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THE CRYSTAL STRUCTURE OF TRIPHENYLTIN ISOTHIOCYANATE

A.M. DOMINGOS* and G.M. SHELDRICK
University Chemical Laboratory, Lensfield Road, Cambridge (Great Britain)
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Summary

The crystal structure of Ph_3SnNCS has been determined by single crystal X-ray diffraction. The crystals are monoclinic, $P2_1$, $a = 19.02(3)$, $b = 11.67(2)$, $c = 15.49(2)$Å, $\beta = 95.64(10)°$, $Z = 8$. The molecules are arranged in infinite zig-zag $=S\cdots Sn—N=C=S\cdots Sn—$ chains similar to those in Me_3SnNCS, but with slightly longer Sn—N, shorter Sn—S bonds, and almost planar SnC_3 units. Principal mean bond lengths and angles are: Sn—N, 2.22(5); N—C, 1.17(8); C—S, 1.58(7); S—Sn, 2.92(1); Sn—C, 2.09(3); C—C, 1.38(2)Å; Sn—N—C, 161(4); C—S—Sn, 97(3); S—Sn—N, 175(3) and C—Sn—C, 119.8(1.5)°.

Introduction

As part of our study of the molecular structures of silyl [1] and organotin [2 - 5] pseudo-halides we have determined the crystal structure of triphenyltin isothiocyanate. The crystal structure of the trimethyltin analogue can be considered to be intermediate between a structure based on tetrahedrally coordinated tin (NC_3), and one with trigonal bipyramidal coordination (NC_3S), the extra $Sn\cdots S$ interactions giving rise to $=S\cdots Sn—N=C=S\cdots Sn—$ chains bent only at sulphur. A similar structure is found in $Me_2Sn(NCS)_2$, but with coordination intermediate between tetrahedral (N_2C_2) and octahedral ($N_2C_2S_2$) [5,6]. We anticipated that the replacement of methyl groups by phenyl might result in a tetrahedral, essentially molecular, structure for steric reasons; in fact the observed changes are all in the opposite direction, towards trigonal bipyramidal coordination.

Experimental

The compound was prepared by the reaction of Ph_3SnCl with NaNCS in refluxing methanol, and purified by repeated fractional sublimation in vacuo.

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* On leave from Laboratorio de Fisica e Engenharia Nuclearis, Sacavém, Portugal.

Colourless needle-shaped crystals were obtained by slow evaporation of a toluene solution; these were sealed into Lindemann glass capillary tubes. Intensities were determined visually from equi-inclination Weissenberg photographs taken with two crystals (*h0l* to *h10l* and *0kl* to *4kl* respectively) and Ni-filtered Cu-K_α radiation. Lorentz, polarisation and absorption corrections were applied. The two sets of data were scaled together, but the data from the second crystal were found to be of poor quality (almost certainly a result of the large differential absorption for a needle-shaped crystal mounted about an axis perpendicular to the needle axis), and so were not used in the final stages of refinement. Unit-cell dimensions were obtained from a least-squares fit to the positions of 55 reflections on the *h0l* and *0kl* Weissenberg photographs.

Crystal data

$C_{19}H_{15}NSSn$, $M = 407.8$, monoclinic, $a = 19.02(3)$, $b = 11.67(2)$, $c = 15.49(2)$Å, $\beta = 95.64(10)°$, $U = 3421$Å^3, $\mu_a = 133.7$ cm^{-1}, $d_c = 1.58$ for $Z = 8$. Systematic absences: $0k0$, $k \neq 2n$. Space group $P2_1$ or $P2_1/m$; attempts at finding a solution in $P2_1/m$ were unsuccessful, and $P2_1$ was confirmed by refinement of the structure. The asymmetric unit consists of four formula units; all atoms occupy the two-fold general positions of the set (x, y, z; $-x$, $\frac{1}{2} + y$, $-z$).

*Structure solution and refinement**

The structure was solved by multisolution tangent refinement, four tin and two sulphur atoms being identified in the best E-map. The remaining non-hydrogen atoms were located by successive difference Fourier syntheses. The structure was refined by full-matrix least-squares, with a weighting scheme $w = 1/(5.62 + |F_o| + 0.00444\, F_o^2)$. In order to reduce the number of parameters (there are 88 non-hydrogen atoms in the asymmetric unit) the coordinates of the benzene ring atoms were constrained so that [7]:

$$x_i = {}^2/_3(x_1 + x_3 + x_5) - x_{7-i}$$

with analogous expressions for y_i and z_i, where $i = 2$, 4 or 6. This results in planar centrosymmetric rings with coincident centroids for atoms 1, 3, 5 and 2, 4, 6, and reduces the number of independent positional parameters per ring from 18 to 9. Removal of these constraints did not lead to a significant improvement in the R index. In the final cycles of refinement a total of 275 parameters were varied independently, including anisotropic temperature factors for the tin atoms only, 10 inter-layer scale factors, and the Zachariasen secondary extinction coefficient, which refined to the value [8] $10^5 Q_o \cdot r^* = 24(4)$ cm^{-1}. Complex neutral-atom scattering factors [9,10] were employed for all atoms; the alternative absolute configuration to the one given in the Tables was rejected because the ratio of generalised R indices was 1.023. The final value of $R = \Sigma|F_o - F_c|/\Sigma F_o$ was 0.149 for a total of 3638 unique non-zero reflections. A final difference Fourier revealed no pronounced features. Atomic coordinates and anisotropic temperature factors from the final least-

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* Structure factor tables are available from the authors.

squares cycle are given in Tables 1 and 2; the resulting bond lengths and angles are given in Tables 3 and 4. Figure 1 shows the atoms of one asymmetric unit in projection down the *Y* axis.

TABLE 1

FRACTIONAL COORDINATES (X 10^4) AND ISOTROPIC TEMPERATURE FACTORS (Å X 10^3)

	x/a	*y/b*	*z/c*	*U*
Sn(1)	4791(2)	8040	199(2)	
Sn(2)	199(2)	8546(5)	4734(2)	
Sn(3)	262(2)	5196(5)	9846(2)	
Sn(4)	4819(2)	4881(5)	5239(2)	
S(1)	5626(6)	4777(15)	—1406(8)	84(4)
S(2)	—636(6)	5327(14)	6413(8)	86(4)
S(3)	—618(8)	8459(18)	11397(10)	100(5)
S(4)	5618(7)	8136(15)	3575(9)	90(4)
N(1)	5089(24)	6732(54)	—695(29)	105(15)
N(2)	—114(21)	7162(43)	5658(27)	90(12)
N(3)	64(22)	6745(47)	10685(26)	106(13)
N(4)	4968(22)	6251(43)	4361(26)	101(13)
C(1)	5266(27)	5899(61)	—939(33)	98(17)
C(2)	—308(24)	6410(49)	5962(30)	82(14)
C(3)	—273(18)	7445(39)	11028(23)	63(10)
C(4)	5254(20)	7179(43)	4066(26)	71(12)
C(11)	3667(23)	9255(46)	—884(28)	131(20)
C(12)	3318(22)	9889(46)	—1606(30)	125(19)
C(13)	3677(23)	10264(46)	—2250(28)	116(17)
C(14)	4385(23)	10006(46)	—2172(28)	149(22)
C(15)	4735(22)	9372(46)	—1450(30)	123(18)
C(16)	4376(23)	8997(46)	—806(28)	92(13)
C(21)	3622(18)	6406(35)	379(22)	86(12)
C(22)	3174(19)	5630(39)	761(24)	148(22)
C(23)	3219(23)	5527(45)	1650(31)	134(20)
C(24)	3711(18)	6200(35)	2157(22)	126(18)
C(25)	4158(19)	6976(39)	1775(24)	116(17)
C(26)	4114(23)	7079(45)	886(31)	69(10)
C(31)	6082(19)	9022(36)	1292(23)	91(12)
C(32)	6819(26)	9094(47)	1596(28)	141(23)
C(33)	7344(28)	8475(59)	1225(37)	195(35)
C(34)	7132(19)	7786(36)	549(23)	159(25)
C(35)	6395(26)	7714(47)	245(28)	156(25)
C(36)	5870(28)	8333(59)	617(37)	70(10)
C(41)	313(18)	10189(39)	6311(25)	90(13)
C(42)	687(21)	10789(37)	6950(25)	123(19)
C(43)	1429(22)	10804(46)	7043(26)	106(16)
C(44)	1797(18)	10219(39)	6497(25)	142(24)
C(45)	1423(21)	9619(37)	5858(25)	97(15)
C(46)	681(22)	9604(46)	5765(26)	75(12)
C(51)	1346(20)	6816(41)	4513(25)	103(16)
C(52)	1816(17)	6107(35)	4139(22)	121(19)
C(53)	1829(25)	6168(51)	3291(36)	173(29)
C(54)	1373(20)	6936(41)	2818(25)	130(21)
C(55)	903(17)	7645(35)	3193(22)	74(11)
C(56)	890(25)	7584(51)	4040(36)	62(10)
C(61)	—1123(18)	9679(34)	3697(22)	89(14)
C(62)	—1862(21)	9758(37)	3443(24)	113(19)
C(63)	—2361(19)	9034(41)	3834(26)	98(15)
C(64)	—2122(18)	8230(34)	4481(22)	104(16)
C(65)	—1383(21)	8152(37)	4736(24)	109(18)
C(66)	—884(19)	8876(41)	4344(26)	71(10)

(Continued)

TABLE 1 (Continued)

	x/a	y/b	z/c	U
C(71)	521(20)	4272(45)	11633(32)	133(20)
C(72)	845(23)	3626(49)	12341(29)	157(25)
C(73)	1428(25)	2998(50)	12274(34)	127(21)
C(74)	1686(20)	3015(45)	11500(32)	173(30)
C(75)	1362(23)	3661(49)	10793(29)	138(22)
C(76)	779(25)	4290(50)	10859(34)	72(10)
C(81)	1567(26)	6289(48)	9218(29)	144(22)
C(82)	1940(17)	6969(36)	8654(24)	153(23)
C(83)	1615(26)	7555(47)	7979(31)	135(20)
C(84)	917(26)	7461(48)	7867(29)	127(19)
C(85)	544(17)	6781(36)	8430(24)	78(11)
C(86)	869(26)	6195(47)	9105(31)	107(17)
C(91)	−1093(32)	5158(55)	8697(40)	144(22)
C(92)	−1790(53)	4864(90)	8481(52)	166(28)
C(93)	−2232(32)	4638(55)	9059(52)	172(29)
C(94)	−1977(32)	4705(55)	9853(40)	268(52)
C(95)	−1279(53)	4999(90)	10068(52)	347(70)
C(96)	−837(32)	5225(55)	9490(52)	181(31)
C(101)	4616(21)	3329(45)	3645(32)	121(20)
C(102)	4230(22)	2600(42)	2977(26)	161(27)
C(103)	3529(27)	2569(52)	2899(29)	128(22)
C(104)	3215(21)	3267(45)	3489(32)	121(22)
C(105)	3602(22)	3996(42)	4157(26)	110(17)
C(106)	4303(27)	4027(52)	4235(29)	89(14)
C(111)	3688(20)	6669(41)	5405(26)	93(14)
C(112)	3213(20)	7367(42)	5814(27)	127(21)
C(113)	3231(21)	7360(44)	6716(31)	124(19)
C(114)	3725(20)	6654(41)	7210(26)	115(18)
C(115)	4200(20)	5956(42)	6801(27)	111(17)
C(116)	4181(21)	5964(44)	5899(31)	92(14)
C(121)	6115(22)	4074(42)	6298(28)	101(16)
C(122)	6840(26)	3838(28)	6572(27)	122(21)
C(123)	7357(24)	4308(56)	6202(34)	138(23)
C(124)	7148(22)	5014(42)	5559(28)	141(22)
C(125)	6423(26)	5250(48)	5285(27)	126(20)
C(126)	5906(24)	4780(56)	5655(34)	114(19)

Discussion

The structure consists of four crystallographically independent chains along the screw diads, possessing similar molecular dimensions. The carbon atoms of the benzene rings exhibit considerable thermal motion, and there are no short non-bonded distances involving atoms in different chains. The mean Sn—S distance of 2.92 Å is longer than an Sn—S single bond (cf. 2.47 Å in

(continued on p. 263)

TABLE 2

ANISOTROPIC TEMPERATURE FACTORS[a] (Å^2 X 10^3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	91(3)	85(5)	81(3)	−10(2)	8(2)	−7(2)
Sn(2)	78(2)	72(4)	75(2)	6(2)	10(2)	4(2)
Sn(3)	96(3)	81(5)	83(2)	10(2)	10(2)	0(2)
Sn(4)	76(2)	61(4)	80(2)	−11(2)	8(2)	0(2)

[a] The temperature factor exponent takes the form: $-2\pi^2(U_{11}\cdot h^2\cdot a^{*2} + U_{22}\cdot k^2\cdot b^{*2} + U_{33}\cdot l^2\cdot c^{*2} + 2U_{23}\cdot k\cdot l\cdot b^*\cdot c^* + 2U_{13}\cdot h\cdot l\cdot a^*\cdot c^* + 2U_{12}\cdot h\cdot k\cdot a^*\cdot b^*)$.

TABLE 3

BOND LENGTHS (Å)

Sn(1)—N(1)	2.18(6)	C(11) —C(12) and C(14) —C(15)	1.45(6)
Sn(2)—N(2)	2.28(5)	C(12) —C(13) and C(15) —C(16)	1.34(7)
Sn(3)—N(3)	2.27(6)	C(13) —C(14) and C(16) —C(11)	1.38(7)
Sn(4)—N(4)	2.13(5)	C(21) —C(22) and C(24) —C(25)	1.41(6)
Mean Sn—N	2.22(5)	C(22) —C(23) and C(25) —C(26)	1.38(7)
		C(23) —C(24) and C(26) —C(21)	1.40(7)
Sn(1)—S(1)	2.92(2)	C(31) —C(32) and C(34) —C(35)	1.44(6)
Sn(2)—S(2)	2.91(3)	C(32) —C(33) and C(35) —C(36)	1.40(9)
Sn(3)—S(3)	2.92(2)	C(33) —C(34) and C(36) —C(31)	1.35(8)
Sn(4)—S(4)	2.92(2)	C(41) —C(42) and C(44) —C(45)	1.36(6)
Mean Sn—S	2.92(1)	C(42) —C(43) and C(45) —C(46)	1.41(6)
		C(43) —C(44) and C(46) —C(41)	1.34(7)
S(1)—C(1)	1.67(7)	C(51) —C(52) and C(54) —C(55)	1.38(6)
S(2)—C(2)	1.59(6)	C(52) —C(53) and C(55) —C(56)	1.32(7)
S(3)—C(3)	1.49(5)	C(53) —C(54) and C(56) —C(51)	1.41(8)
S(4)—C(4)	1.56(5)	C(61) —C(62) and C(64) —C(65)	1.42(5)
Mean S—C	1.58(7)	C(62) —C(63) and C(65) —C(66)	1.45(6)
		C(63) —C(64) and C(66) —C(61)	1.42(7)
C(1)—N(1)	1.10(8)	C(71) —C(72) and C(74) —C(75)	1.42(6)
C(2)—N(2)	1.08(6)	C(72) —C(73) and C(75) —C(76)	1.34(8)
C(3)—N(3)	1.20(6)	C(73) —C(74) and C(76) —C(71)	1.34(7)
C(4)—N(4)	1.32(7)	C(81) —C(82) and C(84) —C(85)	1.42(7)
Mean C—N	1.17(8)	C(82) —C(83) and C(85) —C(86)	1.35(7)
		C(83) —C(84) and C(86) —C(81)	1.33(7)
Sn(1)—C(16)	2.01(5)	C(91) —C(92) and C(94) —C(95)	1.39(11)
Sn(1)—C(26)	2.08(5)	C(92) —C(93) and C(95) —C(96)	1.31(12)
Sn(1)—C(36)	2.12(6)	C(93) —C(94) and C(96) —C(91)	1.28(9)
Sn(2)—C(46)	2.15(5)	C(101)—C(102) and C(104)—C(105)	1.48(6)
Sn(2)—C(56)	2.11(6)	C(102)—C(103) and C(105)—C(106)	1.33(7)
Sn(2)—C(66)	2.12(4)	C(103)—C(104) and C(106)—C(101)	1.40(8)
Sn(3)—C(76)	2.06(6)	C(111)—C(112) and C(114)—C(115)	1.41(7)
Sn(3)—C(86)	2.07(5)	C(112)—C(113) and C(115)—C(116)	1.39(7)
Sn(3)—C(96)	2.10(6)	C(113)—C(114) and C(116)—C(111)	1.42(7)
Sn(4)—C(106)	2.02(5)	C(121)—C(122) and C(124)—C(125)	1.43(7)
Sn(4)—C(116)	2.09(5)	C(122)—C(123) and C(125)—C(126)	1.31(8)
Sn(4)—C(126)	2.11(5)	C(123)—C(124) and C(126)—C(121)	1.33(8)
Mean Sn—C	2.09(3)	Mean C—C	1.38(2)

TABLE 4

BOND ANGLES (°)

Sn(1)—N(1)—C(1)	161(5)	S(1′)—Sn(1)—N(1)	179(3)
Sn(2)—N(2)—C(2)	167(5)	S(2′)—Sn(2)—N(2)	178(4)
Sn(3)—N(3)—C(3)	158(4)	S(3′)—Sn(3)—N(3)	171(3)
Sn(4)—N(4)—C(4)	157(4)	S(4′)—Sn(4)—N(4)	171(3)
Mean Sn—N—C	161(4)	Mean S′—Sn—N	175(3)
N(1)—C(1)—S(1)	169(6)	C(1′)—S(1′)—Sn(1)	97(3)
N(2)—C(2)—S(2)	177(5)	C(2′)—S(2′)—Sn(2)	99(5)
N(3)—C(3)—S(3)	161(5)	C(3′)—S(3′)—Sn(3)	99(3)
N(4)—C(4)—S(4)	170(5)	C(4′)—S(4′)—Sn(4)	92(2)
Mean N—C—S	172(4)	Mean C′—S′—Sn	97(3)
C(16) —Sn(1)—N(1)	90(2)	C(16) —Sn(1)—C(26)	119(2)
C(26) —Sn(1)—N(1)	99(2)	C(16) —Sn(1)—C(36)	116(3)
C(36) —Sn(1)—N(1)	90(3)	C(26) —Sn(1)—C(36)	124(3)
C(46) —Sn(2)—N(2)	94(2)	C(46) —Sn(2)—C(56)	117(2)
C(56) —Sn(2)—N(2)	99(2)	C(46) —Sn(2)—C(66)	116(2)
C(66) —Sn(2)—N(2)	90(2)	C(56) —Sn(2)—C(66)	126(2)
C(76) —Sn(3)—N(3)	94(2)	C(76) —Sn(3)—C(86)	118(3)
C(86) —Sn(3)—N(3)	90(2)	C(76) —Sn(3)—C(96)	127(3)
C(96) —Sn(3)—N(3)	85(3)	C(86) —Sn(3)—C(96)	116(3)
C(106)—Sn(4)—N(4)	88(2)	C(106)—Sn(4)—C(116)	114(3)
C(116)—Sn(4)—N(4)	89(2)	C(106)—Sn(4)—C(126)	127(3)
C(126)—Sn(4)—N(4)	93(3)	C(116)—Sn(4)—C(126)	119(2)
Mean C—Sn—N	91.7(1.3)	Mean C—Sn—C	119.8(1.5)

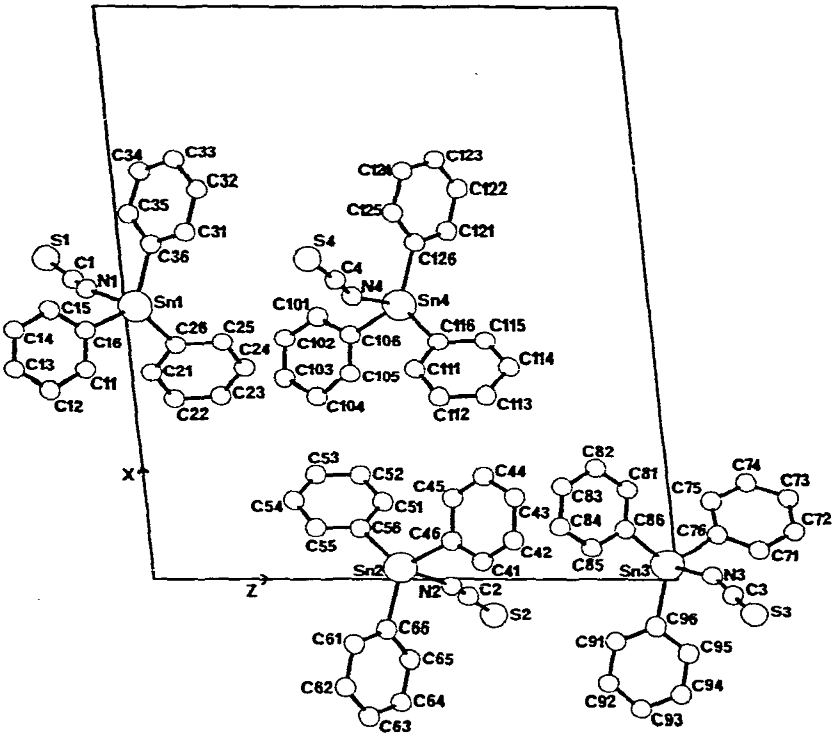

Fig. 1. The asymmetric unit projected perpendicular to Y.

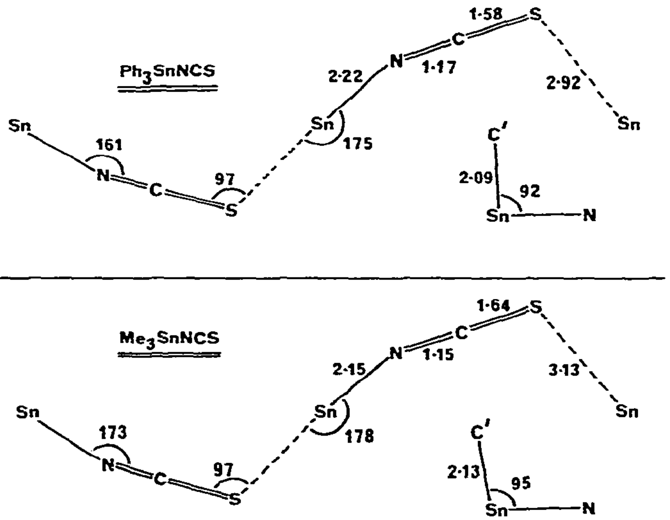

Fig. 2. Comparison of the structures of triphenyltin and trimethyltin isothiocyanate [2]. Mean bond lengths (Å) and angles (°) are given for the former.

Me_3Sn—SC(S)NMe_2 [3]), but is much shorter than expected for a non-bonded distance. The Sn—N distance is appreciably shorter than in $(Me_3SnN)_2C$, where the coordination of tin is trigonal bipyramidal, with two equal axial Sn—N distances of 2.47 Å [5]. The structures of triphenyltin and trimethyltin isothiocyanate are compared in Fig. 2. Similar zig-zag chains are found in the two structures, the chains being fairly linear except for C—S—Sn angles of 97°. Although both structures can be regarded as intermediate between tetrahedral (NC_3) and trigonal bipyramidal (NC_3S), the triphenyl derivative is closer to the five-coordinated structure; thus the Sn—N bond is longer, the Sn—S shorter, and the SnC_3 unit is closer to planarity, with mean bond angles N—Sn—C 91.7, C—Sn—C 119.8°. The shorter Sn—C bonds are consistent with the change from sp^3 to sp^2 hybridised carbon. In contrast to the structure of triphenyltin isothiocyanate reported here, the crystal structure of triphenyltin chloride contains isolated tetrahedral molecules, with no short intermolecular Sn···Cl interactions [11].

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