The Crystal and Molecular Structure of Dimethyltin Bis(*N,N*-dimethyldithiocarbamate)

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The crystal and molecular structure of dimethyltin bis(*N,N*-dimethyldithiocarbamate), $[(CH_3)_2Sn\{S_2CN(CH_3)_2\}_2]$, has been determined by single crystal X-ray diffraction. The crystals are orthorhombic; *Fdd*2; $a=25.478\pm0.008$, $b=35.323\pm0.011$, $c=6.936\pm0.006$ Å, $Z=16$. The tin atom has a distorted octahedral environment. The tin atom and the four sulfur atoms lie approximately on the same plane, with two Sn–S bond distances of 2.515 ± 0.008 and 2.497 ± 0.008 Å and two longer Sn–S distances of 2.954 ± 0.007 and 3.061 ± 0.008 Å, while the methyl groups are in *trans* positions; average Sn–C$=2.15\pm0.04$ Å. The SnSC(S)N skeletons on both sides of the tin atom are approximately planar, and the average bond distances are S–C$=1.72\pm0.03$, C–N$=1.31\pm0.03$, and N–C(Me)$=1.49\pm0.04$ Å.

Many structural investigations have been reported on transition metal complexes of dialkyldithiocarbamates. Most of them have a typical octahedral structure. On the other hand, only a few structures of non-transition metal complexes have been reported.[1]

As a part of the structural studies of organotin compounds, we have recently reported[2] the crystal and molecular structure of dimethyltin chloride *N,N*-dimethyldithiocarbamate (to be abbreviated as Me_2Sn-Cl(dtc) hereafter). It has been found that the coordination around the tin atom is a distorted trigonal bipyramid, the two methyl groups being in equatorial positions.

Dimethyltin bis(*N,N*-dimethyldithiocarbamate)(to be abbreviated as $Me_2Sn(dtc)_2$ hereafter) is the *N,N*-dimethyldithiocarbamate substitute for $Me_2SnCl(dtc)$, and this complex must have a hexa-coordinated structure. IR and PMR investigations[3] have shown that the complex has a distorted octahedral configuration, the two methyl groups being in *trans* positions. In order to determine the exact configuration, crystal structure analysis has been undertaken by means of X-rays.

The present investigation will also contribute to the understanding of the bonding nature of the tin atom in penta- and hexa-coordinated dimethyltin complexes. Schlemper has determined the structure of dimethyltin bis(8-hydroxyquinolinate);[4] he found that the Me–Sn–Me angle ($110.7\pm0.8°$) is remarkably close to the tetrahedral angle. With the aid of a qualitative MO approach, he proposed that the bonding could involve sp^3 hybrid orbitals on the tin participating in the methyl groups and three-center bonds in the oxinate groups. It would be very interesting to determine whether the structure of $Me_2Sn(dtc)_2$ can be understood in terms of such a bonding scheme or not.

Experimental

The crystals were recrystallized from a chloroform-ethanol solution to form colorless needles elongated along the *c* axis.

Approximate unit-cell dimensions were obtained from osillation and Weissenberg photographs taken around the *c* axis, while the accurate cell dimensions were determined on a Rigaku automated four-circle diffractometer.

Crystal Data. $C_8H_{18}N_2S_4Sn$, *F.W.*$=389.1$, orthorhombic, $a=25.478\pm0.008$, $b=35.323\pm0.011$, and $c=6.936\pm0.006$ Å, $U=6242$ Å^3, $D_m=1.650$ and $D_x=1.656$ g·cm^{-3} for $Z=16$. The systematic absences (*hkl*: $h+k\neq2n$, $k+l\neq2n$; 0*kl*: $k+l\neq4n$: *h*0*l*: $h+l\neq4n$; *hk*0: $h\neq2n$, $k\neq2n$; *h*00: $h\neq4n$; 0*k*0: $k\neq4n$, and 00*l*: $l\neq4n$) uniquely define the space group as *Fdd*2.

The three-dimensional intensity data for $2\theta\leqq45°$ were collected on the diffractometer at room temperature, using Zr-filtered Mo$K\alpha$ radiation. The integrated intensity was recorded by the ω-2θ scan technique:

Range of scan (in 2θ)$=(2.0+0.70\tan\theta_c)°$ and

Starting angle of the scan$=(2\theta_c-1.0)°$,

where θ_c is the calculated value of the Bragg angle for $\lambda(\text{Mo}K\alpha_1)=0.70926$ Å. At each end of the scan, the background counts were measured for 10 sec by the stationary crystal-stationary counter technique. The intensity data were corrected for the background counts and for the usual Lorentz and polarization effects. No absorption correction was applied, since the linear absorption coefficient is not very large ($\mu=21.1$ cm^{-1} for Mo$K\alpha$). Finally, two sets of 1143 independent reflections, $F(hkl)$'s and $F(\bar{h}k\bar{l})$'s, were collected in order to consider the anomalous dispersion effect.

Determination and Refinement of the Structure

The initial coordinates of the tin atom were easily determined from the three-dimensional Patterson function computed by using $F(hkl)$'s. The four sulfur atoms could also be located from the Patterson and the minimum function, but two of them were located about 3.0 Å from the tin atom. The first Fourier synthesis was computed with the phases based on the tin atom only, and the four sulfur atoms were found at the positions expected from the Patterson function. The two nitrogen atoms and the four carbon atoms were then found in the Fourier map with the phases based on the tin and the four sulfur atoms. The

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3) M. Honda, M. Komura, Y. Kawasaki, T. Tanaka, and R. Okawara, *J. Inorg. Nucl. Chem.*, **30**, 3231 (1968).

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

remaining four carbon atoms were found in the successive Fourier maps. At this stage, the structure factor calculation gave a discrepancy facor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, of 0.20 for the $F(hkl)$ reflections. The atomic-scattering factors used were taken from those of Hanson and his co-workers.[5]

The block-diagonal least-squares refinement was carried out on a HITAC 5020E computer at the University of Tokyo, and also on a FACOM 230-60 computer at the Kyoto University, with a program, HBLS IV, written by Dr. T. Ashida.[6] Eight cycles of the refinement with isotropic temperature factors for all non-hydrogen atoms gave the R value of 0.17 for a set of $F(hkl)$ data. The anisotropic temperature factors for all non-hydrogen atoms were then introduced, and three cycles of the refinement reduced the R value to 0.095.

At this stage, the corrections for the anomalous dispersion effect were introduced for the tin and the sulfur atoms (for Mo$K\alpha$, $\Delta f'=-0.60$, $\Delta f''=1.90$ for Sn, and $\Delta f'=0.1$, $\Delta f''=0.2$ for S).[7]

The structure was refined using the combined data of $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ by starting from the coordinates representing the molecules of one direction of the polar axis and also from those of the opposite direction. Through refinement, the following weighting scheme was applied;

$$w = 1 \quad \text{for } F_o > 0$$
$$w = 0.2 \quad \text{for } F_o = 0$$

After several cycles, the refinement converged; the values of the R and the residual (defined as $\sum w(|F_o|-|F_c|)^2$) were 0.089 and 7385, respectively, for the coordinates representing the molecules of one direction of the polar axis, while those of the opposite direction were 0.092 and 7638. The relatively small values of the correction for the anomalous scattering of Sn and S atoms might have given such a small difference. This difference might not be significant, but the former structure was chosen as the final result only because it gave the smaller discrepancy. All of the coordinates of this structure are in good agreement with those of the opposite structure within the range of the estimated

TABLE 1. (a) THE FINAL ATOMIC COORDINATES ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
Sn	0.06259(6)	0.08391(4)	0.0000(5)
S(1)	0.00683(24)	0.12223(16)	0.22686(10)
S(2)	0.05927(25)	0.03688(17)	0.2686(10)
S(3)	0.11276(25)	0.01039(17)	−0.0849(9)
S(4)	0.03680(24)	0.16488(19)	−0.1253(11)
N(1)	0.1024(6)	−0.0313(4)	0.232(3)
N(2)	−0.0229(6)	0.1915(4)	0.155(3)
C(1)	0.0917(8)	0.0012(6)	0.147(3)
C(2)	0.0049(8)	0.1635(6)	0.087(3)
C(3)	0.1291(9)	−0.0627(6)	0.133(4)
C(4)	0.0840(9)	−0.0387(7)	0.433(4)
C(5)	−0.0553(10)	0.1887(8)	0.334(5)
C(6)	−0.0218(10)	0.2294(7)	0.055(5)
C(10)	0.0081(10)	0.0692(8)	−0.227(4)
C(20)	0.1406(7)	0.1052(7)	0.017(5)

(b) THE ANISOTROPIC THERMAL PARAMETERS (EACH MULTIPLIED BY 10^4) OF THE FORM:
$\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	14	9	162	−1	7	−1
S(1)	22	9	186	0	35	9
S(2)	24	10	182	4	40	−1
S(3)	23	9	172	4	46	−10
S(4)	18	12	234	0	35	4
N(1)	17	6	217	1	−22	3
N(2)	15	6	291	0	−39	−9
C(1)	16	8	208	1	−7	11
C(2)	13	8	199	−3	−5	−18
C(3)	26	7	318	−1	81	−39
C(4)	20	10	259	−2	18	15
C(5)	25	15	416	10	114	−22
C(6)	23	9	446	4	25	38
C(10)	22	16	204	7	−40	−6
C(20)	9	13	406	1	12	24

TABLE 3. GEOMETRY AROUND THE TIN ATOM (a) BOND DISTANCES AND ANGLES ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES.

Bond distance (Å)		Bond angle (°)	
Sn–S(1)	2.515(8)	S(1)–Sn–S(2)	82.7(0.3)
Sn–S(2)	2.497(8)	S(1)–Sn–S(4)	63.5(0.2)
Sn–S(3)	2.954(7)	S(1)–Sn–C(10)	102.8(0.8)
Sn–S(4)	3.061(8)	S(1)–Sn–C(20)	108 (1)
Sn–C(10)	2.16 (3)	S(2)–Sn–S(3)	65.1(0.2)
Sn–C(20)	2.13 (4)	S(2)–Sn–C(10)	111.1(0.8)
		S(2)–Sn–C(20)	103 (1)
		S(3)–Sn–S(1)	147.4(0.3)
		S(2)–Sn–S(4)	145.7(0.3)
		S(3)–Sn–S(4)	149.1(0.2)
		S(3)–Sn–C(10)	85.5(0.8)
		S(3)–Sn–C(20)	85 (1)
		S(4)–Sn–C(10)	83.1(0.8)
		S(4)–Sn–C(20)	83 (1)
		C(10)–Sn–C(20)	136 (1)

(b) THE LEAST-SQUARES PLANE OF THE FIVE ATOMS, Sn, S(1), S(2), S(3), and S(4):
$-0.84637x-0.34451y-0.40615z+2.38101=0$,
Deviations from the least-squares plane (Å):

Sn	0.010
S(1)	0.107
S(2)	−0.103
S(3)	0.062
S(4)	−0.066

Angle between the least-squares plane and the Sn–C(10) bond: 67.3°,
Angle between the least-squares plane and the Sn–C(20) bond: 69.1°.

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6) "Universal Crystallographic Computation Program System," ed. by Tosio Sakurai, Crystallographic Society of Japan, Tokyo (1967).

7) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham 1962, p. 214.

standard deviations.

The final atomic coordinates and the anisotropic thermal parameters obtained by using the combined data are listed in Table 1. The observed and calculated structure factors are listed in Table 2.[8]

Results and Discussion

The Geometry Around the Tin Atom. The molecular structure and the numbering system of $Me_2Sn(dtc)_2$ are shown in Fig. 1. The bond distances and angles around the tin atom are given in Table 3.

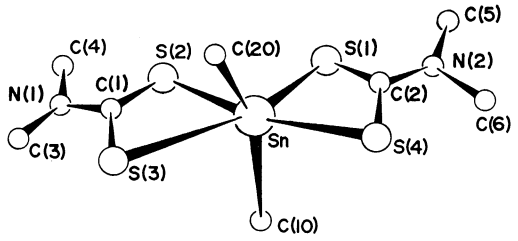

Fig. 1. Molecular structure of dimethyltin bis(*N*,*N*-dimethyldithiocarbamate) with the numbering of atoms.

The configuration about the tin atom could be described as a hexa-coordinated octahedron, with the two methyl groups attached to the tin atom in the *trans* positions. This configuration would be in agreement with the proposed structure. However this description would not correspond to that of the bonding nature.

It may be easily concluded by an inspection of Table 4, which lists the sulfur-metal bond distances and angles in some of the transition and non-transition metal complexes of dithiocarbamates, that there is a remarkable difference between them. In the transition metal complexes, all the sulfur-metal bond distances are almost equal, while there are two kinds of bond distances in the non-transition metal complexes.

In the present compound, the Sn–S(1) and Sn–S(2) bond distances (2.525(8) and 2.497(8) Å) are slightly longer than the sum of the covalent radii of Sn and S(2.44 Å);[22] they are nearly equal to those in $Me_3Sn(dtc)$[20,21] (2.47(1) Å) and the equatorial Sn–S bond in $Me_2SnCl(dtc)$[2] (2.48(1) Å). On the other hand, the Sn–S(3) and Sn–S(4) distances (2.954(7) and 3.061(8) Å) are significantly longer than the Sn–S(1) and Sn–S(2) bonds. These bonds might be considered as weak coordination bonds. Such weak metal-sulfur bonds have been found in other tin and arsenic complexes, but not in transition metal complexes. These facts suggest, that the bonding nature of the tin atom in the present complex is quite different from those in transition metal complexes. Furthermore, the C–Sn–C angle of 136(1)° shows an appreciable deviation from

Table 4. Metal-sulfur bond distances and angles in some metal dithiocarbamates

Compound	M–S (Å)		∠S–M–S (°)	Ref.
$Fe(NO)(S_2CNEt_2)_2$	2.295(2)	2.298(2)	76.2(1)	9)
	2.394(2)	2.308(2)	75.8(1)	
$Co(S_2CNEt_2)_3$	2.255(3)	2.255(3)	76.8(2)	10)
	2.258(2)	2.260(3)	75.9(1)	
$Ni(S_2CNH_2)_2$	2.207(7)	2.224(15)	78.6(3)	11)
	2.210(7)	2.218(15)	78.4(2)	
$Ni(S_2CNEt_2)_2$	2.195(2)	2.207(2)	79.2(2)	12)
$(Cu(S_2CNEt_2)_2)_2$	2.297(2)	2.317(2)	77.3(2)[a]	13)
$(Cd(S_2CNEt_2)_2)_2$	2.547(4)	2.594(3)	70.9(1)[a]	14)
$(Zn(S_2CNMe_2)_2)_2$	2.333(6)	2.429(6)	76.4(2)[a]	15)
$(Zn(S_2CNEt_2)_2)_2$	2.355(3)	2.443(3)	75.8(2)[a]	16)
$Zn(S_2CNMe_2)_2(C_5H_5N)$	2.330(4)	2.598(4)	73.4(3)	17)
	2.325(4)	2.612(4)	72.9(3)	
$PhAs(S_2CNEt_2)_2$	2.330(6)	2.911(6)	67.8(2)	18)
	2.322(6)	2.835(6)	69.1(2)	
$As(S_2CNEt_2)_3$	2.351(3)	2.903(4)		19)
	2.336(2)	2.820(3)		
	2.358(3)	2.810(3)		
$Me_3Sn(S_2CNMe_2)$				
monoclinic	2.47(1)	3.16(1)	62(1)	20)
orthorhombic	2.47(1)	3.16(3)	63(1)	21)
	2.47(1)	3.33(1)	60(1)	
$Me_2SnCl(S_2CNMe_2)$	2.48(1)	2.79(1)	68.2(3)	2)
$Me_2Sn(S_2CNMe_2)_2$	2.515(8)	3.061(8)	63.5(2)	b)
	2.497(8)	2.954(7)	65.1(2)	

a) The metal-sulfur bonds in which the sulfur atom bridges between two metal atoms are omitted.
b) present work

Table 5. The PMR coupling constants, $J(^{119}Sn–CH_3)$, and the C–Sn–C bond angles in some dimethyltin compounds

Complex	$J(^{119}Sn–CH_3)$ (*cps*)	Ref.	∠C–Sn–C(°)	Ref.
$Me_2Sn(C_9H_6NO)_2$	71.5	22)	110.7	4)
$Me_2SnCl(dtc)$	74.0	3)	128	2)
$Me_2Sn(dtc)_2$	84.0	3)	136.5	present work
$Me_2SnCl_2 \cdot Me_2SO$	86	23)	172	25)

8) Table 2 which gives a complete list of the observed and the calculated structure factors has been submitted to, and is kept as Document No. 7205 by, the office of the Bulletin of the Chemical Society of Japan, 1-5 Kanda-Surugadai, Chiyoda-ku, Tokyo. A copy may be secured by citing the Document number and by remitting, in advance, ¥300 for photo prints. Pay by check or money order payable to: Chemical Society of Japan.

22) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell Univ. Press, Ithaca 1960, p. 246.

9) G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc., A*, **1970**, 1275.
10) S. Merlino, *Acta Crystallogr.*, **B24**, 1441 (1968).
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the angle in the exact *trans* position (180°).

From these observations it might be considered that the bonding on the tin atom could involve sp^3 hybrid orbitals participating in covalent bonds to the two methyl groups and two sulfur atoms, S(1) and S(2). Since there are two additional tin-sulfur interactions (Sn–S(3) and Sn–S(4)), which originate from the electronegativity of S(3) and S(4) and the electropositivity of Sn, the steric effects of S(3) and S(4) would increase the C–Sn–C angle from a tetrahedral one to 136(1)° and would decrease the S(1)–Sn–S(2) angle to 82.7(3)°. Such a conception could explain why the sp^3 tin atom occasionally takes an apparently hexa-coordinated octahedral configuration.

Another approach to this problem has been proposed by Schlemper.[4] With regard to the structure of $(CH_3)_2Sn(C_9H_6NO)_2$, he postulated that the sp^3 tin atom has two normal covalent bonds to the methyl

TABLE 6. GEOMETRY OF THE LIGAND, *N,N*-DIMETHYLDITHIOCARBAMATE GROUP.

(a) BOND DISTANCES AND ANGLES ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES.

Bond distance (Å)		Bond angle (°)	
S(1)–C(2)	1.75(2)	Sn–S(1)–C(2)	96.8(0.8)
S(2)–C(1)	1.73(3)	Sn–S(2)–C(1)	96.0(0.9)
S(3)–C(1)	1.73(3)	Sn–S(3)–C(1)	81.1(0.8)
S(4)–C(2)	1.68(2)	Sn–S(4)–C(2)	80.1(0.8)
C(1)–N(1)	1.32(3)	S(1)–C(2)–S(4)	120 (1)
C(2)–N(2)	1.30(3)	S(2)–C(1)–S(3)	118 (1)
N(1)–C(3)	1.48(4)	S(2)–C(1)–N(1)	121 (2)
N(1)–C(4)	1.49(4)	S(3)–C(1)–N(1)	121 (2)
N(2)–C(5)	1.50(4)	S(1)–C(2)–N(2)	117 (2)
N(2)–C(6)	1.50(4)	S(4)–C(2)–N(2)	124 (2)
		C(1)–N(1)–C(3)	123 (2)
		C(1)–N(1)–C(4)	121 (2)
		C(2)–N(2)–C(5)	123 (2)
		C(2)–N(2)–C(6)	120 (2)
		C(3)–N(1)–C(4)	118 (2)
		C(5)–N(2)–C(6)	117 (2)

(b) THE LEAST-SQUARES PLANES OF THE LIGAND GROUPS AND DEVIATIONS FROM THE PLANES (Å):

(1) $-0.80120x-0.32292y-0.50379z+2.26878=0$,

S(1)	−0.057
S(4)	0.074
C(2)	0.000
N(2)	0.011
C(5)	0.077
C(6)	−0.096

(2) $-0.87050x-0.35100y-0.34500z+2.41725=0$,

S(2)	0.003
S(3)	−0.009
C(1)	0.018
N(1)	−0.022
C(3)	0.013
C(4)	−0.001

TABLE 7. COMPARISON OF THE S–C AND C–N BOND DISTANCES AND THE S–C–S ANGLE WITHIN THE DITHIOCARBAMATE GROUP IN VARIOUS COMPOUNDS.

compound	S–C (Å)		C–N (Å)	∠S–C–S (°)	Ref.
$Na^+(S_2CNEt_2)^-$	1.712(7)	1.729(6)	1.344(8)	120.4(4)	27)
$Fe(NO)(S_2CNEt_2)_2$	1.720(6)	1.726(6)	1.323(7)	110.7(3)	9)
	1.720(6)	1.740(6)	1.312(7)	109.7(3)	
$Co(S_2CNEt_2)_3$	1.714(8)	1.714(8)	1.304(15)	109.6(7)	10)
	1.695(9)	1.703(7)	1.327(10)	110.0(4)	
$Ni(S_2CNH_2)_2$	1.68(2)	1.70(3)	1.37(3)	111.9(11)	11)
	1.68(2)	1.70(3)	1.38(3)	111.6(12)	
$Ni(S_2CNEt_2)_2$	1.700(7)	1.713(7)	1.33(1)	110.6(6)	12)
$[Cu(S_2CNEt_2)_2]_2$	1.711(8)	1.713(8)	1.35(1)	114.6(7)[a]	13)
$[Cd(S_2CNEt_2)_2]_2$	1.714(14)	1.725(14)	1.33(2)	120.2(7)[a]	14)
$[Zn(S_2CNMe_2)_2]_2$	1.701(19)	1.748(19)	1.325(25)	120.2(12)[a]	15)
$[Zn(S_2CNEt_2)_2]_2$	1.722(10)	1.725(10)	1.34(1)	117.5(9)[a]	16)
$Zn(S_2CNMe_2)_2$ (C_5H_5N)	1.701(10)	1.727(10)	1.333(13)	118.3(15)	17)
	1.707(10)	1.732(10)	1.342(13)	117.3(15)	
$PhAs(S_2CNEt_2)_2$	1.652(2)	1.781(2)	1.35(3)	119(1)	18)
	1.687(2)	1.756(2)	1.34(3)	118(1)	
$As(S_2CNEt_2)_3$	1.678(6)	1.760(5)	1.338(7)[a]	—	19)
$Me_3Sn(S_2CNMe_2)$					
monoclinic	1.72(1)	1.75(1)	1.31(2)	117(1)	20)
orthorhombic	1.70(3)	1.80(3)	1.35(3)	117(2)	21)
	1.71(3)	1.78(3)	1.34(3)	119(2)	
$Me_2SnCl(S_2CNMe_2)$	1.68(4)	1.74(4)	1.32(5)	120(2)	2)
$Me_2Sn(S_2CNMe_2)_2$	1.68(2)	1.75(2)	1.30(3)	120(1)	b)
	1.73(3)	1.73(3)	1.32(3)	118(1)	

a) Bond distances and angles concering bridged groups are omitted.
b) present work

27) M. Colapietro, A. Domenicano, and A. Vaciago, *Chem. Commun.*, **1968**, 572.

groups, and the two 'three-center bonds' to the oxinate groups. In a way similar to Schlemper's,[4] the angles of C(10)–Sn–M(1), C(20)–Sn–M(1), C(10)–Sn–M(2), C(20)–Sn–M(2), and M(1)–Sn–M(2) were calculated to be 98, 94, 92, 95, and 153° respectively, where M(1) and M(2) are the midpoints of the lines connecting S(2) and S(3), and S(1) and S(4), respectively. None of these values is, however, a tetrahedral angle. It seems, then, that his conception can not be applied to the present compound.

The distortion of the tetrahedral configuration about the tin atom in $Me_3Sn(dtc)$,[20,21] in particular the widening of the average C–Sn–C angles (119(1) and 118(1)° respectively in monoclinic and orthorhombic forms) and the narrowing of the average C–Sn–S angle (95(1) and 95(1)°), can be well understood by the considerations described above. The short non-bonded Sn—S interactions (3.16 and 3.33 Å) affect the slight distortion of the tetrahedral configuration in $Me_3Sn(dtc)$. In $Me_2SnCl(dtc)$, the substitution of a methyl group by a chlorine atom results in an increase in the covalent character of the non-bonded Sn—S interaction, thus giving a shorter Sn—S distance (2.79(1) Å) and a higher distortion of the configuration about the tin atom. In the present complex, $Me_2Sn(dtc)_2$, the substitution of the methyl group by a (dtc) group changes the coordination number of the tin atom and gives a large distortion. The slightly longer Sn–S bond distances and the larger C–Sn–C angle in $Me_2Sn(dtc)_2$ may be due to the difference in the steric effect and the electronegativity of the ligand groups attached to the tin atom.

It has been suggested that a linear relation holds between the degree of *s*-character of the tin orbitals directed to the carbon atom and the PMR coupling constants.[26] The C–Sn–C bond angles and the coupling constants of some dimethyltin complexes are summarized in Table 5. As is shown in Table 5, however, the increase in the C–Sn–C angle is probably due not only to the *s*-character of the Sn–C bond, but also to the steric effect around the tin atom.

Geometry of the Ligand Group. The bond distances and angles in the ligand groups, *N,N*-Dimethyldithiocarbamate, are given in Table 6(a).

One of the two lignad groups is planar within ±0.03 Å; however, in the other group deviations from the least-squares plane are about ±0.1 Å (Table 6(b)). The dihedral angle between these planes is 10.1°.

The S(1)–C(2), S(4)–C(2), S(2)–C(1), and S(3)–C(1) distances are 1.75(2), 1.68(2), 1.73(3), and 1.73(3) Å respectively. These values are close to those in $Me_2SnCl(dtc)$, and also to those in other dialkyldithiocarbamates (Table 7). The differences in these bond distances are not significant within the limits of experimental error. The C(1)–N(1) and C(2)–N(2) distances of 1.32(3) and 1.30(3) Å are equal to those in other dithiocarbamate complexes. These values suggest that the carbon(sp^2)-nitrogen(sp^2) bond has a high double-bond character, as was to be expected from the IR studies; a similar conclusion was suggested for $Me_2Sn(dtc)Cl$. The four N–C (alkyl) bond distances, 1.48(4), 1.49(4), 1.50(4), and 1.50(4) Å, are equal, within the limits of experimental error, to the N–C single-bond distance (1.48 Å).

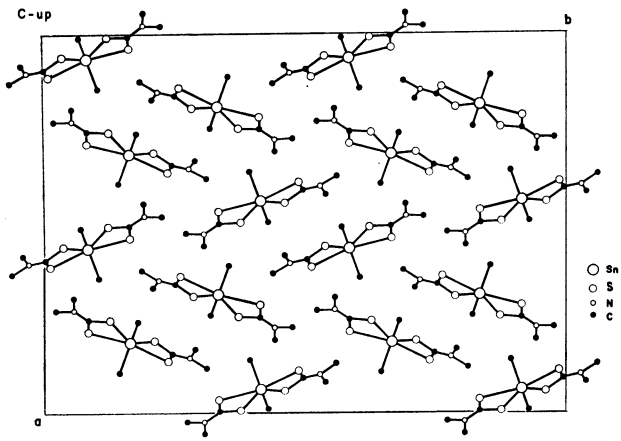

Fig. 2. Crystal structure of dimethyltin bis(*N,N*-dimethyldithiocarbamate) projected onto the (001) plane.

Table 8. The short intermolecular atomic contacts less than 4.0Å

From the unit No. 1,				
To the unit No. 2				
	S(2)–S(2)	3.99Å	S(2)–C(4)	3.82Å
	C(4)–S(2)	3.82		
To the unit No. 3				
	N(1)–C(6)	3.73	C(1)–C(6)	3.71
	C(20)–C(2)	3.72	C(20)–N(2)	3.85
	C(20)–S(4)	3.87		
To the unit No. 4				
	S(1)–C(3)	3.86	N(2)–C(3)	3.99
	C(2)–C(3)	3.69	C(20)–C(3)	3.89
To the unit No. 5				
	C(5)–C(6)	3.82	C(6)–C(6)	3.92

Key				
No. 1	x,	y,	z
2	$-x$,	$-y$,	$-z$
3	$0.25+x$,	$0.25-y$,	$0.25+z$
4	$0.25-x$,	$0.25+y$,	$0.25+z$
5	$-x$,	$0.5-y$,	$0.5+z$

Table 9. Preliminary crystal data of dimethyltin bis (*N,N*-dimethyldiselenocarbamate)

$C_7H_{18}NSe_2Sn$
$F.W.=570.6$
Orthorhombic
Space group *Pnn*2
$a=14.0$Å
$b=18.1$
$c=7.5$
$V=1903$Å^3
$D=1.99$ g.cm^{-3}
for $Z=4$

Crystal Structure. The crystal structure of $Me_2Sn(dtc)_2$ projected onto the (001) plane is shown in Fig. 2. The short intermolecular atomic contacts less than 4.0 Å are summarized in Table 8. None of them is short enough to suggest any significant deviation from

26) J. R. Holmes and H. D. Kasez, *J. Amer. Chem. Soc.*, **83**, 3903 (1961).

the normal van der Waals interaction.

Besides the structure analysis of $(CH_3)_2Sn(S_2CN(CH_3)_2)_2$, preliminary X-ray examinations of $(CH_3)_2Sn(Se_2CN(CH_3)_2)_2$ have been carried out. The crystal data of the compound are listed in Table 9.

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