

# Synthesis and Studies on electronic spectra of Co (II) Complexes with 3-hydroxy-2-Naphthalidene semicarbazone.

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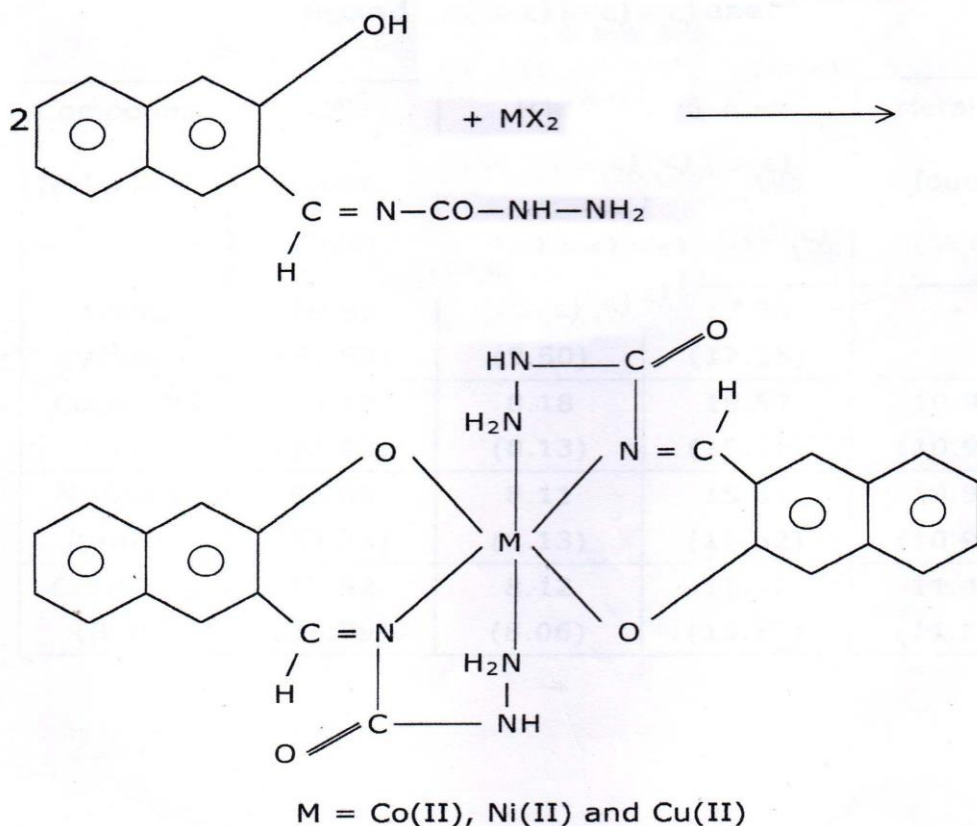
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**Abstract-** The metal complexes have been Synthesised by allowing Co-salts to Condense 3-hydroxy-2-naphthaldehyde with semicarbazide hydrochloride in methanolic solution. The spin orbital coupling vibrational interactions and distortion from cubic symmetry have important effects on the spectra of Co(II) Complexes. The complexes mainly display charge-transfer bands and intraligand transitions in the region 470-200 nm. In a few cases, the complexes display weak band or shoulder near 510-520 nm In the electronic spectra of the complexes.

**Index Terms-** Co-salts, 3-hydroxy-2-naphthaldehyde, octahedral, semicarbazide, squareplanar, tetrahedral.

## I. INTRODUCTION

The metal complexes have been Synthesised by allowing metal salts to Condense 3-hydroxy-2-Naphthaldehyde with semicarbazide hydrochloride in methanolic solution.



## II. RESEARCH METHODOLOGY

Metal salts, aldehyde and semicarbazide have been taken in the molar ratio 1 : 2 : 2. Alcoholic solutions have been used. Products separated out are filtered, washed with alcohol, dried and analyzed. Analytical data and colours have been presented in Table.

## III. RESULTS AND DISCUSSION

### Table

**Analytical data, color and decomposition temperature of ligand and metal complexes**

Compound (color)	C% found (calc)	H% found (calc)	N% found (calc)	Metal % found (calc)
HNSE (yellow)	59.83 (59.50)	9.56 (9.50)	17.53 (17.35)	-
Co(NSC) <sub>2</sub> (red)	53.19 (53.23)	8.18 (8.13)	15.57 (15.52)	10.98 (10.90)

Electronic spectral analyses of complexes give valuable information about the geometry of complexes and hence its application is essentially needed. Most of the complexes of transition elements are highly colored, which means that they are capable of absorbing radiant energy in the visible region of the spectrum. The absorption of light in ultraviolet, visible or infrared region sets valence electrons into oscillation and produces an excitation of the molecule from the ground electronic state to excited electronic state.

It has been found that two general types of electronic transitions are expected to occur with 'd' electrons in complexes<sup>1,2</sup>

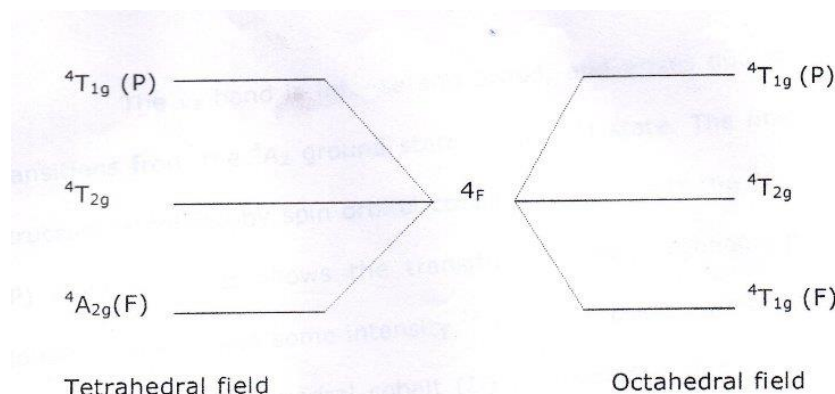
### **ELECTRONIC BEHAVIOUR OF COBALT (II) COMPLEXES:**

Cobalt (II) has  $d^7$  configuration and forms complexes having tetrahedral, square planar and octahedral geometries. The electronic spectral studies of cobalt (II) complexes have been proved quite valuable in differentiating the above mentioned geometries.

Electronic spectra of cobalt (II) complexes are well known. Cobalt (II) forms tetrahedral, square planar and octahedral complexes. Unfortunately, both environments give rise to bands in the vicinity of  $20,000\text{ cm}^{-1}$ , although, tetrahedral complexes more frequently exhibit absorption maxima near  $15,000\text{ cm}^{-1}$ . Thus, the reliable spectral indication of

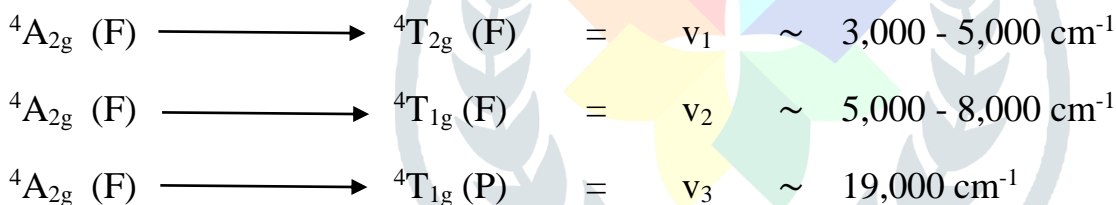
stereochemistry of cobalt (II) complexes is the intensity of absorption band, if the spectrum is not complicated by overlap with strong charge-transfer tail<sup>3</sup>.

Liehr<sup>4</sup> gave the most informative and best explained spectral explanation of cobalt (II). The gaseous cobalt (II) ion has <sup>4</sup>F ground state term and the next higher state of the same multiplicity is <sup>4</sup>P. The splitting of these state in weak octahedral and tetrahedral crystal fields are shown below<sup>5</sup>:



### Simplified energy level energy level diagram of d<sup>7</sup> field

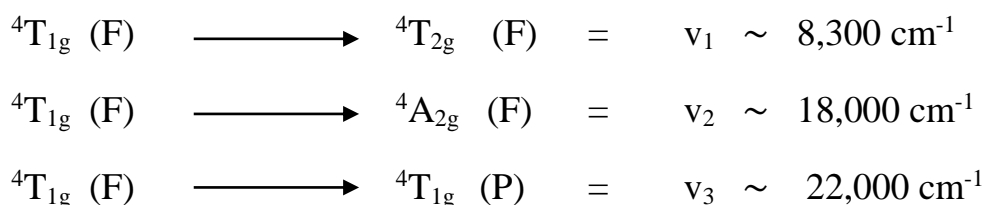
In tetrahedral ligand field, the main spin allowed transitions arising from <sup>4</sup>F and <sup>4</sup>P terms with approximate energies are:<sup>6</sup>



The first transition  $\nu_1$  occurs at the energy of  $10 Dq$ , but the band is mostly unobserved. The band corresponding to  $\nu_2$  is usually and generally observed in the region  $5,000 - 8,000 \text{ cm}^{-1}$ <sup>6</sup>

The  $\nu_3$  band is intense and broad, and arises due to transitions from the <sup>4</sup>A<sub>2</sub> ground state to <sup>4</sup>T<sub>1</sub> (P) state. The fine structure is caused by spin orbital coupling which splits the <sup>4</sup>T<sub>1g</sub> (P) state itself. It allows the transition to the neighbouring doublet state to gain some intensity.<sup>7</sup> The blue colour, which is characteristic of tetrahedral cobalt (II) complexes is due to  $\nu_3$  transition which usually occurs around  $15,000 - 20,000 \text{ cm}^{-1}$ .

In octahedral complexes, the three main transitions arising from <sup>4</sup>F and <sup>4</sup>P terms with their approximate energies are:



However, since the  ${}^4A_{2g}$  state is derived from  $t^3_{2g}, e^4_g$  configuration while the  ${}^4T_{1g}$  (F) state is derived from the  $t^5_{2g}, e^2_g$  configuration. Thus,  ${}^4T_{1g} \rightarrow {}^4A_{2g}$  transition is essentially a two electron process and for this reason it should be weaker (by  $\sim 10^{-2}$ ) than the other transition. Further more, this weak band is very close to the  ${}^4T_{1g}$  (F)  $\rightarrow$   ${}^4T_{1g}$  (P) transition and therefore, the band remains unobserved. The spin orbital coupling, vibrational interactions and distortion from cubic symmetry have important effects on the spectra<sup>8</sup> of cobalt (II) complexes.

In low-spin octahedral cobalt (II) complexes electronic transitions originating from  ${}^2E_g$  and state to  ${}^2T_{1g}, {}^2T_{2g}, {}^4T_{1g}$  etc. states are expected.<sup>9</sup> These bands are generally observed that the complexes do not exhibit spectral band similar to high-spin tetrahedral or octahedral. Cobalt (II) complexes (as discussed above). The complexes mainly display charge-transfer bands and intraligand transitions in the region 470-200nm. In a few cases, the complexes display weak band or shoulder near 510-520 nm region in the electronic spectra of the complexes. This band is probably d-d band assignable to  ${}^2E_g \rightarrow {}^2T_{1g}$  transition of the complexes.

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