Journal of Organometallic Chemistry, 467 (1994) 51–55

Five-coordinate triphenyltin(IV)-sulfur compounds. Crystal structures of the aminoethanethiol and 2-mercaptopyridine-*N*-oxide derivatives

Bruce D. James and Robert J. Magee
Department of Chemistry, La Trobe University, Bundoora, Vic. 3083 (Australia)

Wyona C. Patalinghug [1], Brian W. Skelton and Allan H. White
Department of Chemistry, University of Western Australia, Nedlands, W.A. 6009 (Australia)

(Received June 6, 1993)

Abstract

Single crystal X-ray structure determinations have been carried out on $Ph_3SnS(CH_2)_2NH_2$ (1) and $Ph_3SnSC_5H_4NO$ (2), and have shown that both compounds possess five-coordinate *cis*-chelate structures with Sn–S bonds.

Key words: Tin; Sulfur; Five-coordinate; Crystal structure

1. Introduction

When a triphenyltin(IV) compound contains a fourth group which is potentially chelating, the system is rich with structural possibilities: four-coordinate tetrahedral, monomeric *cis*- and *mer*-five-coordinate and five-coordinate bridged polymers are all feasible [1]. There is particular interest in comparing those systems that have pendant functional groups and those in which similar groups provide internal chelation or intermolecular bonding [2].

Recently, a series of triphenyltin(IV) compounds R_3SnL containing potentially bidentate anionic groups, L, were studied because many of these groups are themselves (like the triphenyltin moiety) biologically active and because the final arrangement about the tin center can affect the toxicity of the compound produced [3]. In this series of compounds, the geometry was deduced by use of well-known generalizations derived from various spectroscopic investigations. Of particular interest among these, are certain complexes of potentially chelating monothioanionic ligands. Triphenyltin species with S-bonding groups tend to display four-coordinate tin environments, whereas higher coordination numbers are achieved with first row donors, and we considered it of interest to examine the coordination geometry of species with a firmly bound sulfur atom but also bearing a first row donor. Among the species studied, two in particular displayed unusual spectroscopic characteristics, which prompted further investigation by single crystal X-ray diffraction methods. The results are presented below.

The aminoethanethiolate compound (L = AET) (1) displayed spectroscopic properties [*e.g.* NMR $\delta(^{119}Sn) = -66.2$ ppm. *vs.* Me_4Sn: Mössbauer $IS = 1.17$ mm s^{-1}, $QS = 1.19$ mm s^{-1}], seemingly consistent with a four-coordinate (Ph_3SnS) tin center in both solution and solid [3]. In contrast, triphenyltin dithiocarbamate compounds, which had been shown to have a similar Ph_3SnS "core" with no interaction of the second sulfur atom of the DTC group with the tin [4], had appreciably different Mössbauer parameters IS = 1.26–1.43 mm

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Correspondence to: Dr. B.D. James.

[1] On leave from Delasalle University, Manila, The Philippines.

0022-328X/94/$7.00
SSDI 0022-328X(93)24018-Z

s^{-1}, $QS = 1.71–1.87$ mm s^{-1} [5]. The interest in compound **1** is therefore centered on the coordination potential of the pendant NH_2 groups.

More intriguing was the thiopyridine-*N*-oxide derivative, (L = PNO) (**2**), which had $\delta(^{119}Sn) = -162.5$ ppm (unaffected by concentration) and $IS = 1.17$ mm s^{-1}, $QS = 1.67$ mm s^{-1}. In comparison with similar data for the known DBM chelate [6], [$\delta(^{119}Sn) = -224.2$ ppm; $IS = 1.07$ mm s^{-1}, $QS = 2.25$ mm s^{-1}] the data for **2** appeared ambiguous. Since a Ph_3SnS core generally does not favour any further interactions at the tin, **2** was regarded as most likely to retain the tetrahedral geometry. In this case, interest centered on the nearness of any approach of the N-oxide oxygen atom to the tin center.

2. Results and discussion

The results of the room temperature single crystal X-ray diffraction studies of **1** and **2** are consistent with the expected stoichiometries and connectivities. Non-hydrogen atom coordinates are given in Tables 1 and 2, and the metal atom geometries in Table 3, and, in comparison with related species, Table 4. The molecular structures are displayed in Fig. 1; in both cases the asymmetric unit of the structure is a single molecule, unsolvated; the crystal packing is uncomplicated, with no unusually short inter-species contacts.

TABLE 1. Non-hydrogen coordinates and isotropic thermal parameters for **1**

Atom	x	y	z	U_{eq} (Å^2)
Sn	0.09500(3)	0.29938(4)	0.92903(4)	0.0399(3)
C(11)	0.0272(5)	0.2466(6)	1.0966(7)	0.047(4)
C(12)	−0.0353(6)	0.1613(7)	1.0907(9)	0.066(5)
C(13)	−0.0783(5)	0.1245(8)	1.201(1)	0.082(7)
C(14)	−0.0572(7)	0.168(1)	1.317(1)	0.086(8)
C(15)	0.0042(6)	0.2544(9)	1.3264(8)	0.076(6)
C(16)	0.0460(5)	0.2905(8)	1.2154(8)	0.060(5)
C(21)	0.1884(4)	0.1600(5)	0.9115(7)	0.044(4)
C(22)	0.1848(5)	0.0588(6)	0.9877(7)	0.052(4)
C(23)	0.2444(7)	−0.0295(6)	0.9732(9)	0.068(6)
C(24)	0.3055(5)	−0.0204(7)	0.881(1)	0.070(6)
C(25)	0.3125(5)	0.0790(8)	0.8074(9)	0.068(6)
C(26)	0.2535(5)	0.1689(6)	0.8214(7)	0.056(5)
C(31)	0.1731(4)	0.4530(5)	0.9481(6)	0.037(4)
C(32)	0.2368(5)	0.4514(6)	1.0368(8)	0.058(5)
C(33)	0.2912(5)	0.5462(7)	1.0495(8)	0.059(5)
C(34)	0.2830(6)	0.6449(7)	0.9749(8)	0.060(5)
C(35)	0.2202(5)	0.6478(6)	0.8851(8)	0.058(5)
C(36)	0.1651(4)	0.5548(6)	0.8729(7)	0.047(4)
S	0.0333(1)	0.2563(2)	0.7206(2)	0.055(1)
C(1)	−0.0443(5)	0.3716(8)	0.6952(8)	0.073(6)
C(2)	−0.0907(5)	0.4062(8)	0.8146(8)	0.069(5)
N(3)	−0.0319(4)	0.4507(5)	0.9124(6)	0.057(4)

TABLE 2. Non-hydrogen positional and isotropic displacement parameters for **2**

Atom	x	y	z	U_{eq} (Å^2)
Sn	0.18459(5)	0.13118(5)	0.17769(6)	0.0375(2)
C(11)	0.2891(8)	0.1701(7)	0.3181(8)	0.039(3)
C(12)	0.2344(8)	0.2252(8)	0.451(1)	0.052(4)
C(13)	0.297(1)	0.247(1)	0.547(1)	0.072(5)
C(14)	0.414(1)	0.214(1)	0.512(1)	0.082(6)
C(15)	0.473(1)	0.157(1)	0.379(1)	0.082(6)
C(16)	0.409(1)	0.1364(9)	0.286(1)	0.056(4)
C(21)	0.0050(7)	0.1940(7)	0.3019(8)	0.040(3)
C(22)	−0.0173(8)	0.3304(8)	0.3298(9)	0.051(4)
C(23)	−0.1332(9)	0.3730(9)	0.402(1)	0.062(4)
C(24)	−0.2299(8)	0.280(1)	0.447(1)	0.060(4)
C(25)	−0.2101(8)	0.1449(9)	0.419(1)	0.055(4)
C(26)	−0.0962(8)	0.1034(8)	0.3470(9)	0.045(3)
C(31)	0.1547(7)	−0.0749(7)	0.1403(8)	0.039(3)
C(32)	0.0992(8)	−0.1688(7)	0.2579(9)	0.048(4)
C(33)	0.0670(8)	−0.2996(8)	0.236(1)	0.056(4)
C(34)	0.0888(9)	−0.3382(8)	0.098(1)	0.059(4)
C(35)	0.1441(9)	−0.2478(9)	−0.021(1)	0.063(4)
C(36)	0.1758(8)	−0.1170(8)	−0.0017(9)	0.054(4)
S	0.2025(2)	0.3128(2)	−0.0236(2)	0.055(1)
C(1)	0.3589(8)	0.3328(8)	−0.0873(8)	0.047(3)
N(2)	0.4257(7)	0.2244(7)	−0.0712(7)	0.046(3)
O	0.3703(5)	0.1056(5)	−0.0118(6)	0.051(2)
C(3)	0.5478(9)	0.235(1)	−0.114(1)	0.059(4)
C(4)	0.609(1)	0.354(1)	−0.179(1)	0.077(5)
C(5)	0.544(1)	0.466(1)	−0.202(1)	0.072(5)
C(6)	0.4210(9)	0.4557(9)	−0.156(1)	0.062(4)

It is clear from Fig. 1 that both the triphenyltin AET and PNO complexes **1** and **2** have five-coordinate *cis* geometry with Sn–S bonds (of lengths 2.426 (2) Å and 2.494 (2) Å respectively). These distances are not in any degree abnormal, and compare with 2.43_4 Å (aver-

TABLE 3. Tin environments: r is the tin-ligand atom distance (Å). Other entries are the angles subtended by the relevant atoms at the head of each row and column (degrees)

Atom		r	C(21)	C(31)	S	N,O
C(11)	**1**	2.132(7)	102.2(3)	116.3(3)	118.0(2)	81.3(2)
	2	2.15(1)	103.3(3)	118.2(3)	115.1(2)	87.2(3)
C(21)	**1**	2.170(1)		101.5(2)	93.2(2)	169.3(2)
	2	2.171(7)		103.4(3)	91.4(2)	163.3(2)
C(31)	**1**	2.142(6)			118.6(2)	85.6(2)
	2	2.127(7)			118.8(2)	82.3(2)
S	**1**	2.426(2)				76.3(1)
	2	2.494(2)				72.2(1)
N	**1**	2.647(6)				
O	**2**	2.364(5)				

In **1**, Sn–S, N–C are 105.1(3)°, 107.9(5)°;
in **2**, Sn–S, O–C,N are 97.7(3)°, 112.5(4)° respectively.
In **1**, ring torsion angles in the Sn–S–1–2–N(3)–Sn bonds (in that order) are −7.9(3)°, 37.7(6)°, −60.1(8)°, 47.9(7)°, −19.8(4)°.
In **2**, Sn, S, O lie 1.21(2), 0.04(1), −0.05(1) Å out of the C_5N pyridine ring plane.

TABLE 4. The tin coordination sphere in five-coordinate triphenyltin derivatives

Angle [a]	AET [b,c,d]	PNO [d]	DBM [e]	SQU [f]	DAT [g]
C(11)–Sn–C(31)	116.3(3)	118.2(3)	99.3(2)	117.6(4)	118.3(2)
C(11)–Sn–C(21)	102.2(3)	103.3(3)	124.0	104.5(4)	106.5(2)
C(21)–Sn–C(31)	101.5(2)	103.4(3)	105.5(2)	100.5(4)	100.1(2)
C(11)–Sn–S	118.0(2)	115.1(2)	120.1(3)	116.9(3)	109.3(1)
C(11)–Sn–N/O	81.3(2)	87.2(3)	85.0(2)	81.8(4)	87.7(2)
C(31)–Sn–S	118.6(2)	118.8(2)	86.0	116.9(3)	121.7(1)
C(31)–Sn–N/O	169.3(2)	163.3(2)	163.7(2)	168.7(3)	163.1(2)
S–Sn–N/O	76.3(1)	72.2(1)	78.1(2)	74.4(2)	69.44(9)

[a] Corresponding atoms in other derivatives have been renumbered according to the scheme given for AET. [b] Angles in degrees. [c] Abbreviations defined in the text. [d] This work. [e] From ref. 6. [f] From ref. 7. [g] From ref. 8.

age) in the quinolinethiolate (SQU) [7], 2.429(1) Å in the dimethylaminothiophenolate (DAT) [8], 2.4582(9) Å in the dithiophosphate (DTP) and 2.481(2)/2.446(2) Å in DTC and monothiocarbamate (MTC) derivatives, previously reported [2,4]. Similarly, the Sn–C distances agree well with those previously reported (range 2.12–2.18 Å) for triphenyltin compounds.

The R_3SnL derivatives with L = AET, PNO, SQU and DAT have geometries around tin which resemble that of the well-known five-coordinate DBM compound [6]. Some parameters are compared in Table 4. There are distortions associated with the shorter Sn–O distances in the DBM compound, and the thio derivatives may reasonably be regarded as a distinct subfamily, but the similarities are obvious, especially the "bite" angles for the chelate and the marked C–Sn–O/N angle reduction from linearity to near 165°.

For the AET derivative, the Sn–N distance [2.647(6) Å] is much shorter than the sum of the van der Waals radii (*ca.* 3.8 Å), as expected, and this again compares with 2.60_1 Å (average) for SQU [7] and is shorter than the 2.89_3 Å observed for DAT [8]. The interaction must then be confirmed as quite strong. Accordingly, the position of the assigned ν(N–H) modes (3380, 3260 cm^{-1} in the solid) near 3400 cm^{-1} is somewhat surprising, since relatively strong NH_2 group interactions with tin exhibit quite large frequency shifts and intensity enhancements in amino acid derivatives [9]. While these infrared features are quite prominent, they are not especially intense, and it is possible that an incorrect assignment was made for the 3380 cm^{-1} peak (*e.g.* it might arise from an overtone or combination band from the very intense absorptions occurring at lower frequencies). In the PNO compound, the Sn–O distance [2,364(5) Å] is only a little longer than the Sn–O(2) distance [2.276(7) Å] in the DBM derivative [6].

It is now clear that it may not be easy to distinguish between tetrahedral and five-coordinate *cis*-triphenyltin compounds by using Mössbauer quadrupolar splitting parameters [10]. A range of 1.6–2.5 mm s^{-1} was suggested for tetrahedral compounds [11], and a value of approximately 1.65 mm s^{-1} was calculated for triphenyltin compounds with the *cis*-five-coordinate structure [6]. In the three β-diketonate derivatives, the quadrupolar splittings were in the wide range 1.38 mm

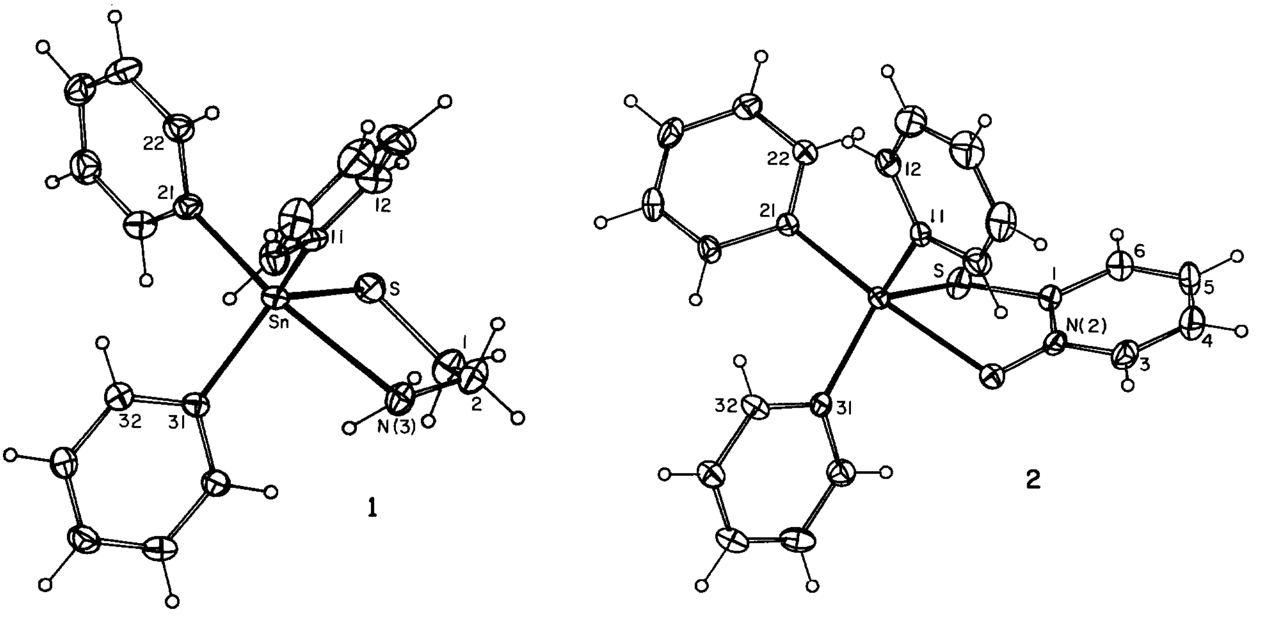

Fig. 1. Molecular projections of 1 and 2. 20% Thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have the arbitrary radii of 0.1 A.

s^{-1} (acetylacetonate) to 2.25 mm s^{-1} (DBM) [10]. The low QS value for the AET derivative opens the way for very low values of this parameter for other five-coordinate triphenyltin–sulfur derivatives. A partial quadrupolar splitting calculation using $\{L\}^{\text{tbe}} = \{\text{thiol}\}^{\text{eq}} = -0.60$ mm s^{-1} [12] and an estimate of $\{L\}^{\text{tba}} = \{\text{amino}\}^{\text{ax}}$ around -0.02 [10] yields $|QS|$ for AET of approximately 0.84. However, a similar result is also calculated for the PNO compound, especially as $\{L\}^{\text{tba}} = \{\text{pyO}\}^{\text{ax}}$ has been estimated to be zero.

The various degrees of distortion from regular trigonal bipyramidal geometry possibly cause marked changes in effective pqs values for the groups so far investigated, and so a very wide QS range is likely for five-coordinate triphenyltin compounds.

For the SQU, DAT, MTC and DTC derivatives the relatively close approach of a second atom into the tin coordination sphere was raised when the structures were reported. Another interesting example is the triphenyltin O-isopropyldithiocarbonato complex which contains a normal Sn–S bond [2.445(1) Å] and an additional Sn–O vector [Sn–O = 2.950(3) Å] [13]. If the oxygen atom is considered to be "bonded" to tin, then a five-coordinate arrangement with two axial phenyl rings is obtained, and the system would be an example of the as-yet-unknown *mer* geometry [1]. The mean angle around the tin atom is 109.4°, however, which is suggestive of a basically tetrahedral arrangement, as argued for the DTC and DTP derivatives. In situations in which abnormal intermolecular interactions are absent, the energetics pertaining to the positioning of the additional atoms in the tin coordination sphere are important, as is the whole continuum of primary bond-secondary bond-no bond interactions and their manifestation in various spectroscopic probes. Further crystallographic studies on triphenyltin-sulfur derivatives appear to be warranted.

3. Experimental details

The two compounds were prepared as described previously [3]. Crystals suitable for study were obtained *via* recrystallization from chloroform.

3.1. Structure determinations

Unique diffractometer data sets were measured at 295 K to $2\theta_{\max} = 50°$ ($2\theta/\theta$ scan mode; monochromatic Mo–Kα radiation source, $\lambda = 0.7106_9$ Å). N independent reflections were obtained, N_0 with $I > 3\sigma\ (I)$ being considered "observed", and used in the full matrix least-squares refinement after Gaussian absorption correction and solution of the structures by vector methods. Anisotropic thermal parameters were used for the non-hydrogen atoms; $(x, y, z, U_{\text{iso}})_{\text{H}}$ were included constrained at estimated values. Residuals on $|F|$ at convergence, R, R' (statistical weights derived from $\sigma^2(I) = \sigma^2(I)_{\text{diff}} + 0.00004\sigma^4(I)_{\text{diff}}$) are quoted. Neutral complex scattering factors were used; for computations the XTAL program system was used, and implemented by Hall [14,15].

3.2. Crystal data

(1) $C_{20}H_{21}NSSn$, $M = 426.2$. Orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), $a = 15.871(9)$ Å, $b = 11.291(4)$ Å, $c = 10.391(4)$ Å, $U = 1862.1$ Å^3. D_c ($Z = 4$) 1.52 g cm^{-3}. $F(000) = 856$. $\mu_{\text{Mo}} = 13.6$ cm^{-1}, specimen: 0.15 × 0.15 × 0.30 mm. $A^*_{\text{min, max}} = 1.18, 1.23$, $N = 1714$, $N_0 = 1593$; $R = 0.029$, $R' = 0.034$ (preferred hand).

(2) $C_{23}H_{19}NOSSn$, $M = 476.2$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 11.689(5)$ Å, $b = 9.827(3)$ Å, $c = 9.622(4)$ Å, $\alpha = 85.97(3)°$, $\beta = 70.93(3)°$, $\gamma = 90.66(3)°$, $U = 1041.4(7)$ Å^3, D_c ($Z = 2$) $= 1.52$ g cm^{-3}, $F(000) = 476$. $\mu_{\text{Mo}} = 12.2$ cm^{-1}; specimen: 0.20 × 0.40 × 0.18 mm, $A^*_{\text{min, max}} = 1.20, 1.28$. $N = 2960$, $N_0 = 2622$; $R = 0.049$, $R' = 0.061$.

Acknowledgment

We thank the Australian Research Council for support of this work.

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