

## Synthesis and Characterization of Co(II), Ni(II) and Cu(II) Complexes with $\alpha$ -(*o*-Hydroxy acetophenone)imino Acetohydroxamic Acid

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The complexes of Co(II), Ni(II) and Cu(II) metals with  $\alpha$ -(*o*-hydroxy acetophenone)imino acetohydroxamic acid in presence of bases containing oxygen and nitrogen as donor atoms have been synthesized and characterized. All the complexes have been found to be octahedral in geometry.

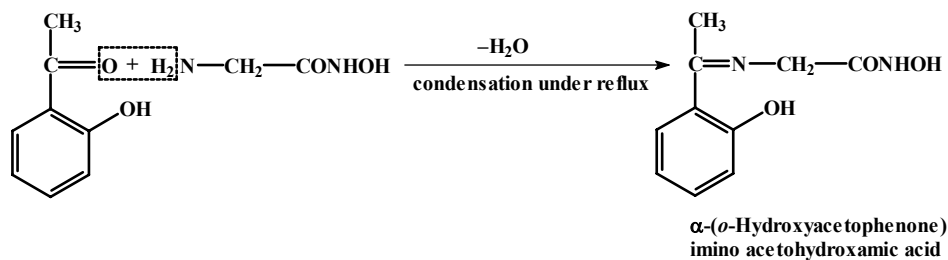
**Key Words:** Cobalt(II), Nickel(II), Copper(II) Complexes,  $\alpha$ -(*o*-Hydroxy acetophenone)imino acetohydroxamic acid.

### INTRODUCTION

In recent years a number of workers have been interested in metal-coordination chemistry<sup>1-3</sup>. In present studies, the synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes of  $\alpha$ -(*o*-hydroxy acetophenone)imino acetohydroxamic acid are reported.

### EXPERIMENTAL

**Preparation of the ligand:** The Schiff base ligand  $\alpha$ -(*o*-hydroxy acetophenone) imino acetohydroxamic acid was prepared by the condensation of  $\alpha$ -amino acetohydroxamic acid and *o*-hydroxy acetophenone in ethanolic medium having equimolar ratio. When the condensation reaction was completed, a yellow colour precipitate separated out and the same was separated by filtration. The compound was found soluble in ethanol, acetone, diethyl ether, *etc.* The compound was analyzed and found to contain C = 57.69 %, H = 5.76 % and N = 13.46 % which corresponds the molecular formula C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>. The chemical reaction occurring during the course of condensation process is given below:



**Preparation of complexes:** The acetate or chloride of Co(II), Ni(II) and Cu(II) were dissolved separately in aqueous-ethanolic solution. The ethanolic solution of the ligand was added to the metal solution in 1:1 ratio. The resulting solution was then refluxed on steam bath in presence of oxygen and nitrogen donor bases separately for about 1 h till the complex separated out. The precipitate thus obtained was separated by filtration and dried over KOH pellets. On the basis of elemental analysis (Table-1), the complexes were found to possess the molecular formula  $[M(L)(B)_3]$ ; where M = Co(II), Ni(II) and Cu(II),  $L^{2-} = C_{10}H_{10}N_2O_2$  and B = water, ammonia and  $\alpha$ -picoline.

TABLE-1  
ELEMENTAL ANALYSIS AND VALUE OF ELECTRICAL  
CONDUCTIVITY AND MAGNETIC SUSCEPTIBILITIES

| Complexes                                                                                                                              | Elemental analysis (Found (Calcd.):) |                  |                |                  | Ohm <sup>-1</sup><br>cm <sup>2</sup><br>mol <sup>-1</sup> | $\mu_{\text{eff}}$<br>(BM) |
|----------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------|------------------|----------------|------------------|-----------------------------------------------------------|----------------------------|
|                                                                                                                                        | M                                    | C                | H              | N                |                                                           |                            |
| [Co(C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> )(H <sub>2</sub> O) <sub>3</sub> ]                                   | 18.30<br>(18.46)                     | 37.40<br>(37.62) | 5.04<br>(5.01) | 8.83<br>(8.78)   | 24                                                        | 4.98                       |
| [Co(C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> )(NH <sub>3</sub> ) <sub>3</sub> ]                                   | 18.52<br>(18.64)                     | 37.77<br>(37.98) | 6.07<br>(6.01) | 22.18<br>(22.15) | 14                                                        | 4.90                       |
| [Co(C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> )(C <sub>6</sub> H <sub>7</sub> N) <sub>3</sub> ] $\alpha$ -picoline | 10.67<br>(10.82)                     | 61.70<br>(61.77) | 5.72<br>(5.69) | 12.90<br>(12.87) | 18                                                        | 4.96                       |
| [Ni(C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> )(H <sub>2</sub> O) <sub>3</sub> ]                                   | 18.20<br>(18.41)                     | 37.48<br>(37.65) | 5.04<br>(5.02) | 8.86<br>(8.78)   | 16                                                        | 3.10                       |
| [Ni(C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> )(NH <sub>3</sub> ) <sub>3</sub> ]                                   | 18.40<br>(18.59)                     | 37.82<br>(38.01) | 6.05<br>(6.01) | 22.20<br>(22.17) | 22                                                        | 2.98                       |
| [Ni(C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> )(C <sub>6</sub> H <sub>7</sub> N) <sub>3</sub> ] $\alpha$ -picoline | 10.60<br>(10.79)                     | 61.62<br>(61.79) | 5.73<br>(5.70) | 12.91<br>(12.87) | 28                                                        | 2.92                       |
| [Cu(C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> )(H <sub>2</sub> O) <sub>3</sub> ]                                   | 19.48<br>(19.62)                     | 36.96<br>(37.09) | 4.98<br>(4.94) | 8.70<br>(8.65)   | 24                                                        | 2.10                       |
| [Cu(C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> )(NH <sub>3</sub> ) <sub>3</sub> ]                                   | 19.68<br>(19.80)                     | 37.30<br>(37.44) | 5.95<br>(5.92) | 21.86<br>(21.82) | 30                                                        | 2.00                       |
| [Cu(C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> )(C <sub>6</sub> H <sub>7</sub> N) <sub>3</sub> ] $\alpha$ -picoline | 11.45<br>(11.57)                     | 61.10<br>(61.25) | 5.68<br>(5.64) | 12.80<br>(12.75) | 22                                                        | 1.96                       |

Electrical conductivities of the solutions of complexes were measured by conductivity meter bridge manufactured by Wiss-Techen Werch Stathen type-LBR at room temperature in DMF. The electronic spectra of the complexes were recorded with Hitachi-320 spectrophotometer at CDRI, Lucknow. The infra red spectra were recorded on Perkin-Elmer-577 spectrophotometer using KBr. The magnetic moment of the complexes were measured by Gouy's method in the University Department of Chemistry, B.R. Ambedkar Bihar University, Muzaffarpur.

## RESULTS AND DISCUSSION

The ligand  $\alpha$ -(*o*-hydroxy acetophenone)imino acetohydroxamic acid behaves like bi-anionic tridentate ligand through potential nitrogen and oxygen donor atoms. In case of IR spectra of the ligand, there are two broad and intense bands around

3480 and 3180  $\text{cm}^{-1}$  indicating the presence of one free -OH group and one hydrogen bonded -OH group in the ligand molecule.

By the perusal of IR spectra of all the complexes (Table-2), it has been found that there is a general disappearance of the band around 3480  $\text{cm}^{-1}$  indicating the deprotonation of free -OH group and participation of phenolic oxygen atom in the bond formation and the presence of a broad and sharp band around 3260  $\text{cm}^{-1}$  in all complexes indicates the presence of one free -OH group with a very weak hydrogen bonding even in the complexes. By the comparison of the IR spectra of the ligand and the complexes, it has been obtained that the bands due to  $\nu(\text{C}=\text{N})$ ,  $\nu(\text{N}-\text{O})$  and  $\nu(\text{C}-\text{O})$  vibrations of the ligand are appreciably changed after complex formation. The reduction in the frequency of  $\nu(\text{C}=\text{N})$  vibration from 1650 to 1590  $\text{cm}^{-1}$  and increase in the frequency of  $\nu(\text{N}-\text{O})$  vibration from 1070 to 1100  $\text{cm}^{-1}$  and in the frequency of  $\nu(\text{C}-\text{O})$  vibration from 1300 to 1380  $\text{cm}^{-1}$  indicate the participation of both aldimino and oximino nitrogen atoms and oxygen atom of (-OH) phenolic group in the complex formation.

TABLE-2  
KEY IR SPECTRAL BANDS ( $\text{cm}^{-1}$ ) OF THE LIGAND AND ITS METAL COMPLEXES

| Assignments              | Ligand | [Co(L)(B) <sub>3</sub> ] | [Ni(L)(B) <sub>3</sub> ] | [Cu(L)(B) <sub>3</sub> ] |
|--------------------------|--------|--------------------------|--------------------------|--------------------------|
| $\nu(\text{O}-\text{H})$ | 3480   | –                        | –                        | –                        |
| $\nu(\text{OH})$         | 3180   | 3260                     | 3260                     | 3260                     |
| $\nu(\text{C}=\text{N})$ | 1660   | 1590                     | 1600                     | 1580                     |
| $\nu(\text{N}-\text{O})$ | 1120   | 1080                     | 1070                     | 1090                     |
| $\nu(\text{C}-\text{O})$ | 1300   | 1370                     | 1380                     | 1360                     |
| $\nu(\text{M}-\text{N})$ | –      | 440                      | 445                      | 435                      |
| $\nu(\text{M}-\text{O})$ | –      | 450                      | 435                      | 445                      |

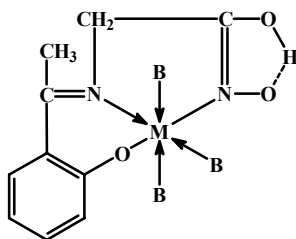
In all the complexes, a new sharp and intense band has been obtained around 440  $\text{cm}^{-1}$  due to  $\nu(\text{M}-\text{N})$  vibrations confirming the participation of both kinds of nitrogen atoms. The deprotonation of -OH group attached to benzene nucleus has been confirmed by the presence of a new sharp and intense band around 550  $\text{cm}^{-1}$  due to  $\nu(\text{M}-\text{O})$  vibrations.

The value of magnetic moment obtained for Co(II) complexes in the range of 4.90-4.98 BM indicates the octahedral nature of the complexes. The value of magnetic moment obtained for Ni(II) complexes in the range of 2.92-2.98 BM indicates the octahedral arrangement of donor atoms around the metal ion. The value of magnetic moment obtained for Cu(II) complexes in the range of 1.90-1.96 BM indicates the octahedral geometry of the complexes<sup>4,5</sup>.

The electronic spectra of Co(II) complexes obtained around 460 nm indicates  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  transition which suggests the octahedral nature of the complexes. The electronic spectra of Ni(II) complexes obtained at 465 nm due to  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$  or CT transition indicates the octahedral geometry of the complexes. The electronic spectra of the Cu(II) complexes obtained as broad and unsymmetrical

band around 410 nm due to  ${}^3B_{1g} \rightarrow {}^2E_g + CT$  transition suggests the distorted octahedral nature of the Cu(II) complex<sup>6</sup>.

On the basis of elemental analysis and electrical conductance, all the complexes of Co(II), Ni(II) and Cu(II) have been found to be monomeric and non-electrolyte in nature. All the complexes have been found to be octahedral in nature as shown below:



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