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**RESEARCH ARTICLE**

# SOLVENT FREE MECHANO CHEMICAL SYNTHESIS AND CHARACTERISATION OF NANOCRYSTALLINE TRANSITION METAL HIPPURATES

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**ABSTRACT**

The nanocrystalline copper (II) complex with hippuric acid have been synthesized by solvent-free Mechano chemical synthesis. Copper (II) hippurate complex was characterized by UV-Vis spectra, fourier transform Infra red spectra, powder X-ray diffraction, High resolution scanning electron microscopic analysis, Transmission electron microscopic analysis, Thermal analysis, and Elemental analysis. The process presented here is operationally simple, environmentally benign and affords excellent yields without the need for any solvent.



## INTRODUCTION

Chemical synthesis using mechanical force also known as mechanochemistry is a well established field of organic synthesis (**James *et al*., 2012 and Stolle *et al*., 2011**). The development of solvent-free reaction is an especially attractive goal in the content of green chemistry. In recent years, solvent-less chemistry is used in both academic and industrial laboratories (**Bala and Coville, 2007**). For instance, one of the major targets in green chemistry is to limit the extensive use of solvents or even better to carry out the synthetic reaction in the absence of them (**Mikhailanko *et al*., 2004 and Rasmussen *et al*., 1997**). Solvent-free or solvent-less reactions are thought to occur in the solid phase (**Rottenberg *et al*., 2001**). Solvent free synthesis involves the use of mechanochemistry with melt phase methods. Mechanochemical method ranges from simply grinding reactants with mortar and pestle to ball-milling process. Melt phase is the induction of the reactants thermochemically by the direct application of heat. This helps to initiate and sustain the chemical reaction due to a rise in temperature .Mechanochemical transformations involving coordination bonds has blossomed to include a variety of coordination polymers and clusters (**Uzarevic *et al*., 2011; Adams *et al*., 2007 and Lewinski *et al*., 2010**).

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A lot of work has been done on solvent free synthesis in metal-organic frameworks (**Pichon *et al*., 2006; Carson *et al*., 2009 and Vuan *et al*., 2010**). Hippuric acid, N-benzoyl glycine, benzoyl amino acetic acid, one of the amino acids, present in the urine of herbivorous animals; also in smaller amounts in human urine. Hippuric acid is a monocarboxylic acid with three types of donar site: the nitrogen and oxygen atom of the carboxylic acid group. This literature reveals that hippuric acid is potentially capable of forming coordinate bonds with many metal ions through a carboxylic oxygen atom as a monodentate or bound through the carboxylic oxygen atoms as a bidentate (**Capilonch *et al*., 2001; Sgarabotto *et al*., 1999; Terron *et al*., 1997; Garcia-Raso *et al*., 1998; Ashby *et al*., 1980; Morelock *et al*., 1982; Morelock *et al*., 1979; Grewe *et al*., 1982; Brzyska *et al*., 1988; Brzyska *et al*., 1988; Brzyska *et al*., 1992 and Sadeek *et al*., 2005**). The NH group of hippuric acid coordinates to the central metal atom only in some complexes (**Moabcotrigiano and Pellacani, 1975 and Allan *et al*., 1991**).

### Experimental

### Materials and instrumentation

All chemicals were reagent grade and were used without further purification . Hippuric acid was purchased from sigma Aldrich and copper nitrate tri hydrate from Merck. The UV-visible spectra were recorded using Varian early 500

UV-VIS-NIR double beam spectrophotometer in the range 190-1100 nm. FT-IR spectra were recorded on Perkin-Elmer FT-IR spectrophotometer (4000-400 $cm^{-1}$) in KBr pellets. Thermal analysis of the metal complex were studied using TGA Q500 V20.10 thermal analyzer. High resolution scanning electron microscopic analysis and elemental analysis were carried out on FEI Quanta FEG 200 scanning electron microscope. High resolution transmission electron microscopic analyses were recorded using JEOL 3010 with a UHR polepiece instrument. Powder X-ray diffraction analyses were recorded on Bruker D8 advanced X-ray diffractometer.

**Synthesis of metal complex**

2 mmol (0.358 g) of hippuric acid and 1 mmol (0.242g) of copper nitrate trihydrate were carefully weighed into an agate mortar which has been washed and dried before use. The reactants were ground together without adding any solvent for fifteen minutes. The reaction was monitored by TLC using chloroform / methanol (9:1) till no traces of reactants were found.

The complexes were heated in a oven at 130° C for two hours. The pale blue porous crystalline products were obtained (Fig. 1).

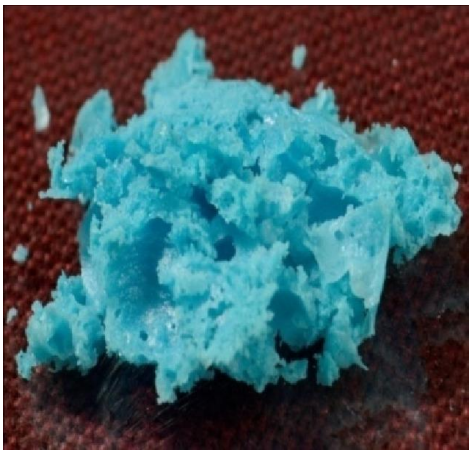

**Fig.1. Copper (II)hippurate complex**

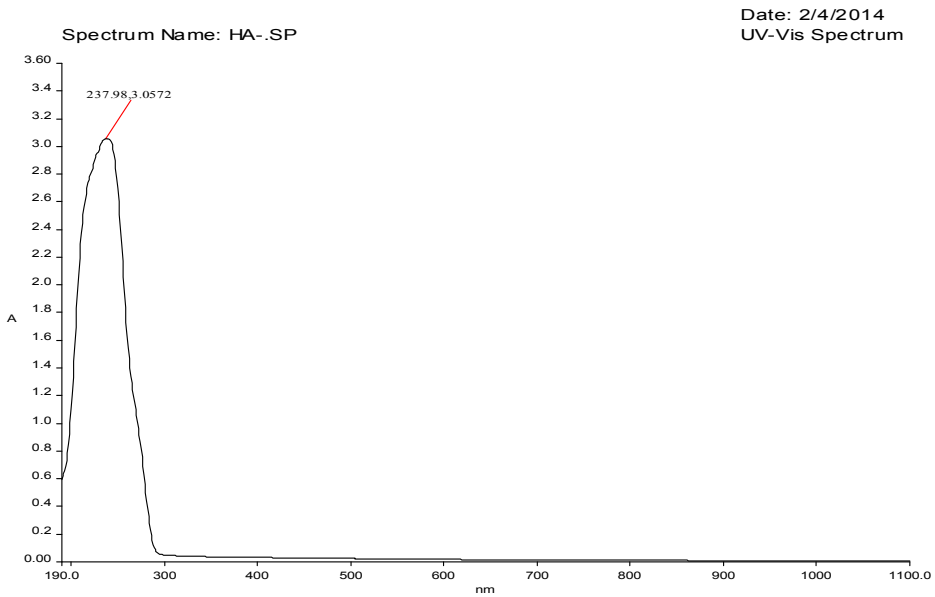


**Fig.2a. UV spectrum of pure HA**

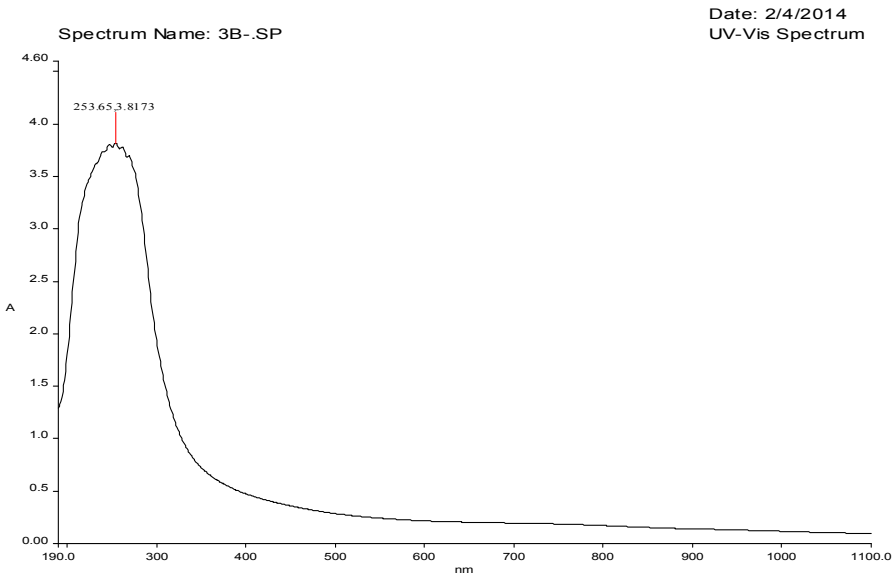


**Fig.2b. UV spectrum of Cu(II) complex**

## Characteristic studies

### UV-visible spectroscopic analysis

The UV-Visible spectra of pure hippuric acid and the synthesized complex is given in Figure 2. The electronic spectra of hippuric acid (HA) shows absorption band at 237 nm was assigned to $\pi$-$\pi^*$ transitions (Barnum *et al*., 1961). But they were shifted to 253 nm in the metal complex due to n-$\pi^*$ intra ligand transitions.

There are evident that the increase in the absorbance (hyperchromic effect) clarified in the metal hippurate complex attributed to the complexation behaviour of hippuric acid towards metal ions, confirming the coordination of the ligand to the metallic ions.

### FT IR spectroscopic analysis

The infra red spectra of pure hippuric acid and the cu(II) complex are shown in Figure 3.

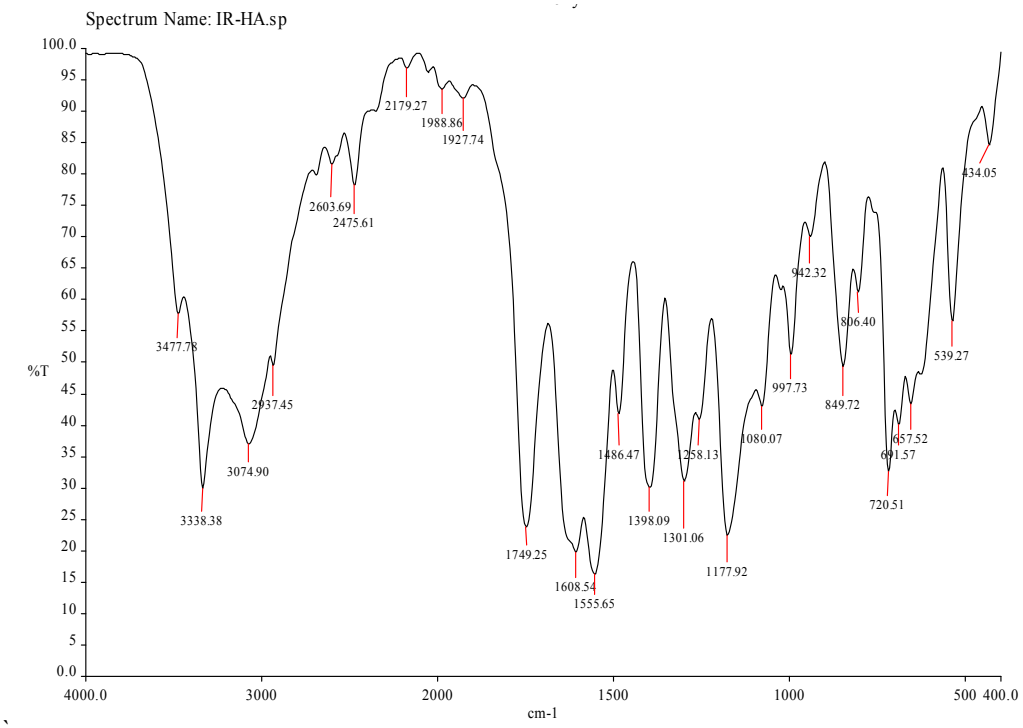


**Fig. 3a. FT-IR spectrum of Pure HA**

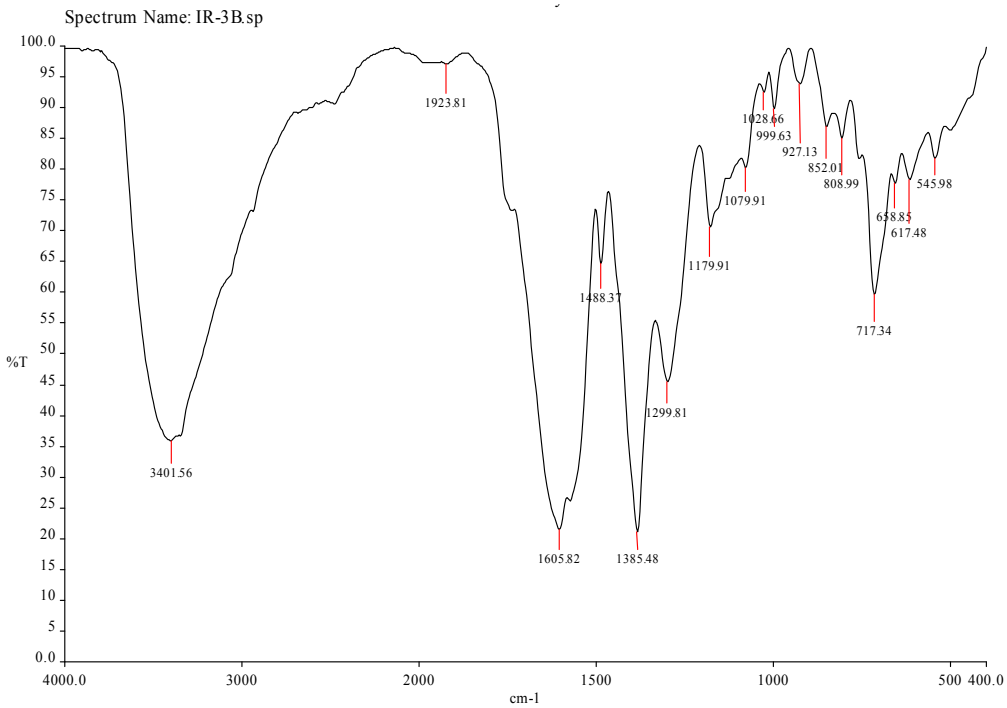


**Fig. 3b. FT-IR spectrum of Cu complex**

The broad peak at 3401 $cm^{-1}$ arising from N-H stretching frequency involved in hydrogen bonding. The band at 1923 $cm^{1}$ is due to aromatic combination. The absence of absorption bands at 1740 and 1555$cm^{-1}$ arising from the carboxylic group of hipurate complex states that the hydrogen ions in the hippuric acid molecules are substituted by the metal ion and the hippurate is the coordination ligand (**Brzyska and Hakim, 1992; Kumar and Srivastava, 1979 and Nakamoto, 1986**). The asymmetric stretching vibration of carboxylate group at 1605$cm^{-1}$ and of the symmetric vibrations at 1385$cm^{-1}$ confirm these hypothesis. The coordination of the metal ions via oxygen carboxylate is confirmed by the M-O bands at 545$cm^{-1}$. According to the above discussion the hippurate is coordinated with the metal ions as a bidentate through the carboxylic group.

**Powder X-ray diffraction analysis**

The powders XRD Pattern of the copper (II) hippurate complex are shown in Figure 4.

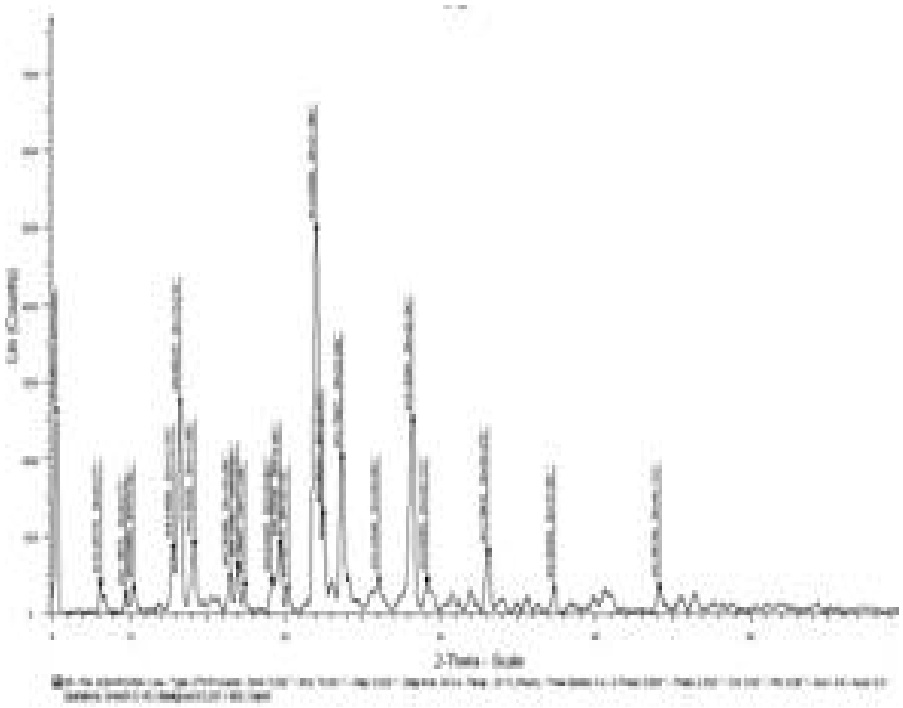

**Fig. 4. PXRD pattern of Cu complex**

X-ray powder diffraction pattern of copper hippurate complex was carried out in order to obtain an idea about the lattice dynamics of the compound. The PXRD pattern of copper hippurate represents a definite compound of a definite structure which is not contaminated with starting materials. This identification of the complex was done by the known method.

**High resolution SEM (HR-SEM) analysis**

Scanning electron microscopic image of copper (II) hippurate complex are shown in Fig.5. Scanning electron microscopy is a technique that enables the study of the microscopic surface morphology of nanoparticles. The SEM image of the complex represents regularly arranged flower like clusters and the nanocrystals are formed in flower like arrangement. It confirms that the copper (II) hippurate comple is nano crystalline in nature.

**High resolution transmission electron microscopic (HR-TEM) analysis**

The HR-TEM micrographs of copper (II) hippurate complex are shown in Figure.6.

**Hippurate complex**

HR-TEM is an instrument for high-magnification studies of nanomaterials. High resolution makes it perfect for imaging materials on the atomic scale. A main advantage of HRTEM over other microscope is that it can simultaneously give informations in real space (in the image mode) and reciprocal space (in the diffraction mode). The HR-TEM micrograph of copper (II) hippuate complex at 100nm and 50 nm respectively shows a wide distribution of nanocrystals of the metal as black dots evenly distributed in the matrix.

The size and morphology of the metal nanoparticles confirms the complex is nanocrystalline solid.

**Thermal analysis**

Thermal analysis curves of the Cu (II) hippurate complex are shown in Fig.7. The thermal decomposition of the complex occurs at four steps. The first degradation step takes place at 115°C, it corresponds to the elimination of water molecule due to a weight loss of 11.78 %. Second step fall in the range 205°C which is assigned to loss of two water molecules and two $C_6H_5$ groups with a weight loss of 31.26%. Third step fall in the range 330°C which is assigned to loss of $C_2H_5NO_3$ group with a weight loss of 33.52%. Fourth step fall in the range of 910°C which is assigned to loss of CO molecule with a weight loss 7.37%.

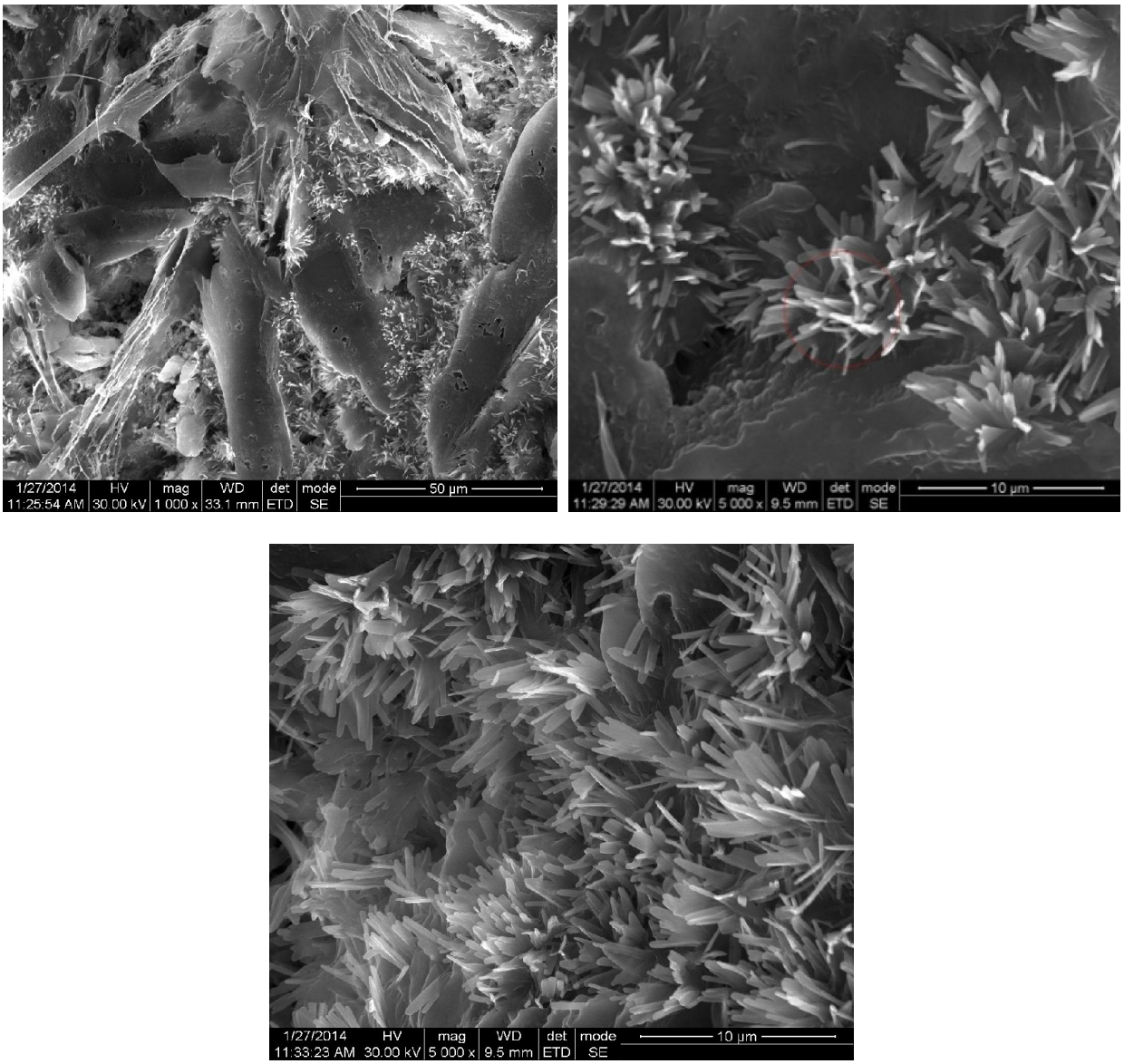


**Fig. 5. Scanning microscopic images of copper (II)hippurate complex**

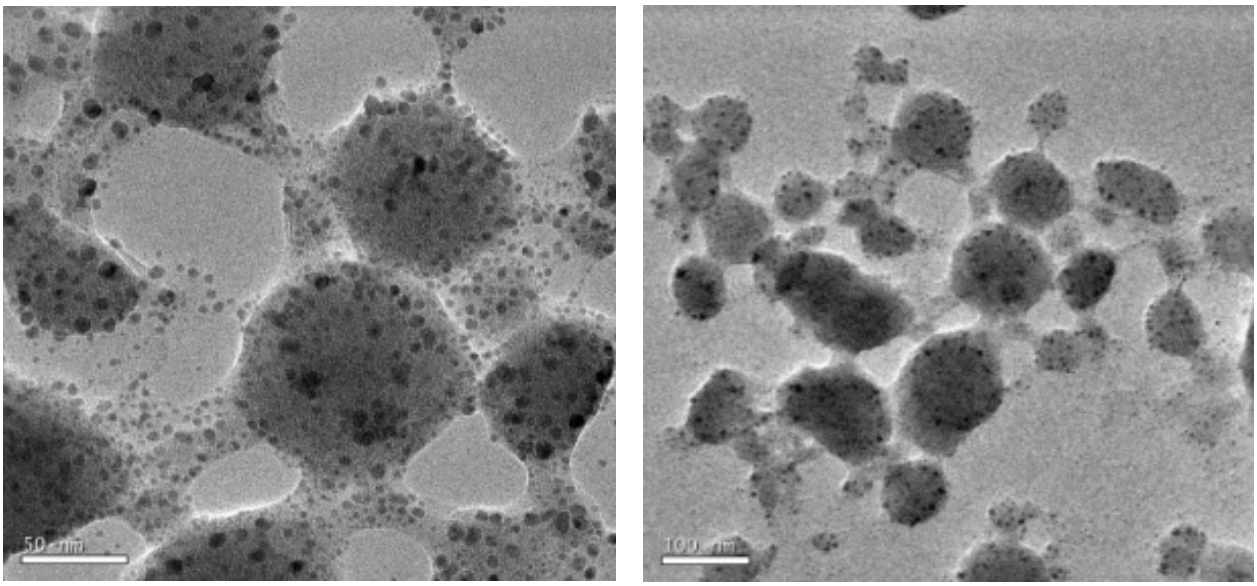


**Fig. 6. HR-TEM images of copper (II) hippurate complex**

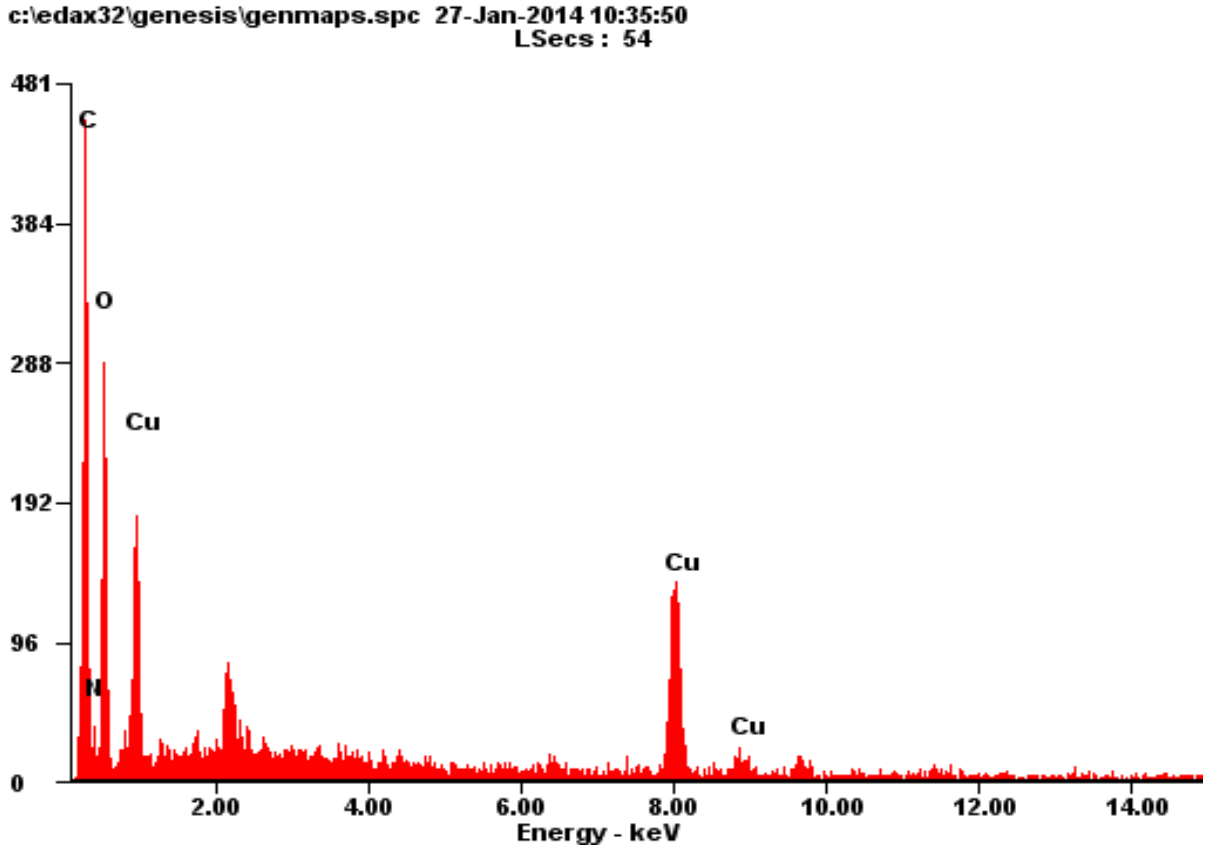


**Fig. 7. TGA**

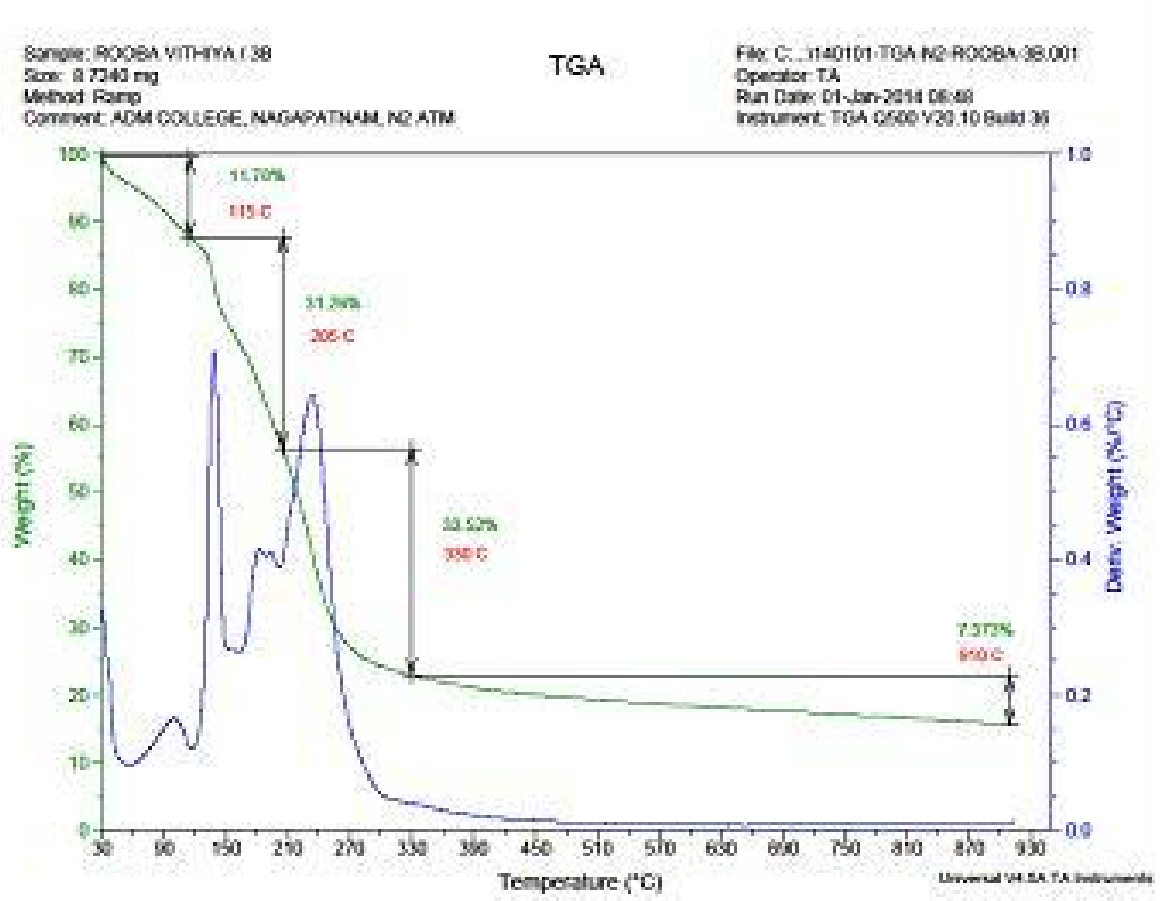


**Fig.8. EDAX (Element Composition Graph)**

The step can be interpreted according to the transform of copper carbonate to CuO. The CuO is the final product remains stable till 910° C.

**Elemental analysis**

The elemental analysis of the complex was carried out using energy dispersive spectroscopy are shown in Fig.8.

The element and its weight present in the complex were shown in the table below.

| *Element* | *Wt%* | *At%* |
|---|---|---|
| *CK* | 39.89 | 58.74 |
| *NK* | 07.41 | 09.36 |
| *OK* | 20.83 | 23.03 |
| *CuK* | 31.87 | 08.87 |
| *Matrix* | Correction | ZAF |

**Conclusion**

Copper (II) complex of hippuric acid have been synthesized by solvent-free mechano chemical method. The fact that an FTIR spectrum confirms the presence of all functional groups and vibrational assignments in the copper (II) hippurate complex. HR-SEM and HR-TEM represents the size and surface morphology of the nanocrystalline complex. Thermal analysis of the complex shows the thermal stability of the copper hippurate complex. Elemental analysis confirms the elements and its percentage weight.

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