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Solid-state synthesis and characterization of Cu (II) complexes of 3,4,5-trihydroxybenzoic acid

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Abstract

Copper(II) complexes of 3,4,5-trihydroxybenzoic acid, formulated as $[\text{Cu}(\text{THB})(\text{CH}_3\text{COO})_2]$ (**1a** and **1b**), prepared by the solid state mechanochemical method (**1a**) of grinding $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and 3,4,5-trihydroxybenzoic acid in a mortar using a pestle in the absence of a solvent, and a solvent-based method of stirring in ethanol at room temperature (**1b**) is herein described. Characterization of the synthesized complexes was done by the methods of FT-IR and UV-Vis spectroscopy, PXRD analysis, elemental analysis, and melting point determination. Data obtained from the analytical and spectroscopic techniques indicated that the synthesized compounds, **1a** and **1b**, are identical. The Cu(II) ion was observed to coordinate to the ligand via the oxygen atom of two of the hydroxyl groups of the ligand resulting in the synthesized $[\text{Cu}(\text{THB})(\text{CH}_3\text{COO})_2]$ complexes having a tetrahedral geometry with the ligand binding in a bidentate manner. The solid state mechanochemical synthesis technique offers a simple, quick and environmentally friendly route towards the preparation of metal complexes at the same time giving quantitative yield compared to the solvent-based method of synthesis.

Keywords: Mechanochemical, solid state, solvent-based, 3,4,5-trihydroxybenzoic acid, copper(II) complex.

1. Introduction

Metal-complex formation ability of aromatic carboxylic acids having the hydroxyl group substituent has being of great interest to researchers due to the excellent ability of this group of carboxylic acids to form complexes when reacted with metal ions (Abu Bakr *et al.*, 1994; Hussain *et al.*, 2013). The trihydroxybenzoic acids are derivatives of benzoic acid which are present in certain plants, such as gallnuts, grapes, tea, hops and oak bark. Gallic acid (3,4,5-trihydroxybenzoic acid), a derivative of the benzoic acids, is a triphenolic compound which exists as free molecular form and as an important part of tannin acid (Badhani *et al.*, 2015). The presence of the hydroxyl and carboxylic acid groups on 3,4,5-trihydroxybenzoic acid makes it a versatile metal-complex formation agent (Hussain *et al.*, 2013). Its uses in the

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pharmaceutical industry span as active agent against the cancer cell, antifungal and antiviral agent, antioxidant, and in the treatment of diabetes (Fazary *et al.*, 2009; Misao *et al.*, 2007; Jittawan and Sirithon, 2008). The presence of the phenolic arrangement greatly influences the antioxidant behavior of gallic acid. Generally, it has been shown that antioxidant character of a particular compound is increased by an increase in the hydroxyl group present on the aromatic ring (Galato *et al.*, 2001; Badhani *et al.*, 2015). In the chemical industry, gallic acid is used as a standard in the determination of the phenolic content of analytes through the Folin-Ciocalteu assay, and in the production of inks and dyes (Fazary *et al.*, 2009).

The ability of gallic acid to form highly stable complexes with iron presents it as a strong chelating agent with the degree of chelating increasing with increase in pH (Li *et al.*, 2000; Rajalakshmi, 1996; Masoud *et al.*, 2012). Lanthanide based metal complexes of gallic acid have also been reported having the general formula $[Ln(C_7H_5O_5)(C_7H_4O_5).nH_2O]$ in which the metal to ligand ratio was reported to be 1:2. Two adjacent hydroxyl groups are observed to be involved in the formation of the complex (Kim *et al.*, 2002) while the other hydroxyl group is suggested to form hydrogen bonding with the COO⁻ group of the second ligand in the same molecule (Dorman *et al.*, 2011; Masoud *et al.*, 2012).

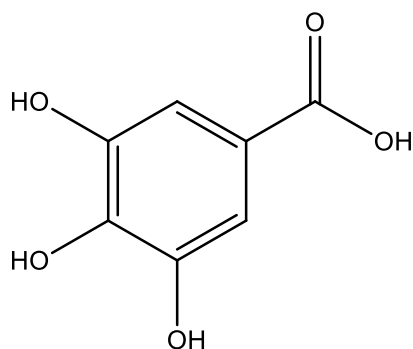


Figure 1: Structure of gallic acid

The need for cleaner and energy-efficient processes and technologies for the protection of the environment is imperative for economic growth and sustainable development. The use of volatile organic solvents on a large scale has been reported to have negative environmental implications (Garay *et al.*, 2007; Sheldon, 2005). Green chemistry therefore plays an important role in the design and development of chemical processes which reduces or eliminates the generation of hazardous chemicals and substances that impact negatively on the environment and human health. (Chandrasekaran *et al.*, 2009; Tella *et al.*, 2011; Chanshetti, 2014). This

concept brings in a new approach to the synthesis and processing of chemical substances so as to limit the threats to the environment and human health.

Mechanochemistry is a solvent-free method of synthesis which involves simply grinding two reactants together using a pestle and mortar, or by ball milling which does not require any physical effort but employs the use of high-speed vibrating ball mill at the same time eliminating the use of solvents which pollutes the environment (Guerard, 2008; Tella *et al.*, 2011, 2014; Suryanarayana, 2001; Garay *et al.*, 2007).

The use of hydroxybenzoic acids in the formation of metal complexes have been reported severally, however, there is no information available on the formation of metal-complexes of gallic acid using the solvent-free method of synthesis and very scarce report on formation of metal complexes of gallic acid via the solvent-based techniques of stirring at room temperature. Thus, this work focuses on the synthesis and stability of metal complexes of gallic acid using both solvent-free and solvent based techniques.

2. Materials and Methods

Copper acetate monohydrate, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (98 %), was obtained from BDH chem. Ltd., England, while gallic acid (3,4,5-trihydroxybenzoic acid (THB), 99 %) was obtained from Sigma Aldrich Co., Germany. All reagents were used as received without further purification.

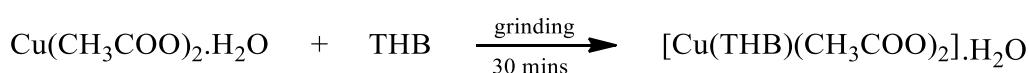
Elemental analysis of the complexes was obtained using a Perkin -Elmer CHN Analyzer 2400 series II, the melting points of the complexes were determined on a Gallen-Kamp melting point apparatus. Powder X-ray diffraction (PXRD) studies were performed on a Bruker D8 Advance X-ray diffractometer using a $\text{CuK}\alpha$ -radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 30 kV and 40 mA. Fourier transform infrared spectroscopy analysis of the complexes were obtained in KBr pellets using a SHIMADZU scientific model 500 FTIR spectrophotometer, while the electronic spectra of the complexes was obtained using a shimadzu UV-1650pc UV-VIS spectrophotometer.

The solvent-free technique described by Tella *et al.* (2011, 2014); Garay *et al.* (2007); Pichon *et al.* (2006) were modified for the solvent-free synthesis of the $[\text{Cu}(\text{THB})(\text{CH}_3\text{COO})_2]$

complexes (**1a**), while the solvent-based synthesis method by Li *et al.*, (2009) was modified for the solvent-based synthesis of [Cu(THB)(CH₃COO)₂] complexes (**1b**).

2.1. Solvent-free mechanochemical synthesis of [Cu(THB)₂] complexes (**1a**):

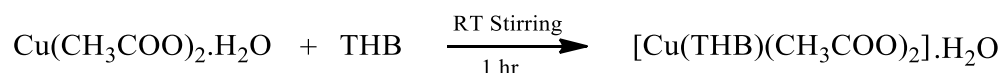
Gallic acid [THB] (2 mmol, 0.340 g) and copper acetate monohydrate, Cu(CH₃COO)₂.H₂O (1 mmol, 0.199 g), were weighed accurately and grinded together in a porcelain mortar using a pestle continuously for 30 minutes. A brownish coloured powder was obtained after 30 minutes, and this was washed with ethanol and dried at room temperature. The reaction is illustrated in scheme 1:



Scheme 1: Reaction of gallic acid with copper acetate monohydrate (solvent-free).

2.2. Solvent-based synthesis of [Cu(THB)(CH₃COO)₂] complexes (**1b**):

Gallic acid (3,4,5-trihydroxybenzoic acid [THB] (2 mmol, 0.340 g) was dissolved in 20 ml ethanol and mixed with a solution of copper acetate monohydrate [Cu(CH₃COO)₂.2H₂O] (1 mmol, 0.199 g) dissolved in 20 ml ethanol. The two solutions were mixed together and stirred at room temperature for 1 hour. The resulting brown powder was filtered, washed with ethanol and dried. The equation of the reaction is illustrated in scheme 2:



Scheme 1: Reaction of gallic acid with copper acetate monohydrate (solvent-based)

3. Results and Discussion

3.1. Elemental analysis result

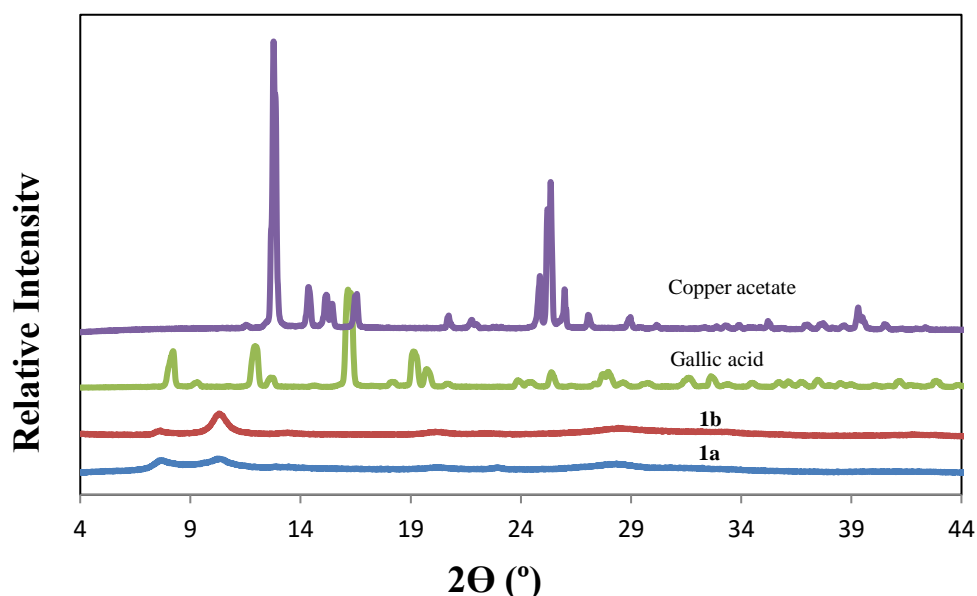
Elemental analysis of the [Cu(THB)(CH₃COO)₂] complexes formed showed the percentage C and H to be 31.01 % and 3.01 % respectively for the solvent-free synthesized [Cu(THB)(CH₃COO)₂] complex while the percentage C and H in the solvent-based synthesized [Cu(THB)(CH₃COO)₂] complex was found to be 31.06 % and 3.07 % respectively indicating that the compounds synthesized via the two different methods are identical. Analytical data for the synthesized complexes are presented in Table 1.

Table 1: Analytical data for [Cu(THB)(CH₃COO)₂] and 3,4,5-trihydroxybenzoic acid (Gallic acid).

Complex/Ligand	Appearance	Molecular weight (g/mol.)	Melting point (°C)	Elemental analysis % found (% calc.)	
				C	H
3,4,5-trihydroxybenzoic acid	White powder	170.12	222-240	-	-
[Cu(THB)(CH ₃ COO) ₂] mechanochemical (1a)	Brown powder	271.28	>400	31.04 (31.25)	3.11 (2.98)
[Cu(THB)(CH ₃ COO) ₂] solvent-based (1b)	Brown powder	271.28	>400	30.99 (31.25)	3.12 (2.98)

3.2. X-ray diffraction studies

A comparison of the X-ray diffraction patterns of the mechanochemical (**1a**) and solvent-based (**1b**) [Cu(THB)(CH₃COO)₂] complexes synthesized is shown in Figure 1. The X-ray diffraction patterns of **1a** and **1b** were observed to be identical; this is consistent with the results obtained in the elemental analysis of **1a** and **1b** and differs from the diffraction patterns of the gallic acid ligand and copper acetate salt used in the syntheses. The 2 θ values observed at 6.79, and 27.43 were observed in both **1a** and **1b** [Cu(THB)(CH₃COO)₂] complexes. The 2 θ values of 9.99, 20.16, 21.60, 32.25 were observed in the **1b** while the 2 θ values of 9.44, 20.16, 21.73, 31.99 were observed in the **1a**. Some 2 θ values observed in the ligands were not found in both the **1a** and **1b** [Cu(THB)(CH₃COO)₂] complexes synthesized which indicates that coordination occurred between the ligand and the Cu(II) ion.

**Figure 1:** Comparison of X-ray diffraction patterns of [Cu(THB)(CH₃COO)₂] : solvent-free (**1a**), solvent-based (**1b**)

3.3. Fourier transform Infra-red (FTIR) Spectra

The FTIR spectra of the synthesized compounds (**1a** and **1b**), and the ligand used in the synthesis are shown in Figure 2. The gallic acid ligand was observed to coordinate with the metal ion through the meta-, and para- hydroxyl group. The $\nu(\text{OH})$ stretching vibration of the alcoholic group observed at 3371.68 cm^{-1} and 3286.81 cm^{-1} in the 3,4,5-trihydroxybenzoic acid ligand was shifted to 3448.84 cm^{-1} in **1a** complex and 3416.05 cm^{-1} in **1b** complex. The $\nu(\text{OH})$ of the carboxylic group in the 3,4,5-trihydroxybenzoic acid ligand observed in the region of $3064.99\text{ cm}^{-1} - 2654.14\text{ cm}^{-1}$ was shifted to the region of $3097.78\text{ cm}^{-1} - 2482.47\text{ cm}^{-1}$ in the mechanochemically synthesized $[\text{Cu}(\text{THB})(\text{CH}_3\text{COO})_2]$ complex (**1a**) and $3095.85\text{ cm}^{-1} - 2671.50\text{ cm}^{-1}$ in the solvent-based $[\text{Cu}(\text{THB})(\text{CH}_3\text{COO})_2]$ complex (**1b**). The bands observed at 1701.27 cm^{-1} due to the $\nu(\text{C}=\text{O})$ stretching of the carboxylic acid group in the free ligand was shifted to 1676.20 cm^{-1} in the $[\text{Cu}(\text{THB})(\text{CH}_3\text{COO})_2]$ **1a** complex and 1685.84 cm^{-1} in the $[\text{Cu}(\text{THB})(\text{CH}_3\text{COO})_2]$ **1b** complex (Tella *et al.*, 2011; 2014). The $\nu(\text{M}-\text{O})$ stretching vibration was observed at 509.22 cm^{-1} and 518.87 cm^{-1} in the **1a** and **1b** complexes respectively.

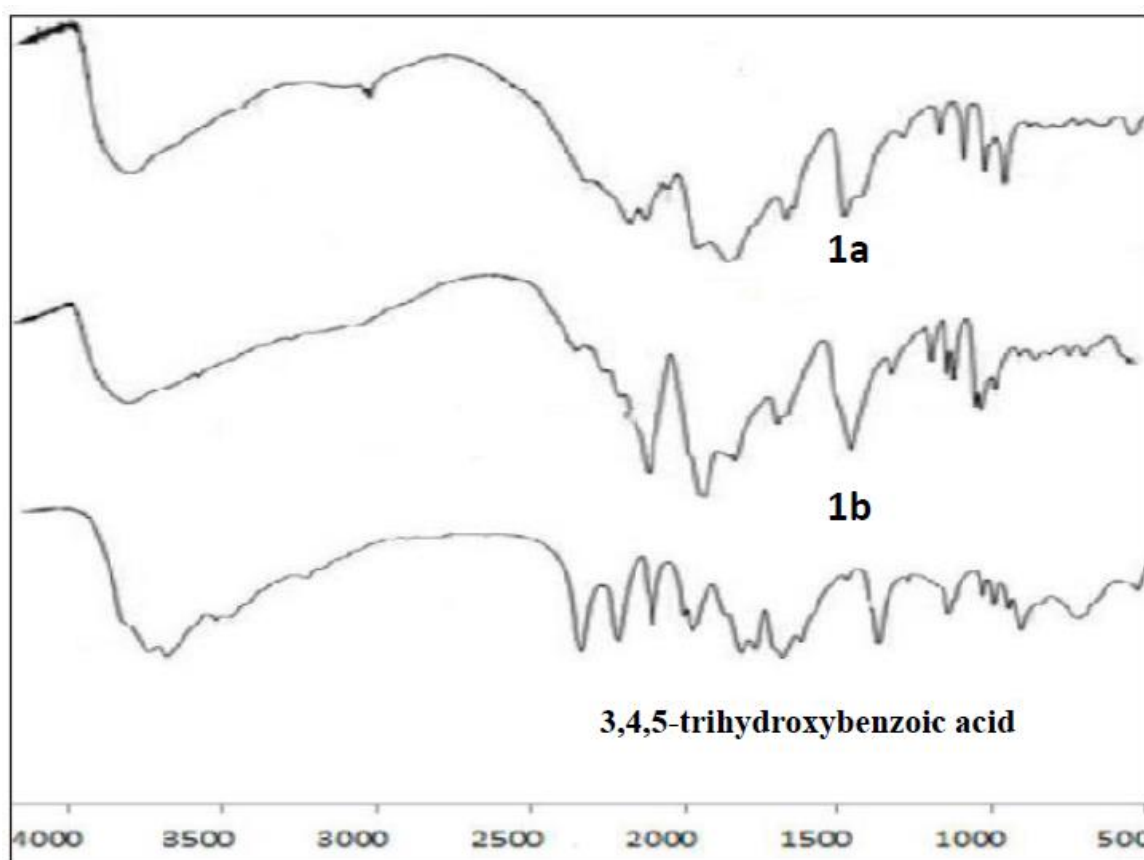


Figure 2: Comparison of the FTIR Spectra of the $[\text{Cu}(\text{THB})(\text{CH}_3\text{COO})_2]$ complex. **1a** (mechanochemical synthesis); **1b** (solvent-based synthesis)

3.4. UV-Visible spectroscopy results

Table 2 presents the UV-Visible spectrum of the [Cu(THB)(CH₃COO)₂] complexes synthesized by the mechanochemical (**1a**) and solvent-based (**1b**) methods. The n-π* transition was observed at 340 nm (29412 cm⁻¹) and 352 nm (28409 cm⁻¹) for the **1a** while the **1b** showed the n-π* transition at 340 nm (29412 cm⁻¹) and 354 nm (28249 cm⁻¹). The π-π* transition observed at 290 nm (34482 cm⁻¹) in **1b** was observed at 306 nm (32679 cm⁻¹) in the **1a**. The complex [Cu(THB)(CH₃COO)₂] has a d⁹ electronic configuration with a ground term of ²T. Bands observed at 698 nm (14327 cm⁻¹) and 694 nm (14409 cm⁻¹) in the **1a** and **1b** respectively were assigned to the ²T_{2g} – ²E_g electronic transition. The MLCT was observed at 398 nm (25126 cm⁻¹) and 394 nm (25381 cm⁻¹) in the **1a** and **1b** respectively (Tella and Obaleye, 2010; Tella *et al.*, 2011).

Table 2: UV-Visible spectroscopy result of the [Cu(THB)₂] complexes (**1a** and **1b**)

Compound/ ligand	Wavelength (nm)	Energy (cm ⁻¹)	Assignment
3,4,5-trihydroxybenzoic acid	220	45455	π-π*
	342	29240	n-π*
[Cu(THB)(CH ₃ COO) ₂] (1a)	306	32679	π-π*
	340	29412	n-π*
	352	28409	n-π*
	398	25126	MLCT
	698	14327	² T _{2g} – ² E _g
[Cu(THB)(CH ₃ COO) ₂] (1b)	290	34482	π-π*
	326	30674	π-π*
	340	29412	n-π*
	354	28249	n-π*
	394	25381	MLCT
	694	14409	² T _{2g} – ² E _g

The observations from characterization of the complexes formed led to the proposed structure shown below:

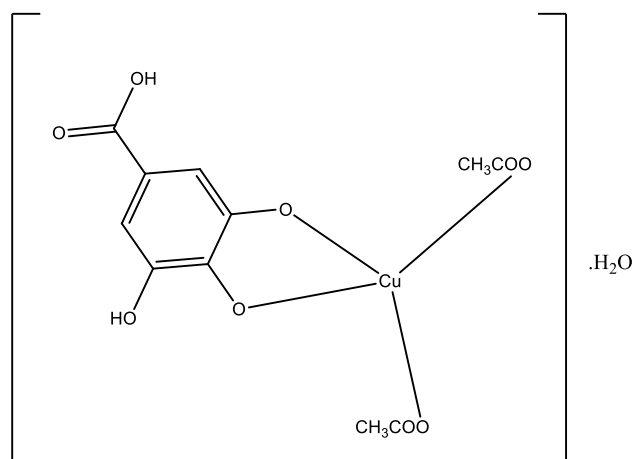


Figure 3: Proposed structure of the $[\text{Cu}(\text{THB})(\text{CH}_3\text{COO})_2]$ complexes synthesized

4. Conclusion

Copper (II) complexes of 3,4,5-trihydroxybenzoic acid (gallic acid) has been synthesized using two different methods: a solvent-free mechanochemical technique and a solvent-based method of stirring in ethanol at room temperature. The products were characterized by spectroscopic techniques and analytical methods. Results of the characterization of the compounds showed that the products are identical and have a tetrahedral geometry with the ligand coordinating to the Cu(II) ion in a bidentate manner through the oxygen atom on two of the hydroxyl groups present in the ligand. The analytical and spectroscopic data of the mechanochemically synthesized $[\text{Cu}(\text{THB})(\text{CH}_3\text{COO})_2]$ complex are in agreement with the analytical and spectroscopic data obtained for the $[\text{Cu}(\text{THB})(\text{CH}_3\text{COO})_2]$ complex synthesized via the solvent based method. It has therefore been proved that the solvent-free mechanochemical method can be used for the preparation of Cu(II) complexes of 3,4,5-trihydroxybenzoic acid and it offers a simple and environmentally friendly method of synthesizing the $[\text{Cu}(\text{THB})(\text{CH}_3\text{COO})_2]$ complex which gives high yield of the product and saves cost and time.

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