

Molecular structures of $[(\text{Ph}_3\text{Sn})_2\text{O}_3\text{Se}]$ and $[(\text{Ph}_3\text{Sn})_2\text{O}_4\text{Cr}](\text{CH}_3\text{OH})$

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Abstract

Molecular structures of $[(\text{Ph}_3\text{Sn})_2\text{O}_3\text{Se}]$ (**1**) and $[(\text{Ph}_3\text{Sn})_2\text{O}_4\text{Cr}](\text{CH}_3\text{OH})$ (**2**) have been determined using spectroscopic techniques and X-ray analysis. Each structure consists of polymers containing two types of tin centres: one of them is bridged by two oxygen atoms of the trifunctional oxyanion into a helical chain while the other is pendant to this chain. In the case of the chromate derivative the pendant tin is also bonded to the oxygen atom of the solvent (methanol); hydrogen bonds between the methanol and the non-coordinated oxygen of the chromate generate a three-dimensional structure containing tin atoms in a trigonal bipyramidal environment. In contrast, the two tin centres in the non-solvated selenite derivative have distinct geometries (tetrahedral and trigonal bipyramidal). Variable temperature Mössbauer spectroscopy data are consistent with the polymeric structure of the selenite derivative while NMR spectroscopy shows the presence of monomeric species in solution.

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1. Introduction

Despite the plethora of organotin carboxylate structures yet determined, derivatives containing triphenyltin moieties have been relatively overlooked [1] and it has been shown that the tin centres adopt one of the four basic configurations defined by Willem et al. [2]. In addition, only a few X-ray structure determinations have been reported for organotin derivatives including inorganic oxyanions as ligands [3]. In the scope of our research work on the coordination ability of various oxyanions in organotin derivatives, we have reported, recently, a spectroscopic study of $[(\text{Ph}_3\text{Sn})_2\text{O}_3\text{Se}]$ [4]. In compounds of general formulae $[\text{XO}_4(\text{SnPh}_3)_n \cdot$

$(\text{H}_2\text{O})_m]$ (X = S, Se, P; $n = 2, 3$; $m = 1, 2$), the oxyanions behave as polydentate ligands while the tin atoms adopt a trigonal bipyramidal or tetrahedral environment; the tetrahedral tin atom can, however, be involved in an additional coordination with a solvent molecule to expand the tin coordination number to five [5]. In a continuation of this interest in organotin derivatives, this present paper deals with the X-ray studies of $[(\text{Ph}_3\text{Sn})_2\text{O}_3\text{Se}]$ (**1**) and $[(\text{Ph}_3\text{Sn})_2\text{O}_4\text{Cr}](\text{CH}_3\text{OH})$ (**2**), their spectroscopic studies, including NMR, and the variable temperature Mössbauer spectroscopy study of the selenite derivatives $(\text{Ph}_3\text{Sn})_2\text{SeO}_3$.

2. Experimental

Ph_3SnOH , $(\text{HO})_2\text{SeO}$, CrO_3 , Et_4NI and ethylenediamine were purchased from Aldrich Chemicals and used without further purification.

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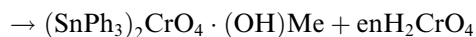
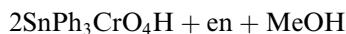
2.1. Spectroscopic characterization

CP-MAS ^{117}Sn spectra were recorded at 89.15 MHz on a Bruker Avance 250 spectrometer, equipped with a 4 MAS broad-band probe. Spinning frequencies are chosen between 5 and 9 kHz. A contact time of 1 ms and a recycling delay of 2 s were employed. The chemical shift reference was set with (cyclo- C_6H_{11}) $_4\text{Sn}$ (−97.35 ppm relative to $(\text{CH}_3)_4\text{Sn}$). ^{119}Sn solution spectra were recorded on a Bruker Avance II 500 spectrometer operating at 186.49 MHz. ^1H , ^{13}C and ^{119}Sn NMR chemical shifts are given in ppm. The coupling constants $nJ(^{119}\text{Sn}-^{13}\text{C}) = {}^nJ$ are given in Hz. The IR and Mössbauer spectra were obtained as reported earlier [6,7]. IR data are given in cm^{-1} . IR abbreviations: (br) broad, (s) strong, (m) medium, (sh) shoulder, (w) weak. Mössbauer parameters are given in mm/s. Mössbauer abbreviations: QS = quadrupole splitting, IS = isomer shift, Γ = full width at half-height.

2.2. Synthesis

$\text{SeO}_3(\text{SnPh}_3)_2$ (**1**) was obtained, as a white precipitate, from the reaction between triphenyltin hydroxide (Ph_3SnOH ; 3.478 g, 9.477 mmol) and selenous acid ($\text{SeO}(\text{OH})_2$; 0.611 g, 4.73 mmol). The mixture has been stirred for several hours and the obtained precipitate was filtered off. On mixing $\text{SeO}_3(\text{SnPh}_3)_2$ (0.590 g, 0.70 mmol in 25 ml CHCl_3) and Et_4NI (0.367 g, 1.40 mmol in 25 ml ethanol) crystals of $\text{SeO}_3(\text{SnPh}_3)_2$ suitable for X-ray diffraction were obtained by slow solvent evaporation. Spectroscopic data of $\text{SeO}_3(\text{SnPh}_3)_2$, including ^1H and ^{13}C NMR in solution, have been yet published [4]. $\delta(^{119}\text{Sn})$ NMR: −69 and −99 ppm (solid state), −97 ppm (CDCl_3 solution).

$[(\text{Ph}_3\text{Sn})_2\text{O}_4\text{Cr}](\text{CH}_3\text{OH})$ (**2**): The reaction between chromic acid (H_2CrO_4 ; 0.400 g, 4.08 mmol in 5 ml water) and triphenyltin hydroxide (Ph_3SnOH ; 1.500 g, 4.08 mmol in 25 ml methanol) gives a yellow precipitate, identified as $\text{Ph}_3\text{SnO}_3\text{Cr}(\text{OH})$. Suitable crystal for X-ray analysis of $[(\text{Ph}_3\text{Sn})_2\text{O}_4\text{Cr}](\text{CH}_3\text{OH})$ were obtained by slow solvent evaporation from a methanolic solution of $\text{Ph}_3\text{SnO}_3\text{Cr}(\text{OH})$ where ethylenediamine (hereafter en) was added in a 2:1 ratio according to the following reaction:



$\text{Ph}_3\text{SnO}_3\text{Cr}(\text{OH})$: *Elemental analyses* [found % (Calc. % for $\text{C}_{18}\text{H}_{16}\text{O}_4\text{CrSn}$): C, 46.33 (46.28); H, 3.38 (3.42). *Infrared*: 3416 br ν_{OH} , 1638 br δ_{OH} 972 w, 856 s $\nu_{\text{O}_4\text{Cr}}$.

$[(\text{Ph}_3\text{Sn})_2\text{O}_4\text{Cr}](\text{CH}_3\text{OH})$: *Elemental analyses* [found % (Calc. % for $\text{C}_{37}\text{H}_{34}\text{O}_5\text{CrSn}_2$): C, 52.16 (52.39); H, 4.13 (4.11). *Infrared*: 935 s, 908 s, 841 br ($\nu_1 + \nu_3$); ν_{SnO} ; 392 w, 345 w ($\nu_2 + \nu_4$); 275 s $\nu_{\text{s}}\text{SnC}_3$; 211 m $\nu_{\text{s}}\text{SnC}_3$. *Mössbauer data*: IS = 1.49; QS = 3.26; Γ = 0.80.

NMR: $\delta(^1\text{H})$ phenyl protons (o) 7.58 [3J = 57], (p, m) 7.42 and 7.38. $\delta(^{13}\text{C})$ C(i) 138.3 [1J = 612], C(o) 136.5 [2J = 47], C(m) 129.2 [3J = 62], C(p) 130.5. $\delta(^{119}\text{Sn})$ NMR: −211 ppm (solid state), −44 ppm (CDCl_3 solution).

Table 1

Crystal data for $[(\text{Ph}_3\text{Sn})_2\text{O}_3\text{Se}]$ (**1**) and $[(\text{Ph}_3\text{Sn})_2\text{O}_4\text{Cr}](\text{CH}_3\text{OH})$ (**2**)

	(1)	(2)
Empirical formula	$\text{C}_{36}\text{H}_{30}\text{O}_3\text{SeSn}_2$	$\text{C}_{37}\text{H}_{34}\text{O}_5\text{CrSn}_2$
Formula weight	826.94	848.02
Temperature (K)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a (Å)	19.9870(2)	12.7140(1)
b (Å)	12.1200(1)	15.6030(1)
c (Å)	27.2260(3)	17.1800(2)
β (°)	100.66	
Volume (Å ³)	6481.41(11)	3408.11(5)
Z	8	4
Density (calculated) (Mg/m ³)	1.695	1.653
Absorption coefficient (mm ^{−1})	2.698	1.809
Theta range (°)	3.11–25.01	3.15–25.03
Reflections collected	62 697	48 652
Independent reflections	11 242 [0.0453]	6000 [0.0582]
[$R(\text{int})$]		
Reflections observed ($>2\sigma$)	9737	5648
Data/restraints/parameters	11 242/0/784	6000/1/411
Final R indices [$I > \sigma(I)$]	$R_1 = 0.0434$, $wR_2 = 0.1017$	$R_1 = 0.0248$, $wR_2 = 0.0535$
R indices (all data)	$R_1 = 0.0531$, $wR_2 = 0.1070$	$R_1 = 0.0285$, $wR_2 = 0.0550$
Largest difference in peak and hole (e Å ^{−3})	3.044 and −0.728	0.430 and −0.906
Deposition number	622160	622161

General crystal and experimental details are reported in Table 1. Data collection was carried out at 150(2) K (for both **1** and **2**) on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream cooling apparatus. The data were corrected for Lorentz and polarization effects. The structures were solved using direct-methods (SHELXS-86) [8] and each refined by a full-matrix least-squares procedure based on F^2 using SHELXL-97 [9] with anisotropic displacement parameters for all non-H atoms. For (**1**), the final electron density map contained several features on the periphery of the phenyl rings, of which the largest is located 2.1 Å from C29. These peaks do not appear to have chemical significance and reflect the quality of the crystal and its associated data set. In the case of (**2**), the asymmetric unit consists of two essentially equivalent but crystallographically distinct molecules; only the one based on Sn(1,2) is discussed in the text. In addition, the phenyl ring based on C(61) attached to Sn(4) of the second molecule in the asymmetric unit is disordered equally over two sites. The absolute configuration of (**2**), which crystallises in the $P2_12_12_1$ space group, was determined from its Flack parameter (−0.021(10)).

3. Results and discussion

3.1. Structure of catena-(μ_3 -selenito)-bis(triphenyl-tin) (**1**)

Fig. 1 shows the asymmetric unit and the labelling scheme used in the text and tables. Key geometric data

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