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## **Synthesis and physico-chemical studies of Cu(II), Ni(II), Co(II) complexes with p-chloroisnitroso acetophenone (P-CIINAP)**

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### **ABSTRACT**

*The Cu(II), Ni(II) and Co(II) complexes of ligand (P-CIINAP) P-Chloro isonitrosoacetophenone derived from isonitrosoacetophenone have been synthesized. The complexes of formula Cu(P-CIINAP)<sub>2</sub>, Ni(P-CIINAP)<sub>2</sub>, Co(P-CIINAP)<sub>2</sub> have characterized on the basis of elemental analysis, molar conductance, magnetic data, electronic spectra etc. and their possible structures are discussed. The diamagnetic nature of Co(II) complex indicates octahedral geometry while the diamagnetic and spectral features of the Cu(II) and Ni(II) complexes suggested square planer geometry.*

**Key word:** planar geometry, magnetic susceptibility, nmr and electronic spectra.

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### **INTRODUCTION**

Metal complexes of bidentate oximes are capable of exhibiting a variety of structures owing to their potential ambidentate character. For many Ni(II) and Cu(II) complexes obtained from isonitroso β diketones asymmetrical ring structures have been reported[1,2]. Patel and co-workers[3] have proposed a symmetrical five member ring structure. The ligand 4-chloro isonitrosoacetophenone (P-CIINAP) has been used for few analytical applications [4, 6]. However, structural studies of the Cu(II), Ni(II) and Co(II) complexes with (P-CIINAP) have not been reported as such. It was therefore considered worthwhile to prepare and characterize them and report their structural features on the basis of magnetic data, electronic, IR and NMR spectral studies

## EXPERIMENTAL SECTION

**Chemicals:** The chemicals used were of A.R. grade. The ligand P-chloroisnitrosoacetophenone was prepared by the method described in the literature [6.7]. The metal complexes are prepared as follows:-

**Preparation of Cu (P-CIINAP)<sub>2</sub> complex :-** 0.625 g of (P-CIINAP) and 0.369 g of copper acetate were dissolved in minimum quantity of alcohol and equal volume of water. The copper acetate solution was added to the reagent solution drop wise with constant stirring. The pH of the resultant was adjusted to 3.5 - 4 with HCl / NH<sub>4</sub>OH. A yellowish green colored complex thus formed was digested on water bath for 20 minutes, it was filtered, washed with water, dried at 90<sup>0</sup>C for several hours. It was recrystallized from chloroform and analyzed for copper, carbon, hydrogen and nitrogen.

**Preparation of Ni (P-CIINAP)<sub>2</sub> Complex:-** 0.326g of (P-CIINAP) and 0.497 g of nickel acetate hydrated was dissolved in minimum quantity of alcohol and equal volume of water. The nickel acetate solution was added to the reagent solution drop wise with constant stirring. The pH of the resultant solution was adjusted to 2.5 to 3. Then the solution was kept in a boiling water bath for 30 minutes, a yellowish colored complex was separated. It was filtered, washed with distilled water, dried at 100<sup>0</sup>C for 4 hours. It was recrystallized from chloroform and analyzed for nickel, carbon, hydrogen and nitrogen.

**Preparation of Co(P-CIINAP)<sub>2</sub> complex :-** 1.746 g of (P-CIINAP) and 0.582 g of cobalt nitrate and was dissolved in minimum quantity of water and digested on boiling water bath for about 30 minutes. A green colored complex was formed. It was filtered washed with 50% alcohol and analyzed for cobalt, carbon, hydrogen and nitrogen.

**Physical Measurements:** Magnetic measurements of solid complexes were carried out from room temperature to liquid nitrogen temperature with Govy balance using mercury tetra-thiocyanato cobalt (II) as magnetic susceptibility standard.

Diamagnetic corrections were calculated by the method given in the literature. Visible and Ultraviolet spectra of the ligand and the complexes were recorded on a Schimat Zq Uv-2000 spectrophotometer. Infrared spectra of the ligand and the complexes were obtained on specord 75 ir in potassium bromide pellets. The conductance measurements were made in nitrobenzene solution.

## RESULTS AND DISCUSSION

Analysis data and some properties of the complexes are reported in Table 1. On the basis of analytical data Cu (II), Ni (II) and Co (II) complexes can be represented as M(P-CIINAP)<sub>2</sub>. The complexes are colored and have good thermal stability. They are insoluble in water and dilute alkali solution suggesting absence of a free oxime group due to removal of oximino proton during complexation. This is supported the infrared spectral studies. The molar conductance values in nitrobenzene indicate their non-electrolytic nature [8].

**Magnetic Measurements:** The result of magnetic susceptibility measurements in a variable temperature data suggest that the Cu(II) and Ni(II) complexes may be diamagnetic with square planer geometries[9,10] and Co(II) complex is diamagnetic which suggest a low spin octahedral coordination. These suggestions are in agreement with spectral observation

**Electronic Spectra:** The electronic spectral data for ligand field transition are summarized in Table 3. The complexes show a group of three or more bands in the 47.84 kK range which can be assigned as  $\pi - \pi^*$  or ligand metal transitions. The electronic spectral of (P-CIINAP) in methanol shows an intense band at 47.84 kK. It splits into two strong bands at 43.10 kK and 42.79 kK. These can be explained by presuming that the symmetric electron system cloud of (P-CIINAP). They may be assigned to  $\pi - \pi^*$  transitions. The electronic spectrum of Cu(II) complex (Table 3) was consistent with a very broad intense band in the 52.35 kK region and band in the 41.32 kK range. A shoulder also appears in the 50.76 kK region. This region screened by the intense charge transfer band exhibited the broad maxima at 51.81 kK. The spectrum resembles with those of Cu(II) complexes tetrahedral environment[11]. The electronic spectrum of Ni(II) complex resemble to those of tetrahedral or square planer Ni(II) complexes[19].

A broad band for Co (II) at 49.50 kK in  $\text{Co(P-CIINAP)}_2$  suggest distorted octahedral geometry. Distorted octahedral species of Co (II) complexes are also characterized by the presence of two main absorption bands [12].

**Infrared Spectra:** I.R. spectra ( $4000-400 \text{ cm}^{-1}$ ) of the complexes are practically identical. The frequencies of some significant band of the free ligand and those of the metal complexes are reported in Table 4. The observed frequencies of different groups in the metal complexes have been assigned on the basis of literature data.

The  $\nu_{\text{O-H}}$  of the oxime group observed at  $3289 \text{ cm}^{-1}$  in (P-CIINAP) is absent in the spectra of the complexes suggesting replacement of the oxime proton by the metal ion during complexation[13]. The peak observed near  $1628, 1622, 1602 \text{ cm}^{-1}$  in spectrum of  $\text{Cu(P-CIINAP)}_2$ ,  $\text{Ni(P-CIINAP)}_2$ , and  $\text{Co(P-CIINAP)}_2$  respectively, may be assigned to the perturbed  $\nu_{\text{C=O}}$  and /or  $\nu_{\text{C=N}}$  stretching vibration involving bonding through oxygen, and nitrogen donor atoms. A band appear in the range  $1300-1200 \text{ cm}^{-1}$  is reported that N-oxide ( $\text{N}\rightarrow\text{O}$ ) stretching mode in aromatic ring compounds [14]. The bands at  $1062, 1089, 1026 \text{ cm}^{-1}$  in  $\text{Cu (P-CIINAP)}_2$ ,  $\text{Ni(P-CIINAP)}_2$ , and  $\text{Co(P-CIINAP)}_2$  respectively are attributed to the N-O stretching in the ligand [15].

It is significant to note that for metal complexes reported to have coordination only through the oxime oxygen or nitrogen atoms only. One medium to strong band at around  $1050$  or  $1200-1250 \text{ cm}^{-1}$  is found leading to a symmetrical six member ring structure [16] or asymmetrical five member ring structure.

**NMR Spectra:** The nuclear magnetic resonance spectrum of (P-CIINAP) in DMSO solution reveals a peak around  $8.64 \delta$  (delta) due to the  $=\text{NOH}$  group. Two groups of bands corresponding to  $-\text{CH}$  and aromatic ring in (P-CIINAP) are observed at  $2.72 \delta$  and  $7.62 \delta$  respectively. It may be mentioned the dioxime solutions of ethyl  $-\alpha$ - isonitrosoacetoacetate

(HEINA), Isonitrosoacetylacetone [16] (HINAA) and Isonitrosoacetophenon [17] (HINAP) show =NOH proton resonance at  $-9.27\delta$ ,  $-8.65\delta$  and  $-8.6\delta$  respectively.

**Table –1 Analytical Data, Color and  $\mu$  eff. at room temp**

COMPLEX	COLOUR	%C	%H	%N	%M	$\mu$ eff.
Cu(P-CIINAP) <sub>2</sub>	Yellowish	44.88	2.26	6.75	14.14	Diamagnetic
	green	(44.80)	(2.33)	(6.53)	(14.81)	
Ni(P-CIINAP) <sub>2</sub>	Yellowish	41.64	2.18	6.72	13.19	Diamagnetic
		(41.32)	(2.36)	(6.60)	(13.85)	
Co(P-CIINAP) <sub>2</sub>	Green	45.38	2.38	6.64	13.20	Diamagnetic
		(45.29)	(2.35)	(6.51)	(13.70)	

**Table 2 Nuclear Magnetic Resonance Signals Observed in P-chloro isonitrosoacetophenone (P-CIINAP) and it's metal complexes**

(P-CIINAP)	Cu(P-CIINAP) <sub>2</sub>	Ni(P-CIINAP) <sub>2</sub>	Co(P-CIINAP) <sub>2</sub>	Assignments
8.64 $\delta$	-	-	-	= NOH
2.72 $\delta$	2.64 $\delta$	2.71 $\delta$	2.72 $\delta$	-CH group
7.62 $\delta$	7.57 $\delta$	7.57 $\delta$	7.57 $\delta$	- Aromatic ring

**Table 3: Electronic Spectral data of complexes**

Complex	Absorption spectra in methanol (nm)	Wave No kK
Cu(P-CIINAP) <sub>2</sub>	193	51.81
	197	50.76
	242	41.32
Ni(P-CIINAP) <sub>2</sub>	222	45.05
	236	42.37
	243	40.98
Co(P-CIINAP) <sub>2</sub>	202	49.50
	210	47.62
	218	45.87

**Table 4: Infrared Spectral Frequencies (4000 to 400 cm<sup>-1</sup>) of ligand and metal complexes**

Ligand	Cu(II)	Ni(II)	Co(II)	Assignment of group
3290	---	---	---	OH, Ar-H
---	3430	3415	3390	Ar-H
1640	---	---	---	C=O
---	1630	1620	1600	C=N, C=O
---	1260	1195	1286	N O
1080	1060	1090	1030	N-Oxide
---	840	802	840	N-O
763	757	756	761	Para Sub.
693	695	601	617	

NMR spectra Cu(P-CIINAP)<sub>2</sub>, Ni(P-CIINAP)<sub>2</sub>, and Co(P-CIINAP)<sub>2</sub> in DMSO solution exhibit peaks due to methyl methylene, and aromatic ring proton and do not show any proton signal due to the =NOH group. This suggests that these complexes have been formed by the replacement of the proton of the =NOH group by the metal ion. It is interesting to note that the peaks due to methyl proton Cu(P-CIINAP)<sub>2</sub> appear at lower value compared to that of methyl proton in the

reagent (P-CIINAP). Further signals of the aromatic ring group in these complexes occur at higher field side with respect to that of aromatic ring signal in (P-CIINAP)

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