Journal of Organometallic Chemistry, 69 (1974) 207—212

THE CRYSTAL STRUCTURE OF *N*-(TRIMETHYLSTANNYL)-*N*-NITROMETHYLAMINE

A.M. DOMINGOS* and G.M. SHELDRICK
University Chemical Laboratory, Lensfield Road, Cambridge, (Great Britain)
(Received September 7th, 1973)

Summary

The crystal structure of $Me_3SnN(Me)NO_2$ has been determined by single crystal X-ray diffraction. The crystals are monoclinic, $P2_1/c$, with a 12.52(2), b 9.91(2), c 14.34(2) Å, β 98.6(1)°, Z 8. Planar trimethyltin groups are linked by planar *N*-nitromethylamine groups to form infinite —$Sn(Me_3)$—N(Me)—N(O)—O—$Sn(Me_3)$— chains in the Y axis direction. There are two sets of crystallographically non-equivalent chains, but the bond lengths and angles agree within experimental error. The coordination of tin is approximately trigonal bipyramidal, with axial nitrogen and oxygen. Mean bond lengths are: Sn—C, 2.16; Sn—N, 2.33; N—C, 1.45; N—N, 1.29; N—O, 1.24; and O—Sn, 2.39 Å.

Introduction

N-(Trimethylstannyl)-*N*-nitromethylamine was first prepared by Winters and Hill [1], who proposed a monomeric structure with five-coordinated tin and a chelating nitromethylamine ligand on the basis of the Mössbauer and infrared spectra of the solid. We have determined the crystal structure in order to compare the coordination of tin with that in the trimethyltin halides and pseudohalides, where it has been found to be intermediate between tetrahedral and trigonal bipyramidal with equatorial methyl groups.

Experimental

The compound was prepared [1] by the reaction of trimethyltin chloride with $AgN(NO_2)Me$ in benzene. The solution was filtered hot to remove AgCl, and the solvent evaporated under vacuum to yield a white solid. Very thin needle shaped crystals were obtained by recrystallisation from benzene.

---

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

(Found: C, 20.4; H, 5.0; N, 11.2. $C_4H_{12}N_2O_2Sn$ calcd.: C, 20.1; H, 5.1; N, 11.7 %.) The infrared spectrum agreed with the reported spectrum [1].

Intensities were determined on a Stoe Stadi-2 two-circle diffractometer (layers $h0l$ to $h10l$ inclusive), with Mo-K_α radiation (λ 0.71069 Å), from a crystal sealed into a Lindemann glass capillary tube and mounted about the Y (needle) axis. The data were collected in an approximately 'constant count' mode; where a prescan indicated that the count could not be achieved within a specified time, the reflexion was ignored. 1190 reflexions were measured, of which 88 were rejected because of background imbalance or because the net count was less than 3σ based on counting statistics; averaging of equivalent reflexions led to 600 unique observed reflexions. Lorentz, polarisation and absorption corrections were applied, the latter being calculated for a cylinder having $\mu \cdot r = 0.41$, where μ is the linear absorption coefficient and r the radius of the cylinder. Unit-cell dimensions were obtained from diffractometer measurements.

Crystal data

$C_4H_{12}N_2O_2Sn$, mol. wt. 238.8, monoclinic, a 12.52(2), b 9.91(2), c 14.34(2) Å, β 98.6(1)°, U 1772 Å^3, μ(Mo-K_α) 28.5 cm^{-1}, d_c 1.79 for Z 8. Systematic absences: $0k0$ $k \neq 2n$; $h0l$, $l \neq 2n$. These uniquely determine the space group as $P2_1/c$. The reflections $h0l$ with $h \neq 2n$ are also very weak. All the atoms occupy four-fold general positions of the set $\pm(x, y, z; x, \frac{1}{2}-y, \frac{1}{2}+z)$; there are two formula units in the asymmetric unit.

Structure solution and refinement

Coordinates for the two tin atoms were obtained by interpretation of the Patterson function; the remaining atoms were located from difference electron

TABLE 1

ANALYSIS OF VARIANCE

N is the number of reflections in the group; V is 100 times the r.m.s. deviation of a reflection of unit weight on an absolute scale of F.

(a) As a function of the parity of the indices

	ggg	ugg	gug	uug	ggu	ugu	guu	uuu	all
N	127	108	88	86	10	9	85	87	600
V	793	497	790	763	963	896	873	671	744

(b) As a function of sin θ

sin θ	0.00 – – 0.14	0.14 – – 0.18	0.18 – – 0.20	0.20 – – 0.22	0.22 – – 0.24	0.24 – – 0.26	0.26 – – 0.28	0.28 – – 0.31	0.31 – – 0.34	0.34 – – 0.45
N	65	77	41	63	62	57	59	77	44	55
V	1278	789	616	760	518	580	538	549	628	770

(c) As a function of F_o

$(F_o/F_{max})^{1/2}$	0.00 – – 0.33	0.33 – – 0.35	0.35 – – 0.37	0.37 – – 0.39	0.39 – – 0.41	0.41 – – 0.43	0.43 – – 0.47	0.47 – – 0.50	0.50 – – 0.55	0.55 – – 1.00
N	75	49	60	69	64	51	66	57	53	56
V	855	761	667	701	645	785	734	920	668	639

(d) As a function of equi-inclination layer number

k	0	1	2	3	4	5	6	7	8	9	10
N	57	111	59	99	62	82	47	46	18	8	11
V	1025	990	608	760	640	618	443	478	473	402	487

TABLE 2

FRACTIONAL COORDINATES (X 10^4) AND ISOTROPIC TEMPERATURE FACTORS (Å^2 X 10^3)

	x/a	y/b	z/c	U
Sn(1)	370(4)	5018(3)	3001(4)	
Sn(2)	4669(4)	7440(3)	1965(3)	
N(1)	1143(29)	3248(36)	3947(27)	35(12)
N(2)	927(31)	2036(35)	3571(32)	37(12)
N(3)	4052(33)	5643(38)	1001(29)	37(12)
N(4)	4345(32)	4512(36)	1324(29)	27(11)
O(1)	1231(31)	1021(39)	3944(26)	56(12)
O(2)	385(30)	2021(32)	2708(26)	43(12)
O(3)	4079(29)	3425(35)	923(24)	51(11)
O(4)	4904(30)	4453(35)	2098(32)	59(13)
C(1)	1009(50)	6434(64)	4103(47)	54(20)
C(2)	−1279(47)	4434(57)	2965(42)	37(22)
C(3)	1256(35)	4761(54)	1905(29)	21(14)
C(4)	1823(41)	3268(48)	4876(39)	50(15)
C(5)	6356(52)	6812(73)	1974(44)	55(23)
C(6)	4074(55)	8809(66)	875(48)	62(22)
C(7)	3676(50)	6828(69)	3111(41)	45(22)
C(8)	3319(44)	5596(53)	127(41)	57(17)

density maps, taking into account that the unit cell is approximately quartered in the [010] projection. The structure was refined by full-matrix least-squares, with a weighting scheme $w = 1/(55.07 + |F_o| + 0.00374|F_o|^2)$. Complex neutral-atom scattering factors were employed for all atoms [2,3]. An attempt to refine an isotropic secondary extinction parameter did not result in a significant improvement, so extinction was ignored. In the final cycles of refinement, a total of 93 parameters were varied independently, including anisotropic temperature factors for the tin atoms and isotropic temperature factors for the remaining atoms. Since it was also necessary to refine the 10 inter-layer scale factors, the values of U_{22} for the tin atoms have large estimated errors, although in fact the numerical values are entirely reasonable. The final value of $R_w = \Sigma w^{½} \cdot |F_o - F_c|/\Sigma w^{½} \cdot |F_o|$ was 0.059, with a corresponding unweighted R index of 0.057. All the peaks in the final difference electron density synthesis were less than 0.9 electrons Å^{-3}, but no attempts were made to locate hydrogen atoms. An analysis of variance is presented in Table 1; atomic coordinates and anisotropic temperature factors from the final least-squares cycle are given in Tables 2 and 3; the resulting bond lengths and angles are given in Tables 4 and 5. Lists of observed and calculated structure factors may be obtained from the authors.

TABLE 3

ANISOTROPIC TEMPERATURE FACTORS (Å^2 X 10^3)

The anisotropic temperature factor takes the form: $\mathrm{Exp}[-2\pi^2(U_{11}h^2a^{\star 2} + U_{22}k^2b^{\star 2} + U_{33}l^2c^{\star 2} + 2U_{23}klb^{\star}c^{\star} + 2U_{31}lhc^{\star}a^{\star} + 2U_{12}hka^{\star}b^{\star})]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	30(2)	37(10)	41(3)	−4(3)	−6(2)	−1(3)
Sn(2)	34(2)	34(10)	36(3)	2(3)	8(2)	1(8)

TABLE 4

BOND LENGTHS (Å)

Sn(1)—C(1)	2.17(7)	Sn(2)—C(5)	2.20(7)
Sn(1)—C(2)	2.14(6)	Sn(2)—C(6)	2.12(7)
Sn(1)—C(3)	2.07(5)	Sn(2)—C(7)	2.29(6)
Sn(1)—N(1)	2.34(4)	Sn(2)—N(3)	2.32(4)
Sn(1)—O(2′)	2.36(5)	Sn(2)—O(4′)	2.42(5)
N(1)—C(4)	1.47(6)	N(3)—C(8)	1.44(6)
N(1)—N(2)	1.33(5)	N(3)—N(4)	1.25(5)
N(2)—O(1)	1.17(5)	N(4)—O(3)	1.24(5)
N(2)—O(2)	1.32(5)	N(4)—O(4)	1.22(5)

Discussion

The structure consists of infinite zig-zag chains along the *Y* (needle) axis, formed by Me$_3$Sn groups linked by approximately planar *N*-nitromethylamine units. The Me$_3$Sn groups are almost planar (the sum of C—Sn—C angles is 358° at Sn(1) and 360° at Sn(2)). The coordination of tin is approximately trigonal bipyramidal, with equatorial methyl groups, an axial amino nitrogen atom, and the remaining axial position occupied by an oxygen atom of a neighbouring formula unit. The geometry of the chain involving Sn(1) is illustrated in Fig. 1; the bond lengths and angles in the two crystallographically non-equivalent chains are consistent within experimental error. The mean Sn—N and Sn—O bond lengths [2.33(4) and 2.39(5)] indicate perhaps a slightly higher Sn—N than Sn—O bond order. The Sn—N bond length can be compared with the values of 2.333(9) and 2.338(9) in Me$_3$SnN(CN)$_2$ [4] and with 2.47(1) Å in (Me$_3$Sn)$_2$N$_2$C [5], in both of which the tin atom is coordinated by two axial nitrogen atoms and three equatorial methyl groups in a trigonal bipyramidal configuration. The Sn—O distance is a little longer than in Me$_3$SnOMe [2.20(2) and 2.26(2) Å] [6], in which there is the corresponding coordination geometry involving two axial oxygens and three equatorial methyl groups. The dimensions of the CNNO$_2$ units are very similar to those of the approximately planar CNNO$_2$ units in *N*,*N′*-dinitroethylenediamine [7]; mean bond lengths are

TABLE 5

BOND ANGLES (°)

C(2) —Sn(1)—C(1)	116(2)	C(6) —Sn(2)—C(5)	115(3)
C(3) —Sn(1)—C(1)	117(2)	C(7) —Sn(2)—C(5)	123(3)
C(3) —Sn(1)—C(2)	125(2)	C(7) —Sn(2)—C(6)	122(3)
C(1) —Sn(1)—N(1)	89(2)	C(5) —Sn(2)—N(3)	91(2)
C(2) —Sn(1)—N(1)	97(2)	C(6) —Sn(2)—N(3)	90(2)
C(3) —Sn(1)—N(1)	97(2)	C(7) —Sn(2)—N(3)	93(2)
C(1) —Sn(1)—O(2′)	81(2)	C(5) —Sn(2)—O(4′)	96(2)
C(2) —Sn(1)—O(2′)	84(2)	C(6) —Sn(2)—O(4′)	85(2)
C(3) —Sn(1)—O(2′)	90(2)	C(7) —Sn(2)—O(4′)	85(2)
N(1) —Sn(1)—O(2′)	170(2)	N(3) —Sn(2)—O(4′)	173(2)
N(2) —N(1) —Sn(1)	114(3)	N(4) —N(3) —Sn(2)	115(3)
C(4) —N(1) —Sn(1)	130(3)	C(8) —N(3) —Sn(2)	131(3)
C(4) —N(1) —N(2)	116(4)	C(8) —N(3) —N(4)	114(4)
O(1) —N(2) —N(1)	124(5)	O(3) —N(4) —N(3)	124(5)
O(2) —N(2) —N(1)	116(4)	O(4) —N(4) —N(3)	118(4)
O(2) —N(2) —O(1)	120(4)	O(4) —N(4) —O(3)	117(4)
Sn(1)—O(2′) —N(2′)	122(3)	Sn(2)—O(4′) —N(4′)	126(3)

TABLE 6

NON-BONDED DISTANCES LESS THAN 3.8 Å

Within chain			
Sn(1)—O(2)	3.00		
Sn(1)—N(2)	3.12	Sn(2)—O(4)	2.98
Sn(1)—N(2′)	3.26	Sn(2)—N(4)	3.05
Sn(1)—O(1′)	3.33	Sn(2)—N(4′)	3.30
Sn(1)—C(4)	3.48	Sn(2)—O(3′)	3.34
N(1)—O(1)	2.21	Sn(2)—C(8)	3.44
N(1)—O(2)	2.24	N(3)—O(3)	2.20
N(1)—C(1)	3.17	N(3)—O(4)	2.12
N(1)—C(3)	3.31	N(3)—C(6)	3.14
N(1)—C(2)	3.36	N(3)—C(5)	3.23
N(2)—C(4)	2.37	N(3)—C(7)	3.34
N(2)—C(2)	3.65	N(4)—C(8)	2.26
N(2)—C(3)	3.67	N(4)—C(5)	3.42
N(2)—C(2′)	3.46	N(4)—C(7)	3.63
N(2)—C(3′)	3.53	N(4)—C(7′)	3.64
O(1)—O(2)	2.16	O(3)—O(4)	2.10
O(1)—C(4)	2.65	O(3)—C(8)	2.55
O(1)—C(2′)	3.17	O(3)—C(5′)	3.53
O(1)—C(3′)	3.41	O(3)—C(7′)	3.34
O(2)—C(2)	3.23	O(4)—C(5)	2.98
O(2)—C(3)	3.20	O(4)—C(7)	3.27
O(2)—C(4)	3.57	O(4)—C(8)	3.40
O(2)—C(1′)	2.96	O(4)—C(5′)	3.43
O(2)—C(2′)	3.01	O(4)—C(6′)	3.06
O(2)—C(3′)	3.14	O(4)—C(7′)	3.19
C(1)—C(2)	3.66	C(5)—C(6)	3.64
C(1)—C(3)	3.61	C(6)—C(8)	3.45
C(1)—C(4)	3.43		
C(2)—C(3)	3.73		
Between chains, first atom transformed by:			
(1—x, 0.5 + y, 0.5—z)		(x, 0.5—y, 0.5 + z)	
N(2)—C(5)	3.61	O(1)—C(8)	3.31
O(1)—C(5)	3.56	O(3)—C(4)	3.43

[*N*-(trimethylstannyl)-*N*-nitromethylamine given first]: N—C, 1.45(6), 1.463(4); N—N, 1.29(5), 1.301(4); and N—O, 1.24(5), 1.238(3).

The structure reported here was rejected by Winters and Hill [1] because the triethyltin analogue was found to be monomeric in benzene, and because there was a weak infrared absorption at 512 cm^{-1} which could be assigned to the

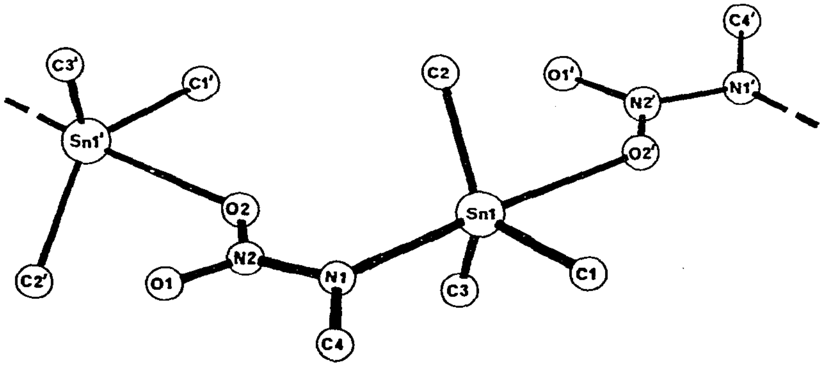

Fig. 1. The repeat unit of the chain involving Sn(1).

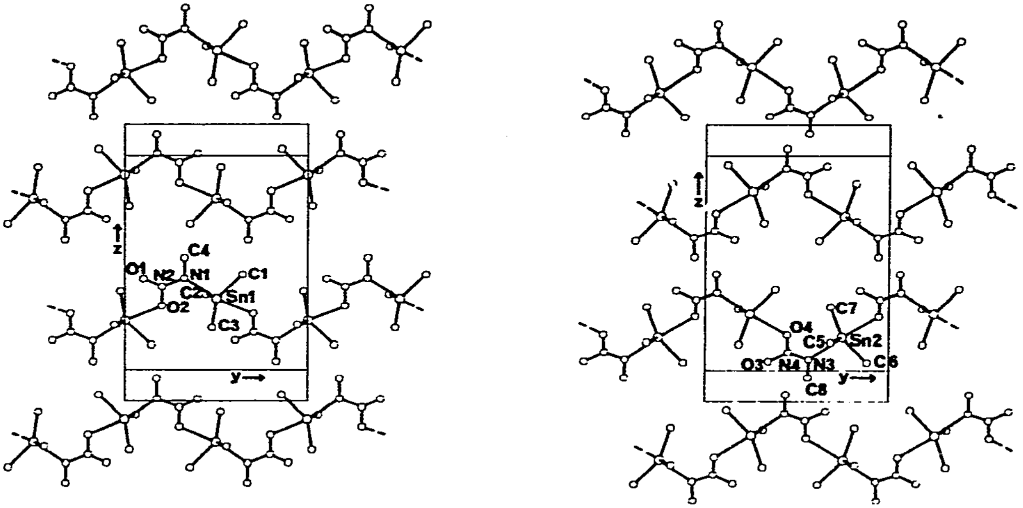

Fig. 2. Packing diagram, showing the projection of the structure perpendicular to X. The two halves of this diagram should be superimposed.

symmetric SnC_3 stretching mode. It is not clear to us whether this band has been incorrectly assigned, or whether the symmetric SnC_3 stretching mode is sufficiently strong to be observed because the site symmetry of the $SnMe_3$ groups in the crystal is lower than D_3 or C_{3h}. The splitting of the asymmetric SnC_3 stretch (541 and 556 cm^{-1}) could also be attributed to the lower site symmetry. It seems likely that the compound has a different structure in solution, possibly similar to the monomeric structure proposed by Winters and Hill.

The packing of the chains is illustrated in Fig. 2, which has been split into two parts for clarity. There are no short intermolecular distances between the chains.

Acknowledgements

We are grateful to the Science Research Council for the provision of the diffractometer, and to the University Computer Laboratory for computing facilities. The calculations were performed using the IBM 370 computer and programs written by G.M.S.; the plots were produced using the program PLUTO written by Dr. S. Motherwell.

References

1 L.J. Winters and D.J. Hill, Inorg. Chem., 4 (1965) 1433.
2 D.T. Cromer and J.T. Waber, Acta Crystallogr., 18 (1965) 104.
3 D.T. Cromer, Acta Crystallogr., 18 (1965) 17.
4 Y.M. Chow, Inorg. Chem., 10 (1971) 1938.
5 R.A. Forder and G.M. Sheldrick, J. Chem. Soc. A, (1971) 1107.
6 A.M. Domingos and G.M. Sheldrick, in preparation.
7 J.W. Turley, Acta Crystallogr., Sect. B, 24 (1968) 942.