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CRYSTAL AND MOLECULAR STRUCTURE OF THE TRIPHENYLPHOSPHINE OXIDE ADDUCT OF TRI-3-THIENYLTIN BROMIDE, $Ph_3PO \cdot SnBr(C_4H_3S)_3$

DAVID W. ALLEN, D. JANE DERBYSHIRE, IAN W. NOWELL,

Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB (Great Britain)

and JOHN S. BROOKS

Department of Applied Physics, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB (Great Britain)

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Summary

The solid state structure of the triphenylphosphine oxide (TPPO) adduct of tri-3-thienyltin bromide has been investigated by both single crystal X-ray analysis and Mössbauer spectroscopy. The crystal structure consists of discrete molecules and there is no evidence of any intermolecular tin–sulphur interactions. Each tin atom is found to be in a five-coordinate trigonal bipyramidal environment in which the three thienyl groups occupy equatorial positions. The metal atom is displaced by 0.182 Å out of the equatorial plane and towards the axial bromine. Two of the thienyl ligands exhibit rotational disorder and the lack of disorder in the remaining heteroaryl ligand is attributed to the close proximity of this group to a phenyl ligand. The Mössbauer parameters are also in accord with five-coordination for tin and are indicative of the aryl groups being equatorial.

Introduction

As part of our study of heteroaryltin(IV) compounds, we have investigated the solid state structure of a number of triorganotin halides. In order to substantiate Mössbauer data [1] an X-ray analysis of tri-3-thienyltin bromide was attempted. A preliminary study shows the molecule to be extensively disordered, with rotational disorder about the Sn–Br bond and also about each of the three Sn–C (thienyl) bonds. While it has not proven possible to gain detailed structural data, it has been established that the tin atom occupies a tetrahedral environment and that no intermolecular tin–sulphur interactions are present; a result in accord with the Mössbauer data. More recently we have prepared the triphenylphosphine oxide (TPPO) adduct of tri-3-thienyltin bromide and herein we present the X-ray analysis of this compound.

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Experimental

Tri-3-thienyltin bromide and its TPPO adduct were prepared as previously described [1].

Mössbauer data. ^{119}Sn Mössbauer spectra were obtained using a constant acceleration spectrometer. A 15mCi Ba^{119}SnO$_3$ source was used at room temperature, the samples were sealed in perspex discs and cooled to 80 K using a continuous flow nitrogen cryostat with helium exchange gas. The Mössbauer isomer shift and quadrupole splitting parameters were obtained from computer least squares fits to the spectra using Lorentzian line shapes.

^{119}SnNMR. ^{119}Sn NMR spectra were recorded on a Jeol FX60Q instrument in 10 mm tubes at 22.24 MHz. The field frequency lock was to external D$_2$O.

Crystal data. $C_{30}H_{24}BrOPS_3Sn$, $M_r = 726.7$, triclinic, $P\bar{1}$, a 14.700(10), b 11.002(8), c 9.805(7) Å, α 104.05(6), β 95.04(5), γ 101.71(5)°, U 1490.5 Å^3, $Z = 2$, D_c 1.62 Mg m^{-3}, D_m 1.58 Mg m^{-3}, μ(Mo-K_α) 2.36 mm^{-1}, $F(000) = 720$.

Data collection and reduction

Intensities were measured for a crystal, approximate dimensions 0.10 × 0.18 × 0.38 mm, mounted on a glass fibre with the c-axis coincident with the ω-axis of a Stöe Stadi-2 two circle diffractometer. Monochromatic Mo-K_α radiation was used and the background-ω scan-background technique employed to give 4989 independent reflections, of which 4375 had $I \geqslant 3\sigma(I)$ and were used for subsequent analysis. Corrections were made for Lorentz and polarisation effects, but no correction was applied for absorption.

Structure determination and refinement

Preliminary photographs showed the crystal to be triclinic and subsequent analysis confirmed the space group to be $P\bar{1}$. The approximate positions of the tin and bromine atoms were calculated from a three-dimensional Patterson synthesis and the remaining atoms were located from successive difference Fourier maps. While one of the 3-thienyl groups is ordered, the other two contain rotational disorder such that two thienyl groups (having approximately 50% occupancy) are related to each other by a pseudo two-fold axis about the Sn–C(n1) (n = 4,6) bonds. Each of the disordered 3-thienyl entities were given ideal geometries and included in the least squares refinement with common isotropic temperature factors applied to atoms related by the pseudo symmetry. The population parameters applied to each pair of thienyl units were refined, the final values corresponding to occupancies of 55 and 45% for the C(n1), C(n2A), S(n3A), C(n4A), C(n5A) and C(n1), C(n2B), S(n3B), C(n4B), C(n5B) moieties respectively. Hydrogen atoms were located for the three phenyl and ordered 3-thienyl groups, but given ideal geometry (C–H 1.08 Å). Common isotropic temperature factors were applied to the phenyl hydrogens and also to the thienyl hydrogens, which refined to final values of U 0.088(9), 0.081(13) Å^2 respectively. Scattering factors were calculated using an analytical approximation [2] and the weighting scheme $w = 0.956/[\sigma^2(F_o) + 0.006(F_o)^2]$. All ordered, non-hydrogen, atoms were given anisotropic temperature factors and refinement converged at $R = 0.055$, $R' = 0.067$. Final position parameters are given in Table 1, bond

TABLE 1

FINAL POSITIONAL PARAMETERS ($\times 10^5$ for Sn and $\times 10^4$ for other atoms) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES [a]

Atom	*x*	*y*	*z*
Sn	27036(3)	44611(4)	20342(4)
Br	3314(1)	2338(1)	1139(1)
P	2349(1)	7775(1)	2983(1)
O	2174(3)	6341(3)	2805(4)
C(11)	2381(4)	8601(5)	4818(6)
C(12)	2425(4)	7924(6)	5828(6)
C(13)	2406(5)	8531(8)	7230(7)
C(14)	2366(5)	9791(8)	7622(8)
C(15)	2327(6)	10454(7)	6650(10)
C(16)	2343(5)	9905(6)	5216(8)
C(21)	3422(4)	8402(5)	2371(6)
C(22)	4122(4)	9421(6)	3242(7)
C(23)	4936(5)	9825(7)	2716(8)
C(24)	5075(5)	9242(8)	1351(8)
C(25)	4379(5)	8257(7)	506(7)
C(26)	3551(4)	7834(6)	1018(7)
C(31)	1381(4)	8139(5)	2018(6)
C(32)	1445(5)	8587(7)	825(7)
C(33)	625(7)	8715(9)	51(9)
C(34)	−232(6)	8372(8)	459(9)
C(35)	−277(5)	8012(7)	1692(10)
C(36)	520(4)	7873(7)	2476(8)
C(41)	1640	3608	3070
C(42A)	1060	4292	3766
S(43A)	169	3246	4207
C(44A)	699	1990	3796
C(45A)	1480	2305	3193
C(42B)	1698	2556	3556
S(43B)	615	1927	3955
C(44B)	247	3309	4017
C(45B)	868	4145	3526
C(51)	3997(4)	5578(5)	3262(6)
C(52)	4771(5)	6023(8)	2722(9)
S(53)	5666(2)	6941(2)	3996(4)
C(54)	5059(6)	6778(7)	5251(9)
C(55)	4157(5)	5999(6)	4764(7)
C(61)	2297	4590	−50
C(62A)	2762	4177	−1156
S(63A)	2293	4550	−2633
C(64A)	1396	5047	−1843
C(65A)	1488	5055	−454
C(62B)	1760	5419	−292
S(63B)	1407	5096	−2088
C(64B)	2437	4658	−2366
C(65B)	2769	4234	−1252
H(12)	2447	6920	5508
H(13)	2451	8018	8034
H(14)	2326	10259	8712
H(15)	2322	11463	6985
H(16)	2305	10444	4435
H(22)	4026	9873	4310
H(23)	5471	10628	3374

TABLE 1 (continued)

Atom	x	y	z
H(24)	5732	9540	977
H(25)	4465	7824	−574
H(26)	3008	7044	356
H(32)	2117	8809	463
H(33)	676	9069	−881
H(34)	−851	8468	−146
H(35)	−952	7812	2052
H(36)	465	7534	3418
H(52)	4833	5794	1604
H(54)	5317	7248	6359
H(55)	3656	5736	5444

[a] Two of the three 3-thienyl groups are disordered. The first is comprised of C(41), C(42A), S(43A), C(44A), C(45A) and C(41), C(42B), S(43B), C(44B), C(45B) rings and the second of C(61), C(62A), S(63A), C(64A), C(65A) and C(61), C(62B), S(63B), C(64B), C(65B).

distances and angles in Table 2. The labelling scheme adopted is shown in Fig. 1. Lists of structure factors, thermal parameters and mean planes data are available on request from the authors (IWN).

TABLE 2

BOND DISTANCES (Å) AND BOND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS FOR ORDERED ATOMS IN PARENTHESES

Distances (Å)

Sn–Br	2.651(1)	P–O	1.510(4)
Sn–O	2.335(4)	P–C(11)	1.799(5)
Sn–C(41)	2.121	P–C(21)	1.803(6)
Sn–C(51)	2.122(5)	P–C(31)	1.805(6)
Sn–C(61)	2.125		
C(41)–C(42A)	1.369	C(41)–C(42B)	1.369
C(42A)–S(43A)	1.720	C(42B)–S(43B)	1.720
S(43A)–C(44A)	1.703	S(43B)–C(44B)	1.704
C(44A)–C(45A)	1.359	C(44B)–C(45B)	1.365
C(45A)–C(41)	1.441	C(45B)–C(41)	1.439
C(51)–C(52)	1.349(10)		
C(52)–S(53)	1.694(7)		
S(53)–C(54)	1.606(10)		
C(54)–C(55)	1.396(10)		
C(55)–C(51)	1.416(8)		
C(61)–C(62A)	1.366	C(61)–C(62B)	1.369
C(62A)–S(63A)	1.723	C(62B)–S(63B)	1.719
S(63A)–C(64A)	1.704	S(63B)–C(64B)	1.704
C(64A)–C(65A)	1.355	C(64B)–C(65B)	1.377
C(65A)–C(61)	1.446	C(65B)–C(61)	1.433

TABLE 2 (continued)

	n = 1	*n* = 2	*n* = 3
C(*n*1)–C(*n*2)	1.381(9)	1.399(7)	1.379(10)
C(*n*2)–C(*n*3)	1.381(9)	1.379(10)	1.417(12)
C(*n*3)–C(*n*4)	1.360(12)	1.388(11)	1.362(13)
C(*n*4)–C(*n*5)	1.338(13)	1.369(9)	1.363(14)
C(*n*5)–C(*n*6)	1.393(11)	1.393(10)	1.400(11)
C(*n*6)–C(*n*1)	1.407(9)	1.370(8)	1.379(9)

Angles (°)

Br–Sn–O	179.4(1)	C(51)–Sn–C(61)	121.5(2)
Br–Sn–C(41)	95.1	P–O–Sn	146.9(2)
Br–Sn–C(51)	95.6(2)	O–P–C(11)	110.0(3)
Br–Sn–C(61)	94.0	O–P–C(21)	112.4(2)
O–Sn–C(41)	85.5	O–P–C(31)	109.8(2)
O–Sn–C(51)	84.3(2)	C(11)–P–C(21)	109.7(2)
O–Sn–C(61)	85.5	C(11)–P–C(31)	105.8(3)
C(41)–Sn–C(51)	119.0(2)	C(21)–P–C(31)	108.9(3)
C(41)–Sn–C(61)	117.4		
Sn–C(41)–C(42A)	121.9	Sn–C(41)–C(42B)	122.0
Sn–C(41)–C(45A)	125.0	Sn–C(41)–C(45B)	125.3
C(42A)–C(41)–C(45A)	112.9	C(42B)–C(41)–C(45B)	112.1
C(41)–C(42A)–S(43A)	109.1	C(41)–C(42B)–S(43B)	108.4
C(42A)–S(43A)–C(44A)	93.3	C(42B)–S(43B)–C(44B)	92.8
S(43A)–C(44A)–C(45A)	111.2	S(43B)–C(44B)–C(45B)	111.0
C(41)–C(45A)–C(44A)	111.9	C(41)–C(45B)–C(44B)	111.5
Sn–C(51)–C(52)	124.9(5)		
Sn–C(51)–C(55)	124.6(4)		
C(52)–C(51)–C(55)	110.4(5)		
C(51)–C(52)–S(53)	112.8(6)		
C(52)–S(53)–C(54)	92.5(4)		
S(53)–C(54)–C(55)	113.3(6)		
C(51)–C(55)–C(54)	110.9(6)		
Sn–C(61)–C(62A)	122.2	Sn–C(61)–C(62B)	121.6
Sn–C(61)–C(65A)	124.1	Sn–C(61)–C(65B)	125.7
C(62A)–C(61)–C(65A)	113.7	C(62B)–C(61)–C(65B)	109.3
C(61)–C(62A)–S(63A)	108.9	C(61)–C(62B)–S(63B)	109.3
C(62A)–S(63A)–C(64A)	93.8	C(62B)–S(63B)–C(64B)	88.4
S(63A)–C(64A)–C(65A)	111.2	S(63B)–C(64B)–C(65B)	110.5
C(61)–C(65A)–C(64A)	111.8	C(61)–C(65B)–C(64B)	110.9

	n = 1	*n* = 2	*n* = 3
P–C(*n*1)–C(*n*2)	118.8(4)	122.0(5)	124.1(5)
P–C(*n*1)–C(*n*6)	120.7(5)	118.1(4)	116.6(5)
C(*n*2)–C(*n*1)–C(*n*6)	120.5(5)	119.9(5)	119.2(6)
C(*n*1)–C(*n*2)–C(*n*3)	119.2(6)	118.8(6)	119.9(7)
C(*n*2)–C(*n*3)–C(*n*4)	120.5(8)	121.5(6)	120.5(9)
C(*n*3)–C(*n*4)–C(*n*5)	120.5(7)	119.0(7)	118.9(8)
C(*n*4)–C(*n*5)–C(*n*6)	122.1(7)	120.4(6)	121.7(7)
C(*n*1)–C(*n*6)–C(*n*5)	117.0(7)	120.4(5)	119.5(7)

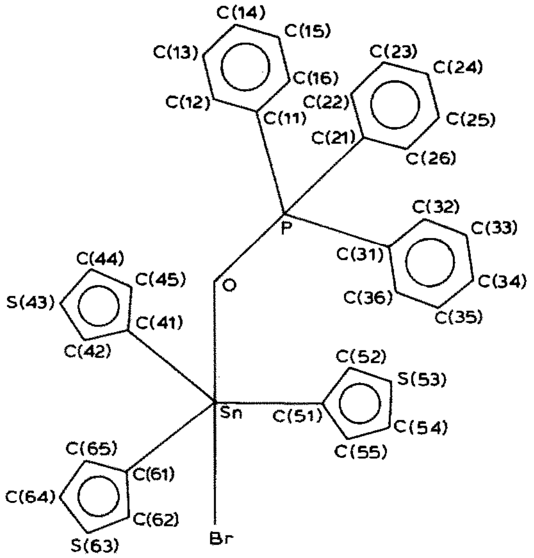

Fig. 1. Labelling scheme adopted for tri-3-thienyltin bromide·triphenylphosphine oxide. Two of the 3-thienyl groups are disordered with a common C(*n*1) (*n* = 4 or 6) atom and the remaining atoms designated A or B.

Discussion

The TPPO adducts of triphenyltin halides have been predicted, on the basis of partial quadrupole splitting calculations [3,4], to have a trigonal bipyramidal structure with equatorial aryl groups. The observation of similar Mössbauer parameters for the related 3-thienyl compounds (Table 3) suggests that they also adopt a similar geometry. ^{119}Sn NMR solution studies [5] are also indicative of an increase in coordination number for tin. The ^{119}Sn NMR signal shifts to a considerably lower frequency for the adduct compared with the unassociated tin species.

TABLE 3

MÖSSBAUER DATA FOR TRI-3-THIENYL, TRIPHENYLTIN HALIDES AND THEIR TRIPHENYLPHOSPHINE OXIDE ADDUCTS

	Isomer shift [a] δ(mm s^{-1} $\pm$0.02)	Quadrupole splitting Δ (mm s^{-1} $\pm$0.02)
Ph_3SnCl	1.37	2.45 Ref. 13
Ph_3SnBr	1.37	2.46
$(3\text{-}C_4H_3S)_3SnCl$	1.21	2.29
$(3\text{-}C_4H_3S)_3SnBr$	1.25	2.08
$Ph_3SnCl \cdot Ph_3P{=}O$	1.28	3.23 Ref. 3
$Ph_3SnBr \cdot Ph_3P{=}O$	1.29	3.20 Ref. 3
$(3\text{-}C_4H_3S)_3SnCl \cdot Ph_3P{=}O$	1.18	3.08
$(3\text{-}C_4H_3S)_3SnBr \cdot Ph_3P{=}O$	1.21	3.30

[a] Relative to $BaSnO_3$.

The present single crystal X-ray study confirms that the TPPO adduct of tri-3-thienyltin bromide does adopt a trigonal bipyramidal arrangement in the solid state, in which bromine and oxygen (TPPO) occupy axial positions, while the aryl groups are equatorial (Fig. 2). Although there is only a slight angular distortion from a regular trigonal bipyramidal arrangement, the bond angles do reveal that the tin atom lies out of the trigonal equatorial plane (0.182 Å), and in a direction towards the bromine atom. Thus the C–Sn–Br angles lie in the range 94.0–95.6°, while the C–Sn–O angles are significantly smaller, ranging from 84.3–85.5°. In general, the structure is reminiscent of an early S_N2-like transition state for substitution at tin.

The disordered 3-thienyl groups show an almost equal preference for the two possible sites with population parameters of 55 and 45%. The apparent ease with which these thienyl units may rotate about the Sn–C bond appears to be a consequence of the lack of any significant inter- and/or intra-molecular interactions involving the heteroaryl group. Rotational disorder of this type has previously been observed for 2-thienyl groups attached to tin [6]. Similar disorder has been found both for 3-thienyl and for 2-thienyl groups attached to phosphorus [7,8]. In contrast, the C(51), C(52), S(53), C(54), C(55) ligand is completely ordered and this may be a direct consequence of the close proximity of one of the phenyl groups (C(21)–C(26)), thereby inhibiting rotation about the Sn–C(51) bond.

The Sn–Br distance (2.651(1) Å) is increased relative to that found in the parent tri-3-thienyltin bromide molecule (2.49 Å), and is significantly longer than the sum of the covalent radii (2.54 Å). This would appear to reflect an increase in the coordination number of tin, from four to five. Similar lengthening of the tin–halogen bond has been observed for trimethyltin chloride on complexation with hexa-

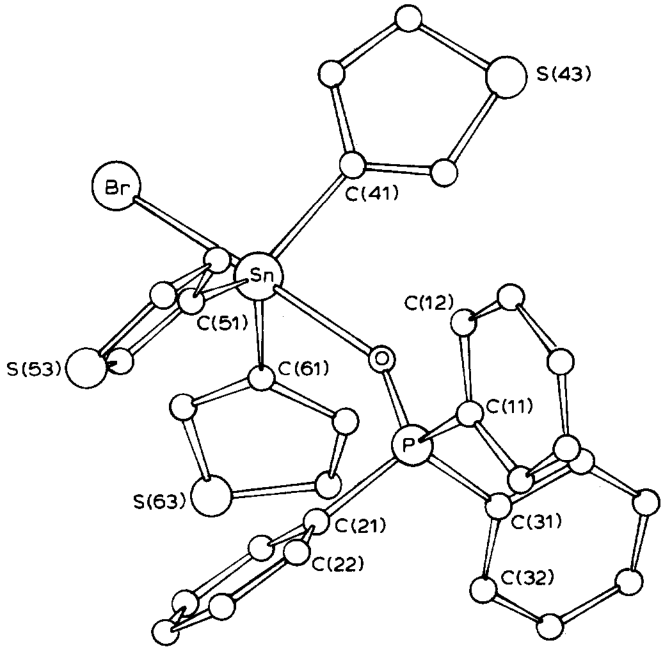

Fig. 2. Molecular structure of $Ph_3PO \cdot SnBr(C_4H_3S)_3$. For clarity, only one conformation of the two disordered 3-thienyl ligands is shown.

methyltriamido phosphate (from 2.36 to 2.52(2) Å [9]). The length of the Sn–O bond (2.335(4) Å), which is considerably greater than the sum of the covalent radii (2.13 Å), is also significantly longer than Sn–O distances reported for many tin complexes, including for example dimethylchlorotin acetate (shortest Sn–O 2.165(6) Å) [10] and μ-bis(diphenylphosphinyl)ethane-bis(nitratotriphenyltin), Sn–O 2.220(5) Å [11]. It would appear that the tin–oxygen interaction in the present TPPO adduct is relatively weak and certainly the P–O distance shows only a slight lengthening upon coordination (from a mean value of 1.475 to 1.510(4) Å). The resulting P–O bond length is considerably shorter than the sum of the covalent radii (1.83 Å) and is indicative of the presence of substantial π-character. The coordination of the TPPO ligand is similar to that found in nitratotriphenyl (triphenylphosphine oxide)tin(IV) [12], where the Sn–O and P–O distances are 2.29(2) and 1.47(2) Å respectively. The Sn–O–P angle in this nitrato complex is 153(1)° and may be compared to that found in the present study (146.9(2)°).

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