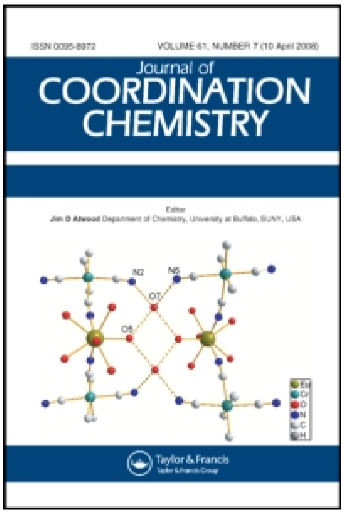

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Siang-Guan Teoh[a]; Soon-Beng Teo[a]; Leong-Kok Lee[a]; Zainudin Arifin[b]; Seik-Weng Ng[c]
[a] School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia [b] Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia [c] Institute of Advanced Studies, University of Malaya, Kuala Lumpur, Malaysia

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TIN-SULPHUR COORDINATION IN A TRIPHENYLTIN(IV) DERIVATIVE OF MONOTHIOBENZOIC ACID. CRYSTAL STRUCTURE OF TRIPHENYL(MONOTHIOBENZOATO)TIN(IV)

SIANG-GUAN TEOH,* SOON-BENG TEO, LEONG-KOK LEE

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

ZAINUDIN ARIFIN[a] and SEIK-WENG NG[b]

*[a]Department of Chemistry; [b]Institute of Advanced Studies, University of Malaya,
59100 Kuala Lumpur, Malaysia*

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Reaction of triphenyltin(IV) chloride with monothiobenzoic acid results in the formation of triphenyl (monothiobenzoato) tin (IV), $C_{25}H_{20}OSSn$, which crystallizes in the orthorhombic system, space group $P2_12_12_1$ (No. 19), with $a = 8.2959(8)$, $b = 16.900(4)$, $c = 31.453(2)$ Å, $V = 4410(1)$ Å^3, $D_c = 1.468$g cm^{-3}, $F(000) = 1952$, $\mu = 12.64$ cm^{-1} for $Z = 8$. Refinement converged to $R = 0.037$ and $R_w = 0.041$ ($w = [\sigma^2(F) + (0.02F)^2 + 1]^{-1}$) based on 3282 unique reflections and 2191 observed reflections such that $I > 3\sigma(I)$. The ligand functions as a monodentate anion coordinating to the tin atom through its sulphur atom and conferring a tetrahedral geometry about the tin atom. The average bond length between tin and sulphur is 2.430(5)Å.

KEYWORDS: triphenyl(monothiobenzoato)tin(IV), triphenyltin(IV) chloride, tetrahedral, X-ray structure

INTRODUCTION

Although the coordinating ability of monothiocarboxylate ligands to transition metals have been extensively studied,[1–6] there have only been a few such studies on corresponding organotin(IV) compounds.[7–10] A recent structural investigation[11] has shown that in dimethyldi(monothiobenzoato)tin(IV), each of the two monothiobenzoato ligands functions as a unidentate anion coordinating to tin through its sulphur atom.

In this paper, we report the synthesis and a full X-ray structure analysis of the title compound.

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* Author for correspondence.

EXPERIMENTAL

Synthesis of triphenyl(monothiobenzoato)tin(IV), $C_{25}H_{20}OSSn$

A reaction mixture consisting of triphenyltin chloride (0.5 mmol) and monothiobenzoic acid (0.5 mmol) in 50 cm^3 of ethanol was continuously stirred for 1 hr at room temperature. The mixture was allowed to stand, whereupon the crystals which were formed were filtered and then recrystallized from ethanol. Yield 70%; m.p. 107–109°C.

Anal. Calcd. for $C_{25}H_{20}OSSn$: C, 61.64; H, 4.13%. Found: C, 61.38; H, 4.10% IR (KBr): ν, 1624 ($S\text{-}C=O_{assym}$); 1430 ($S\text{-}C=O_{symm}$); 925 (C-S); NMR (^1H, $CDCl_3$, 25°C): δ, 7.43–8.10(m,aromatic) ppm. The carbon, hydrogen and nitrogen analyses were carried out on a Control Equipment Corporation 240 XA elemental analyzer at the School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia. The tin analysis was performed using an Instrumental Laboratory aa/ee 357 atomic spectrophotometer. IR data were recorded using a Perkin Elmer FTIR 1650 spectrophotometer in the frequency range 4000–450 cm^{-1} with the samples in KBr discs. ^1H NMR spectra were recorded on a Brüker 300 MHz AC-P NMR spectrometer.

Determination of crystal structure of $C_{25}H_{20}OSSn$

An irregularly-shaped crystal measuring about 0.35 × 0.35 × 0.35 mm^3 was used for diffraction analysis on an Enraf-Nonius CAD4 diffractometer (graphite-monochromatized Mo-$K\alpha$ radiation, 0.71073 Å). The cell constants were calculated from 25 random reflections in the $\theta = 8\text{–}12°$ range, and were refined as an orthorhombic cell type.[12] The 3282 unique reflections were measured at room temperature by using w-2θ scans up to $2\theta_{max} = 50°$ (collection range: $h = 0$ to 8, $k = 0$ to 18, $l = 0$ to 33). Three reflections used to monitor crystal quality after every hour showed a fluctuation of 0.01%. The data were corrected for Lorentz and polarization factors, and also for absorption effects (av.corr. = 0.9947) by using a set of psi scans.[13] The structure was solved by the Patterson method from 2191 $I \geq 3\sigma(I)$ reflections and refined on F by full-matrix, least-squares procedures; anistropic temperature factors were used for non-H atoms; H-atoms were generated geometrically (C-H = 0.95Å, $B = 5Å^2$) and were allowed to ride on their parent C-atoms. Refinement of 508 variables converged to a final R index of 0.037; $Rw = 0.041$ ($w = [\sigma^2(F) + (0.02F)^2 + 1]^{-1}$)[14] and $S = 0.475$. The final difference map was diffuse and had peaks varying from $-0.13(7)$ to $0.34(7)$ $eÅ^{-3}$ Scattering factors and anomalous dispersion coefficients were taken from *International Tables for X-ray Crystallography,* Vol. IV (1974). Computations were carried out with the MolEN package[15] running on a MicroVAX minicomputer. Crystal data and refinement parameters are given in Table 1. Fractional atomic coordinates and their equivalent isotropic displacement parameters are given in Table 2 and bond distances and angles in Table 3. The molecular structure of $C_{25}H_{20}OSSn$ with atom labelling is shown in Figure 1.

Table 1 Crystal data and refinement details for $C_{25}H_{20}OSSn$.

Formula	$C_{25}H_{20}OSSn$
Formula weight	487.19
Crystal system	Othorhombic
Space group	$P2_12_12_1$(No.19)
Cell constants	a = 8.2959(8) Å
	b = 16.900(4) Å
	c = 31.453(2) Å
	V = 4410(1) Å^3
Z	8
F(000)	1952
Dc	1.468 g cm^{-1}
μ	12.64 cm^{-1}
Radiation	M_0K^α (= 0.71073 Å)
Range of h k l	h: 0→8; k: 0→18; l: 0→33
No. of unique reflections	3282
No. of observed reflections	2191, $I > 3\sigma(I)$
R	0.037
R_w	0.041, $w = [\sigma^2(F) + (0.02F)^2 +]^{-1}$

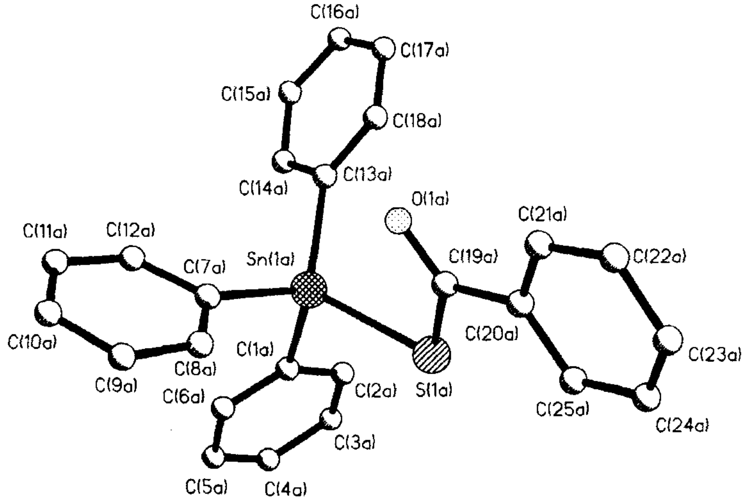

Figure 1 The molecular structure of $C_{25}H_{20}OSSn$.

RESULTS AND DISCUSSION

The assymetric unit of the title compound consists of two crystallographically independent molecules; the structure of one such molecule is shown in Figure 1. The tin atom in triphenyl(monothiobenzoato)tin(IV) possesses a slightly distorted tetrahedral geometry; tetrahedral angles subtended at the tin atom by the three phenyl groups and the sulphur atom of the monothiobenzoate ligand range from 99.3(5) to 116.8(6)°. The monothiobenzoate ligand functions as a unidentate anion

Table 2 Atomic coordinates and equivalent isotropic displacement coefficients (Å^2 × 10^3).

Atom	*x/a*	*y/b*	*z/c*	*B*(Å^2)	Atom	*x/a*	*y/b*	*z/c*	*B*(Å^2)
Sn1a	0.0516(1)	0.11111(6)	0.11458(3)	4.77(2)	Sn1b	0.4636(1)	0.13443(5)	0.37267(3)	4.29(2)
S1a	-0.0933(5)	0.1587(3)	0.1767(1)	6.7(1)	S1b	0.6053(5)	0.0854(3)	0.3105(1)	6.2(1)
O1a	-0.229(1)	0.2163(6)	0.1088(3)	6.1(3)	O1b	0.728(1)	0.0246(6)	0.3786(3)	5.7(2)
C1a	0.230(2)	0.0383(8)	0.1457(4)	4.8(3)	C1b	0.282(2)	0.2056(8)	0.3425(4)	4.0(3)
C2a	0.343(2)	0.0747(9)	0.1730(5)	5.9(4)	C2b	0.182(2)	0.1727(9)	0.3143(5)	5.9(4)
C3a	0.455(2)	-0.0298(9)	0.1935(5)	6.7(4)	C3b	0.065(2)	0.2143(9)	0.2952(5)	6.9(4)
C4a	0.455(2)	-0.0496(8)	0.1873(5)	7.1(4)	C4b	0.046(2)	0.291(1)	0.3033(5)	8.1(4)
C5a	0.350(2)	-0.0851(8)	0.1605(5)	6.9(4)	C5b	0.146(2)	0.328(1)	0.3302(6)	8.1(5)
C6a	0.232(2)	-0.0379(8)	0.1387(5)	5.6(4)	C6b	0.265(2)	0.2853(8)	0.3507(5)	5.7(4)
C7a	-0.099(2)	0.0379(9)	0.0787(4)	5.1(3)	C7b	0.624(2)	0.2078(7)	0.4090(4)	4.6(3)
C8a	-0.248(2)	0.009(1)	0.0900(5)	7.6(5)	C8b	0.783(2)	0.2212(9)	0.3994(5)	6.0(4)
C9a	-0.338(2)	-0.044(1)	0.0677(6)	9.2(5)	C9b	0.870(2)	0.270(1)	0.4234(7)	9.0(6)
C10a	-0.280(2)	-0.070(1)	0.0305(6)	8.9(5)	C10b	0.810(2)	0.305(1)	0.4590(6)	9.1(5)
C11a	-0.137(2)	-0.0439(9)	0.0157(5)	8.3(5)	C11b	0.658(2)	0.288(1)	0.4694(6)	8.9(6)
C12a	-0.048(2)	0.0085(8)	0.0400(4)	6.5(4)	C12b	0.560(2)	0.2428(8)	0.4444(4)	5.9(4)
C13a	0.178(2)	0.1971(8)	0.781(5)	5.5(4)	C13b	0.334(2)	0.0477(8)	0.4090(4)	4.6(3)
C14a	0.320(2)	0.176(1)	0.0600(5)	9.3(6)	C14b	0.382(2)	-0.0258(8)	0.4200(5)	6.9(4)
C15a	0.409(3)	0.229(1)	0.0347(5)	10.9(5)	C15b	0.287(2)	-0.072(1)	0.4439(6)	9.6(5)
C16a	0.362(3)	0.304(1)	0.0302(6)	11.2(6)	C16b	0.145(2)	-0.050(1)	0.4594(5)	9.5(5)
C17a	0.221(2)	0.326(1)	0.0486(6)	10.5(5)	C17b	0.097(2)	0.025(1)	0.4484(5)	8.0(5)
C18a	0.133(2)	0.272(1)	0.0715(6)	8.4(5)	C18b	0.187(2)	0.0732(8)	0.4239(5)	6.5(4)
C19a	-0.240(2)	0.2097(8)	0.1472(5)	5.3(4)	C19b	0.747(2)	0.0314(8)	0.3410(4)	4.7(3)
C20a	-0.378(2)	0.2461(8)	0.1713(4)	4.9(3)	C20b	0.885(2)	-0.0009(7)	0.3179(4)	3.8(3)
C21a	-0.497(2)	0.2873(7)	0.1501(5)	5.3(4)	C21b	1.000(2)	-0.0432(8)	0.3421(4)	5.8(4)
C22a	-0.625(2)	0.3212(8)	0.1702(6)	6.7(4)	C22b	1.133(2)	-0.0727(9)	0.3222(5)	6.9(4)
C23a	-0.638(2)	0.310(1)	0.2127(6)	7.9(5)	C23b	1.160(2)	-0.0618(9)	0.2801(6)	7.2(5)
C24a	-0.519(2)	0.2712(9)	0.2348(5)	6.9(4)	C24b	1.051 (2)	-0.0214(9)	0.2565(5)	6.5(4)
C25a	-0.390(2)	0.2373(7)	0.2151(4)	4.7(3)	C25b	0.913(2)	0.0078(8)	0.2748(4)	4.8(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)*[a^2 *B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos \text{gamma})*B(1,2) + ac(\cos \text{beta})*B(1,3) + bc(\cos \text{alpha})*B(2,3)]$.

coordinating to tin through sulphur, whereas the carbonyl oxygen atom, O1, is uncoordinated and is situated at an average distance of 2.90(1) Å form the tin atom. The average Sn-S distance (2.430(2) Å) is comparable to those observed for diorgano- and triorganotin compounds with sulphur-containing ligands.[11,16–20]

It is found that $\nu_{S\text{-}H}$ in the IR spectrum of the free monothiobenzoic acid disappears upon complexation with Ph_3SnCl while the S-H signal at $\delta = 4.50$ ppm in the ^{1}H NMR spectrum of the ligand is absent in the spectrum of the complex. Such observations are in accord with deprotonation of the thiol proton and the coordination of sulphur to tin.

Evidence for unidentate coordination had been obtained earlier by Tsipis *et al.*[7] by comparing the IR band separation, $\nu_{\text{assym}}(\text{S-C = O})\text{-}\nu_{\text{symm}}(\text{S-C = 0})$ with those of the ionized and free acid. However, our present crystal structure study establishes unidentate sulphur atom coordination to the tin atom.

Supplementary Material

Tables of hydrogen coordinates and their corresponding atomic displacement parameters, anisotropic atomic displacements for the non-hydrogen atoms and structural factors are available from the authors.

Table 3 Bond distances (Å) and angles (°) with e.s.d.'s in parentheses for non-hydrogen atoms.

Sn1a-S1a 2.432(5)	S1a-Sn1a-C1a 99.3(5)	Sn1b-S1b 2.428(5)	S1b-Sn1b-C1b 100.1(4)
Sn1a-C1a 2.16(2)	S1a-Sn1a-C7a 109.5(6)	Sn1b-C1b 2.15(2)	S1b-Sn1b-C7b 109.0(5)
Sn1a-C7a 2.09(2)	S1a-Sn1a-C13a 116.8(6)	Sn1b-C7b 2.15(2)	S1b-Sn1b-C13b 116.0(6)
Sn1a-C13a 2.13(2)	C1a-Sn1a-C7a 108.4(7)	Sn1b-C13b 2.15(2)	C1b-Sn1b-C7b 110.3(7)
S1a-C19a 1.76(2)	C1a-Sn1a-C13a 107.4(8)	S1b-C19b 1.77(2)	C1b-Sn1b-C13b 105.4(7)
O1a-C19a 1.22(2)	C7a-Sn1a-C13a 114.1(7)	O1b-C19b 1.20(2)	C7b-Sn1b-C13b 114.9(6)
C1a-C2a 1.41(2)	Sn1a-S1a-C19a 94.6(7)	C1b-C2b 1.34(2)	Sn1b-S1b-C19b 93.6(6)
C1a-C6a 1.31(2)	Sn1a-C1a-C2a 119(1)	C1b-C6b 1.38(2)	Sn1b-C1b-C2b 120(1)
C2a-C3a 1.36(2)	Sn1a-C1a-C6a 120(1)	C2b-C3b 1.34(3)	Sn1b-C1b-C6b 122(2)
C3a-C4a 1.35(2)	C2a-C1a-C6a 121(2)	C3b-C4b 1.33(3)	C2b-C1b-C6b 118(2)
C4a-C5a 1.35(3)	C1a-C2a-C3a 120(2)	C4b-C5b 1.35(3)	C1b-C2b-C3b 122(2)
C5a-C6a 1.44(3)	C2a-C3a-C4a 119(2)	C5b-C6b 1.38(3)	C2b-C3b-C4b 121(2)
C7a-C8a 1.37(3)	C3a-C4a-C5a 122(2)	C7b-C8b 1.37(2)	C3b-C4b-C5b 120(2)
C7a-C12a 1.38(2)	C4a-C5a-C6a 119(2)	C7b-C12b 1.37(2)	C4b-C5b-C6b 119(2)
C8a-C9a 1.36(3)	C1a-C6a-C5a 118(2)	C8b-C9b 1.33(3)	C1b-C6b-C5b 120(2)
C9a-C10a 1.34(3)	Sn1a-C7a-C8a 128(2)	C9b-C10b 1.36(3)	Sn1b-C7b-C8b 125(2)
C10a-C11a 1.34(3)	Sn1a-C7a-C12a 120(1)	C10b-C11b 1.34(4)	Sn1a-C7b-C12b 116(1)
C11a-C12a 1.39(3)	C8a-C7a-C12a 112(2)	C11b-C12b 1.37(3)	C8b-C7b-C12b 119(2)
C13a-C14a 1.36(3)	C7a-C8a-C9a 127(2)	C13b-C14b 1.35(2)	C7b-C8b-C9b 120(2)
C13a-C18a 1.34(3)	C8a-C9a-C10a 118(3)	C13b-C18b 1.38(3)	C8b-C9b-C10b 123(3)
C14a-C15a 1.40(3)	C9a-C10a-C11a 121(3)	C14b-C15b 1.34(3)	C9b-C10b-C11b 117(3)
C15a-C16a 1.35(4)	C10a-C11a-C12a 119(2)	C15b-C16b 1.32(4)	C10b-C11b-C12b 123(3)
C16a-C17a 1.36(4)	C7a-C12a-C11a 123(2)	C16b-C17b 1.38(3)	C7b-C12b-C11b 119(2)
C17a-C18a 1.37(3)	Sn1a-C13a-C14a 119(2)	C17b-C18b 1.34(3)	Sn1b-C13b-C14b 128(2)
C19a-C20a 1.50(2)	Sn1a-C13a-C18a 127(2)	C19b-C20b 1.46(2)	Sn1b-C13b-C18b 114(2)
C20a-C21a 1.38(2)	C14a-C13a-C18a 115(2)	C20b-C21b 1.41(2)	C14b-C13b-C18b 118(2)
C20a-C25a 1.39(2)	C13a-C14a-C15a 122(3)	C20b-C25b 1.38(2)	C13b-C14b-C15b 120(2)
C21a-C22a 1.36(2)	C14a-C15a-C16a 121(3)	C21b-C22b 1.37(3)	C14b-C15b-C16b 125(3)
C22a-C23a 1.35(3)	C15a-C16a-C17a 117(3)	C22b-C23b 1.35(3)	C15b-C16b-C17b 115(2)
C23a-C24a 1.37(3)	C16a-C17a-C18a 120(3)	C23b-C24b 1.36(3)	C16b-C17b-C18b 123(2)
C24a-C25a 1.37(2)	C13a-C18a-C17a 124(3)	C24b-C25b 1.37(3)	C13b-C18b-C17b 120(2)
Sn1a..O1a 2.93(1)	S1a-C19a-O1a 121(2)	Sn1b..O1b 2.88(1)	S1b-C19b-O1b 120(1)
	S1a-C19a-C20a 117(2)		S1b-C19b-C20b 116(2)
	O1a-C19a-C20a 121(2)		O1b-C19b-C20b 124(2)
	C19a-C20a-C21a 120(2)		C19b-C20b-C21b 117(1)
	C19a-C20a-C25a 121(2)		C19b-C20b-C25b 125(2)
	C21a-C20a-C25a 119(2)		C21b-C20b-C25b 118(2)
	C20a-C21a-C22a 123(2)		C20b-C21b-C22b 119(2)
	C21a-C22a-C23a 117(2)		C21b-C22b-C23b 122(2)
	C22a-C23a-C24a 121(2)		C22b-C23b-C24b 120(2)
	C23a-C24a-C25a 122(2)		C23b-C24b-C25b 120(2)
	C20a-C25a-C24a 118(2)		C20b-C25b-C24b 121(2)

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