value (107.5 ± 3.5°), only one of the six independent measurements being larger than 109.5° (see Table III). The C(8)–N–B angle (average 116.0 ± 2.1°) is significantly larger than the other two corresponding angles (average 108.9 ± 0.8°), apparently because of the larger steric repulsions involving the C(8) group, which is in "gauche" orientation with respect to both of the bulky substituents on the boron atom.

The

group is planar within experimental error. The msd's from the average plane are 0.018 and 0.027 Å for cations a and b, respectively; the equations of the corresponding planes, in terms of fractional coordinates, are $0.6388x + 0.6753y + 0.3640z - 1.1072 = 0$, for a, and $0.6611x + 0.6389y + 0.3885z - 6.7044 = 0$, for b. The dihedral angles between the picolinic group and the Br–B–N(1) and N(2)–B–N(1') planes are (average) 40.0 ± 2.5 and 81.0 ± 0.3°, respectively; the larger dihedral angle involving the bulkier $-N(CH_3)_3$ group is very likely due to larger steric repulsions. As it is shown in Figure 4, the pyridine ring is nearly orthogonal to the N–B–N plane (average value of the dihedral angle 82 ± 1°); the departure from the 90° value seems to be due to the necessity of increasing the intramolecular Br···H distance (2.7 Å, see Figure 4; the distance has been evaluated assuming the H atom in the normal stereochemical position), which still falls short of the sum of the van der Waals radii (3.1 Å).[9]

The geometry of the pyridine ring of the picolinic residue does not differ, within experimental error, from that established for pyridine by microwave measurements.[10] As expected in an ionic structure, ions with the same charge tend to avoid close contacts. As reported in Figure 2, where hydrogen atoms are neglected, the shortest interatomic distance between different cations is 3.70 Å (Br···C); as for the PF_6^- ions the F···F distances are never shorter than 4 Å. On the other hand, interatomic contact between ions of opposite charge can be as close as 3.12 Å ($F\cdots CH_3$) and 3.39 Å (F···N of the picolinic ring).

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(9) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

(10) B. Bank, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.*, **22**, 2013 (1954).

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The Crystal and Molecular Structure of Dimeric Tetramethyl-1,3-diisothiocyanatodistannoxane, $[((CH_3)_2SnNCS)_2O]_2$

BY YEH MEI CHOW

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The crystal structure of dimeric tetramethyl-1,3-diisothiocyanatodistannoxane has been determined from three-dimensional X-ray diffraction data. It forms monoclinic crystals in space group $C2/m$ with a = 21.73 (4) Å, b = 7.88 (1) Å, c = 10.96 (2) Å, and β = 134.7 (2)°. The intensities of 546 independent reflections were obtained by visual estimation of film data. The structure was solved by Patterson and Fourier syntheses and refined by the least-squares method to a conventional R factor of 8.0%. The dimeric molecule has $2/m$ symmetry with a central planar four-membered $Sn(2)_2O_2$ ring. Secondary bonding (2.84 (4) Å) between the isothiocyanate nitrogens of these tin atoms and the exocyclic tins forms two additional planar Sn(2)OSn(1)···N(2) rings. The endocyclic tin is thus pentacoordinate, approximately trigonal bipyramidal. Still further weak Sn(1)···S(2) linkage (3.33 (3) Å) between dimers results in distorted octahedral hexacoordination for the exocyclic tin atom and infinite chains parallel to [001]. Distances are Sn(1)–O = 2.05(5), Sn(1)–N(1) = 2.06 (4), Sn(1)–CH_3(1) = 2.07 (3), Sn(2)–O = 1.99 (3), Sn(2)–O = 2.15 (4), Sn(2)–N(2) = 2.39 (8), and Sn(2)–CH_3(2) = 2.15 (3) Å. Both NCS groups are linear with distances N(1)–C(1) = 1.17 (7), C(1)–S(1) = 1.61 (6), N(2)–C(2) = 1.10 (7), and C(2)–S(2) = 1.64 (5) Å.

Introduction

The crystal structure reported here is a part of a general investigation of donor–acceptor interactions between pseudohalogens and heavy atoms in the solid state. Many tetraalkyldistannoxane derivatives $(XR_2Sn)_2O$ and the related hydroxides $XR_2SnOSnR_2OH$ are known (X = halogen, pseudohalogen, carboxylate, nitrate, alkoxide, or phenoxide). Pfeiffer and Brack[1] in 1914 assumed that the compound $(XR_2Sn)_2O$ had the structure I; however, Harada[2] argued the case for a cyclic structure II where the tin atoms have coordination numbers of 4 and 5; on rather insecure evidence he

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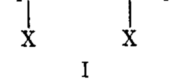
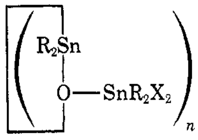
(1) P. Pfeiffer and O. Brack, *Z. Anorg. Allg. Chem.*, **87**, 229 (1914).

(2) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

proposed that the value $n = 3$. On the basis of ^1H and ^{119}Sn magnetic resonance spectroscopy and vapor pressure osmometry, Alleston, *et al.*,[3] were unable to choose between III and IV as the structure for $(XR_2Sn)_2O$ (X = halogen, carboxylate, sulfonate, or thiocyanate). Recently accumulated evidence has supported the four-membered ring skeleton IV in which tetra- or pentacoordinated tin is involved.[4] In addition ladder-type structures V and VI have been used to explain the infrared spectra of $SCNR_2SnOSnR_2NCS$ and $SCNR_2SnOSnR_2OH$; in these structures all tin atoms are pentacoordinated. The ladder-type structure has been confirmed by the X-ray study[5] of $[((CH_3)_2SnOSi(CH_3)_3)_2O]_2$, which is the only known crystal structure of this type.


I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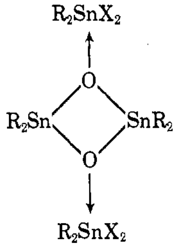
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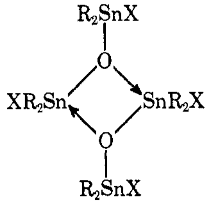
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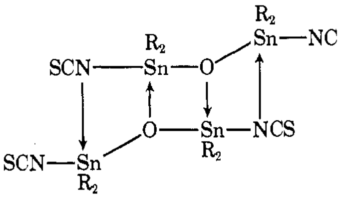
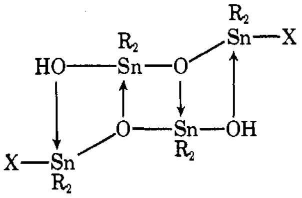

V


VI

The investigation of tetramethyl-1,3-diisothiocyanatodistannoxane was motivated by the recent determination of the crystal structures of dimethyltin diisothiocyanate[6] and trimethyltin isothiocyanate.[7] These crystal structures consist of infinite polymeric chains. In dimethyltin diisothiocyanate, the discrete molecules are linked by the donor–acceptor bonding between two sulfur atoms with the tin atom of the adjacent molecule leading to a hexacoordinated tin. It seemed to us that there was the possibility of a donor–acceptor interaction between sulfur and tin atoms in the distannoxane reported here, in which case hexacoordinated tin might be involved.

Experimental Section

Preparation and Properties.—Tetramethyl-1,3-diisothiocyanatodistannoxane was prepared by the same method as the corresponding ethyl, *n*-propyl, and *n*-butyl compounds.[8] Dimethyltin diisothiocyanate and dimethyltin oxide (mole ratio 1:1) were refluxed in benzene for several hours. Crystals of $[((CH_3)_2SnNCS)_2O]_2$ were formed by slow evaporation of the filtrate. *Anal.* Calcd: C, 16.77; H, 2.82; N, 6.52; S, 14.92. Found: C, 16.81; H, 2.84; N, 6.35; S, 14.88. The melting point and the infrared frequency of C–N stretching vibrations are compared with those of related compounds in Table I. The melting point of $[((CH_3)_2SnNCS)_2O]_2$ is higher than that of the similar ethyl, propyl, or butyl compounds. In addition, the higher C–N stretching frequencies in the solid and the lower solubilities in inert organic solvents may suggest the presence of sulfur bridging similar to that in dimethyltin diisothiocyanate.

TABLE I

MELTING POINTS AND INFRARED FREQUENCIES (CM^{-1}) OF C–N STRETCHING VIBRATIONS OF $(CH_3)_2Sn(NCS)_2$ AND $[(R_2SnNCS)_2O]_2$

		$[(R_2SnNCS)_2O]_2$, R =			
	$(CH_3)_2Sn(NCS)_2$[a]	CH_3	C_2H_5[a]	n-C_3H_7[a]	n-C_4H_9[a]
Mp, °C	194–196	205–207	178–179	108–108.5	83.5–84.5
Nujol mull	2088	2058	2037	2042	2041
	2062	2010	1959	1961	1953
Soln		1998[b]	2030[c]	2020[c]	2016[c]
		1955	1957	1959	1960

[a] See ref 8 and M. Wada and R. Okawara, *J. Organometal. Chem.*, **8**, 261 (1967). [b] In CCl_4 solution. [c] In CCl_4 or benzene solution.

Space Group and Unit Cell.—Oscillation and Weissenberg photographs were taken with Mo Kα radiation (λ 0.7107 Å) with rotation about the needle axis (crystallographic c axis). Precession pictures were taken with c^* as the spindle axis. The crystal is monoclinic with $a = 21.73$ (4) Å, $b = 7.88$ (1) Å, $c = 10.96$ (2) Å, and $\beta = 134.7$ (2)°; errors are estimated to be 1 part in 600 due to crystal setting accuracy with the precession camera. From the 215-Å^3 molecular volume of $(CH_3)_2Sn(NCS)_2$ it was reasonable to assume that this compound had four molecules per unit cell. This would give a calculated density of 2.13 g/cm^3, which agrees with a value of 2.12 (1) g/cm^3 measured by flotation in a mixture of CH_2I_2 and CCl_4. Systematic extinctions $h + k$ odd in hkl indicated $C2$, Cm, or $C2/m$ to be the space group. The spoon test[9] for pyroelectricity gave a positive result, which would rule out $C2/m$ as a possible space group, but the refined structure showed that $C2/m$ is the space group. One possible explanation is that there is a transition to an acentric phase on cooling the crystal to the temperature of liquid nitrogen; however, the transition does not cause the crystal to powder. Another is that distortions from $C2/m$ symmetry are too small to be detected by this study.

A crystal elongated along c with a length of 0.32 mm and with approximate widths 0.08 mm for the (010) and 0.08 mm for the (100) faces was used for intensity measurements. Using unfiltered Mo Kα radiation, precession intensity data were collected for layers $h0l$ to $h4l$, $0kl$ to $8kl$, and $(3k)kl$ to $(3k - 14)kl$. All intensities were estimated by visual comparison with an intensity strip. There were 546 independent reflections with observable intensities. No unobserved reflections were included in the structure determination. The estimated transmission factors for reflections with widest variation were 0.73–0.76; no absorption correction was carried out ($\mu = 40.0$ cm^{-1}).

Determination of Structure.—It was possible to find the tin atom positions from the Patterson map. Both of the atoms appeared to have approximately the same y coordinate. Using only the two tin atoms differing by 0.01 in y coordinates gave

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[3] D. L. Alleston, A. G. Davis, M. Hancock, and R. F. M. White, *J. Chem. Soc.*, 5469 (1963).

[4] R. Okawara and M. Wada, *Advan. Organometal. Chem.*, **5**, 137 (1967).

[5] R. Okawara, N. Kasai, and K. Yasuda, 2nd International Symposium on Organometallic Chemistry, Madison, Wis., 1965, p 128.

[6] Y. M. Chow, *Inorg. Chem.*, **9**, 794 (1970).

[7] J. B. Hall, Ph.D. Thesis, University of Minnesota, 1969.

[8] M. Wada, M. Nishika, and R. Okawara, *J. Organometal. Chem.*, **3**, 70 (1965).

[9] C. W. Bunn, "Chemical Crystallography," 2nd ed, Oxford University Press, London, 1960, p 321.

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.28$ and $r = (\Sigma w|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4 = 0.63$. The subsequent electron density map confirmed the chosen positions of tin and revealed the positions of all other atoms, in an arrangement that corresponded to space group $C2/m$, which had earlier been discarded. A full-matrix least-squares refinement was carried out on the positional parameters and the isotropic temperature parameters for all atoms minimizing the function r. The weighting scheme was $w = 1.0$ for $F_o < 17.7$ and $w = (17.7/F_o)^4$ for $F_o > 17.7$. A difference Fourier map based on the parameters from this refinement gave significant peaks only around the tin atom positions. The course of subsequent refinement is as follows (r, R): all atoms isotropic, 0.0563, 0.098; only Sn anisotropic, 0.0446, 0.085; all atoms anisotropic, 0.0392, 0.080. Hamilton's tables indicate that the hypothesis of all atoms being anisotropic is confident at the 99% level.[10] Therefore, these parameters are chosen as the final set and are given in Table II. No parameters changed by more than 0.04 of its estimated standard deviation during the final cycle. The corresponding principal axes of the ellipsoids of vibration of all atoms are given in Table III. However, the error of the ellipsoids of vibration of some light atoms seems to be exceedingly large. An examination of the errors in the positional parameters and the orientation of the thermal ellipsoids failed to reveal any trends that would suggest that the space group should have been $C2$ or Cm rather than $C2/m$. The observed and calculated structure factors are given in Table IV.

TABLE II

Positional Parameters

	X	Y	Z
Sn(1)	−0.0835 (2)	0	0.1619 (4)
Sn(2)	0.0942 (2)	0	0.2008 (5)
S(1)	−0.3564 (10)	0	−0.4309 (18)
S(2)	0.2136 (10)	0	0.7773 (20)
O	0.0322 (17)	0	0.0608 (33)
N(1)	−0.2074 (28)	0	−0.0812 (54)
N(2)	0.1000 (28)	0	0.4269 (59)
C(1)	−0.2711 (34)	0	−0.2272 (73)
C(2)	0.1454 (30)	0	0.5671 (57)
$CH_3(1)$	−0.0728 (26)	0.2472 (45)	0.2388 (58)
$CH_3(3)$	0.1408 (25)	0.2563 (47)	0.2530 (57)

Thermal Parameters ($\times 10^4$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn(1)	44 (2)	178 (10)	139 (7)	0	57 (4)	0
Sn(2)	43 (2)	175 (10)	143 (7)	0	56 (4)	0
S(1)	53 (8)	247 (34)	156 (24)	0	44 (11)	0
S(2)	44 (6)	283 (35)	149 (23)	0	55 (11)	0
O	21 (11)	410 (97)	92 (45)	0	38 (21)	0
N(1)	34 (18)	96 (70)	151 (77)	0	23 (32)	0
N(2)	58 (23)	160 (85)	268 (104)	0	107 (46)	0
C(1)	44 (28)	170 (116)	233 (120)	0	85 (54)	0
C(2)	43 (24)	156 (93)	135 (81)	0	65 (40)	0
$CH_3(1)$	100 (28)	149 (78)	454 (130)	−55 (37)	199 (58)	−122 (73)
$CH_3(2)$	66 (20)	146 (74)	350 (105)	−41 (33)	124 (42)	−77 (65)

TABLE III

Parameters for the Ellipsoids of Vibration

	Rms amplitude, Å	Angle with—		
		a axis, deg	*b* axis, deg	*c* axis, deg
Sn(1)	0.197 (10)	120 (16)	90	15 (16)
	0.234 (9)	151 (16)	90	75 (16)
	0.237 (6)	90	0	90
Sn(2)	0.205 (8)	115 (22)	90	20 (22)
	0.232 (11)	155 (22)	90	70 (22)
	0.234 (7)	90	0	90
S(1)	0.22 (2)	80 (5)	90	55 (5)
	0.28 (2)	90	0	90
	0.32 (4)	170 (5)	90	35 (5)
S(2)	0.21 (2)	99 (80)	90	36 (80)
	0.24 (5)	171 (80)	90	54 (80)
	0.30 (2)	90	0	90
O	0.11 (21)	164 (61)	90	30 (61)
	0.17 (3)	106 (61)	90	120 (61)
	0.36 (4)	90	0	90
N(1)	0.17 (6)	90	0	90
	0.18 (6)	116 (18)	90	109 (18)
	0.32 (5)	154 (18)	90	19 (18)
N(2)	0.19 (31)	168 (47)	90	33 (47)
	0.23 (6)	90	0	90
	0.29 (4)	78 (47)	90	57 (47)
C(1)	0.17 (15)	177 (51)	90	43 (51)
	0.23 (8)	90	0	90
	0.27 (7)	87 (51)	90	48 (51)
C(2)	0.15 (36)	143 (65)	90	8 (65)
	0.22 (7)	90	0	90
	0.23 (5)	53 (65)	90	82 (65)
$CH_3(1)$	0.17 (43)	161 (197)	85 (319)	28 (57)
	0.18 (7)	101 (326)	160 (94)	94 (301)
	0.40 (4)	74 (18)	109 (8)	63 (17)
$CH_3(2)$	0.18 (6)	62 (33)	33 (28)	98 (27)
	0.24 (4)	28 (33)	115 (31)	140 (22)
	0.34 (5)	86 (20)	109 (16)	51 (21)

TABLE IV

Observed and Calculated Structure Factors

H	L	OBS	CALC
K=0			
2	1	84	83
2	2	66	-22
4	0	282	-242
4	2	152	148
4	3	166	169
4	4	47	50
4	5	121	-118
4	6	68	-65
4	8	54	56
6	0	272	-258
6	2	187	188
6	3	84	78
6	5	52	-53
10	0	121	114
10	2	100	-99
10	3	70	-68
10	5	72	53
12	0	79	80
16	0	73	-70
0	-2	292	-252
0	-3	283	-292
0	-5	170	162
0	-6	53	40
0	-8	58	-59
2	-2	73	-64
2	-3	217	-217
2	-5	105	101
2	-6	142	157
2	-8	98	-98
2	-9	61	-65
4	-3	121	110
4	-4	61	-53
4	-7	57	-48
6	-1	310	-276
6	-2	180	168
6	-3	425	444
6	-4	71	70
6	-5	222	-216
6	-6	226	-232
6	-8	87	93
8	-1	70	-62
8	-2	114	112
8	-5	133	-147
8	-6	165	-153
8	-8	89	86
8	-9	122	128

H	L	OBS	CALC
8	-11	54	-53
8	-12	47	-41
10	-1	105	102
10	-2	68	-67
10	-3	146	-145
10	-7	35	-36
12	-1	108	115
12	-2	69	-71
12	-3	165	-176
12	-4	175	-186
12	-5	146	143
12	-6	189	205
12	-7	67	68
12	-8	108	-99
12	-9	123	-114
14	-3	74	-79
14	-5	64	70
14	-6	76	71
14	-8	70	-68
14	-9	92	-77
14	-11	70	75
14	-12	64	64
16	-1	60	-64
16	-3	61	69
16	-4	65	67
16	-5	53	-54
18	-1	52	-38
18	-4	63	64
18	-6	96	-93
18	-7	57	-52
18	-8	69	74
18	-9	101	97
18	-11	56	-52
20	-6	54	-55
20	-9	55	63
20	-11	62	-53
20	-12	53	-50
20	-14	49	41
K=1			
1	0	327	362
1	1	132	145
1	2	107	-111
1	3	189	-196
1	5	45	47
1	6	44	44
3	0	41	-30
3	1	67	-59

H	L	OBS	CALC
3	2	131	143
3	3	110	110
3	5	83	-84
3	6	63	-65
5	0	207	-221
5	2	148	145
5	3	162	169
5	5	72	-73
5	6	62	-62
7	0	221	-229
7	2	77	79
7	3	66	67
9	0	76	83
9	2	42	-48
9	3	51	-51
11	0	138	137
11	2	69	-74
11	3	58	-62
1	-1	200	179
1	-2	222	-216
1	-3	210	-204
1	-4	44	-41
1	-5	165	162
1	-6	104	110
1	-8	70	-71
1	-9	64	-50
3	-3	77	-78
3	-4	95	-91
3	-5	96	95
3	-6	91	99
3	-8	87	-95
3	-9	60	-59
3	-11	65	44
5	-1	136	-136
5	-2	137	128
5	-3	192	194
5	-4	88	90
5	-5	129	-149
5	-6	109	-112
7	-1	142	-148
7	-2	115	140
7	-3	278	270
7	-4	94	95
7	-5	233	-223
7	-6	185	-185
7	-8	129	149
7	-9	78	77

H	L	OBS	CALC
7	-11	59	-43
9	-1	39	32
9	-3	37	-35
9	-6	111	-108
9	-8	76	72
9	-9	91	94
9	-11	66	-64
9	-12	55	-34
11	-1	75	77
11	-2	51	-55
11	-3	173	-172
11	-4	95	-90
11	-5	88	82
11	-6	92	95
11	-7	49	55
11	-8	42	-42
11	-9	39	-35
13	-1	76	76
13	-3	163	-173
13	-4	121	-118
13	-5	97	97
13	-6	233	210
13	-7	48	51
13	-8	106	-112
13	-9	117	-114
13	-11	91	84
15	-6	33	26
15	-9	56	-56
15	-11	54	36
15	-12	53	53
17	-3	83	87
17	-4	91	58
17	-6	76	-74
17	-8	58	45
17	-9	51	54
19	-4	55	64
19	-6	88	-76
19	-7	52	-49
19	-9	131	121
19	-11	82	-72
19	-12	65	-63
K=2			
0	0	368	462
0	4	38	-34
2	1	90	76
2	4	40	-42

H	L	OBS	CALC
4	0	151	-146
4	1	58	-42
4	2	98	98
4	3	173	170
4	4	54	56
4	5	115	-113
4	6	61	-64
4	8	56	52
6	0	226	-219
6	1	52	-48
6	2	169	165
6	3	75	80
6	5	54	-52
8	5	32	33
10	0	114	119
10	1	51	54
10	2	89	-96
10	3	68	-67
10	5	42	49
12	0	77	73
16	0	71	-64
16	1	52	7
0	-1	107	106
0	-2	101	-115
0	-3	273	-250
0	-5	156	143
0	-8	60	-57
2	-1	49	39
2	-3	165	-174
2	-5	81	84
2	-6	144	150
2	-8	93	-91
2	-9	64	-60
2	-11	60	43
4	-1	115	88
4	-2	89	-67
4	-7	54	-52
6	-1	176	-172
6	-2	139	127
6	-3	330	305
6	-4	71	78
6	-5	151	-140
6	-6	212	-210
6	-9	50	49
8	-1	92	-92
8	-2	99	88

H	L	OBS	CALC
8	-3	50	53
8	-4	71	65
8	-5	142	-137
8	-6	147	-145
6	-8	84	85
8	-8	76	81
8	-9	107	113
10	-1	60	60
10	-2	91	-89
10	-3	81	-74
10	-7	56	-5
12	-1	104	110
12	-2	59	-61
12	-3	167	-160
12	-4	181	-164
12	-5	127	124
12	-6	212	183
12	-7	70	67
12	-8	87	-87
12	-9	113	-108
12	-11	48	46
14	-3	67	-72
14	-4	61	-58
14	-5	63	63
14	-6	107	108
14	-8	101	-93
14	-9	75	-75
14	-11	76	71
14	-12	60	54
16	-1	62	-61
16	-3	66	68
16	-4	44	50
16	-5	51	-53
18	-3	54	62
18	-4	65	70
18	-6	90	-98
18	-7	69	-66
18	-8	75	75
18	-9	115	104
18	-11	53	-57
20	-6	53	-56
20	-9	77	78
20	-11	72	-64
K=3			
1	0	297	260
1	1	95	102

H	L	OBS	CALC
1	2	88	-92
1	3	160	-135
3	1	44	-49
3	2	104	96
3	3	94	89
3	5	65	-70
3	6	53	-53
5	0	236	-183
5	2	142	121
5	3	136	137
5	5	71	-64
5	6	65	-51
7	0	212	-175
7	2	64	60
7	3	51	53
9	0	71	71
9	2	49	-42
9	3	59	-42
11	0	98	114
11	2	56	-63
11	3	51	-52
17	0	48	-46
1	-1	123	134
1	-2	152	-163
1	-3	180	-174
1	-4	37	-33
1	-5	139	137
1	-6	91	93
1	-8	58	-60
1	-9	50	-40
3	-3	69	-63
3	-4	69	-65
3	-5	82	79
3	-6	75	78
3	-8	71	-77
3	-9	59	-48
5	-1	143	-107
5	-2	130	102
5	-3	166	157
5	-4	73	73
5	-5	96	-102
5	-6	83	-91
7	-1	136	-112
7	-2	107	90
7	-3	234	213
7	-4	80	82

H	L	OBS	CALC
7	-5	170	-171
7	-6	146	-153
7	-8	104	109
7	-9	54	65
9	-6	79	-83
9	-8	60	58
9	-9	78	76
11	-1	62	67
11	-2	38	-43
11	-3	117	-138
11	-4	68	-71
11	-5	57	67
11	-6	97	83
11	-8	40	-38
11	-9	37	-32
13	-1	53	59
13	-3	137	-133
13	-4	105	-94
13	-5	87	75
13	-6	199	169
13	-7	40	42
13	-8	95	-94
13	-9	101	-95
13	-11	73	69
13	-12	45	37
15	-9	49	-46
15	-11	51	44
15	-12	52	44
17	-1	51	-52
17	-3	73	71
17	-4	47	47
17	-6	67	-61
17	-9	53	45
19	-4	51	49
19	-6	79	-78
19	-7	52	-42
19	-9	113	99
19	-11	59	-59
19	-12	57	-51
K=4			
0	0	357	366
0	6	46	30
2	0	82	66
2	1	53	38
4	0	170	-142
4	2	101	94

H	L	OBS	CALC
4	3	108	108
4	4	38	29
4	5	79	-80
4	6	46	-45
4	8	38	39
6	0	199	-164
6	2	134	118
6	3	56	52
6	5	48	-38
10	0	82	77
10	2	73	-67
10	3	62	-47
12	0	59	58
0	-1	72	75
0	-2	156	-145
0	-3	178	-180
0	-5	102	106
2	-1	46	40
2	-2	48	-50
2	-3	144	-134
2	-5	69	74
2	-6	122	107
2	-8	63	-66
2	-9	54	-44
4	-3	65	65
6	-1	197	-154
6	-2	119	102
6	-3	306	255
6	-4	47	51
6	-5	145	-129
6	-6	157	-145
6	-8	58	63
8	-1	46	-39
8	-2	91	65
8	-3	38	24
8	-4	46	42
8	-5	81	-78
8	-6	97	-100
8	-8	55	61
8	-9	79	87
8	-11	39	-39
10	-1	81	70
10	-2	42	-37
10	-3	92	-87
12	-1	84	79
12	-2	51	-45

H	L	OBS	CALC
12	-3	120	-115
12	-4	109	-112
12	-5	90	94
12	-6	137	134
12	-7	48	42
12	-8	65	-69
12	-9	72	-78
14	-3	48	-50
14	-5	40	45
14	-6	44	48
14	-7	37	29
14	-8	57	-48
14	-9	43	-56
16	-1	46	-41
16	-3	46	48
18	-3	48	54
18	-6	61	-66
18	-7	43	-36
18	-8	53	49
18	-9	59	65
K=5			
1	0	142	157
1	1	50	59
1	2	55	-63
1	3	92	-97
3	2	59	52
3	3	50	52
3	5	50	-44
3	6	40	-37
5	0	146	-116
5	2	86	75
5	3	96	90
5	5	53	-46
7	0	128	-116
7	2	45	41
11	0	93	79
11	2	66	-45
11	3	60	-37
13	0	33	26
1	-1	72	76
1	-2	83	-103
1	-3	92	-109
1	-5	68	87
1	-6	60	66
3	-2	36	-15
3	-3	42	-37

H	L	OBS	CALC
3	-5	54	51
3	-6	54	55
3	-8	53	-51
3	-9	42	-33
5	-1	88	-70
5	-2	71	66
5	-3	117	102
5	-4	40	42
5	-5	67	-61
5	-6	53	-53
7	-1	79	-72
7	-2	64	63
7	-3	151	139
7	-4	54	52
7	-5	115	-105
7	-6	109	-97
7	-8	70	72
7	-9	50	47
9	-6	52	-55
11	-1	63	48
11	-3	111	-90
11	-4	50	-43
11	-5	51	49
11	-6	62	54
13	-1	49	46
13	-3	112	-93
13	-4	60	-61
13	-5	56	55
13	-6	115	111
13	-8	59	-63
13	-9	68	-68
19	-6	57	-59
19	-9	65	68
19	-11	48	-41
K=6			
0	0	182	163
4	0	70	-65
4	2	48	44
4	3	73	76
4	5	55	-55
4	6	38	-31
6	0	109	-96
6	2	69	70
10	0	60	57
10	2	57	-46
12	0	48	37

H	L	OBS	CALC
0	-1	47	44
0	-2	64	-55
0	-3	120	-106
0	-5	68	64
2	-3	80	-76
2	-5	45	45
2	-6	78	73
6	-1	74	-69
6	-2	56	56
6	-3	132	127
6	-5	59	-57
6	-6	64	-89
8	-5	45	-56
8	-6	59	-66
8	-8	51	42
8	-9	52	53
12	-1	62	53
12	-3	85	-72
12	-4	71	-67
12	-5	50	57
12	-6	85	83
12	-9	48	-52
K=7			
1	0	80	85
5	0	73	-72
5	3	51	53
7	0	59	-60
11	0	51	47
1	-2	58	-55
1	-3	59	-70
5	-1	47	-37
5	-3	56	62
7	-3	78	79
7	-5	52	-58
7	-6	50	-60
11	-1	50	32
11	-3	62	-51
11	-5	48	29
13	-3	47	-46
13	-6	67	64
K=8			
0	0	98	101
6	0	53	-52
0	-2	54	-45
0	-3	55	-55
6	-3	80	78

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[10] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

Discussion

The dimeric molecule with $2/m$ symmetry is shown in Figure 1. The individual bond distances and angles are shown in Table V and are compared to those found in other related compounds in Table VI. The molecule contains a central planar four-membered $Sn(2)_2O_2$ ring. The Sn(2)–O distances are 1.99 (3) Å for the equatorial bond and 2.15 (4) Å for the axial bond of the endocyclic pentacoordinated tin. Neither differs much from the sum of covalent radii or from the distances of 2.10 (1) and 2.11 (1) Å found in $(CH_3)_2Sn(C_9H_6NO)_2$.[11] In dimeric $[((CH_3)_2SnOSi(CH_3)_3)_2O]_2$, the Sn–O distances of the central ring are 2.2 and 2.8 Å and the difference between them is 0.6 Å.[4] One might consider the 2.8-Å Sn–O bond to be a weak donor–acceptor bond and hence regard this molecule as formed from two recognizable monomers. However in the present structure, the difference between the two Sn–O distances is only 0.16 (5) Å. We would rather believe that this is caused by the difference of the equatorial and axial covalent bonding in the trigonal-bipyramidal geometry, and hence no monomeric part can be identified. The angles for the very distorted trigonal-bipyramidal pentacoordinated Sn(2) are quite different from those in most trimethyltin derivatives. The exocyclic Sn(1)–O distance 2.05 (5) Å is equal to the sum of the single-bond covalent radii. Secondary bonding between the isothiocyanate nitro-

Table V

Selected Interatomic Distances (Å) and Angles (deg) in $[((CH_3)_2SnNCS)_2O]_2$

Sn(1)–O	2.05 (5)	Sn(2)–O	1.99 (3)
			2.15 (4)
Sn(1)–N(1)	2.06 (4)	Sn(2)–N(2)	2.39 (8)
Sn(1)–N(2)	2.84 (4)	Sn(2)–N(1)	3.51 (3)
Sn(1)–CH_3(1)	2.07 (3)	Sn(2)–CH_3(2)	2.15 (3)
N(1)–C(1)	1.17 (7)	N(2)–C(2)	1.10 (7)
C(1)–S(1)	1.61 (6)	C(2)–S(2)	1.64 (5)
N(1)–Sn(1)–O	91 (1)	Sn(1)–O–Sn(2)	124 (1)
N(2)–Sn(1)–O	69 (2)	CH_3(2)–Sn(2)–O	110 (1)
N(1)–Sn(1)–S(2)[a]	75 (1)	CH_3(2)–Sn(2)–CH_3(2)	140 (2)
N(2)–Sn(1)–S(2)[a]	125 (2)	N(2)–Sn(2)–O	156 (1)
CH_3(1)–Sn(1)–CH_3(1)	141 (4)	Sn(2)–N(2)–C(2)	142 (7)
Sn(1)–N(1)–C(1)	169 (3)	N(2)–C(2)–S(2)	180 (8)
N(1)–C(1)–S(1)	177 (4)	Sn(2)–O–Sn(2)	105 (2)

[a] Sulfur atom of adjacent molecule.

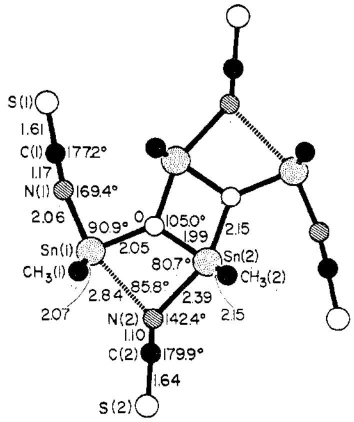

Figure 1.—Molecular structure of $[((CH_3)_2SnNCS)_2O]_2$.

Table VI

Interatomic Distances (Å) and Angles (deg) for $[((CH_3)_2SnNCS)_2O]_2$ and Related Compounds

Atoms	Compd	Value	Ref
	Distances		
Sn–O	$[((CH_3)_2SnNCS)_2O]_2$	1.99 (3)	*a*
		2.15 (4)	
		2.05 (5)	
	$[((CH_3)_2SnOSi(CH_3)_3)_2O]_2$	2.2	*b*
		2.8	
	$(CH_3)_2Sn(C_9H_6NO)_2$	2.11 (1)	*c*
		2.10 (1)	
Sn–N	$[((CH_3)_2SnNCS)_2O]_2$	2.06 (4)	*a*
		2.39 (8)	
		2.84 (4)	
	$(CH_3)_2Sn(NCS)_2$	2.10 (2)	*d*
	$(CH_3)_3SnNCS$	2.15 (6)	*e*
N–C	$[((CH_3)_2SnNCS)_2O]_2$	1.10 (7)	*a*
		1.17 (7)	
	$(CH_3)_3SnNCS$	1.15 (7)	*e*
	$(CH_3)_2Sn(NCS)_2$	1.15 (5)	*d*
	Some other isothiocyanates and bridged thiocyanates	1.07–1.3	*f–h*
C–S	$[((CH_3)_2SnNCS)_2O]_2$	1.61 (6)	*a*
		1.64 (5)	
	$(CH_3)_3SnNCS$	1.64 (7)	*e*
	$(CH_3)_2Sn(NCS)_2$	1.60 (4)	*d*
	Some other isothiocyanates and bridged thiocyanates	1.55–1.80	*f–h*
Sn–S	$[((CH_3)_2SnNCS)_2O]_2$	3.33 (3)	*a*
	$(CH_3)_3SnNCS$	3.12 (2)	*e*
	$(CH_3)_2Sn(NCS)_2$	3.21 (1)	*d*
	Sum of van der Waals radii[k]	4.05	
Sn–CH_3	$[((CH_3)_2SnNCS)_2O]_2$	2.07 (3)	*a*
		2.15 (3)	
	$(CH_3)_3SnNCS$	2.15 (5)	*e*
		2.15 (6)	
	$(CH_3)_2Sn(NCS)_2$	2.14 (3)	*d*
	$(CH_3)_2Sn(CN)_2$	2.11 (5)	*i*
	$(CH_3)_2SnF_2$	2.06 (1)	*j*
	Angles		
O–Sn–N	$[((CH_3)_2SnNCS)_2O]_2$	91 (1)	*a*
		81 (2)	
N–Sn–N	$(CH_3)_2Sn(NCS)_2$	84.1 (1.6)	*d*
NC–Sn–CN	$(CH_3)_2Sn(CN)_2$	85.3 (3.7)	*i*
CH_3–Sn–CH_3	$[((CH_3)_2SnNCS)_2O]_2$	141 (4)	*a*
		140 (2)	
	$(CH_3)_2Sn(NCS)_2$	145.9 (1.4)	*d*
	$(CH_3)_2Sn(CN)_2$	148.7 (3.5)	*i*
Sn–N–C	$[((CH_3)_2SnNCS)_2O]_2$	169 (3)	*a*
		142 (7)	
	$(CH_3)_2Sn(NCS)_2$	168.2 (2.6)	*d*
	$(CH_3)_3SnNCS$	173 (5)	*e*
M–N–C	Some other isothiocyanates and bridged thiocyanates	111–180	*f–h*
N–C–S	$[((CH_3)_2SnNCS)_2O]_2$	177 (4)	*a*
		180 (8)	
	$(CH_3)_2Sn(NCS)_2$	179.3 (2.8)	*d*
	$(CH_3)_3SnNCS$	175 (6)	*e*
Sn–S–C	$[((CH_3)_2SnNCS)_2O]_2$	103 (3)	*a*
	$(CH_3)_2Sn(NCS)_2$	90.7 (1.1)	*d*
	$(CH_3)_3SnNCS$	97 (2)	*e*

[a] This work. [b] Reference 4. [c] Reference 11. [d] Reference 6. [e] R. A. Forder and G. M. Sheldrick, *J. Organometal. Chem.*, **21**, 115 (1970). [f] A. Ferrari and A. Braibanti, *Acta Crystallogr.*, **18**, 367 (1965). [g] J. R. Knox and K. Eriks, *Inorg. Chem.*, **7**, 84 (1968). [h] A. C. Hazell, *J. Chem. Soc.*, 5745 (1963). [i] J. Konnert and D. Britton, unpublished work. [j] E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, **5**, 995 (1966). [k] van der Waals radius of Sn was estimated to be 2.20 Å.

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(11) E. O. Schlemper, *Inorg. Chem.*, **6**, 2012 (1967).

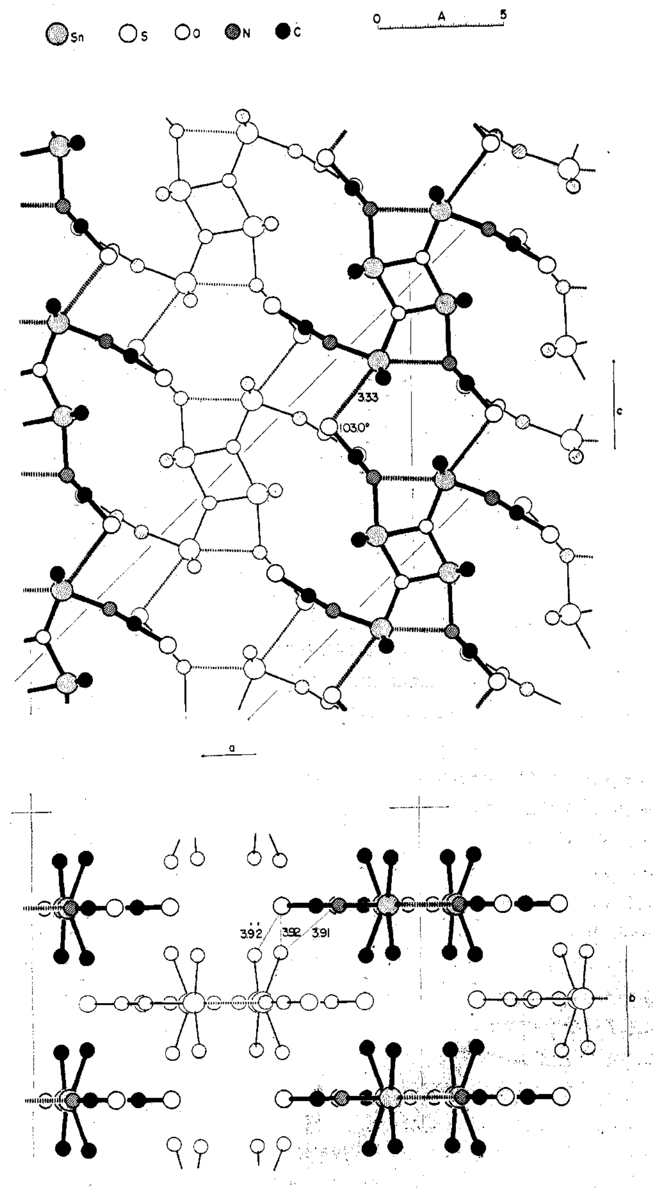
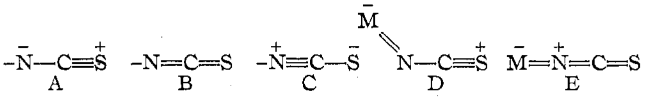


Figure 2.—Packing of molecules within the crystal: top, view along *b* axis; bottom, view along *c** axis.

gens N(2) of endocyclic Sn(2) atoms and the exocyclic Sn(1) atoms forms two additional planar Sn(2)O–Sn(1)···N(2) rings within the dimeric molecule. The large Sn(2)–N(2) distance of 2.39 Å and the small O–Sn(2)–N(2) angle of 80.7° lead us to believe that the Sn(1)–N(2) distance of 2.89 Å is not just an accidentally short intramolecular distance but in fact reflects an energetically favorable interaction. Still further the intermolecular Sn(1)···S(2) interaction results in distorted octahedral hexacoordination for the exocyclic Sn(1) atom and a polymeric crystal structure. The bond lengths and angles of the hexacoordinated Sn(1) are similar to that in dimethyltin dicyanide and dimethyltin diisothiocyanate and are different from that in regular octahedrally coordinated tin in dimethyltin difluoride.[12]

The isothiocyanate groups are different in the present structure. The NCS(1) coordinates terminally to a hexacoordinated tin. The NCS(2) is not only bonded to a pentacoordinated tin, but also provides a nitrogen bridge to a hexacoordinated tin in the dimer and a sulfur bridge to another hexacoordinated tin of the adjacent molecule. Comparing the C–N and C–S distances with those in dimethyltin diisothiocyanate and other isothiocyanates, nothing unusual is found. If the following five resonance forms are considered for the bound NCS group, form A favors N as the electron donor and



$$\underset{\text{A}}{-\overset{-}{\text{N}}-\text{C}\equiv\overset{+}{\text{S}}}\quad \underset{\text{B}}{-\text{N}=\text{C}=\text{S}}\quad \underset{\text{C}}{-\overset{+}{\text{N}}\equiv\text{C}-\overset{-}{\text{S}}}\quad \underset{\text{D}}{\overset{\overset{\overset{-}{\text{M}}}{\diagdown}}{\text{N}}-\text{C}\equiv\overset{+}{\text{S}}}\quad \underset{\text{E}}{\overset{-}{\text{M}}=\overset{+}{\text{N}}=\text{C}=\text{S}}$$

would result in lowering of the C–N stretching frequency, and form C favors S as the electron donor and would increase the C–N stretching frequency. These two resonance forms apparently compensate the effect of each other. The lowering of the C–N stretching frequency in CCl_4 solution could be interpreted as indicating lack of sulfur intermolecular bridging in solution. Because of the large uncertainties the differences in bond distances within NCS(1) and NCS(2) cannot be considered as significant. If the lower C–N stretching frequency is assigned to the NCS group with longer C–N distance, then it corresponds with C(1)–N(1) which is a nonbridging group.

The crystal structure is shown in Figure 2. The presence of the intermolecular donor–acceptor bonding between sulfur atoms in one molecule and the tin atoms in the adjacent molecules leads to the formation of infinite chains along the *c* axis. The 3.33 (3) Å Sn(1)–S(2) distance is slightly longer than that in dimethyltin diisothiocyanate and trimethyltin isothiocyanate. Perhaps the presence of the nitrogen bridging weakens this interaction. There is no indication of any interaction other than van der Waals between nearest chains.

In some aspects this structure is different from what was predicated from the infrared spectra of the ethyl, propyl, and butyl compounds. The similarity of the C–N stretching frequencies in solid and solution of other distannoxanes may suggest the absence of intermolecular bridging through the sulfur atoms in their crystal packing.

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(12) E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, **5**, 995 (1966).