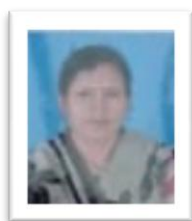


Study of Copper (II) Complex with Semicarbazide

Abstract

The complexes of copper (II) with semicarbazide of the formula (CuL_2) ($L=NH-NH.CO.NH_2$), has been prepared and characterised. The structure of the complex has been established on the basis of its elemental analysis, ir, uv and magnetic moment studies. The complex is paramagnetic and square planar.

Keywords: Semicarbazide, Ligand, Spectra, Semicarbazide, Enolic Ligand, Band, Stretch, Attributed, Sharp, Repertionin, Enolisation, Subsequent Chelation, Attributed, Corresponding, Symmetry, Obviously, Regarding, Semicarbazone, Enolic Content.



Dazy Kumari

Lecturer,
Dept. of Chemistry,
Urdu College,
Gopalganj, Bihar, India

Introduction

A brief survey of literature showed numerous organic reagent – 6] containing nitrogen and oxygen, which form four co-ordinated copper (II) complexes, but no mention has been made of the formation of copper (II) complex with semicarbazide. The present work shows complex, bissemicarbazide Cu (II) of the formula, $[Cu(CH_4ON_3)_2]$.

Preparation of Complex

Copper (II) complex was prepared by taking 30 c.c. of cu (II) solution (1% $CuSO_4 \cdot 5H_2O$ solution) and treating it with 1-2 drops of conc. H_2SO_4 and slight excess of aq. Or aq. alcoholic ligand, followed by an immediate addition of 0.1 (N) NaOH or Na_2CO_3 solution in cold. The orange yellow complex was washed with cold water and dried in air.

Results and Discussion

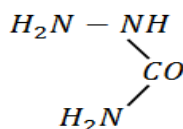
On analysis, it was found: Cu 30.03, C 11.30, H 3.72 and N 39.5 percent. For $[Cu(CH_4ON_3)_2]$ calculated: Cu 30.04, C 11.34, H 3.72 and N 39.70 Percent.

Infra-Red spectra

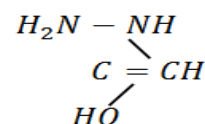
I.R. spectra of ligand and complex in range $200-4000\text{ cm}^{-1}$ along with the assignments of few important bands are given in (table 1).

The band at $3400-20\text{ cm}^{-1}$ due to (NH_2) in the ligand lowered to 2930 cm^{-1} in the complex, shows co-ordination to Cu through N atom of NH_2 . Goel and Gupta [7] suggested $\nu(NH_2)$ at $3480-3500\text{ cm}^{-1}$. Jensen [8] established co-ordination through nitrogen in M (II) -semicarbazide complexes. Furthermore, Cu- O bond be formed either by donation of lone pair by oxygen of CO or by replacement of H of enolic ligand.

The latter possibility is supported by the presence of a clear band at 1140 cm^{-1} due to (C-o) bond in the spectra of complex which has been earlier confirmed by Goel and Gupta [7], who reported bands at $1040-1120\text{ cm}^{-1}$ and $1170-1190\text{ cm}^{-1}$ for (C-O). Singh



(Keto form)



(Enol form)

Table 1

$\text{CH}_4\text{ON}_3\text{HCl} \cdot \text{cm}^{-1}$	$\text{Cu}(\text{CH}_4\text{ON}_3)_2 \text{ cm}^{-1}$	Assignments
3400-3420 w	- CONH ₂ , CONH, -OH stretch
	2930 vs	-OH. =NH or v (NH ₂)
2840-50 bs	2860 vs	-N-C=, -O-H, or=NH or overtones
2300-40 w	NH ₂ or -N-C=O
1990-2000 ms	C=N and NH ₂ + combination.
1900-50 ms
1650 s	1640 s	Amide I, δ (NH), CONH ₂ C=N or NH ₂ bend.
1420-50 s	1450—60 s	C=N, δ (N-H) or =OH bend.
1340-65 ms	1370 vs	δ (NH). -OH bend; =NH bend or C-N
1200-20 vs	OH bend.
1180-90 ms	1140 ms	(C-O) of =C-OH
750-60 s	620 ms	NH rocking or deform.
700-10 s	Y (-OH)
	500-20 ms	Cu-N
	460-80 ws	Cu-N+Cu-O
	430 ws	Cu-O
	300 w	

Srivastava and Prakash [9] reported 1170 cm^{-1} for C-N stretch. and 758 cm^{-1} for NH rock-ing. The bands at 1340-65 and 1370 and 750-60 and 620 cm^{-1} in the ligand and complex may be attributed to C-N and NH rock-ing. Sharp band at 1650 and 1640 cm^{-1} in the ligand and complex are due to C=N which are in accord with the values reperatioion the literab by Goel and Gupta. The bands at 284-50 and 2860 cm^{-1} and 1420-50 and 1450-60 cm^{-1} and 2860 cm^{-1} may be due γ (NH) and NH or δ (NH) respectuey.

Slight differences in the band positions of ligand and complex are due to enolisation and subsequent chelation.

Some new bands at 500-20 cm^{-1} and 430 cm^{-1} in the spectra of complex may be attributed to Cu-N and Cu-O bond vibrations.

U.V. Spectra

Compound	λ_{Max} , m μ
CH ₅ ON ₃	400-390 s
	380-360 o
Cu(CH ₄ ON ₃) ₂	430-360 b sh
	360-300 b sh
	290 w

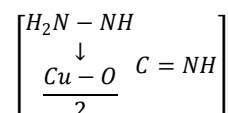
Broad sholder band at 430-360 m may byattributed to the splitting of orbital corresponding to 2B₂→E δ in D_{4h} symmetry. The orange yellow colour of complex may be due to charge transfer band tailing off into the blue end of visible spectra. Other bands are too weak to be detected. No clear indication about geometry of complex has been obtained.

Magnetic moment:

Magnetic moment has been found to be 2.01 BM, a value obviously greater than 1.732 BM corresponding to spin only value but less than 2.82 BM, which amounted for two unpaired electrons. Thus although actual geometry seems to be vague but interpretation regarding considerable distortion of octahedral or tetrahedral geometry leading to square planar geometry can be made. High value of μ_{eff} may be due to moment corresponding to one unpaired electron plus orbital contribution. The square planar complex may involve dsp² hybridisation.

Structure of Semicarbazide Copper (II) Complex

Like other nitrogen oxygen containing ligands such as Benz aldehyde, semicarbazone 10, etc, semicarbazide co-ordinates to Cu through N atom of NH₂. The hydrogen of enolic ligand is replaced by Cu. 1680-1750 cm^{-1} inligand or complex further confirms ex stence of enolic content of ligand Moreover the clear banddue to (C-O) has been observed in the complex the structure can be represented as follows: Dipheny1 semicarbazide [11] forms Mg (II)-complex in NaOH medium in similar manner.



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