

Research Article

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Synthesis, crystal structure and catalytic activity of 2-methoxycarbonylethyltin dichlorotin hydroxide

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Abstract: 2-methoxycarbonylethyltin hydroxide, $\text{CH}_3\text{OCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})$ (**1**), has been synthesized by hydrolysis reaction and characterized by elemental analysis, FT-IR, ^1H NMR spectroscopy, and X-ray single crystal diffraction. Compound **1** is a centrosymmetric dimer, and the tin atom approximates to octahedral geometry *via* an intramolecular carbonyl-to-tin coordination and hydroxo-bridging. The compound display high selectivity and good catalysis activity on the transesterification reaction of ethyl acetoacetate with an alcohol.

Supporting information: FT-IR, ^1H NMR, X-Ray, GC/MS analyses, Cif file.

Keywords: organotin, 2-methoxycarbonylethyltin chloride, crystal structure, catalysis, transesterification.

1. INTRODUCTION

Organotin compounds, a class of important organometallics, are widely used as the reaction catalysts, PVC stabilizers, biocides, and wood preservatives [1]. 2-Alkoxy carbonylethyltin trichlorides [2], the excellent PVC stabilizer intermediates [3], have received considerable attention due to the variety of coordination geometries about the tin atom [4-6]. Their crystal structures and spectra [2-6] have been extensively studied. However, to our knowledge, little attention has been paid to their hydroxides and use of these compounds in the catalysis reactions. Here, we report the synthesis, crystal structure and catalytic property of 2-methoxycarbonylethyltin dichlorotin hydroxide, $\text{CH}_3\text{O-COCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})$ (**1**).

2. EXPERIMENTAL

All chemicals were of reagent grade and were used without further purification. 2-methoxycarbonylethyltin trichloride was prepared according to the reported method by the reaction of $\text{CH}_2=\text{CHCO}_2\text{CH}_3$ with SnCl_2 and HCl [2]. Carbon and hydrogen analyses were determined using a Perkin Elmer 2400 Series II elemental analyzer. IR spectra were recorded on a Nicolet 470 FT-IR spectrophotometer using KBr discs in the range 4000-400 cm^{-1} . ^1H NMR spectral data were collected using a Bruker Avance DMX500 NMR spectrometer with CD_3OD as solvent and TMS as internal standard. GC/MS analyses were carried out on an HP GC6890/MS5973 equipped with an HP-5MS capillary column (length: 30 m, inner diameter: 0.25 mm) with helium as carrier gas.

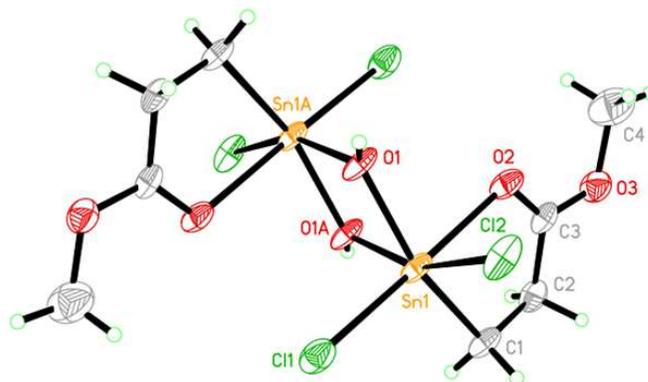


Figure 1: The molecular structure of **1**.

2.1 Synthesis of **1**

A solution of 2-methoxycarbonylethyltin trichloride (0.31 g, 1 mmol) in acetone (20 mL) with a little added water was stirred for 3 h at room temperature, and then was filtered. The solution was evaporated slowly at room temperature. The colorless crystals were obtained in 58% yield. M.p. 118.7-119.9 °C. Anal. Found: C, 16.24; H, 2.58. Calcd for $\text{C}_4\text{H}_8\text{Cl}_2\text{O}_3\text{Sn}$: C, 16.36; H, 2.75%. IR (KBr)/ cm^{-1} : 3430 (broad, OH), 1652 [vs, n(C=O)], 1268, 1233 [vs, n(C-O)], 545 [m, n(Sn-O)]. ^1H NMR (500 MHz, CD_3OD)/ δ : 3.92 (3H, s, CH_3O), 2.84 (2H, t, $J = 7.6$ Hz, $^3J(^1\text{H}-^{119}\text{Sn}) = 184.5$ Hz, COCH_2), 1.81 (2H, br, $^2J(^1\text{H}-^{119}\text{Sn}) = 115.6$ Hz, CH_2Sn).

2.2 X-ray crystallography

The colorless single crystal of **1** was obtained from methanol by slow evaporation at room temperature. Diffractions measurements were performed on a Bruker Smart Apex imaging-plate area detector fitted with graphite monochromatized Mo-K α radiation (0.71073 Å) using the *j* and *w* scan technique. The structures were solved by direct-methods and refined by a full-matrix least squares procedure based on F^2 using SHELXL-97 [7]. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at calculated positions. Crystal data, collection procedures and refinement results are summarized in Table S1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 930555.

2.3 Transesterification catalyzed by **1**

The transesterification of ethyl acetoacetate with 1-butanol were carried out in a 50 ml round-bottomed flask equipped with a condenser. A mixed solution of ethyl acetoacetate (6.50 g, 50 mmol), 1-butanol (7.41 g, 100 mmol), and **1** (0.15 g, 0.5 mmol)

was refluxed for 4 h. The final composition of the reaction mixture was monitored by GC-MS techniques (see Figure S3).

RESULTS AND DISCUSSION

Compound **1** was obtained by hydrolysis of 2-methoxycarbonylethyltin trichloride in acetone. The equation is as follows:



This compound is colorless crystal, and can be soluble in methanol and acetone.

In the IR of **1**, the strong and broad $\nu(\text{OH})$ band appeared at $\sim 3430\text{ cm}^{-1}$ indicates that the chlorine atom on the tin is substituted by the hydroxyl. This is further proved by the appearance of a medium band at 545 cm^{-1} , assignable to the Sn-O stretching vibration [8]. The stretching vibration of carbonyl in the $1640\sim 1740\text{ cm}^{-1}$ region is known to depend on the nature of coordination of the carbonyl oxygen to metal [4, 9]. The $\nu(\text{C}=\text{O})$ band of **1** appears at 1652 cm^{-1} , clearly indicating that the carbonyl is coordinated to tin atom. The fact that there is almost no variation of $\nu(\text{C}=\text{O})$ between the pure compound (in KBr discs) and a solution of methanol for **1** indicates the intramolecular $\text{C}=\text{O}\rightarrow\text{Sn}$ coordination still remains in solution [4].

In CD_3OD , the proton resonances of CH_2Sn and COCH_2 appear at 1.81 and 2.84 ppm, respectively, and the couplings with tin nuclei, $^2J(^1\text{H}-^{119}\text{Sn})$ and $^3J(^1\text{H}-^{119}\text{Sn})$, are 115.6 and 184.5 Hz, respectively. The δ values of the CH_3O protons (3.92 ppm) show a downfield shift compared with that in methyl propionate (3.67 ppm) because the coordination of carbonyl to tin causes the deshielding of CH_3O protons.

The molecular structure of **1** is shown in Figure 1. The selected bond lengths and bond angles are listed in Table 1. The compound crystallizes in monoclinic space group $C2/c$ and is a centro-symmetric dimer built up around a planar four-membered cyclic Sn_2O_2 unit, in which the hydroxyl groups

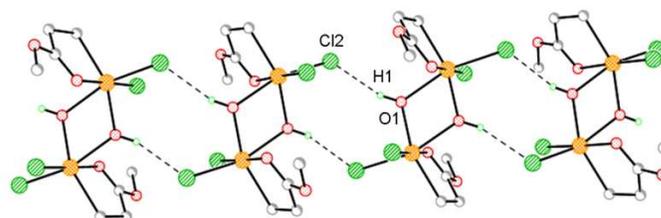


Figure 2. The double-chain formed by the intermolecular O-H...Cl interactions. All hydrogen atoms except H(1) atom are omitted for

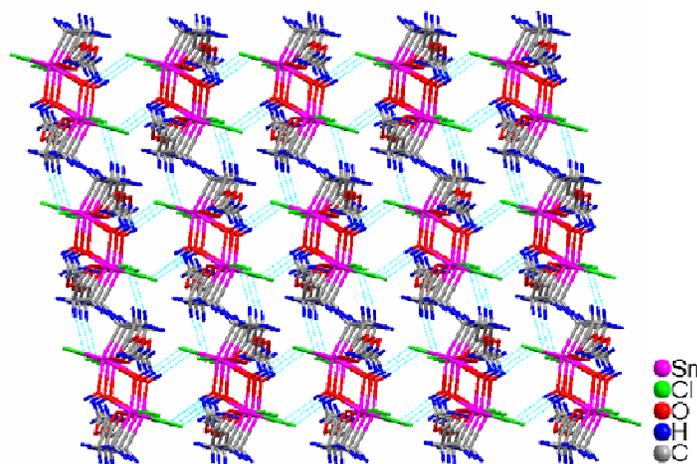
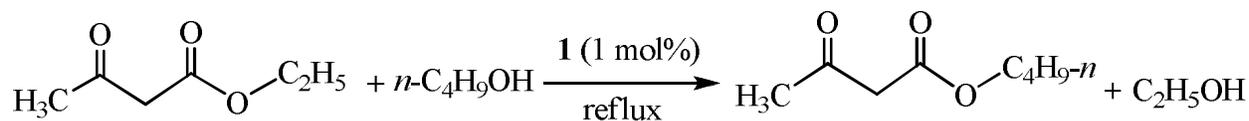


Figure 3. The three-dimensional connectivity formed by the intermolecular O-H...Cl and C-H...Cl interactions in **1**.

bridge the two tin atoms. Each tin atom is coordinated by two chloride atoms occupying mutually *cis* positions and a carbon and a carbonyl oxygen from the chelating COCH_2CH_2 moiety. The remaining positions in the distorted octahedral coordination geometry about each tin atom are occupied by two μ_2 -hydroxide

Table 1. Selected bond lengths (Å) and angles (°) for **1**. Symmetry code A: $-x, -y, -z$.

Sn(1)-O(1)	1.987(4)	Sn(1)-Cl(1)	2.375(2)
Sn(1)-C(1)	2.084(7)	Sn(1)-Cl(2)	2.4414(19)
Sn(1)-O(1A)	2.180(4)	O(2)-C(3)	1.187(6)
Sn(1)-O(2)	2.304(5)	O(3)-C(3)	1.282(9)
O(1)-Sn(1)-C(1)	155.2(2)	O(2)-Sn(1)-Cl(1)	177.42(12)
O(1)-Sn(1)-O(1A)	69.57(18)	O(1)-Sn(1)-Cl(2)	91.88(13)
C(1)-Sn(1)-O(1A)	94.1(2)	C(1)-Sn(1)-Cl(2)	100.7(2)
O(1)-Sn(1)-O(2)	81.16(18)	O(1A)-Sn(1)-Cl(2)	159.93(14)
C(1)-Sn(1)-O(2)	79.0(2)	O(2)-Sn(1)-Cl(2)	84.12(14)
O(1A)-Sn(1)-O(2)	85.45(19)	Cl(1)-Sn(1)-Cl(2)	94.09(8)
O(1)-Sn(1)-Cl(1)	97.06(16)	Sn(1)-O(1)-Sn(1A)	110.43(18)
C(1)-Sn(1)-Cl(1)	103.2(2)	C(3)-O(2)-Sn(1)	111.2(5)
O(1A)-Sn(1)-Cl(1)	95.71(16)	C(2)-C(1)-Sn(1)	109.0(5)



Scheme 1 Compound **1** catalyzed transesterification of ethyl acetoacetate.

groups. The major distortions in the tin atom geometries may be traced to the acute angles induced by the Sn_2O_2 ring [O(1)-Sn(1)-O(1A) $69.57(18)^\circ$, symmetry code A: -x, -y, -z.] and five-membered chelate CSnO ring [C(1)-Sn(1)-O(2) $79.0(2)^\circ$]. The Sn-O distances in the four-membered Sn_2O_2 ring are not symmetrical, with the bond *trans* to a carbon atom being shorter [Sn(1)-O(1) $1.987(4)$ Å] than that *trans* to a chlorine atom [Sn(1)-O(1A) $2.180(4)$ Å], which are comparable with those found in $[\text{n-BuSn}(\text{OH})\text{Cl}_2(\text{H}_2\text{O})_2]$ [8], $[\text{MeSn}(\text{OH})\text{Cl}_2(\text{H}_2\text{O})_2]$ [10], $[\text{H}_2\text{NCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})_2]$ [11]. The Sn-O distance in the five-membered chelate ring is Sn(1)-O(2) $2.304(5)$ Å, which is slightly shorter than that ($2.351(2)$ Å) of the six-coordinated $\text{CH}_3\text{CH}_2\text{OCOCH}_2\text{CH}_2\text{SnCl}_3\cdot\text{OSBu}_2$ [5]. The two Sn-Cl distances around each tin center are significantly different ($2.375(2)$ and $2.4414(19)$ Å), which is similar to those observed in $[\text{n-BuSn}(\text{OH})\text{Cl}_2(\text{H}_2\text{O})_2]$ [8] and $[\text{H}_2\text{NCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})_2]$ [11].

The molecules of **1** are linked by a pair of intermolecular O-H...Cl hydrogen bonds over a center of inversion [H(1)...Cl(2)^{#1} 2.28 Å, O(1)...Cl(2)^{#1} $3.125(6)$ Å, O(1)-H(1)...Cl(2)^{#1} 171° , symmetry code #1: -x, y, -z+1/2] to form an infinite zigzag double-chain (Figure 2). The one-dimensional supramolecular chains are further joined by the weaker intermolecular C-H...Cl interactions [H(2A)...Cl(1)^{#2} 2.74 Å, C(2)...Cl(1)^{#2} $3.703(7)$ Å, C(2)-H(2A)...Cl(1)^{#2} 170° , symmetry code #2: -x+1/2, y+1/2, -z+1/2] to complete a form of three-dimensional connectivity (Figure 3).

Tin-based Lewis acids like mono- and dialkyltin compounds and tetraalkyldistannoxane derivatives are very efficient catalysts for transesterification reactions [12]. Compound **1** possessed the similar structure to distannoxanes, and is also an effective transesterification catalyst. In order to prove the catalytic activity of **1** in transesterification reactions, we initially conduct a blank reaction, in which ethyl acetoacetate is reacted with 2 equiv of *n*-butanol at reflux without **1**. The GC-MS analysis shows that the desired *n*-butyl ester is obtained in only trace amounts even after 12 h. When the same reaction is conducted using 1 mol% of **1** at reflux, the *n*-butyl acetoacetate is obtained in 87.2% yield within 4 h, and the ketal products, $\text{CH}_3\text{C}(\text{OC}_2\text{H}_5)_2\text{CH}_2\text{COOC}_2\text{H}_5$ (ethyl 3,3-dibutoxybutanoate), is not observed (Scheme 1).

The catalytic activity of **1** on the transesterification of ethyl acetoacetate with an alcohol is higher than that of the distannoxane catalyst, $\text{ClBu}_2\text{SnOSnBu}_2\text{OH}$, reported by Otera [13]. In addition, the preparation of **1** is easier than the distannoxane derivatives and the other mono- and dialkyltin compounds [2]. Hobbs [14] reported that 2-methoxycarbonyl ethyltin trichloride, $\text{CH}_3\text{O-COCH}_2\text{CH}_2\text{SnCl}_3$, undergo a facile auto-catalyzed transesterification reaction with an alcohol. In the **1**-catalyzed transesterification of ethyl acetoacetate, catalyst **1** itself could also conduct transesterification with *n*-butanol, but the product formed, $\text{n-C}_4\text{H}_9\text{OCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})$, can continue to catalyze this reaction. This reaction catalyzed by **1** with good yields, higher

selectivity and easier operation provides a convenient way for preparing acetoacetates.

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