

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 chromato 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 selenito derivative have distinct geometries (tetrahedral and trigonal bipyramidal). Variable temperature Mössbauer spectroscopy data are consistent with the polymeric structure of the selenito 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 $[\text{XO}_4(\text{SnPh}_3)_n]$

($\text{H}_2\text{O})_m$] ($\text{X} = \text{S, Se, P}$; $n = 2, 3$; $m = 1, 2$), 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 selenito 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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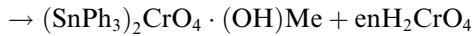
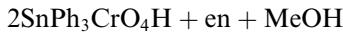
2.1. Spectroscopic characterization

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}) 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 $nJ(\text{Sn}^{119}-\text{C}^{13}) = ^nJ$ 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]. $\delta(\text{Sn}^{119})$ 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 νOH , 1638 br δOH 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 ($\nu_1 + \nu_3$); νSnO ; 392 w, 345 w ($\nu_2 + \nu_4$); 275 s $\nu_s\text{SnC}_3$; 211 m $\nu_s\text{SnC}_3$. 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	62697	48652
Independent reflections	11242 [0.0453] [$R(\text{int})$]	6000 [0.0582]
Reflections observed ($>2\sigma$)	9737	5648
Data/restraints/parameters	11242/0/784	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

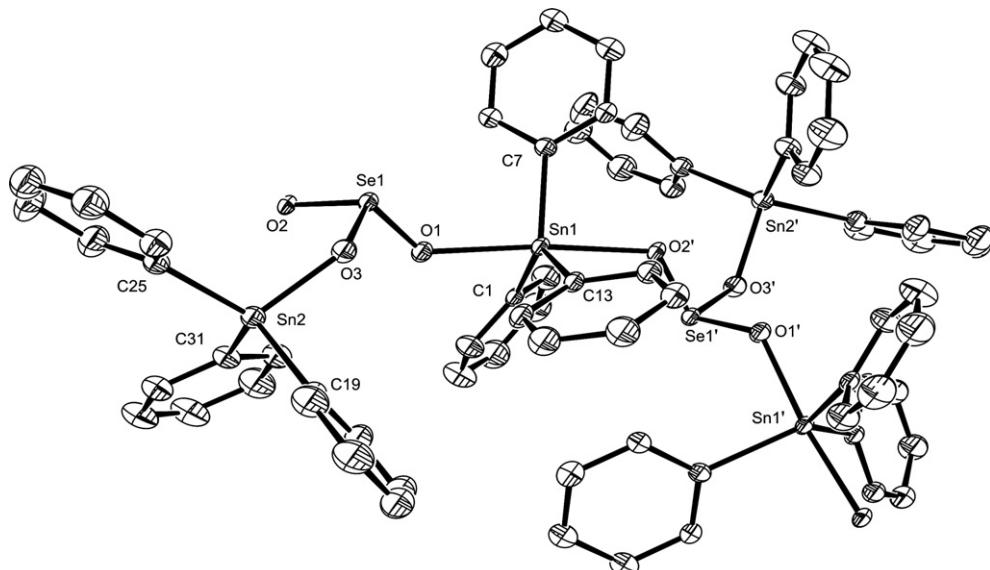


Fig. 1. The asymmetric unit of (1) showing the labelling scheme used in the text and tables. Only one of two essentially equivalent but crystallographically distinct molecules is shown for clarity. Thermal ellipsoids are at the 30% probability level and only the α -carbons of the phenyl rings are numbered for clarity of the figure; C1 thus represents the ring containing C1–C6, etc.

are given in Table 2. One of the two tin centres in the repeat unit [Sn1], forms part of a one-dimensional polymeric chain in which metal centres are bridged by two of the oxygen atoms [O1, O2] of the tri-functional selenite ligand, while the other tin centre is pendant to this chain via O3 of the ligand. There are no interactions between adjacent polymer chains. The structure thus contains two types of tin centres: one in a trigonal bipyramidal environment [Sn1] (involved in the polymer chain) while the other is in a tetrahedral environment [Sn2] (the pendant triphenyltin) confirming our previous conclusions based on spectroscopic studies [4].

The tetrahedral tin in the repeat unit [Sn2] has a shorter bond to oxygen [Sn2–O3 = 2.030(3) Å] than the trigonal bipyramidal tin centers [Sn1] [Sn1–O1 = 2.193(3), Sn1–O2 = 2.253(3) Å]; the Sn–O bonds in the O_2SnC_3 moieties are different. The O1–Sn1–O2 angle [173.10(12)°] deviates slightly from linearity. The Se1–O bond distances

[1.678(3) and 1.681(3) Å], which form part of the O_2SnC_3 group in the chain, are almost equivalent and slightly shorter than the Se1–O3 linked to the tetrahedral tin centre [Se1–O3 = 1.724(3) Å]. The values of the O–Se–O angles (average 100°) are consistent with the pyramidal geometry around the Se atoms due to the presence of a non-bonding electron pair.

3.2. Structure of catena-(μ_3 -chromato)-methanol-bis(triphenyl-tin) (2)

The asymmetric unit, indicated by unprimed atoms in Fig. 2, consists of three triphenyltin moieties, one chromato and one methanol molecule; a segment of the $CrO_4SnPh_3SnPh_3HOCH_3$ lattice viewed perpendicular to the (ac) plane is shown in Fig. 3. Key metrical data are given in Table 3. The chromato derivative has a structure similar to $SO_4SnPh_3SnPh_3OH_2$ [5a] and is constituted by polymeric chains formed by two Ph_3Sn moieties [based on $Sn(2,2')$] linked to CrO_4 entities; the CrO_4 group being also bonded to a pendant $Ph_3SnO(H)CH_3$ unit [Sn(1)]; the chromato behaving as a tridentate ligand. Adjacent chains are linked by hydrogen bonds involving the methanol of the pendant $SnPh_3HOCH_3$ and the O(4) atom of the chromato (symmetry operation: $x + 1, y + 1/2, -z + 3/2$), the only oxygen of the ligand not involved in a direct bond to the metal. The O(4)–O(5) distance is 2.72 Å, while the H(5)–O(4) separation is 1.89 Å; the $\angle O(5)–H(5A)–O(4)$ is 155.6°. The sheet structure that is generated (Fig. 3) contains 28 atom rings.

Each $[O_4Cr]$ coordinates three tin atoms with significantly different Sn–O distances [Sn1–O1 = 2.153(2) Å, Sn2–O3 = 2.201(2) Å, Sn2''–O3 = 2.244(2) Å]. The Sn–O distances are not equivalent, the largest difference being

Table 2
Selected interatomic bond distances (Å) and angles (°) for (1)

Sn1–O1	2.193(3)	Sn1–O2	2.252(3)
Sn2–O3	2.030(3)	Sn1–C1	2.130(5)
Sn1–C7	2.137(5)	Sn1–C13	2.155(5)
Sn2–C19	2.139(5)	Sn2–C31	2.114(5)
Sn2–C25	2.134(5)	Se1–O1	1.681(3)
Se1–O2	1.678(3)	Se1–O3	1.724(3)
O1–Se1–O2	101.80(17)	O1–Se1–O3	101.41(17)
O2–Se1–O3	99.36(16)	O1–Sn1–C1	87.07(16)
O1–Sn1–C7	97.28(16)	O1–Sn1–C13	92.04(16)
O1–Sn1–O2	173.10(12)	C1–Sn1–C7	115.02(19)
C1–Sn1–C13	128.88(18)	C7–Sn1–C13	115.77(19)
Se1–O1–Sn1	128.76(18)	Se1–O2–Sn1	121.71(17)
Se1–O3–Sn2	126.10(19)		

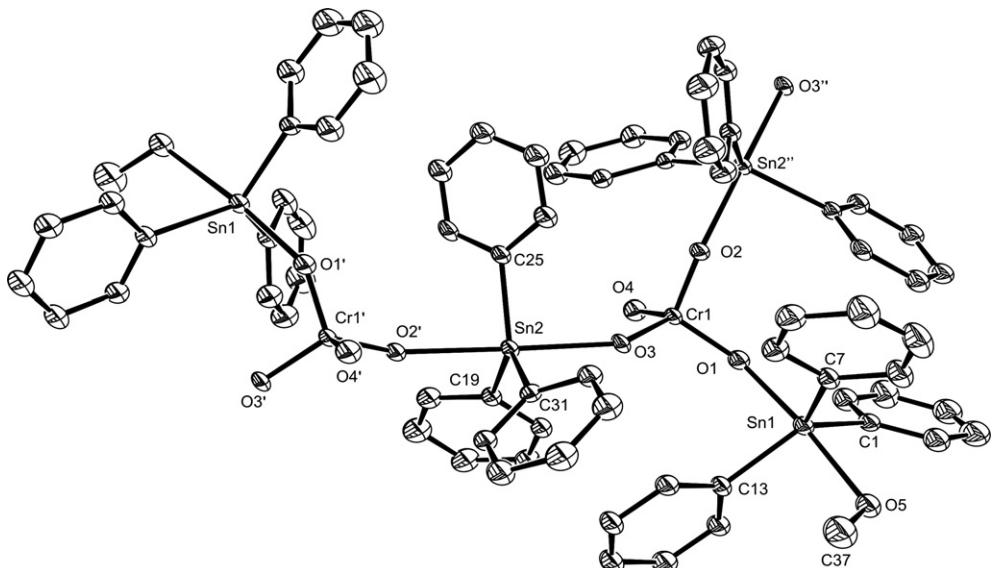


Fig. 2. The asymmetric unit of (2) showing the labelling scheme used in the text and tables. Thermal ellipsoids are at the 30% probability level only the α -carbons of the phenyl rings are numbered for clarity of the figure; C1 thus represents the ring containing C1–C6, etc.

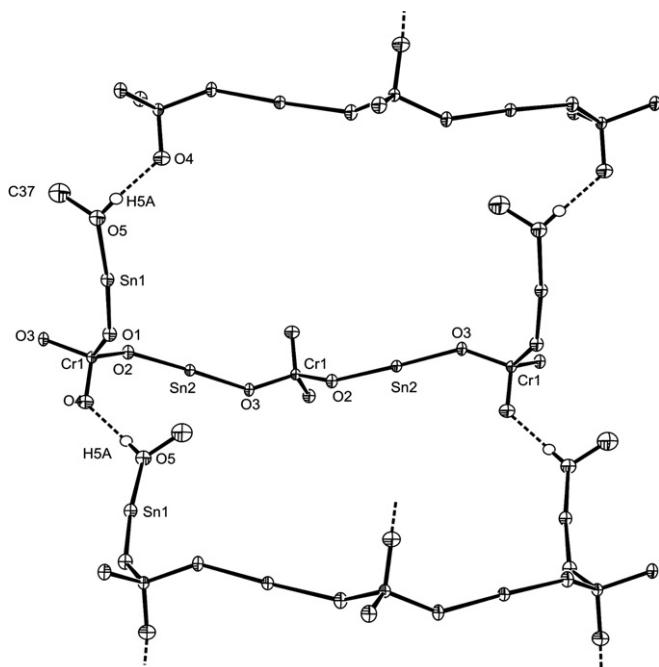


Fig. 3. Polymer propagation in (2) by chromate bridging along a and hydrogen bonds along b. Phenyl groups linked to tin have been omitted for clarity.

observed in the pendant methanol triphenyltin(IV)–O–chromato groups, [Sn1–O1(chromate) = 2.153(2) Å and the corresponding Sn1–O5 (methanol) = 2.361(3) Å]. The Sn1–O(5) bond length in the methanoltriphenoxytin group is in the normal range of those reported for Sn–OH₂ [2.14–2.47] [5d].

These modes of coordination lead to trigonal bipyramidal geometries around both tin centres. The slight distortion from the ideal trigonal bipyramidal geometry is

Table 3
Selected interatomic bond distances (Å) and angles (°) for (2)

Sn1–C1	2.118(4)	Sn1–C7	2.120(4)
Sn1–C13	2.131(4)	Sn1–O1	2.153(2)
Sn1–O5	2.361(3)	Sn2–O2	2.244(2)
Sn2–O3	2.201(2)	Sn2–C25	2.132(4)
Sn2–C19	2.133(4)	Sn2–C31	2.137(3)
Cr1–O1	1.669(2)	Cr1–O2	1.647(2)
Cr1–O3	1.660(2)	Cr1–O4	1.608(3)
O1–Sn1–O5	174.69(10)	O2–Sn2–O3'	176.75(9)
C1–Sn1–C7	119.91(15)	C1–Sn1–C13	119.37(15)
C7–Sn1–C13	119.94(14)	C19–Sn2–C25	119.19(14)
C19–Sn2–C31	121.50(14)	C25–Sn2–C31	119.14(14)
O4–Cr1–O2	109.59(13)	O4–Cr1–O3	109.49(14)
O2–Cr1–O3	108.85(12)	O4–Cr1–O1	109.45(13)
O2–Cr1–O1	109.87(13)	O3–Cr1–O1	109.58(13)

Symmetry operation: 'x + 1/2, -y + 3/2, -z + 1.

surely due to steric hindrance (in the O₂SnC₃ moieties) and/or the non-equivalence of the groups in axial positions.

The O–Sn–O angles deviate only slightly from linearity (O1–Sn1–O5 = 174.69(10)°, O2–Sn2–O3'' = 176.75(9)°). The Cr1–O bond distances (1.660(2), 1.647(2) and 1.669(2) Å), which form part of the O₂SnC₃ group in the chain, are almost equivalent and slightly longer than the Cr1–O₄ (non-tin coordinated oxygen) (1.608(8) Å). The environment around the chromium atom is tetrahedral and the O–Cr–O angles are very close to 109°.

4. Spectroscopic characterization

4.1. Infrared spectroscopy

Infrared spectroscopic studies of (1) have been already published [4]; the splitting of the bands corresponding to

the stretching vibrations (ν_3 and ν_1) into three bands (935, 908 and 841 cm^{-1}) in the IR spectrum of the chromato derivative (**2**) is indicative of C_{3v} symmetry for the chromate. The presence of the medium band at 211 cm^{-1} , due to vsSnC_3 , in the IR spectrum allows to conclude to the presence of non-planar SnC_3 moieties.

4.2. Variable temperature Mössbauer study of $\text{SeO}_3(\text{SnPh}_3)_2$ (**1**)

The temperature dependence of the absorber free-recoil fraction f_a in the Debye model is given by the relationship:

$$\begin{aligned} d[\ln f_a]/dT &= -6E_r/K\theta^2 = -3E_v^2/Kc^2M\theta^2 \\ &= -3KE_v^2/h^2c^2MW_L^2 \end{aligned}$$

The values of the slope $a = -d\ln f_a/dT$ gives interesting information on the lattice dynamics of the molecule. From the relationship between the area of the resonance peaks (A) and the absorber free-recoil fraction (f_a), the following equation is obtained:

$$a = -d[\ln A(\text{tot})]/dT = -d[\ln f_a]/dT = 3E_v^2/MC^2K_B\vartheta_D$$

where E_v is the energy of the Mössbauer transition, M , is the effective vibration mass, K_B is the Boltzmann constant and ϑ_D is the Debye temperature.

Data recorded over the temperature 80–140 K are shown in Fig. 4. From systematic studies dealing with plots of $\ln A$ vs. T [10], there are some overlap of the $-a$ values among the four (rod, zig-zag, stretched and helical) classes, but for phenyl tin compounds in general rigid polymers give rise to $-a$ values of the order 0.011 K^{-1} and for the non-interacting molecules $-a$ values are in the range 0.014 – 0.028 K^{-1} [10c]. The value of $-a$ in the case of the selenito derivative (0.0116 K^{-1}) is consistent with polymer structure and is well correlated to the structure obtained by X-ray.

The value of the Mössbauer quadrupole splitting in the chromato derivative (**2**), 3.26 mm s^{-1} , is consistent with the presence of trigonal bipyramidal SnC_3 framework [11] as evidenced by the X-ray structure of (**2**).

4.3. NMR spectroscopy

Compound **1** in CDCl_3 solution shows a broad ^{119}Sn resonance at -97 ppm , whereas in the solid state two resonances are observed at -69 and -99 ppm . All these chemical shifts appear in the range generally reported for tetra-coordinated triphenyltin compounds [12]. Tetra-coordination is expected in solution and already observed earlier [4], and is explained by cleavage of the polymeric chain, thus destroying the trigonal bipyramidal geometry of one of the tin centres.

In the solid state, the tin resonance at -99 ppm is attributed to the tetra-coordinated tin atom of the pendant triphenyltin selenate. In contrast to what could have been expected, the second tin resonance does not occur in the

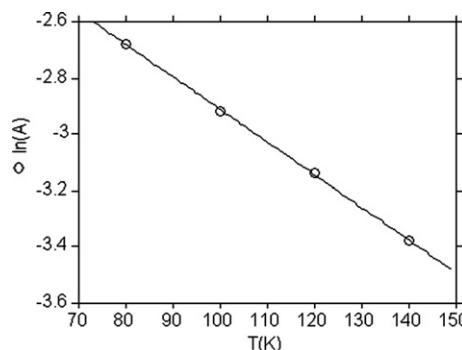


Fig. 4. Variable temperature Mössbauer data for $\text{SeO}_3(\text{SnPh}_3)_2$ (**1**).

region of penta-coordinated triphenyltin compounds (-180 to -280 ppm) [12], but surprisingly and interestingly, at -69 ppm . This indicates that the tin atom experiences a weaker covalent bonding, which is somewhat reflected in a longer bond distance, but it is believed that the main cause for this observation is to be found in some ionic character of the triphenyltin selenite bond, which could be written in an extreme resonance form as $[\text{Ph}_3\text{SnO}-\text{SeO}_2^-][\text{Ph}_3\text{Sn}]^+$. Support for this statement can be found in the tin chemical shifts of triphenyltin carboxylates, showing less negative values when strongly electronegative substituents are present in the carboxylic acid residue ($\text{Ph}_3\text{SnO}-\text{COCF}_3$ at -64 ppm , versus $\text{Ph}_3\text{SnOCOCH}_3$ at -121 ppm) [13]. Compound **2** shows isotropic chemical shifts in the solid state at -205 , -211 and -214 ppm , in accordance with the expected five-coordination as seen from X-ray diffraction studies. The slight differences in chemical shift are due to crystal packing effects. In solution, the tin resonance at -44 ppm reflects four-coordination due to disruption of the polymeric chains in solution. The value observed for the (unresolved) $^1J(^{13}\text{C}-^{117/119}\text{Sn})$ coupling constant (612 Hz) is also typical for a tetrahedral environment [14].

Appendix A. Supplementary material

CCDC 622160 and 622161 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2007.01.038.

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