Synthesis of Nanocrystalline Copper Oxide using Copper (II) Semicarbazone Derivative

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ABSTRACT:

The Semicarbazone derivatives of 2-4, dihydroxy acetophenone is synthesized and characterized by physico-chemical techniques such as melting point, Ultra Violet-Visible Spectrophotometer, Fourier Transform Infra-Red (FTIR), proton nuclear magnetic resonance (^{1}HNMR) spectroscopy and used as a chelating agent to form complex with Copper as Copper (II) semicarbazone derivative. The synthesised Copper (II) semicarbazone complex was also studied for its complex formation IR analysis, decomposition studies using TGA. The synthesised Copper (II) semicarbazone complex was successfully employed as precursor for synthesis of nano crystalline Copper oxide and its formation was confirmed by UV-Visible spectroscopy and XRD analysis. The method successfully employed use of Copper (II) semicarbazone complex for synthesis of nano Copper oxide.

KEYWORDS: Copper oxide, Semicarbazone, Nanocrystalline, Copper (II) semicarbazone, nano particles.

INTRODUCTION:

Complex formation with Schiff base, semicarbazone, thiosemicarbazones, triazoles, amino acids, are largely studied for quantitative estimation of metal ions by coupling with various instrumental techniques. Literature survey reveals that there are large number of research papers on complex formation and characterization[2,3]. Several complexes are applied for the biological activity studies by examining for antibacterial, antimicrobial, antiviral etc. activities. Some authors studied the coordination chemistry of the complex and its application as biological active complex. Here we present a unique application for metal ligand complex by using it as a precursor for synthesis of nano crystalline Copper (II) oxide[4].

MATERIALS AND METHODOLOGY:

All the chemicals and solvents used for the synthesis are analytical grade. semicarbazide hydrochloride, 2',4'-dihydroxy acetophenone and other chemicals were purchased from sigma Aldrich or Merck. The FTIR spectra were recorded using KBr discs on a Perkin-Elmer spectrum FTIR system. The NMR spectra were recorded in Bruker Ultra shield 300 spectrophotometer. The electronic spectra in the range 200–1000 nm was obtained in acetonitrile on a UV-1800 Shimadzu spectrophotometer. Thermogravimetric measurements were carried out on a Mettler Toledo TGA/DSC instrument.

The synthesis of complex was done in two steps, 1) the synthesis of ligand 2) the synthesis of the complex.

1) The synthesis of ligand[1] was done by equimolar mixture of sodium acetate and semicarbazide hydrochloride is dissolved in minimum quantity of water and then it is added to methanolic solution of 2',4'-Dihydroxy acetophenone. After addition warm the solution and stir the solution about one hour. The light pink colored compound is precipitate out, which is washed and then recrystallized by using 50% ethyl alcohol as solvent.

Fig. No. 1. Synthesis of Ligand (Reagent)

2) The synthesis of complex was done by direct reaction of ligand (Reagent)[5,6] with Copper (II) sulphate. The light-yellow colored complex[12,13] is precipitate out, which is washed and then recrystallized by using 50% ethyl alcohol as solvent. The powdered complex was then dried and used for further studies.

Fig. No. 2. Synthesis of Copper complex preparation of Cu-(2, 4-DHA) semicarbazone

RESULT AND DISCUSSIONS:

In order to find application of metal ligand complex as a precursor for synthesis of nanocrystalline Copper the synthesis of different semicarbazone complex were done. The synthesised of Ligand (reagent) 2,4 dihydroxy acetophenone semicarbazone[19,20] was first characterised by obtaining IR and NMR[7,8] and the synthesised complex was then characterised and compared with IR[9,10]. The interpretation of data is shown in table no 1, 2 and 3 which confirms the formation of a ligand(reagent), Cu (II) complex respectively. The correspond figures of the interpreted results are also included as figure no 3, 4, 5, 6 and 7 for different instrumental techniques[14,15].

Fig. No. 3. IR of Semicarbazone derivative(ligand)

Table No. 1 IR Spectral Studies of Ligand (Reagent)

Frequency (cm^{-1})	Functional group
3483	$\nu_{(O-H)}$ stretching
3095	$\nu_{(CH)}$ aromatic stretching
1593	$\nu_{(C=N)}$ stretching
1520	$\nu_{(C=C)}$ stretching
1680	$\nu_{(C=O)}$ stretching
1458	C-O-H bending
1323	Ph-C-O stretching
1284	C-N stretching
1375	In plane bonds due to aromatic substituted benzene ring
1173	
1155	
1116	
854	Substituted benzene ring
758	$\nu_{(C-H)}$ stretching due to substituted benzene ring
538	Benzene ring deformation
1375	(CH_3-C) bending

Fig. No. 4. H NMR of Semicarbazone derivative

Table No. 2. ^{1}H NMR Spectral Studies of Ligand (Reagent)

Solvent	No. of protons	δ in ppm	Assignment
d^6-DMSO	s, 3H	3.39	CH_3-C=N
	s,2H	2.14	-NH_2
	s,1H	2.48	-NH-
	two d, 2H s,1H	6.1 to 7.3	Aromatic Proton
	d, 2H	12.98	-OH

Fig. No. 5. IR of Cu (II) Complex

Table No. 3. IR Spectral Studies of Cu (II) Complex

Frequency (cm^{-1})	Functional group
3046	$\nu_{(C-H)}$ aromatic stretching
1585	$\nu_{(C=N)}$ stretching
1486	$\nu_{(C=C)}$ stretching
1660	$\nu_{(C=O)}$ stretching
1375	Ph-C-O- stretching
1170	C-N stretching
538	$\nu_{(M-N)}$ stretching
476	$\nu_{(M-O)}$ stretching

Decomposition Studies TGA Studies:

The decomposition studies[16,17] of the complexes were done by means of Thermogravimetric analysis[11]. The decomposition of the complex was studied at different temperature in the range 28°C to 900°C. Thermogravimetric (TG) weight loss curves and the corresponding differential thermogravimetric (DTG) curves for the complex are shown in Figure no 3. The complex showed three well-defined steps at 170°C, 270°C and 413°C together with final steps above 413°C. The loss in weight in the first step is 7.358% which should be due to the two co-ordinated water molecules. The second, and third weight losses are 29.211% and 46.858%, respectively, totalling 72.46%. This large weight drop can be explained by considering that the residue is a $C_8H_6N_2$ and CuO (calculated weight loss 72.46%). The table no 4 shows the details of the decomposition studies.

Fig No. 6. TGA for Metal Complex

Table No. 4. Thermo Gravimetric Analytical Data for Metal Complex

Molecule	Temperature (°C)		Weight loss In %
	Commencement	Completion of	Observed

	of decomposition	decomposition	
H_2O	28	170	7.358
NH_3	170	270	29.211
CO_2	270	413	46.858
$C_8H_6N_2$	413	900	72.46

XRD STUDIES:

Particle size of the copper oxide was determined by using Scherrer's formula given below. Average particle size of the CuO was found to be 35nm size.

$$D = \frac{0.89\,\lambda}{\beta \cos\theta}$$

Where, $\lambda = 1.54060\ A^0$ ($Cu\ K_\alpha$)

β = Full width half maxima in radian.

Fig No. 7. XRD of Copper oxide

CONCLUSION:

From the above studies it can be seen that the compounds containing Copper chalcogen bond can be used for the preparation of Copper chalcogenide nanoparticles[18]. It is found that the semicarbazone derivative result in Copper oxide. In conclusion, the presence of direct Copper-chalcogen bond is important in getting these materials. Also, it is evident that the simple decomposition technique can lead to Copper oxide nano crystallites. As these nano crystallites have wide range of applications still some are awaiting which are to be finding out.

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