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Preparation and structure of $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$

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Abstract

The novel estertin, $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$, has been prepared and examined. The crystal ($Pna2_1$; a 13.626(3), b 7.323(2), c 12.727(3) Å; $Z = 4$; $R = 0.046$) adopts a distorted octahedral arrangement with the five- and six-membered fused rings via two carbonyl oxygen-to-tin coordinations. However, IR and multinuclear NMR spectroscopy in solution suggests that one carbonyl group of the tin compound is released from the tin atom, which results in a five coordinate tin atom in solution.

Introduction

A large number of estertin compounds and their derivatives have been prepared and established because of the variety of coordination geometries around the tin atom and their applicability as a PVC stabilizer with low mammalian toxicity [1–8]. In order to extend the estertin chemistry, we report here the preparation and structural properties of a novel estertin, $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$.

Experimental

All chemicals were of reagent grade and used without further purification. All solvents were dried by standard methods before use. Chemical analysis was carried out by the Chemical Analysis Laboratory at KIST. The molecular weight was determined cryoscopically in water by use of a Cryette A Automatic Cryoscope. The IR spectrum was measured in the 4000–400 cm^{-1} region on both KBr pellet and CH_2Cl_2 solution with an Analect Instrument FX 6160 FT-IR spectrometer. The NMR spectra were recorded on a Bruker AM-200 operating at 200 (^1H) and 74.63 MHz (^{119}Sn) in pulse mode with Fourier transform at ambient temperature. The chemical shifts are relative to internal Me_4Si (^1H) and external Me_4Sn (^{119}Sn) for indicated nuclei.

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The title compound was prepared by a procedure similar to that a solution of $CH_3OOCCH_2CH_2SnCl_3$ [1]: $SnCl_2$ (94.8 g, 500 mmol) and dimethyl itaconate (79.7 g, 500 mmol) in 300 ml of diethyl ether were placed in a 1000 ml three-necked flask equipped with a mechanical stirrer, reflux condenser, and gas inlet tube. Through the stirred suspension was buffled for 2 h gaseous anhydrous hydrogen chloride (13.8 g, 500 mmol) at 20 °C. The solvent was removed at reduced pressure, and the residue was washed with ethyl ether to produce white crystalline solids in 95% yield. The analytical-grade sample was recrystallized from a dichloromethane–petroleum ether solvent mixture (1 : 1) to give colorless crystalline solids suitable for X-ray crystallography, mp, 154–155 °C. Anal. Found: C, 21.70; H, 2.87. $C_7H_{11}O_4Cl_3Sn$ calcd: C, 21.88; H, 2.89% M.W. measured (in H_2O): 362 (calcd. 384.21), IR(KBr pellet; CH_2Cl_2 solution, cm^{-1}): ν(C=O), 1672(vs), 1656(sh); 1738(vs), 1664(vs), (1687(sh)). ^1H NMR (acetone-d_6; δ, ppm): 3.99 (s, 3H); 3.73(s, 3H); 3.52–3.64 (m, 1H); 3.06–3.10(dd, J 6, 2Hz, 2H); 2.29–2.39(dd, J 8, 4Hz, 1H); 2.07–2.17(dd, J 8, 4Hz, 1H). ^{13}C NMR (CD_2Cl_2; δ, ppm): 182.6 (C=O); 173.4 (C=O); 81.2 (–CH–); 56.9 (CH_3O–); 53.8 (CH_3O–); 37.2 (–CH_2–); 34.3 (–CH_2Sn). ^{119}Sn NMR (CD_2Cl_2; δ, ppm) = −180.1.

All the crystallographic data were obtained on an Enraf–Nonius CAD4 diffractometer with graphite-monochromated molybdenum radiation ($\lambda = 0.71072$ Å). The structure was solved by use of the conventional heavy-atom method and difference Fourier techniques, and refined by means of full-matrix least squares procedure; formula, $C_7H_{11}O_4Cl_3Sn$ (384.21); orthorhombic; $Pna2_1$; a 13.626(3), b 7.323(2), c 12.727(3) Å; V 1269.9(4) Å^3; $Z = 4$; d_{cal}, 2.01 gcm^{-3}; crystal size, $0.34 \times 0.40 \times 0.52$ mm; μ, 24.38 cm^{-1}; T = 23(2) °C; scan method, $\omega/2\theta$; data collected, h, k, l, $1 \leq \theta \leq 25°$; total number of observations, 1327; number of unique data, $I > 3\sigma(I)$, 1022; number of parameters refined, 135; largest shift/esd, 0.02; largest peak, 1.27 eÅ^{-3} (1.01 Å from Sn); R (R_w) = 0.046 (0.050); GOF = 0.95.

Results and discussion

The ORTEP drawing and atomic labeling scheme of the present compound is presented in Fig. 1, along with selected bond distances and angles. The compound is a discrete molecule with no close intermolecular contacts. The geometry of the tin atom is hexacoordinate with Cl(1), Cl(2), Cl(3), O(1), O(3), and C(1) in a distorted octahedral arrangement. The distortion appears to be caused by the small bite angles of O(1)–Sn–C(1) (76.5(6)°), C(1)–Sn–O(3) (78.2(7)°), and O(1)–Sn–O(3) (79.9(4)°) with a concomitant splaying of the Cl–Sn–Cl angles (95.9(2); 96.9(2); 97.7(2)°). The mono-charged potential tridentate ligand is bonded to the tin atom in a trihapto fashion which is essentially facial, to provide a suitable bite angle, resulting in the fused rings having either five or six members. The rings are puckered from the typical form, but retain the facial tridentate mode. The bond lengths of Sn–O(1) (2.400(1) Å), Sn–O(3) (2.469(8) Å), and Sn–C(1) (2.127(18) Å) are slightly longer than those (Sn–O, 2.347(5); Sn–C, 2.139(8) Å) of its pentacoordinate analog, $CH_3OOCCH_2CH_2SnCl_3$ [3] owing to a decrease of the Lewis acidity of the tin atom by the crowded coordination sphere. On the other hand, the Sn–O(1) distance in the five-membered ring is slightly shorter than that of Sn–O(3). This indicates a weaker coordination in the six-membered chelate than in the five-membered chelate in the solid state.

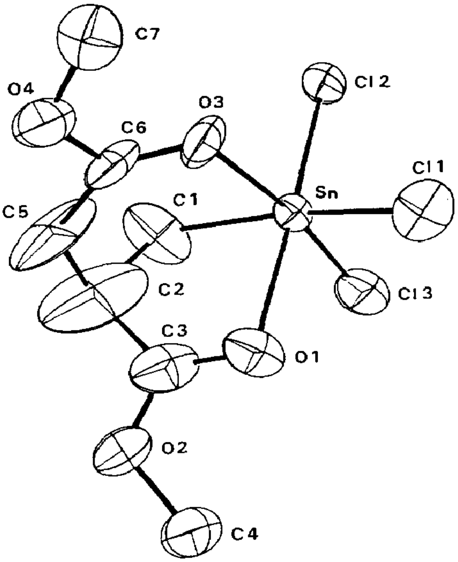

Fig. 1. ORTEP drawing of $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$ with thermal ellipsoids shown at the 50% probability level; selected bond lengths (Å) and angles (°): Sn–Cl(1) 2.315(4) Sn–Cl(2) 2.379(4), Sn–Cl(3) 2.371(4), Sn–C(1), 2.127(18), Sn–O(3) 2.469(8); Cl(2)–Sn–Cl(1) 95.9(2), Cl(3)–Sn–Cl(1) 96.9(2), Cl(3)–Sn–Cl(2) 97.7(2), C(1)–Sn–Cl(1) 150.1(5) C(1)–Sn–Cl(2) 104.3, C(1)–Sn–Cl(3) 101.8(7), O(1)–Sn–Cl(1) 81.1(3), O(1)–Sn–Cl(2) 173.5(3), O(1)–Sn–Cl(3) 88.3(4), O(1)–Sn–C(1) 76.5(6), O(3)–Sn–Cl(1) 78.7(2), O(3)–Sn–Cl(2) 94.0(3), O(3)–Sn–Cl(3) 167.9(3), O(3)–Sn–C(1) 78.2(7), O(3)–Sn–O(1) 79.9(4).

The $\nu(C{=}O)$ band (1672, 1656(sh) cm^{-1}) of the present compound in the solid state appear at the same region as that (1650 cm^{-1}) of $CH_3OOCCH_2CH_2SnCl_3$ [3], whereas exhibits a remarkable red shift from that (1727 cm^{-1}) of $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)_2Cl$ [9], in which the carbonyl group is not coordinated to the tin atom. However, the $\nu(C{=}O)$ band of the compound in CH_2Cl_2 solution was prominently separated in a coordinated carbonyl (1664 cm^{-1} region) and a free carbonyl group (1738 cm^{-1}). The result indicates that the two carbonyls are coordinated to the tin atom in the solid, where one carbonyl is not coordinated to the tin atom in solution state. $\delta(^{119}Sn)$ of the present compound supports the IR data. The tin chemical shift ($\delta(^{119}Sn) = -180.1$ ppm) is near to that of pentacoordinate compound, $CH_3OOCCH_2CH_2SnCl_3$ (-145.1 ppm in $CDCl_3$) [10]. In addition, ^1H NMR ($\delta(CH_3O-) = 4.0$, 3.7 ppm in acetone) and ^{13}C NMR ($\delta(C{=}O) = 182.6$, 173.4 ppm, $\delta(CH_3O-) = 56.9$, 53.8 ppm in dichloromethane) suggest that the bonding fashion of the carbonyl groups in solution is different from that in the solid state. According to our previous result, $\delta(^1H)$ for CH_3O- and $\delta(^{13}C)$ for C=O and CH_3O- could be used for elucidating the behavior of the ester group bonded to tin atom. For example, $\delta(^1H) = 4.0$ ppm (CH_3O-) and $\delta(^{13}C) = 181.0(C{=}O)$, 54.2 ($CH_3O$-) ppm in the carbonyl oxygen-to-tin coordinated compound, $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)Cl_2$, is deshielded by approximately 0.3 ppm, 6 ppm, and 3 ppm, respectively, relative to those in $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)_2Cl$, in which the carbonyl group is not coordinated to the tin atom [9]. Thus the separated values for $\delta(^1H)$ for CH_3O-, and $\delta(^{13}C)$ for C=O and CH_3O- in the present compound indicate that one carbonyl group presumably involved in the six-membered chelate is released from the tin atom in solution, so that the tin atom is pentacoordinate in solution (both coordinating and noncoordinating solvent) in contrast to hexacoordinate in the solid state.

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