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THE CRYSTAL STRUCTURE OF TRIMETHYLTIN ISOTHIOCYANATE

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SUMMARY

The crystal structure of Me_3SnNCS has been determined by single crystal X-ray diffraction. The crystals are orthorhombic, *Pbca*, $a = 13.20(1)$, $b = 10.28(1)$, $c = 12.01(1)$ Å, $Z = 8$. The molecules are arranged in infinite zig-zag =S–Sn–N=C=S–Sn– chains, linear except at sulphur. The principal bond lengths and angles are: Sn–N, 2.15(6); N–C, 1.15(7); C–S, 1.64(7); S–Sn, 3.13(2); Sn–C(H_3) (mean), 2.13(3); angle N–Sn–C(H_3) (mean), 95(2)° and angle C–S–Sn, 97(2)°.

INTRODUCTION

The crystal structure[1] of trimethyltin cyanide consists of infinite linear –Sn–C–N–Sn– chains with planar Me_3Sn and disordered cyanide groups; however trimethylgermanium cyanide was found[2] to be monomeric in the crystal. Mössbauer studies[3] of trialkyltin isothiocyanates suggest that the trialkyltin groups are planar, with five-coordinated tin; the IR spectra of the crystals[4] are consistent with a R_3Sn–N=C=S rather than a R_3Sn–S–C≡N structure, with a significant non-bonded S–Sn interaction and a chain structure bent at nitrogen. It is interesting that the ratio of the intensities of the IR bands assigned to the symmetric and asymmetric SnC_3 stretching modes of trimethyltin isothiocyanate is much smaller in the crystal than in solution, consistent with a wider N–Sn–C angle and hence monomeric structure in solution[4]. On the other hand the IR spectra of organolead selenocyanates suggest that the lead atom is bonded to selenium rather than nitrogen[5]. In view of the ambiguities in the interpretation of the spectroscopic data, and also for comparison with the structure of silyl isothiocyanate[6], where linearity at nitrogen provides evidence of involvement of the silicon 3*d* orbitals in the bonding, we have determined the crystal structure of trimethyltin isothiocyanate*.

EXPERIMENTAL

Needle shaped crystals were obtained by recrystallisation from benzene; these were sealed into Lindemann glass capillary tubes. Intensities were determined visually from equi-inclination Weissenberg photographs taken with a crystal mounted

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* For a preliminary report see ref. 7.

TABLE 1

OBSERVED AND CALCULATED STRUCTURE FACTORS

Since the interlayer scale factors were refined, it is necessary to multiply these values (which are on an absolute scale) by 1.000, 1.058, 0.951, 0.947, 0.893, 1.061 and 0.702 for *hk*0, *hk*1, ..., *hk*6 for use in the weighting function.

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
2	0	0	154	173	3	5	1	137	139	1	1	3	49	42	1	5	4	43	27
4	0	0	253	246	4	5	1	91	97	2	1	3	68	64	2	5	4	49	40
6	0	0	223	251	5	5	1	39	36	3	1	3	63	71	3	5	4	50	41
8	0	0	76	60	6	5	1	40	33	7	1	3	38	36	0	6	4	57	49
10	0	0	109	107	7	5	1	55	72	9	1	3	46	39	1	6	4	81	65
12	0	0	90	82	8	5	1	74	79	0	2	3	48	45	5	6	4	56	58
2	1	0	291	227	9	5	1	43	50	1	2	3	200	189	6	6	4	36	36
4	1	0	142	172	10	5	1	30	31	2	2	3	56	45	7	6	4	30	29
6	1	0	50	55	0	6	1	133	127	3	2	3	35	29	1	7	4	25	23
8	1	0	135	151	1	6	1	53	44	4	2	3	34	24	2	7	4	56	51
10	1	0	71	71	2	6	1	54	47	5	2	3	143	151	3	7	4	50	49
12	1	0	45	38	4	6	1	69	70	6	2	3	49	52	4	7	4	51	45
14	1	0	47	44	5	6	1	46	48	7	2	3	79	89	0	8	4	84	71
0	2	0	200	149	6	6	1	70	72	9	2	3	33	29	1	8	4	44	36
2	2	0	88	72	2	7	1	58	48	11	2	3	56	57	2	8	4	36	32
4	2	0	76	73	4	7	1	42	37	1	3	3	155	153	4	8	4	44	39
6	2	0	129	122						2	3	3	97	85	5	8	4	43	39
8	2	0	36	32						3	3	3	204	216	6	8	4	49	51
10	2	0	64	60						4	3	3	58	57	1	9	4	19	26
12	2	0	45	40						5	3	3	48	49	2	9	4	35	41
2	3	0	93	90	1	0	2	129	175	6	3	3	36	25	3	9	4	42	48
4	3	0	79	67	2	0	2	40	45	7	3	3	88	106					
8	3	0	60	59	3	0	2	41	39	8	3	3	46	35					
10	3	0	23	21	4	0	2	52	55	9	3	3	82	95	1	1	5	19	13
0	4	0	79	63	5	0	2	142	154	13	3	3	41	39	2	1	5	67	67
4	4	0	31	30	6	0	2	56	60	0	4	3	68	63	3	1	5	27	27
2	5	0	93	88	7	0	2	90	97	1	4	3	195	179	4	1	5	57	59
4	5	0	83	75	9	0	2	45	37	2	4	3	45	32	6	1	5	18	14
6	5	0	21	23	11	0	2	83	71	3	4	3	38	31	8	1	5	50	47
8	5	0	55	61	12	0	2	33	26	4	4	3	40	33	0	2	5	120	117
0	6	0	173	192	13	0	2	31	18	5	4	3	132	145	1	2	5	28	21
2	6	0	90	76	1	1	2	129	130	6	4	3	44	37	2	2	5	47	45
4	6	0	103	102	2	1	2	104	114	7	4	3	72	88	4	2	5	56	58
6	6	0	108	114	3	1	2	150	174	9	4	3	28	29	5	2	5	16	20
2	7	0	118	122	4	1	2	93	106	11	4	3	57	62	6	2	5	70	75
4	7	0	63	75	5	1	2	42	31	1	5	3	84	76	10	2	5	40	36
6	7	0	32	24	6	1	2	35	28	3	5	3	113	117	1	3	5	21	23
8	7	0	55	67	7	1	2	91	100	5	5	3	31	30	2	3	5	110	117
0	8	0	123	120	8	1	2	61	62	7	5	3	58	60	3	3	5	40	37
2	8	0	45	43	9	1	2	91	91	9	5	3	54	62	4	3	5	55	58
4	8	0	56	65	10	1	2	24	23	13	5	3	25	27	6	3	5	28	24
6	8	0	64	75	13	1	2	44	41	0	6	3	30	25	8	3	5	56	59
2	9	0	79	98	0	2	2	127	121	1	6	3	101	100	10	3	5	27	31
4	9	0	59	71	1	2	2	210	198	2	6	3	31	26	0	4	5	199	187
0	10	0	61	72	2	2	2	114	89	3	6	3	22	17	1	4	5	38	29

1	1	1	76	92
2	1	1	56	60
3	1	1	140	153
5	1	1	37	36
6	1	1	29	25
7	1	1	70	67
8	1	1	27	23
9	1	1	46	44
0	2	1	179	159
1	2	1	131	125
2	2	1	70	64
3	2	1	19	8
4	2	1	83	95
5	2	1	96	113
6	2	1	80	97
7	2	1	64	60
10	2	1	48	43
11	2	1	43	34
12	2	1	42	30
2	3	1	153	147
3	3	1	76	75
4	3	1	137	134
5	3	1	31	26
6	3	1	51	45
7	3	1	47	56
8	3	1	99	108
9	3	1	42	42
10	3	1	40	32
12	3	1	29	28
0	4	1	191	177
1	4	1	154	138
2	4	1	107	98
4	4	1	101	100
5	4	1	115	129
6	4	1	129	144
7	4	1	56	62
9	4	1	30	29
10	4	1	53	62
11	4	1	42	40
12	4	1	40	37
1	5	1	73	72
2	5	1	140	131
3	2	2	43	40
4	2	2	70	67
5	2	2	139	155
6	2	2	95	109
7	2	2	88	88
9	2	2	46	29
10	2	2	34	35
11	2	2	59	58
1	3	2	74	64
3	3	2	95	90
4	3	2	44	39
5	3	2	33	21
7	3	2	43	37
9	3	2	52	41
0	4	2	62	55
1	4	2	25	15
2	4	2	36	25
4	4	2	27	24
6	4	2	43	31
1	5	2	48	32
3	5	2	57	49
4	5	2	36	28
7	5	2	40	29
0	6	2	37	17
1	6	2	90	93
5	6	2	76	79
6	6	2	23	21
7	6	2	53	45
1	7	2	79	74
2	7	2	69	66
3	7	2	104	117
4	7	2	53	42
5	7	2	34	25
7	7	2	59	61
8	7	2	33	30
9	7	2	56	53
0	8	2	67	69
1	8	2	89	100
2	8	2	41	30
4	8	2	41	38
5	8	2	83	85
6	8	2	47	45
7	8	2	46	49
1	9	2	48	37
3	9	2	53	60
5	6	3	80	82
6	6	3	33	35
7	6	3	48	48
11	6	3	30	35
1	7	3	46	40
3	7	3	57	62
1	0	4	86	131
2	0	4	68	92
4	0	4	64	72
5	0	4	126	134
6	0	4	118	124
7	0	4	63	62
9	0	4	35	35
10	0	4	51	49
11	0	4	51	40
12	0	4	34	29
1	1	4	41	42
2	1	4	102	111
3	1	4	98	109
4	1	4	82	92
5	1	4	39	34
6	1	4	42	34
7	1	4	55	65
8	1	4	67	76
9	1	4	50	44
10	1	4	25	24
0	2	4	168	147
1	2	4	49	42
2	2	4	60	51
4	2	4	72	80
5	2	4	57	56
6	2	4	72	72
7	2	4	29	27
10	2	4	36	29
1	3	4	48	32
2	3	4	50	39
3	3	4	75	65
4	3	4	18	17
7	3	4	34	32
0	4	4	51	44
1	4	4	62	35
5	4	4	39	28
2	4	5	72	59
4	4	5	88	97
5	4	5	21	23
6	4	5	90	96
8	4	5	19	20
10	4	5	46	44
12	4	5	31	35
1	5	5	30	22
2	5	5	123	128
3	5	5	43	38
4	5	5	85	86
6	5	5	21	22
8	5	5	60	70
10	5	5	28	30
0	6	5	70	69
1	6	5	20	16
2	6	5	35	30
4	6	5	36	33
6	6	5	48	50
10	6	5	22	25
1	0	6	51	87
2	0	6	54	67
4	0	6	67	67
5	0	6	75	76
6	0	6	99	102
7	0	6	52	35
10	0	6	56	43
1	1	6	27	18
2	1	6	91	102
3	1	6	53	51
4	1	6	77	87
7	1	6	30	33
8	1	6	63	64
0	2	6	112	94
2	2	6	46	33
4	2	6	58	51
6	2	6	59	52
2	3	6	49	36
3	3	6	52	29
0	6	6	62	51
1	6	6	62	46

about the Z(needle) axis and Ni-filtered Cu-K_α radiation (layers $hk0$–$hk6$ inclusive). We were not successful in obtaining good Weissenberg photographs for a crystal mounted about another axis. Lorentz, polarisation and absorption corrections were applied, the latter being calculated exactly for a cylinder with $\mu t = 1.6$, where μ is the linear absorption coefficient and t the diameter of the cylinder. Unit-cell dimensions were obtained from powder photographs, taken with a Guinier focussing camera and silicon internal calibrant ($a = 5.4306$ Å), and indexed using the approximate unit-cell constants and intensity data from the Weissenberg photographs. The estimated standard deviations in the unit-cell dimensions were multiplied by a factor of two to allow for possible systematic errors.

Crystal data

C_4H_9NSSn, $M = 221.9$, orthorhombic, $a = 13.20\,(1)$*, $b = 10.28\,(1)$, $c = 12.01\,(1)$, $U = 1629.4$, $d_c = 1.82$ for $Z = 8$. This value of Z was consistent with the interpretation of the Patterson function. Systematic absences: $0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$; $hk0$, $h \neq 2n$. These determine the space group uniquely as *Pbca*. The asymmetric unit consists of one formula unit; all atoms occupy the eight-fold general positions of the set $\pm(x,y,z;\ \tfrac{1}{2}+x, \tfrac{1}{2}-y, -z;\ -x, \tfrac{1}{2}+y, \tfrac{1}{2}-z;\ \tfrac{1}{2}-x, -y, \tfrac{1}{2}+z)$.

Structure solution and refinement

A three-dimensional Patterson synthesis was interpreted to give a self-consistent set of coordinates for the tin atoms. The remaining atoms were located from difference electron density syntheses, but no attempt was made to locate the hydrogen atoms. The structure was refined by full-matrix least-squares, initially with isotropic temperature factors for all the atoms; the weighting scheme adopted on the basis of an analysis of variance was $w = 1/(|F_o| - 0.00181 F_o^2)$. In the final stages of refinement a total or 46 parameters were varied simultaneously, including the inter-layer scale factors, anisotropic temperature factors for the tin and sulphur atoms only, and the Zachariasen secondary extinction coefficient[8]. Complex neutral-atom scattering factors were employed for all atoms[9,10]. The final value of $R = (\Sigma w^{\frac{1}{2}}(F_o - F_c)/\Sigma w^{\frac{1}{2}} \cdot F_o)$ was 0.118 for a total of 344 unique non-zero reflections; the corresponding unweighted "R index" was 0.112. A final difference Fourier revealed no pronounced features. Observed and calculated structure factors are shown in Table 1, and the results from the final full-matrix least-squares cycle are given in Tables 2 and 3. These results together with the full covariance matrix and the estimated standard deviations in the unit cell dimensions were used to calculate the bond lengths and angles given in Table 4 and Fig. 1. The shortest "non-bonded" distances are listed in Table 5. Fig. 2 shows the structure in projection down the X axis.

DISCUSSION

The structure consists of zig-zag chains along the Z axis, all the atoms except those of the methyl groups lying approximately in planes perpendicular to the X axis. As shown in Fig. 1, the S–Sn–N–C–S skeleton is linear within experimental error,

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* Throughout this paper estimated standard deviations (in parentheses) are given in units of the least significant digit of the quantity to which they refer.

TABLE 2

ATOM COORDINATES AND ISOTROPIC VIBRATIONAL AMPLITUDES ($Å^2 \times 1000$) WITH ESTIMATED STANDARD DEVIATIONS

Atom	x/a	y/b	z/c	$\bar{U}$
N	0.1667(31)	0.3236(48)	0.2914(55)	68(16)
C	0.1646(39)	0.4052(64)	0.3567(52)	92(19)
C(1)	0.0923(37)	0.0404(46)	0.2586(48)	72(16)
C(2)	0.0695(35)	0.3032(51)	0.0514(43)	83(18)
C(3)	0.3202(46)	0.1780(63)	0.1258(55)	122(25)

TABLE 3

ATOM COORDINATES AND ANISOTROPIC VIBRATIONAL AMPLITUDES ($Å^2 \times 1000$) WITH ESTIMATED STANDARD DEVIATIONS[a,b]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn	0.1595(2)	0.1873(4)	0.1553(4)	68(2)	53(3)	150(30)	3(3)	2(3)	2(2)
S	0.1572(16)	0.5120(17)	0.4575(21)	148(16)	64(10)	238(46)	−24(13)	−14(19)	−11(11)

[a] The anisotropic temperature factor takes the form: $\exp[-2\pi^2(U_{11}\cdot h^2\cdot a^{*2}+U_{22}\cdot k^2\cdot b^{*2}+U_{33}\cdot l^2\cdot c^{*2}+2U_{23}k\cdot l\cdot b^*\cdot c^*+2U_{31}l\cdot h\cdot c^*\cdot a^*+2U_{12}h\cdot k\cdot a^*\cdot b^*)]$. [b] The Zachariasen secondary extinction coefficient refined to the value $8.2(1.7)\times 10^{-7}$.

TABLE 4

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°)

Atoms	Distance	Atoms	Angle
Sn–N	2.15(6)	Sn–N–C	173(5)
C–S	1.64(7)	C(1)–Sn–N	92(2)
Sn–C(2)	2.10(5)	C(3)–Sn–N	96(3)
S′–Sn	3.13(2)	C(2)–Sn–C(3)	119(2)
N–C	1.15(7)	S′–Sn–N	178(1)
Sn–C(1)	2.15(5)	N–C–S	175(6)
Sn–C(3)	2.15(6)	C(2)–Sn–N	96(2)
		C(1)–Sn–C(2)	121(2)
		C(3)–Sn–C(1)	118(2)
		C′–S′–Sn	97(2)

the chains being bent at sulphur. The N–Sn–C(H_3) angle of 95(2)° is smaller than the tetrahedral angle expected for a monomer, possibly accounting for the observation that the IR band assigned to the SnC_3 symmetric stretch is weaker in the solid than in solution. The molecule should definitely be considered to be an isothiocyanate rather than a thiocyanate, since the Sn–S distance is appreciably longer than the value of 2.47 Å found for the Sn–S "single" bond in $Me_3SnSC(S)NMe_2$[11], although it is close to the values for the short "non-bonded" Sn–S distance in that compound. No other precise Sn–N bond lengths are available for comparison, but the value obtained for the trimethyltin isothiocyanate is close to that predicted from the sum of covalent radii. The N–C and C–S distances are found to be 1.22 and 1.56 Å in HN=C=S[12] and 1.16 and 1.68 Å in MeS–C≡N[13]. Despite the large estimated standard deviations,

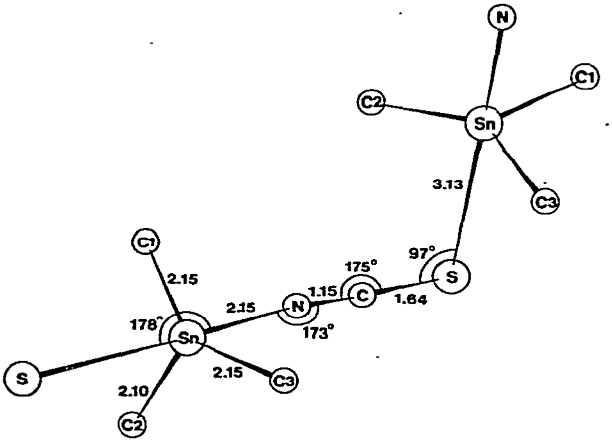

Fig. 1. The molecular dimensions of Me_3SnNCS.

TABLE 5

SHORTEST NON-BONDED DISTANCES (Å), WITH TRANSFORMATIONS RELATING THE COORDINATES OF THE SECOND ATOM TO THOSE OF THE CORRESPONDING ATOM IN THE SAME ASYMMETRIC UNIT AS THE FIRST ATOM

Atoms	Non-bonded distance	Transformations		
N–S	2.78	x	y	z
N–C(1)	3.10	x	y	z
Sn–S	3.13	x	$0.5-y$	$-0.5+z$
N–C(2)	3.16	x	y	z
N–C(3)	3.21	x	y	z
Sn–C	3.30	x	y	z
C–C(2)	3.41	x	$0.5-y$	$0.5+z$
S–C(3)	3.54	x	$0.5-y$	$0.5+z$
N–C(2)	3.62	x	$0.5-y$	$0.5+z$
S–C(2)	3.62	x	$0.5-y$	$0.5+z$
C(2)–C(3)	3.66	x	y	z
C(1)–C(2)	3.69	x	y	z
C(1)–C(3)	3.69	x	y	z
C–C(1)	3.69	$0.5-x$	$0.5+y$	z
Sn–C	3.71	x	$0.5-y$	$-0.5+z$
S–C(1)	3.76	x	$0.5-y$	$0.5+z$
S–C(3)	3.79	$0.5-x$	$1-y$	$0.5+z$
C(1)–C(2)	3.88	x	$0.5-y$	$0.5+z$
N–C(1)	3.90	$-x$	$0.5+y$	$0.5-z$
C–C(1)	3.92	$-x$	$0.5+y$	$0.5-z$

it is interesting that the "short" N=C and "long" C=S bond lengths in Me_3SnNCS are consistent with a structure intermediate between the valence bond extremes:

$$=\mathrm{S} \qquad \mathrm{Sn{-}N{=}C{=}S} \qquad \mathrm{Sn{-}N{=}C{=}}$$

$$-\mathrm{S}-\overset{-}{\mathrm{Sn}}-\overset{+}{\mathrm{N}}\equiv\mathrm{C}-\mathrm{S}-\overset{-}{\mathrm{Sn}}-\overset{+}{\mathrm{N}}\equiv\mathrm{C}-$$

and

$$-\mathrm{S}^- \qquad \mathrm{Sn}^+ \qquad \mathrm{N}\equiv\mathrm{C}-\mathrm{S}^- \qquad \mathrm{Sn}^+ \qquad \mathrm{N}\equiv\mathrm{C}-$$

In all three structures there are two or more "lone pairs" on the sulphur atom, consistent with the C–S–Sn angle of 97(2)°. The second structure requires an *sp* hybridised nitrogen atom with a linear Sn–N–C arrangement; the contribution of this valence bond extreme is presumably sufficient to make this rehybridisation of the nitrogen atom energetically profitable. An appreciable contribution from this structure is also consistent with the short Sn–S contact. The short Sn–N bond length required by the second structure would be counterbalanced by the long Sn–N distance required by the third. This bonding scheme is similar to that required to account for the crystal structure of trimethyltin cyanide. The stereochemical inactivity of the nitrogen lone pair is consistent with the above scheme, and does not imply "p_π–d_π" bonding from nitrogen to tin.

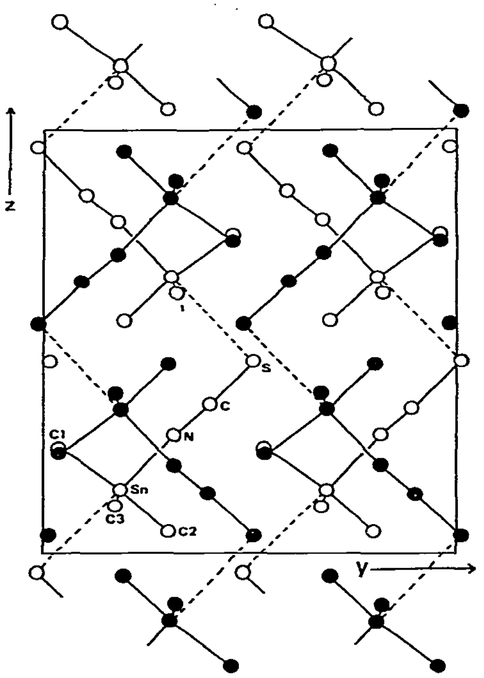

Fig. 2. The crystal structure seen in projection along the *X* axis.

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