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## Synthesis and Characterization of a Water Soluble Triphenyltin (IV) Carboxylate Fungicide

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**Abstract** Triphenyltin (IV) monopotassium 3-carboxy-3-hydroxy-pentanedioate (A) was synthesized by reacting monopotassium 3-carboxy-3-hydroxypentanedioate with triphenyltin (IV) hydroxide (Ph<sub>3</sub>SnOH) in the ratio of 1:1 in methanol. The product was isolated by evaporation of the solvent at 313 K for 72 h; and characterized by FTIR. Tin content analyses and its aqueous solubility was determined afterwards. The spectroscopy and tin content data indicated that the product was completely formed. The solubility test data showed the product to have a solubility of 20 % in water, which is sufficient to enable direct fungicidal preparation of their crystalline concentrates in aqueous media.

**Keywords** triphenyltin (IV), carboxylate, fungicide, water soluble, characterization, synthesis

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### Introduction

The properties, biological worth, industrial relevance and picture of organotin (IV) complexes are roundly documented. They have a broad gamut of applications, being used in anti-fouling paints [1], PVC stabilization, as homogeneous catalysts, and as ion carriers in electrochemical membrane design [2,3,4]. Among organotin (IV) complexes, organotin (IV) carboxylates show significant antifungal[5], antibacterial[6] and antitumor activities [7] which is essentially related to the number and nature of the organic groups attached to the central Sn atom, therefore, the role of the carboxylate ligand cannot be ignored [8]. Usually triorganotin (IV) compounds display a higher biological activity than their di- and mono-organotin (IV) correspondents, which has been related to their ability to bind to proteins [9,10]. In addition to their biological activities, the organotin (IV) carboxylates also present an interesting structural diversity. Depending on the mode of attachment of the carboxylate group, the resultant triorganotin (IV) complex can either be tetra or penta-coordinated. A tetrahedral complex result when the carboxylate group acts as a monodentate ligand [11]. For a bridged carboxylate group, a penta-coordinated polymer usually results while a chelated monomeric compound is formed when the carboxylate ligand acts as a non-bridging bidentate ligand [12]. Generally, triorganotin (IV) carboxylates with bulky R groups attached to the Sn atom will favour tetrahedral monomeric structures, while sterically less demanding R groups would favour bridged polymeric structures [13]. Among diorganotin (IV) bis(carboxylates) the coordination geometry around the Sn atom is usually found to be skew trapezoidal [14]. In such type of structural theme, the Sn atom is hexa-coordinated and carboxylate ligands chelate the Sn atom, forming disparate Sn–O bond distances.



Modern agriculture as a major commercial and developmental enterprise entails the use of chemicals (pesticides), which require some distribution of the active substances during field application. However, organotin (IV) fungicides are mostly insoluble in water, which presents a formidable challenge to their convenient, cost effective field application, considering the large hectares cultivated. The relative insolubility of organotin (IV) fungicides in water is primarily due to their non-polar nature. In general, they are soluble in many organic solvents, such as alcohols, ethers and halogenated hydrocarbons [14, 15].

The poor aqueous solubility of the organotin (IV) compounds has remained a problem in agricultural applications, especially as appreciable solubility is necessary for minimizing the handling of large volume of solvents during concentrate preparations which eventually render them very expensive; and a minimum of aqueous solubility is required to free the organotin (IV) moiety enabling it to more effectively interfere with the physiological processes of target pests [15].

The present investigation deals with synthesis, characterization and solubility study of a novel water soluble triphenyltin (IV) monopotassium 3-carboxy-3-hydroxy-pentanedioate.

### Experimental

The acid 3-carboxy-3-hydroxypentanedioic acid,  $\text{Ph}_3\text{SnOH}$ , KOH and Methanol used were Aldrich products of analytical grade, with purity greater than 99%, imported directly from the factory in Germany and used without further purification.

### Apparatus

Glasswares were thoroughly washed with soapy detergent, repeatedly rinsed with distilled water and oven dried. A Dean-Stark apparatus was employed for reflux- distillation.

Crystals of the acid salt and the organotin (IV)<sup>nt+</sup> compound synthesized were dried in an oven (Model: Leader UK) at 313 K - 333 K. Thermometers used were calibrated to 633 K. Tin content analysis was carried out according to the method reported by Farnsworth and Pekola [9], using porcelain crucibles, gas Bunsen Burners, electric furnace (Carbolite ELF 11/6B, Thermal Engineering Service, UK) and vacuum desiccator. Weights were taken using an analytical balance (model: ADAM AAA 100L) and infrared data was generated using a Mattson Infrared Spectrophotometer (Genesis IIFIR).

### Synthesis of Monopotassium Salt of 3-Carboxy-3-hydroxypentanedioic acid

Potassium hydroxide (0.0500 mol, 2.8547g) and 3-carboxy-3-hydroxypentanedioic acid (0.0500 mol, 9.6214 g) were weighed and dissolved in distilled water in a 250 cm<sup>3</sup> beaker. The mixture was stirred thoroughly using a glass rod until there was complete dissolution. Water was removed by evaporating in an oven at 313 K for 72 h; during which a progressively viscous solution resulted and eventually dried to a white crystalline solid [16].

### Reaction between Monopotassium 3-Carboxy-3-hydroxypentanedioate and Triphenyltin (IV) Hydroxide

Equimolar amounts of triphenyltin (IV) hydroxide (0.0050 mol, 1.8351 g) and monopotassium 3-carboxy-3-hydroxypentanedioate (0.0050 mol, 1.1505 g) were suspended in methanol and the mixture was simultaneously refluxed and stirred vigorously on a magnetic stirrer for 4 hours. The mixture was initially a cloudy, white dispersion, largely insoluble in methanol. During refluxing the mixture became clear and the solvent distilled over at 347 K for a greater part of the time of refluxing; then there was an abrupt drop in thermometer reading to 327 K, apparently due to a near complete removal of the solvent. Any remaining solvent was evaporated in the oven at 313 K for 30 minutes, to a progressively sticky, glassy mass and finally, the solution dried up to a white crystalline solid [16-19].



## Characterization

### Tin Content Analysis

Triphenyltin (IV) monopotassium 3-carboxy-3-hydroxy-pentanedioate ( $\approx 0.25$  g) in a porcelain crucible was heated strongly (up to  $\approx 1,173$  K) in an electric furnace (Carbolite ELF 11/6B, Thermal Engineering Service, UK) until a uniformly yellow solid ( $\text{SnO}_2$ ) was obtained. This was cooled in a desiccator, weighed as  $\text{SnO}_2$  and the tin content of the sample was then worked out [20-25]

### Solubility of the Organotin (IV) Compound

0.2g of sample B was weighed and  $1\text{cm}^3$  of distilled water added at room temperature (308 K). The mixture was gently swirled and the tube vortexed vigorously for 1–2 minutes. It was observed that the sample dissolved. The solubility was then calculated as a percentage of the mass of the solute divided by the volume of water at which complete dissolution occurred, as shown in the table below. Assuming the density of water was always  $1.000\text{ g/cm}^3$  [8, 26-29]

$$\text{Solubility} = \frac{\text{weight of solute}}{\text{Weight of water}} \times 100 \% \text{ (at fixed temperature).}$$

### FTIR of Acid, Organotin (IV)<sup>nt</sup> Compound, Acid Salts and Organotin (IV) Carboxylate [10, 17-19]

The FTIR Spectra of 3-carboxy-3-hydroxy-pentanedioic acid, its monopotassium salt, the triphenyltin (IV) hydroxide and the Triphenyltin (IV) monopotassium 3-carboxy-3-hydroxy-pentanedioate in nujol mull were measured on a Mattson Infrared Spectrophotometer, (Genesis II FTIR) in the range of  $4000 - 400\text{ cm}^{-1}$  at 32 runs per minute. The samples were scanned at normal laboratory temperature and placed in constant path-length NaCl cells (Shedda Science and Technology Complex – SHESTCO, Abuja, Nigeria). The spectrophotometer calibration was checked and confirmed using polystyrene (Mattson) at ambient temperature, and the reference point for the data were determined with 3-carboxy-3-hydroxypentanedioic acid  $>99.9\%$  purity (Aldrich, GmbH). Percentage transmittance bands and intensities were then obtained using a 'winFIRST' Plot Composer Software.

## Results and Discussion

The result of tin content analysis as carried out by the method reported by Farnsworth and Pekola [11] are reported in the table 1.

**Table 1:** Results of tin content analysis

Sample	Crucible(g)	Crucible+ Sample (g)	Sample (g)	Crucible + SnO <sub>2</sub> (g)	SnO <sub>2</sub> (g)	Sn (g)	% Sn OBS	% Sn CALC
A	85.530	85.788	0.258	85.607	0.077	0.061	23.643	20.162

The agreement between the observed and calculated value lies within 4 percentage points; though the observed was greater than the calculated.

### FTIR Spectroscopic Results

The FTIR data of 3-carboxy-3-hydroxy-pentanedioic acid, its monopotassium salt, the triphenyltin (IV) hydroxide and the triphenyltin (IV) monopotassium 3-carboxy-3-hydroxy-pentanedioate is as tabulated in table 2.

By comparison of the FTIR data obtained with the data reported in literature for other organotin (IV) compounds formed with {O} donor atom containing anionic groups the following assignments are made for the compound studied in this work: The  $\nu_{\text{OH}}$  band of  $\text{Ph}_3\text{SnOH}$  ( $3614\text{ cm}^{-1}$ ) is not found in the spectra of the corresponding product, A, indicating a reaction had occurred. Also, there is the appearance of strong  $-\text{C}-\text{H}$  out-of-plane (OOP) deformation bands at  $724\text{ cm}^{-1}$  for A, which was synthesized from  $\text{Ph}_3\text{SnOH}$ . The  $-\text{C}=\text{O}$  stretching vibrations of the free acid were observed at  $1745$  and  $1694\text{ cm}^{-1}$  (citric acid). Upon formation of the carboxylate anion ( $-\text{COO}^-$ ) in the acid salt, other bands appeared at lower frequencies at  $1729\text{ cm}^{-1}$  and  $1583\text{ cm}^{-1}$  (monopotassium citrate). These are related



to the  $-\text{COO}^-$  anions. There are, however, few “anomalous” shoulders due probably to atmospheric water vapour. Upon complexation, the  $\nu_{\text{C=O}}$  band shifted towards lower frequencies:  $1723\text{cm}^{-1}$  and  $1618\text{cm}^{-1}$  (A), and split in two components for the citrates, which, are related to the antisymmetrical and symmetrical stretching vibrations, respectively of the  $-\text{COO}^-$  group.

**Table 2:** FTIR data for the organotin (IV) carboxylates prepared, the organotin (IV) compounds, carboxylic acids and their potassium salts

Sample	$\text{OH}_{\text{str}}$ $\text{cm}^{-1}$	$-\text{C}=\text{O}^{\text{asy}}$ $\text{cm}^{-1}$	$\text{C-O(H)}$ $\text{cm}^{-1}$	$\text{C-H}_{\text{Ph}}$ $\text{cm}^{-1}$	$\text{C-H}_{\text{oop}}$ $\text{cm}^{-1}$	$\text{Sn-Bu}$ $\text{cm}^{-1}$
$\text{Ph}_3\text{SnOH}$	3614	-	-	1077	721 <i>st, s</i>	-
A	3126	1723, 1618		1073	724	
Citric acid	3294	1745 1694	1138			
K citrate	3298	1729 1583	1092	-		

A further change in the electronic system of the affected  $-\text{COO}^-$  groups (deprotonation of OH group, interaction with the {Sn} atom and formation of an O-Sn bond) is confirmed by a shift of  $\nu_{\text{C-O(H)}}$  and by changing into  $\nu_{\text{C-O(Sn)}}$ . The  $\text{Ph}_3\text{Sn}$  (IV) compound showed the usual benzene ring absorption:  $\text{Ph}_3\text{SnOH}$  has the band at  $1077\text{cm}^{-1}$  and its complex has it at  $1073\text{cm}^{-1}$  (A). These bands, assigned to C-H in-plane deformation vibrations, are characteristic of the phenyltin (IV) group.

### Solubility Results

**Table 3:** Solubility of the triphenyltin (IV) carboxylate

Sample	Sample mass (g)	Water volume ( $\text{cm}^3$ )	% Solubility (water)
B	0.2	1	20

This result shows significant solubility for samples B. It is possible that the phenyltin (IV) exhibited the observed solubility due to its bulky structure augmented by the ionic carboxylate end of the compound.

### Conclusions

The aqueous solubility of the synthesized compound was developed through amphiphilic micellization as in fatty acid soaps, where they have both hydrophilic and hydrophobic ends, coupled with their bulky nature, which allows the hydrophilic end to force the compounds into aqueous solvation. The compound was tested for solubility in aqueous media and the result obtained confirmed sufficient aqueous solubility.

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