

TRIMETHYLTIN(IV) NAPHTHOATES: X-RAY STRUCTURE OF THE 2-ISOMER

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Abstract—The isomeric trimethyltin(IV) 1- and 2-naphthoates have been prepared in high yield from trimethyltin chloride and the appropriate sodium naphthoate in THF solution. Spectroscopic data for the compounds point to the presence of monomers, probably with a tetrahedral structure in CDCl_3 solution, but five-coordinate trigonal bipyramidal units in the donor solvent DMSO. An X-ray structure of the 2-isomer shows an infinite zig-zag chain structure in which the carboxylate group bridges asymmetrically between pairs of tin atoms, which have distorted trigonal bipyramidal geometry. Much of the distortion can be traced to a weak residual chelating effect from the carboxylate group.

Carboxylates are versatile ligands toward heavier Main Group metals and can coordinate either as unidentate, chelating or bridging groups. These coordination patterns have been observed in a range of organotin(IV) species, but it has become clear that, in the absence of other donor groups within the carboxylate ligand, polymeric five-coordinate structures with bridging carboxylates are the dominant structural type.¹ There are still some ambiguities in this area as, for example, triphenyltin thiophene-2-carboxylate is monomeric,² while the trimethyl analogue is a one-dimensional polymer with bridging carboxylates.³ Further, more remote changes in constitution can have a significant effect, as found with two triphenyltin chlorobenzoates, where the *p*-isomer is a chelated monomer and the *o*-isomer a chain polymer.⁴

It has been suggested, however, that tetrahedral unidentate structures may be stabilized by employing bulky anions and/or by using anions of very weak acids (high $\text{p}K_a$ values), where the electronegativities of methyl and oxygen are more similar

and prefer to bind to tin using orbitals which allow a more equitable mix of *s* and *p* character.⁵ In the light of these factors, we have prepared trimethyltin derivatives of 1- and 2-naphthoic acids ($\text{p}K_a = 3.7$ and 4.2, respectively) and determined the crystal structure of the latter.

EXPERIMENTAL

The trimethyltin naphthoates were prepared by refluxing equimolar mixtures of trimethyltin chloride and the appropriate sodium naphthoate for 14 h in THF. Precipitated sodium chloride was filtered off and the THF removed *in vacuo* to give the products in ca 95% yield. The compounds were crystallized from 1:1 methanol-THF to give $\text{Me}_3\text{Sn}(1\text{-O}_2\text{CC}_{10}\text{H}_7)$, m.p. 158–162°C. Found: C, 50.4; H, 4.9; Sn, 35.0. Calc. for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{Sn}$: C, 50.2; H, 4.8; Sn, 35.5%. $\text{Me}_3\text{Sn}(2\text{-O}_2\text{CC}_{10}\text{H}_7)$, m.p. 136–138°C. Found: C, 50.5; H, 5.0; Sn, 34.8. Calc. for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{Sn}$: C, 50.2, H, 4.8; Sn, 35.5%.

NMR spectra were measured using a Bruker AC-300F spectrometer, with TMS, CDCl_3 , $\text{DMSO-}d_6$ and tetramethyltin as standards, and the results are

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Table 1. NMR parameters in CDCl₃ and DMSO-*d*₆ solutions

Parameter	Me ₃ Sn(1-O ₂ CC ₁₀ H ₇)		Me ₃ Sn(2-O ₂ CC ₁₀ H ₇)	
	CDCl ₃	DMSO- <i>d</i> ₆	CDCl ₃	DMSO- <i>d</i> ₆
¹¹⁹ Sn data				
δ (ppm)	138.0	-10.9	138.7	-6.6
¹ H data				
δ(Me) (ppm)	0.65 (s)	0.63 (s)	0.63 (s)	0.63 (s)
δ(ligand) (ppm)	7.20–8.60 (m)	7.20–8.60 (m)	7.20–8.60 (m)	7.20–8.60 (m)
² J(¹¹⁹ Sn– ¹ H) (Hz)	56.9	71.0	56.8	69.0
Me–Sn–Me angle estimated (°)	110.4	120.8	110.4	118.9
¹³ C data				
δ(Me) (ppm)	0.54	0.54	0.54	0.54
δ(ligand) (ppm)	162.4, 133.9 132.9, 130.9 128.7, 128.5 127.4, 125.9 124.6		170.4, 134.5 132.4, 131.9 130.0, 129.9 127.6, 127.5 127.4, 126.4 126.3	
¹ J(¹¹⁹ Sn– ¹³ C) (Hz)	385.7	526.0	389.3	525.6
Me–Sn–Me angle estimated (°)	110.6	122.8	110.9	122.8

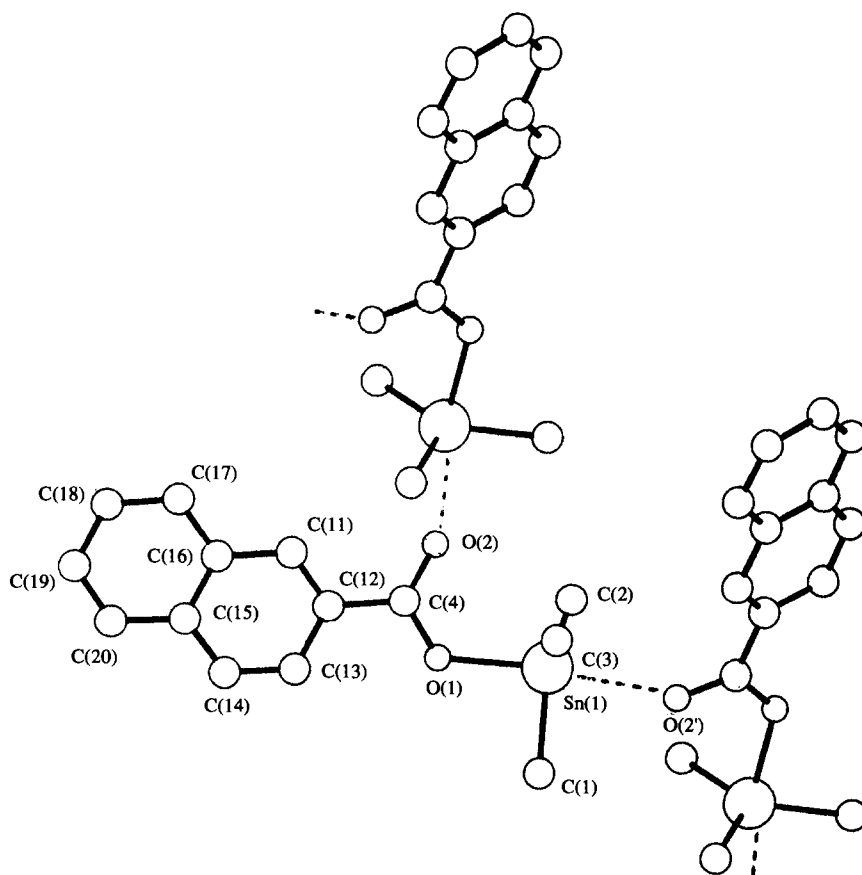


Fig. 1. Structure of trimethyltin(IV) 2-naphthoate, showing the atom numbering scheme.

summarized in Table 1. IR spectra were recorded using a Perkin-Elmer 1430 spectrometer and Raman spectra using a Ramanlab spectrometer and a Spectra Physics argon ion laser. Molecular weights were determined by cryoscopy in benzene solution.

X-ray crystallography

Crystals of the 2-naphthoate suitable for X-ray investigation were obtained by slow recrystallization from methanol-THF. Crystal data: $C_{14}H_{16}O_2Sn$, $M = 334.7$, orthorhombic, $P2_12_12_1$, $a = 6.436(2)$, $b = 10.001(3)$, $c = 21.619(7)$ Å, $V = 1391.5$ Å³, $Z = 4$, $D_c = 1.60$ g cm⁻³, $F(000) = 664$, $\mu = 18.3$ cm⁻¹, $T = 294$ K, crystal size $0.4 \times 0.25 \times 0.1$ mm, $\lambda(Mo-K\alpha) = 0.71069$ Å.

The lattice parameters were refined using 12 reflections in the range $22^\circ < 2\theta < 28^\circ$. Data were collected on a Hilger and Watts Y290 diffractometer with graphite monochromated Mo- $K\alpha$ radiation for 1466 reflections in the range $0^\circ < 2\theta < 50^\circ$ ($0 < h < 7$, $0 < k < 11$, $0 < l < 25$). 1190 unique reflections with $I > 3\sigma(I)$, corrected for Lorentz and polarization effects but not for absorption, were used in the structure solution and refinement. Crystallographic calculations used the CRYSTALS programs⁶ and scattering factors for neutral atoms.⁷ The position of the tin atom was obtained from a three-dimensional Patterson synthesis and subsequent cycles of full matrix least squares refinement and difference Fourier syntheses revealed the other non-hydrogen atoms. After refinement with anisotropic thermal parameters and application of a three-coefficient Chebyshev weighting scheme, a difference Fourier synthesis showed positions for the hydrogen atoms. These were included in the final cycles of refinement with isotropic thermal parameters and the refinement converged at $R = 3.81\%$ ($R_w = 6.70\%$) for 218 least squares parameters. The maximum shift: e.s.d. in the final cycle was 0.03 and the maximum and minimum residual electron densities were 0.66 and -0.25 e Å⁻³, with all large peaks in the vicinity of the tin atom. The absolute structure was confirmed as the inverted form had a significantly higher R value (4.02%).

DISCUSSION

The two compounds can be prepared in high yield by metathesis reactions in THF between trimethyltin chloride and the sodium salt of the appropriate naphthoic acid. The products are white, non-hygroscopic crystalline solids, which dissolve readily in a range of common organic solvents. Molar con-

Table 2. Important bond lengths (Å) and angles (°) for $Me_3Sn(2-O_2CC_{10}H_7)$, with e.s.d.s in parentheses

Sn(1)—C(1)	2.10(2)
Sn(1)—C(2)	2.12(2)
Sn(1)—C(3)	2.11(2)
Sn(1)—O(1)	2.14(1)
Sn(1)—O(2)	3.25(1)
Sn(1)—O(2')	2.57(1)
O(1)—C(4)	1.29(2)
O(2)—C(4)	1.26(2)
C(4)—C(12)	1.47(2)
C(11)—C(12)	1.34(2)
C(11)—C(16)	1.45(2)
C(12)—C(13)	1.42(2)
C(13)—C(14)	1.36(3)
C(14)—C(15)	1.36(2)
C(15)—C(16)	1.42(3)
C(15)—C(20)	1.42(2)
C(16)—C(17)	1.41(3)
C(17)—C(18)	1.37(3)
C(18)—C(19)	1.38(4)
C(19)—C(20)	1.37(4)
C(1)—Sn(1)—C(2)	118.2(9)
C(1)—Sn(1)—C(3)	116.5(9)
C(1)—Sn(1)—O(1)	90.5(6)
C(1)—Sn(1)—O(2)	132.1(6)
C(1)—Sn(1)—O(2')	80.7(6)
C(2)—Sn(1)—C(3)	123.3(10)
C(2)—Sn(1)—O(1)	98.7(7)
C(2)—Sn(1)—O(2)	71.1(6)
C(2)—Sn(1)—O(2')	83.0(6)
C(3)—Sn(1)—O(1)	94.7(7)
C(3)—Sn(1)—O(2)	83.5(6)
C(3)—Sn(1)—O(2')	92.0(6)
O(1)—Sn(1)—O(2)	42.7(5)
O(1)—Sn(1)—O(2')	170.6(5)
O(2)—Sn(1)—O(2')	145.1(5)
Sn(1)—O(1)—C(4)	125(1)
O(1)—O(4)—O(2)	121(1)
O(1)—C(4)—C(12)	116(1)
O(2)—C(4)—C(12)	122(1)
C(12)—C(11)—C(16)	122(1)
C(4)—C(12)—C(11)	120(1)
C(4)—C(12)—C(13)	120(1)
C(11)—C(12)—C(13)	120(2)
C(12)—C(13)—C(14)	119(2)
C(13)—C(14)—C(15)	123(2)
C(14)—C(15)—C(16)	119(2)
C(14)—C(15)—C(20)	124(2)
C(16)—C(15)—C(20)	116(2)
C(11)—C(16)—C(15)	117(2)
C(11)—C(16)—C(17)	121(2)
C(15)—C(16)—C(17)	122(2)
C(16)—C(17)—C(18)	120(3)
C(17)—C(18)—C(19)	119(3)
C(18)—C(19)—C(20)	123(2)
C(15)—C(20)—C(19)	120(2)

Atoms carrying a prime are related to unprimed atoms by the symmetry operation $1-x, y-0.5, 0.5-z$.

ductivities in nitrobenzene solution are less than $1 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, clearly indicating that they remain unionized, and cryoscopy in benzene points to monomers in solution [molecular weights of 328 and 330 (calc. 335) for the 1- and 2-isomers, respectively].

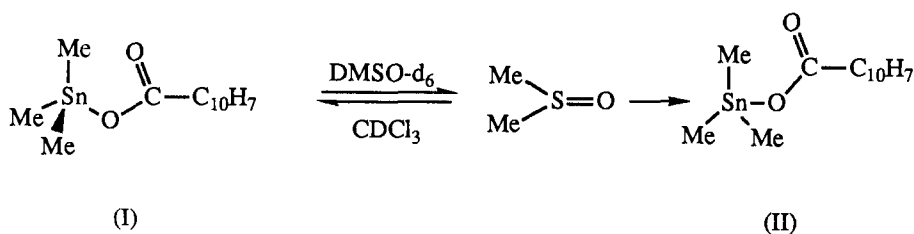
The observation of bands at 1620 and 1580 cm^{-1} [$\nu(\text{C}=\text{O})$], 1550 cm^{-1} [$\nu_a(\text{COO})$] and 540 cm^{-1} [$\nu_a(\text{SnC}_3)$] in their IR spectra and a single peak at 521 cm^{-1} , assigned to $\nu_s(\text{SnC}_3)$, in their Raman spectra are consistent with the presence of a planar Me_3Sn moiety and an unsymmetrical carboxylate in these solids. However, in carbon tetrachloride solution, the IR spectra show bands at both 540 and 510 cm^{-1} , which are assigned, respectively, to the antisymmetric and symmetric SnC_3 stretches. This rules out the presence of the planar SnC_3 unit and suggests the possibility of the quasi-tetrahedral structure (I).

^{119}Sn NMR spectra show singlets at 138.0 and 139.0 ppm, respectively, for the 1- and 2-isomers in CDCl_3 solution, which shift to higher field (-10.9 and -6.6 ppm, respectively) in $\text{DMSO}-d_6$. Similarly, these compounds show substantial differences in both $^1J(^{119}\text{Sn}-^{13}\text{C})$ and $^2J(^{119}\text{Sn}-^1\text{H})$ in non-coordinating (CDCl_3) and coordinating ($\text{DMSO}-d_6$) solvents, implying substantial structural changes with change of solvent. It is most likely, therefore, that in the presence of DMSO, a strong Lewis base, the tetrahedral monomers in CDCl_3 are solvated to give five-coordinate trigonal bipyramidal adducts. The $\text{Me}-\text{Sn}-\text{Me}$ angles estimated from the coupling constants (see Table 1) are qualitatively in agreement with this change in geometry about tin from four-coordinate quasi-tetrahedral (I) to five-coordinate trigonal bipyramidal with axial naphthoate and DMSO molecules (II).

bridges between pairs of tin atoms to give an infinite zig-zag chain parallel to the *a*-axis, similar to that in a number of previous structures, and the hope of stabilizing a monomeric, tetrahedral structure with a bulky carboxylate anion derived from a very weak acid is not realized.

Carboxylate bridging is, in fact, substantially more asymmetric than usually observed in these systems, with $\text{Sn}-\text{O}$ distances of 2.14(1) and 2.57(1) Å for $\text{Sn}(1)-\text{O}(1)$ and $\text{Sn}(1)-\text{O}(2')$, respectively. The $\text{C}-\text{O}$ separations are 1.29(2) and 1.26(2) Å, respectively, and the $\text{O}(1)-\text{C}(4)-\text{O}(2)$ angle at 121(1) $^\circ$ is normal. Geometry about the tin atom is, as expected, trigonal bipyramidal, but there is substantial distortion as shown by angles between the equatorial methyl groups of 116.5 $^\circ$, 118.2 $^\circ$ and 123.3 $^\circ$ (mean 119.3 $^\circ$), and a value of 170.6(5) $^\circ$ for the angle between the oxygen atoms in the two axial positions.

There is a residual interaction [$\text{Sn}(1) \cdots \text{O}(2)$ 3.25(1) Å], again as observed in other structures of this type, between tin and the formally double bonded oxygen atom of the carboxylate group, so that as well as bridging, the carboxylate group also shows weak chelating character. The interaction is clearly very weak (*cf* 3.69 Å, the sum of the tin and oxygen van der Waals radii), but is maximized by the low $\text{Sn}(1)-\text{O}(1)-\text{C}(4)-\text{O}(2)$ torsion angle (1.3 $^\circ$). This weak interaction is then probably responsible for, at least, some of the distortion of the trigonal bipyramid about tin, i.e. the increase in the $\text{C}(2)-\text{Sn}(1)-\text{C}(3)$ equatorial angle from the ideal 120 $^\circ$ to 123.3 $^\circ$ and the axial-equatorial $\text{O}(1)-\text{Sn}(1)-\text{C}(2)$ and $\text{O}(1)-\text{Sn}(1)-\text{C}(3)$ angles from the ideal 90 $^\circ$ to 98.7(7) $^\circ$ and 94.7(7) $^\circ$, respectively.



The structure of the 2-isomer in the solid state and, by implication that of the 1-isomer also, follows from the X-ray diffraction study. Table 2 includes a listing of the important bond distances and angles and the structure is illustrated in Fig. 1, which also shows the atom numbering scheme. As shown in Fig. 1, the carboxylate group

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