

## Synthesis and Characterization of a Series of Cobalt (II), Nickel (II), And Copper (II) Complexes with a Schiff Base Ligand H<sub>2</sub>hamme

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### Abstract

Inner complexes of the type, [M (hamme)] are obtained when H<sub>2</sub>hamme reacts with metal acetates [M= Co (II), Ni (II), Cu (II)]. The preparation of the complexes has been achieved by isolating the ligand first and then complexing with the metal ion or by adopting an “*in situ*” method involving the metal ion catalyzed template synthesis of the ligand and simultaneous isolation of the complexes, [M (hamme)] with better yield. Characterization has been done on the basis of magnetic, conductivity and spectral studies. Square planar structure has been proposed for the complexes.

**Key Words:** Co (II), Ni (II), Cu (II), complexes, Schiff base ligand, square planar geometry

### 1.0 INTRODUCTION

Schiff base ligands and their metal complexes is the most exciting field of research during recent years due to their applications in varieties of field<sup>1-12</sup>. Consequently, the present communication describes preparation properties and use of a series of inner complex salts of the type [M (hamme)] where M= Co (II), Ni (II), Cu (II) and hamme is the dianion of the Schiff base ligand H<sub>2</sub>hamme. H<sub>2</sub>hamme stands for 2,9-dihydroximino – 4,7-diaza 5,6: methylbenzo -3,8 –dimethyl – 3,7 – decadiene.

### 2.0 EXPERIMENTAL

The present section is devoted to the experimental procedure adopted for the preparation of the imine-oxime chelating ligand, H<sub>2</sub>(hamme) and its metal

complexes and the measurements of their physical properties. The constituent parts of each compound have been estimated by established analytical methods such as copper by iodometry, nickel as bis-(dimethylglyoximate)nickel(II), cobalt as its oxinate, and carbon, hydrogen and nitrogen by semi micro combustion methods.

### 2.1 PREPARATION OF THE LIGAND, H<sub>2</sub>hamme

2,3-diaminotoluene (6.2 g, 0.05 mol) was mixed with diacetymonoxime (10.1 g, 0.1 mol) with the help of agate and mortar when they went into homogenous liquid after triturating them together for fifteen minutes. The solution was transferred into a beaker and it was stirred vigorously with a glass rod for more than an hour. During the course of stirring the reaction mixture gradually become more and more viscous.

It was slightly cooled by dipping the beaker in ice cold water when the viscous liquid immediately solidified and the compound was dried under vacuum. The compound, which possessed an yellow color, was recrystallised from ethanol and analyzed. The melting point of the compound was found to be  $182 \pm 2^{\circ}\text{C}$ . The compound is susceptible to moisture.

## 2.2 PREPARATION OF [Cu (hamme)]

### 2,9-dihydroximinato-4, 7-diaza-3, 8-dimethyl-5,6:(methylbenzo) 3, 7-decadienecopper (II), [Cu(hamme)]

The ligand (2.89 g, 0.01 mol) was dissolved in a minimum, amount of absolute alcohol on warming. To the ligand solution thus formed, an alcoholic solution of finely ground cupric acetate monohydrate (2.0 g,0.01mol) was added. An yellowish green crystalline compound was immediately obtained. The quantity of the solid product increased on allowing the solution to stand for some time. it was filtered, washed with alcohol and finally with ether and analyzed after drying.

## 2.3 PREPARATION OF [Co (hamme)]

### 2, 9-dihydroximinato-4,7-diaza-3, 8-dimethyl-5,6:(methylbenzo) 3, 7-decadienecobalt (II) ,[Co (hamme)]

An alcoholic solution of cobalt (II) acetate tetrahydrate (2.5 g,0.01mol) was allowed to react with the ligand (2.89 g, 0.01 mol) dissolved in absolute alcohol when the color of solution immediately changed to dark brown . Solid compound was not obtained immediately. However, slow evaporation of the resulting dark brown solution at room temperature resulted in appearance of dark brown crystals which

were filtered, washed with alcohol and analyzed after drying.

## 2.4 PREPARATION OF [Ni (hamme)]

### 2,9-dihydroximinato-4,7-diaza-3,8-dimethyl-5,6:(methylbenzo) 3,7-decadienenicke (II), [Ni (hamme)]

Nickel (II) acetate tetra hydrate (2.5 g, 0.01 mol) dissolved in a minimum amount of absolute alcohol was added to an alcoholic solution of the ligand (2.89 g, 0.01 mol) and the reaction mixture was vigorously shaken for a few minutes. The color of the mixture solution immediately changed from green to deep red and fine red crystals were obtained and quantity of the solid product gradually increased on allowing the solution to stand for some time. It was filtered, washed with alcohol, followed by ether, dried under vacuum and subsequently analyzed for its different constituents.

The analytical results are shown in Table I

## 3.0 RESULTS AND DICUSTIONS

The spectra of all the metal complexes show two sharp and strong bands in the vicinity of  $1600\text{ cm}^{-1}$  which have been attributed to C... N stretching vibrations of azomethine and oxime C=N bands respectively. The characteristic behavior of the I R bands is the shift of the azomethine and oxime C=N bands respectively toward red and blue region of the spectra as compared with the free ligand H<sub>2</sub>hammer. It suggests that in the inner complexes salts, the oxime ligand acts as an endoquadridentane ligand coordinating through its nitrogen atoms and the structure may be represented as shown below.

Table I

Analytical Data of metal complexes [M (hamme)]

Compounds	% of elements Found (Calculated)			
	% C	% H	% N	% M
H <sub>2</sub> hamme	62.46 (62.50)	6.98 (6.94)	19.42 (19.44)	–
[Co(hamme)]	51.21 (51.17)	5.22 (5.21)	16.22 (16.23)	17.00 (17.10)
[Ni(hamme)]	51.13 (51.17)	5.20 (5.21)	16.20 (16.23)	17.12 (17.10)
[Cu(hamme)]	51.38 (51.49)	5.12 (5.14)	16.00 (16.02)	18.02 (18.18)

Inner complexes salt of nickel (II) is diamagnetic. Its electronic spectrum exhibits a broad band in the region 20000-24000 cm<sup>-1</sup> in the visible range which represents a group of two to three bands amongst the three spin allowed d-d transitions, <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>A<sub>2g</sub>, <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>B<sub>2g</sub>, and <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>E<sub>g</sub> for d<sup>8</sup> diamagnetic square planar complex.

The inner complex salt of cobalt II has the magnetic moment 2.0 B.M. The low magnetic moment of characteristic of square planar environment of the ligand about cobalt II ion. It shows a broad band in the region 20000-22000 cm<sup>-1</sup> suggest cobalt II ion to be in a square planar environment and the band presumably arises due to the transition <sup>2</sup>A<sub>1g</sub>→b<sub>1g</sub>(d<sub>x<sup>2</sup>-y<sup>2</sup>) where <sup>2</sup>A<sub>1g</sub> is probably the ground state for low spin cobalt II ion in square planar environment and b<sub>1g</sub> is the empty antibonding orbital.</sub>

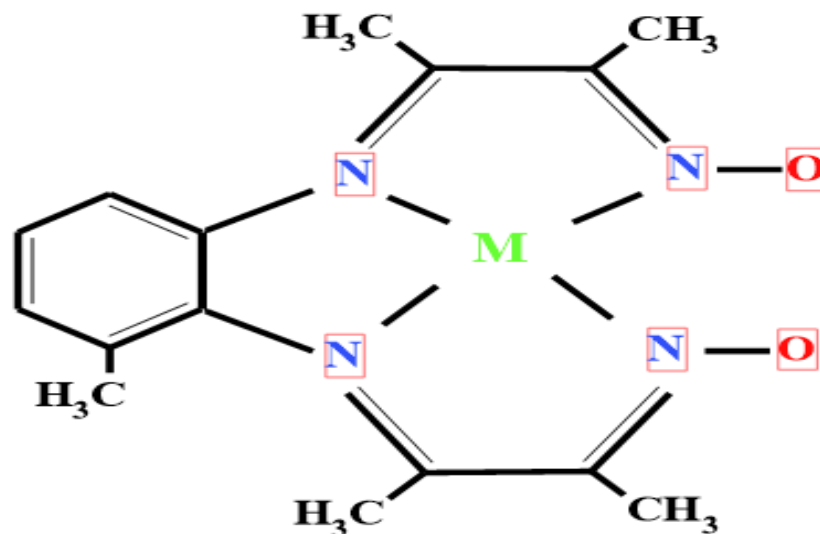
During the course of present investigation the nickel II inner complexes [Ni(hamme)] is diamagnetic and possesses a singlet ground term <sup>1</sup>A<sub>1g</sub>. The electronic spectrum exhibits a broad band in the region 20000-22000 cm<sup>-1</sup>. The width of the spectra manifests that the band represents a group of two to three transitions assignable to the transitions, <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>A<sub>2g</sub>, <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>B<sub>2g</sub>, and <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>E<sub>g</sub> under a square planar environment possessing the chromophore, NiN<sub>4</sub>.

The cobalt II inner complex salt isolated during the course of the present investigation is of low-spin type possessing magnetic moment 2.0 B.M. The spectrum shows a broad band in the region 20000-22000 cm<sup>-1</sup> with some amount of structure which manifest that the cobalt II ion is placed in a square planar ligand field. The spectral data can be logically assigned to number of spin-

allowed transitions from the ground state  $^2A_2$ . However, the high intensity of these bands lead us to believe that one or more charge transfer transitions partly contribute to this part of the spectra. It is likely that these ligands possess low energy  $\pi^*$  orbitals. The third ionization

potential energy of cobalt II ion being low, the charge transfer band may be metal  $\rightarrow$  ligand in nature.

On the basis of above discussion, the square planar structure (fig . 1) may be proposed for the complexes [M (hamme)]



M= Co (II), Ni (II) or Cu (II)

Fig. 1

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