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

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Abstract :- Synthesis of transition metal semicarbazone complexes and their characterization by analytical and spectroscopic methods have been the subject of extensive investigation by many workers. In the present investigation semicarbazide derivatives of 3-hydroxy-2-napthaldehyde legends have been used for the synthesis of Cu(II) complexes. The metal complexes have been synthesized by allowing Cu salts to catalyze the condensation of 3-hydroxy- 2-napthaldehyde with semi carbazide hydrochloride in methanolic solution.

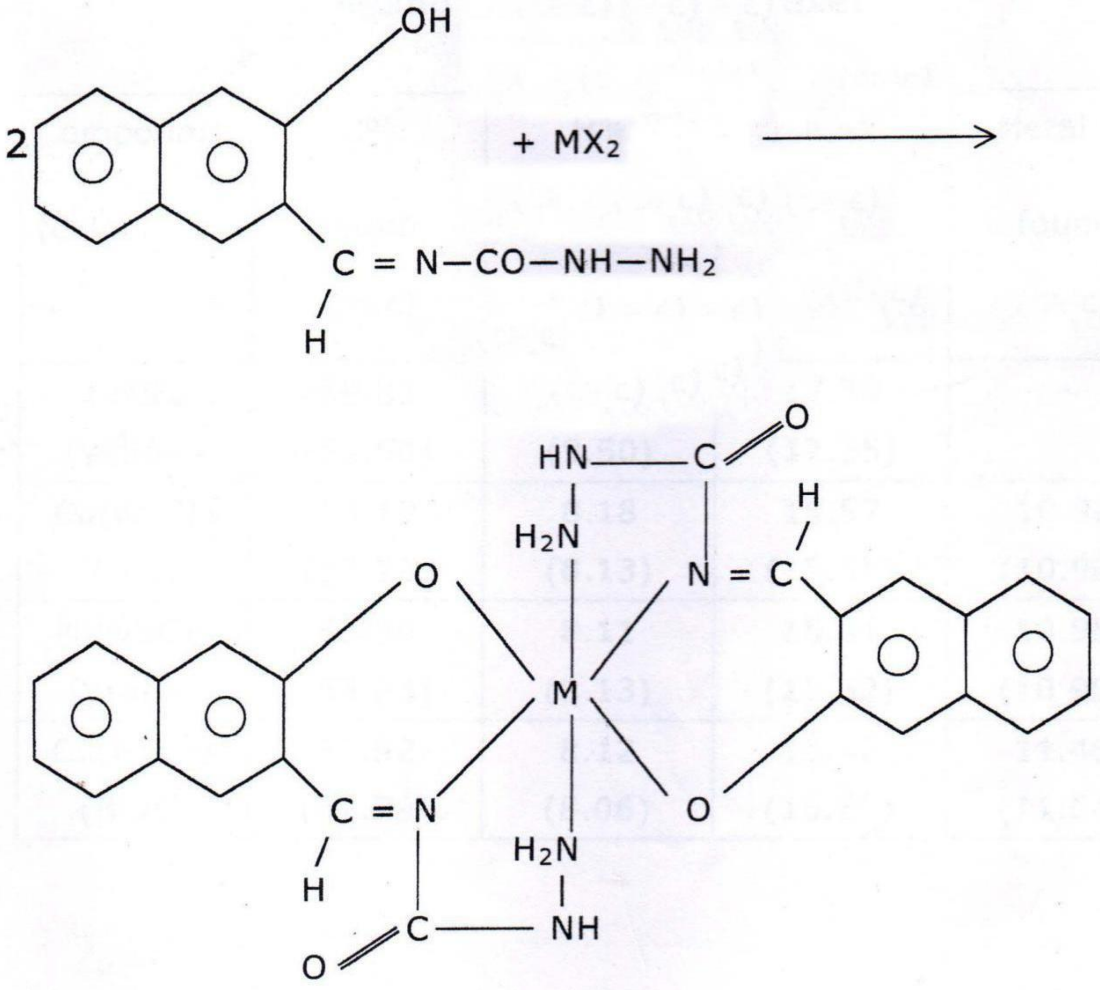
Electronic spectral analyzed give valuable information about the geometry of complexes and hence its application is essentially needed. The complexes have the general formula [ML_2] where M is the metal and L is the tridentate ligand. All these complexes have octahedral geometry.

The electronic absorption and reflectance spectra of complexes have been recorded in the range 800-200 nm. The electronic absorption spectrum in ethanolic or acetone solution of copper (II) complex does not exhibit any d-d band rather it exhibit two intense bands near 225 nm and 270 nm respectively. Ligand also exhibits two electronic absorption band in the u.v region which are located at 225 and 275 nm respectively. These bands are attributed to ligand absorption.

Index Term :- Copper salts, 3-hydroxy-2-napthaldehyde, octahedral, semi carbazide hydrocholoride, tridentate.

I. Introduction

Synthesis of transition metal semicarbazone complexes and there and their characterization by analytical and spectroscopic method have been the subject of extensive investigation by many workers[1-3]. In the present investigation semicarbazide derivatives of 3-hydroxy-2-nepthaldehyde ligand have been used for the synthesis of Cu(II) complexes. The metal complexes have been synthesized by allowing Cu salt to catalyse the condensation of 3-hydroxy-2-naphthaldehyde with semicarbazide hydrochloride in methanolic solution.



M = Cu(II)

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The absence of d-d bands in solution is probably due to intense absorption bands of the ligand molecules which abscures the weak d-d band expected for copper(II) complexes. However the solid reflectance spectra of the complexes exhibit broad asymmetric band between 620-750 nm. This broad and asymmetric band is assigned to combination of $^2B_{2g}$

$^2B_{1g}$, $^2E_g \rightarrow$ $^2B_{1g}$ and $\rightarrow$ $^2A_{1g}$ $^2B_{1g}$ $\rightarrow$

Transition resulting from distorted tetragonal ligand field.

II. RESERACH METHODOLOGY

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

III. RESULTS AND DISCUSSION

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)	-
$Cu(NSC)_2$ (Blue)	52.92 (52.79)	8.12 (8.06)	15.42 (15.39)	11.46 (11.64)

The electronic transitions occur, when electron within the molecules or ions move from one energy level to another. Therefore, absorption spectra reveal (a) which are the energy level that are populated (the ground state) and which are the nearly empty energy level into which electrons may be excited and (b) what are the probabilities for the various possible absorption to occur.

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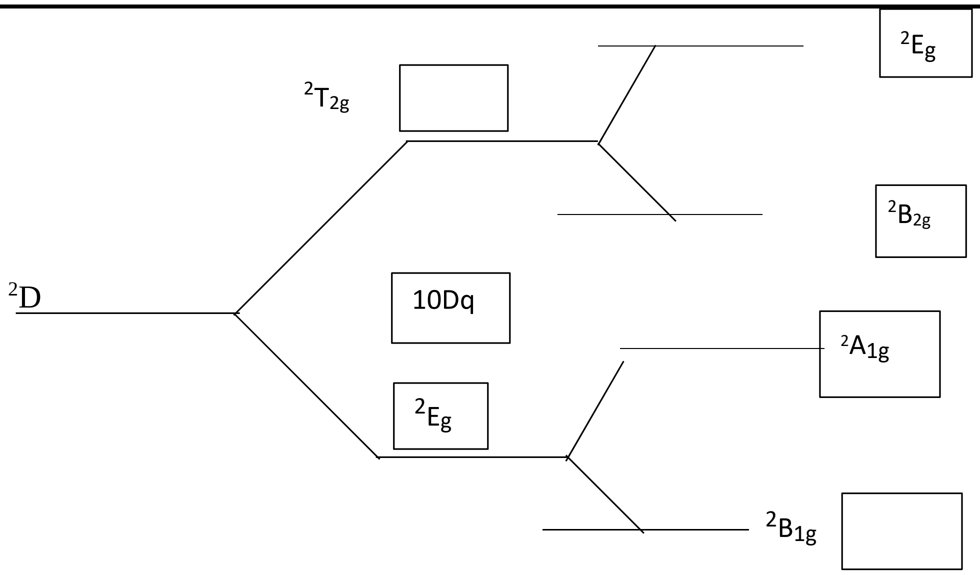
ELECTRONIC BEHAVIOUR OF COPPER (II) COMPLEXES

The G.S term for copper (II) is ^2D. Copper (II) form generally square planar, tetrahedral or distorted octahedral complexes.

The degenerate d-levels are split up in the presence of octahedral field as shown below[4]



SPILITING IN CUBIC FIELD IN TETRAGONAL FIELD

Only one absorption band arising from d-d transition E_g T_{2g} is observed in the spectra of octahedral complexes. In excited state, the three electrons in e_g could be so arranged as to lead to two different possible configurations i.e., $(d_z{}^2)^2$ $(d_x{}^2y^2)^1$ or $(d_z{}^2)^1$ $(d_x{}^2\text{-}y^2)^2$. in the former case the more repulsion is expected between metal ion ligand electrons along the $d_z{}^2$ axis than along $d_x{}^2\text{-}y^2$ axis because there is high electron density in $d_z{}^2$, thereby elongating the bond along z-axis. In the latter case, we can similarity predict four long bonds along $d_x{}^2\text{-}y^2$ and two short ones along $d_z{}^2$. The more common distortion involves lengthening of the bonds along $d_z{}^2$. Under such circumstances the e_g and t_{2g} levels no longer constitute degenerate sets and splitting of the d-orbitals occurs to remove this degeneracy. Thus more stable distorted complex results because metal ion electrons do not repel ligand electron density as much as in the undistorted structure. Hence, in the distorted crystal field the doubly degenerate ground E_g as well as the upper state T_{2g} are, each, split into two other compounds.

The existence of a planar or distorted octahedral ligand field results in the appearance of three transition :

$^2B_{1g}$ $^2B_{2g}$ →

$^2B_{1g}$ ^2E_g →

$^2B_{1g}$ $^2A_{1g}$ →

And these are generally very asymmetric. It is found [5-7] that the d-d bond due to planar or octahedral field appears generally at higher energy (around 19000 cm^{-1} for planar, and around 15000-18000 cm^{-1} for octahedral complexes) than those of pseudo-tetrahedral arrangement (around 8000 - 11500 cm^{-1})[8-10]. In case of distorted tetragonal or week distorted octahedral field (D_{4h} symmetry) an asymmetric contour is located in the range of 10000 - 14000 cm^{-1}

The polarized absorption spectrum of $CuSO_4 .5H_2O$ shows that three transitions are found in the range of 19000 - 14000 cm^{-1} [11]. The absorption spectrum of $[Cu(H_2O)_6]^{2+}$ shows one very asymmetric band which can be resolved at least into two bands. It is believed that the asymmetric band is due to Jahn-Teller effect which cause distortion of the octahedral coordination of water molecules around Cu(II) ions[4]. Bjerrum et al[12] and Jorgensen[13] have reported spectral data of many Cu(II) complexes in solution. They observed that most of the distorted octahedral copper(II) complexes show one asymmetric band which, in some cases, has been resolved into two or three overlapping bands.

IV. ACKNOWLEDGEMENT

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