thiopyruvic hydroxamic acid (ACPTH) and 2-amino-3 ; 5-dimethyl phenyl thiopyruvic hydroxamic acid (AMPHTH) containing nitrogen, oxygen as well as sulphur as potential donor atoms with some metal ions.

This thesis, compiled into five chapters, describes the preparation, properties and probable structures of the complexes of copper (II), nickel (II), cobalt (II), cadmium (II), mercury (II) and lead (II) with the ligands.

There is a brief survey of donor properties of ligands containing N, O & S donor atoms.

### KEYWORDS :

*Co-ordination Behaviour , Thiopyruvic Hydroxamate Ligand(S) , probable structures .*

## INTRODUCTION

The "PREPERATION AND ELEMENTAL ANALYSIS OF LEGANDS AND THEIR COMPLEXES" describes the preparation of ligands and its complexes with Cu (II), Co (II), Ni (II), Cd (II), Hg (II) and Pb (II) have been described. The procedures of elemental analysis have also been included in this chapter. On the basis of elemental analysis, the molecular formula of the complexes have been found of the types  $[MLXB]_nH_2O$   $M=Co$  (II), Ni (II), Cu (II) ;  $L=ACPT, AMPT$  ;  $B = H_2O, Py, \alpha - pic$  ;  $n = 0, 1, 2$  ;  $[ML]Cl$  ;  $[MLCl]$  ; ( $M = Hg(II), Cd(II), Zn(II), Pb(II)$   $L =$  as usual. The ligands act as tetra dentate monobasic ligand. The supporting facts of these molecular formula of complexes have been discussed in the forthcoming chapters.

The "MAGNETIC MEASUREMENTS OF THE COMPLEXES" deals with the results and discussions of magnetic moment determination.

A theoretical approach of magnetic behavior of copper (II), Cobalt (II), nickel (II) complexes has been incorporated in this chapter. The magnetic moment of complexes have been determined. The values are noted here with the respective complexes.  $[Cu.L.Cl.H_2O] H_2O$  (1.75 B.M.) ;  $[Cu.L'.(CH_3COO)]$  (1.90 B.M.) ;  $[Cu.L.HCOOH_2O]$  (1.80 B.M.) ;  $[Cu.L'.Cl.Py]$  (1.85 B.M.) ;  $[Cu.L'.Cl.H_2O]$  (1.75 B.M.) ;  $[Cu.L'.CH_3COO]$  (1.80 B.M.) and  $[Cu.L'.Cl.Py]$  (1.90 B.M.). Thus the magnetic moment values of Cu (II) complexes fall in the range (1.75 to 1.90 B.M.). These values correspond the values required for tetrahedral octahedral copper (II) complexes.

Cobalt (II) complexes show magnetic moment values in the range 2.40 to 2.10 B.M. at 3030 K, such as  $[Co.L.H_2O] H_2O$  ;  $[Co.L.Cl.Py]$  ;  $[Co.L.Cl. (\alpha - pic)]$  ;  $[Co.L'.Cl.H_2O]$  ;  $[Co.L'.Cl.Py]$  ;  $[Co.L'.Cl.(\alpha-pic)]$  show magnetic moment values 2.30, 2.40, 2.35, 2.10, 2.20 and 2.25 B.M. respectively. The  $\mu_{eff}$  values of cobalt complexes are in between those high-spin octahedral and low-spin octahedral or planar cobalt (II) complexes. The lower magnetic moment values may also be apprehended due to a mixture of planar cobalt (II) complexes surrounded by octahedral or tetrahedral species.

The magnetic moment values of nickel (II) complexes have been determined at 3030 K and the values in B.M. are noted with the complexes.  $[Ni.L.H_2O] H_2O$  (2.60 B.M.) ;  $[Ni.L.Cl.Py]$  (2.80 B.M.) ;  $[Ni.L'.Cl.H_2O] H_2O$  (2.85 B.M.) ;  $[Ni.L'.Cl.Py]$  (2.65 B.M.) ;  $[Ni.L.Cl(\alpha-pic)]$  (2.75 B.M.) and  $[Ni.L'.Cl(\alpha-pic)]$  (2.70 B.M.).

The magnetic moment values of the complexes as observed fall in the range 2.70 to 2.85 B.M. The values are straight forward in the range accepted for octahedral nickel (II) complexes. The magnetic moment values of mixed ligand complexes have lower values than high-spin octahedral complexes. The lower values of nickel (II) complexes may be attributed to the presence of some square planar species surrounded by octahedral or tetrahedral complexes.

The complexes of Zinc (II), cadmium (II), mercury (II) and lead (II) were found to be diamagnetic.

The "ELECTRONIC SPECTRAL STUDIES OF METAL COMPLEXES" deals with the results and discussion on electronic absorption spectra behavior of complexes. The electronic absorption spectra of the complexes have been recorded in the range 200 nm (50000  $cm^{-1}$ ) to 850 nm (21758  $cm^{-1}$ ). In this range only ligand absorption arising from (C = S) / (C = N) group could be observed, but except in few case no d-d band could be located due to high ligand absorption and expected low intensity of six co-ordinated nickel (II) complexes.

In concentrated ethanolic solution LH and L'H complexes exhibit ligand to metal charge transfer band near 375 and d-d transition at 460-465 nm. The last peak is attributed to presence of planar species present in the complexes. However, the solid reflected spectra of complexes exhibit expected weak d-d transition of nickel (II) ions. Though the exact assignments of band are not possible since the spectra have been measured in the range 350-1000 nm, however, tentative assignments and their

band positions have been made. The strong electronic reflectance band at 380 nm of  $[ML] 2H_2O$  is assigned to a combination of  $3A_2g \rightarrow 3T_2g$  (P) and a charge transfer band. In addition to  $3A_2g \rightarrow 3T_1g$  (P),  $3A_2g \rightarrow 3T_1g$  (F) and  $3A_2g \rightarrow 3T_2g$  (F) transition,  $[MIL] 2H_2O$  exhibit spin forbidden transition  $3A_2g \rightarrow 3Eg$  at 675 nm. From the energy of  $3A_2g \rightarrow 3T_2g$  transition, the value of ligand field parameter is found to be 825 nm for  $|Ni| 2H_2O$ . Thus from values, it appears that the present ligand can be placed in the strong end of spectrochemical series.

The electronic spectra of cobalt(II) complexes under investigation has been recorded in ethanol and also some reflectance spectra have also been taken. In solution no d-d bands are observed but they exhibit strong ligand absorption to  $n \rightarrow \pi^*$ . Bands 325 are assigned  $\pi \rightarrow \pi^*$  where as bands 410 nm are assigned to charge transfer transitions. Weak and broad band 470 and 590 nm of reflectance spectra and assigned to  $4T_1g \rightarrow 4A_2g$  and  $4T_1g \rightarrow 4T_2g$  respectively. The band corresponding to  $4A_2g \rightarrow 4A_2g$  is not observed in solution spectra due to obscuring of ligand absorptions.

The weak and broad bands in the region 470-590 nm are assigned to some tetragonal distortion of octahedral species in the presence of base molecules.

The electronic reflectance or absorption spectra of the copper(II) complexes under investigation are of a little significance, since the strong charge-transfer transition originating from back bonding of thioamide sulphur to copper atom obscures the expected d-d bands in the majority of copper (II) complexes and some electronic and reflectance spectral curves.

In Nujol mull the copper (II) complexes display three or four bands due to charge-transfer and intraligand  $n \rightarrow \pi^*$  or  $\pi \rightarrow \pi^*$  electronic transition. All other bands are either shoulders or weak and broad band. The charge transfer band which absorbs as strong band near 400-420 nm. The reflectance spectra of some copper (II) complexes show shoulders or weak and broad band near 400 nm due to the charge transfer. The broad shoulder observed near 650-710 nm in the electronic spectra of mononuclear complexes fall in the range of spectral band assignable to  $Eg \rightarrow T_2g$  transition for octahedral or distorted octahedral copper (II) complexes. Therefore, it is suggested that the copper (II) complexes have distorted octahedral structures.

The "INFRARED SPECTRA OF LIGAND AND ITS COMPLEXES" describes the I.R. spectral mode of ligands to metal ions. The absorption band at 3265 / 3270  $cm^{-1}$  owing to N - H stretching vibration in the I.R. spectrum of the ligand shifts to lower frequency by approximately about  $20 \pm 5 cm^{-1}$  in I.R. spectra of the metal complexes. This indicates the involvement of NH group in coordination to the metal ion through nitrogen atom. Further confirmation of N-bonding to the metals in the complexes is obtained by the appearance of low frequency spectral absorptions to (M-N) interactions in the region 350-250  $cm^{-1}$ . In the spectra of metal complexes under study, the absorption bands in the region 290-350  $cm^{-1}$  are tentatively assigned to (M-N).

The sharp absorption band at 1650 / 1655  $cm^{-1}$  owing to C = O stretching vibrations in the I.R. spectrum of the ligand shifts to lower frequency in metal complexes and is found in the region 1600-1575  $cm^{-1}$ . This indicates that oxygen atom of the carboxyl group is involved in co-ordination to the metal ions in the metal complexes. The appearance of a new band near 640  $cm^{-1}$  assignable to M-O support the coordination of C = O.

The weak absorption band observed at 2560  $cm^{-1}$  in the I.R. spectrum of the ligand due to -S-H stretching vibrations is washed of completely from the I.R. spectra of the metal complexes, however the C = S band (near 875) shifts to lower frequency ( $840 \pm 5$ ) indicates the co-ordination of thione sulphur. This is supported by appearance of a new band ( $280 \pm 5$ ) assignable to  $\nu$  (M-S). Further confirmation of S-bonding to the metals in the complexes is obtained by appearance of low frequency spectral absorptions due to (M-S) in the range 350-200  $cm^{-1}$ . In the spectra of metal complexes under study, the absorption bands in region 250-290  $cm^{-1}$  are tentatively assigned to (M-S).

The data of the I.R. spectra of the ligand and metal complexes with reference to above mentioned three groups and (M-N) are given in the text. Narayan et.al. while discussing structure of complexes prepared from multisubstituted chalcone – oxime having this type of system adduced similar arguments.

In general, amide – II and  $\nu$  (N-O) bands were recorded to have shifted to lower frequency in complexes. Amide – II bands 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 acids unless alkyl or aryl system possesses it. The retention of amide band in spectra of complexes, of course, at lower 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.

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