

# Molecular Motions in $(\text{CH}_3)_3\text{XCl}$ , $\text{X}=\text{Sn}$ and $\text{Pb}$ . NMR Investigations and Crystal Structure Study of $(\text{CH}_3)_3\text{PbCl}$ and $\text{CH}_3\text{SnBr}_3$

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The molecular motion in  $(\text{CH}_3)_3\text{XCl}$ ,  $\text{X}=\text{Sn}$  and  $\text{Pb}$  has been investigated by measurement of the second moment  $M_2(^1\text{H})$  as function of temperature in the range  $95 < T/\text{K} < 345$ . The methyl groups in both compounds rotate freely over the whole temperature range studied. In  $(\text{CH}_3)_3\text{SnCl}$  the  $\text{C}_3$ -rotation of  $(\text{CH}_3)_3\text{Sn}$ -group about the  $\text{Sn}-\text{Cl}$  axis sets in above 273 K. To explain the NMR and INS results, the crystal structures of  $(\text{CH}_3)_3\text{PbCl}$  and  $\text{CH}_3\text{SnBr}_3$  were determined by single X-ray diffraction.  $(\text{CH}_3)_3\text{PbCl}$  crystallizes in a monoclinic space group  $\text{C}_2^3-\text{C}_2$ ,  $a=1276.7(3)$  pm,  $b=982.3(3)$  pm,  $c=547.0(2)$  pm,  $\beta=91.12(1)^\circ$ ;  $Z=4$ ,  $R=0.035$ .  $\text{CH}_3\text{SnBr}_3$  crystallizes in an orthorhombic space group  $\text{D}_{2h}^{16}-\text{Pnma}$ ,  $a=643.0(3)$  pm,  $b=1005.3(4)$  pm,  $c=1148.0(4)$  pm;  $Z=4$ ,  $R=0.057$ .

## Introduction

Molecular dynamics in the solid state is an interesting subject which has been studied intensively in recent years. Using various experimental methods such as nuclear magnetic resonance (NMR), study of the spin-lattice relaxation time ( $T_1$ ) as well as the second moment ( $M_2$ ), and inelastic neutron scattering (INS) technique detailed informations about internal motions of molecules or functional groups in solid state can be obtained. Recently we have reported on the rotational tunneling of methyl groups in various methyl group-IVa halides  $(\text{CH}_3)_{4-n}\text{M}^{\text{IV}}\text{X}_n$  with  $\text{M}=\text{Sn}, \text{Pb}$ ;  $\text{X}=\text{F}, \text{Cl}, \text{Br}$  [1], studied by inelastic neutron scattering. For the methyl group-IVa halide compounds, tunnel splittings between 0.3 and 50  $\mu\text{eV}$  at  $T=4$  K have been observed. Only in  $\text{CH}_3\text{SnCl}_3$  no tunnel splitting has been found. The molecular motions in  $(\text{CH}_3)_3\text{SnF}$  with known crystal structure [2] have been investigated, using NMR techniques, by Ulrich et al. [3]; the authors measured the spin-lattice relaxation time  $T_1$  and the second moment in the range  $60 < T/\text{K} < 540$ .

In the present paper we report an NMR study of molecular motion in trimethyl-tin(lead) chloride via the second moment  $M_2(^1\text{H})$  as a function of temperature. To explain the results from NMR studies and

INS investigation [1], the crystal structures of trimethyllead chloride,  $(\text{CH}_3)_3\text{PbCl}$ , and methyltin tribromide,  $\text{CH}_3\text{SnBr}_3$ , have been determined and are reported here, too.

## Experimental

The three compounds studied have been synthesized according to the literature:  $(\text{CH}_3)_3\text{SnCl}$  [4],  $(\text{CH}_3)_3\text{PbCl}$  [5], and  $\text{CH}_3\text{SnBr}_3$  [6]. The compounds are air sensitive and have to be handled in a dry inert gas atmosphere.

### Crystal Structure Determination

The crystal structures of  $(\text{CH}_3)_3\text{PbCl}$  and  $\text{CH}_3\text{SnBr}_3$  were determined by single-crystal X-ray diffraction at room temperature. The experimental conditions are given in Table 1, together with crystal structure data (space groups, lattice constants etc.).

### Nuclear Magnetic Resonance Measurements

The NMR line widths as well as the second moment  $M_2(^1\text{H})$  in  $(\text{CH}_3)_3\text{SnCl}$  and  $(\text{CH}_3)_3\text{PbCl}$  were measured in the temperature range  $95 < T/\text{K} < 345$ , respectively. The NMR-spectra were recorded by lock-in technique as the derivative of the absorption curve with a Robinson type oscillator [7, 8] operating at a constant frequency of 8.1 MHz by slowly varying

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Table 1. Experimental conditions for the crystal structure determinations and structure data of trimethyllead chloride,  $(\text{CH}_3)_3\text{PbCl}$ , and methyltin tribromide  $\text{CH}_3\text{SnBr}_3$ .

Compound	$(\text{CH}_3)_3\text{PbCl}$	$\text{CH}_3\text{SnBr}_3$
Crystal habitus	needle	prisma
Crystal size/mm <sup>3</sup>	$0.1 \times 0.08 \times 1.6$	$0.24 \times 0.24 \times 2.2$
Diffractionmeter		Stoe-Stadi 4
Wavelength/pm		71.069 (MoK $\alpha$ )
Monochromator		Graphite (002)
T/K	297	300
Absorption coefficient $\mu/\text{m}^{-1}$	25 011	18 950
Scan	$2\theta/\omega$	
$(\sin \theta/\lambda)_{\text{max}}/\text{pm}^{-1}$	0.005385	0.005946
Measured reflexions	1010	1950
Symmetry independent reflexions	480	696
Reflexions consid.	466	665
$[(F_0 \geq 2\sigma(F_0))]$		
Number of free parameters	55	29
$F(000)$	495.93	656
$R(F)$	0.0348	0.0573
$R_w(F)$	0.0349	0.0512
Lattice constants	$a/\text{pm}$ 1276.7(3) $b/\text{pm}$ 982.3(3) $c/\text{pm}$ 547.0(2)	$a/\text{pm}$ 643.0(3) $b/\text{pm}$ 1005.3(4) $c/\text{pm}$ 1148.0(4)
$\beta/^\circ$	91.12(1)	90
$V \cdot 10^{-6}/(\text{pm})^3$	685.9(6)	742.1(9)
Space group	$\text{C}_3^1\text{-C2}$	$\text{D}_{2h}^{16}\text{-Pnma}$
Formula units per unit cell	$Z=4$	$Z=4$
$\rho_{\text{calc}}/\text{Mg m}^{-3}$	2.785(2) ( $T=297\text{ K}$ )	3.34(1) ( $T=300\text{ K}$ )
$\rho_{\text{pykn}}/\text{Mg m}^{-3}$	2.76 ( $T=295\text{ K}$ )	3.3 ( $T=296\text{ K}$ )
Point position:	in $\text{C}_3^1\text{-C2}$ all atoms in 4c:	in $\text{D}_{2h}^{16}\text{-Pnma}$ Sn, Br <sup>(1)</sup> , and C in 4c:
	$x, y, z; \bar{x}, \bar{y}, \bar{z};$ $\frac{1}{2}+x, \frac{1}{2}+y, z;$ $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}.$	$x, \frac{1}{4}, z; \bar{x}, \frac{3}{4}, \bar{z};$ $\frac{1}{2}-x, \frac{3}{4}, \frac{1}{2}+z;$ $\frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z.$
	Br <sup>(2)</sup> in 8d: $x, y, z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z;$ $\bar{x}, \frac{1}{2}+y, \bar{z}; \frac{1}{2}-x, \bar{y}, \frac{1}{2}+z;$ $\bar{x}, \bar{y}, \bar{z}; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z;$ $x, \frac{1}{2}-y, z; \frac{1}{2}+x, y, \frac{1}{2}-z.$	

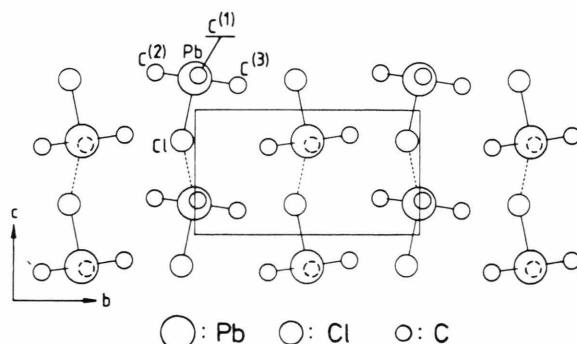


Fig. 1. Projection of the crystal structure of trimethyllead chloride,  $(\text{CH}_3)_3\text{PbCl}$  for  $0 \leq x \leq 0.5$  along  $[100]$ . The hydrogen atoms are not shown. --- Shortest  $\text{Pb} \cdots \text{Cl}$  distance between two  $(\text{CH}_3)_3\text{PbCl}$  molecules, one behind the other.

the magnetic induction  $B_0$  within a range of  $\Delta B = \pm 2 \cdot 10^{-3}\text{ T}$ .

The line width was taken as distance (in Tesla) between points of maximum and minimum of the dispersion curve. The second moment  $M_2(^1\text{H})$  was calculated using a numerical integration procedure, in which appropriate corrections for the finite modulation amplitude were incorporated [9].

## Results

### Crystal Structures of $(\text{CH}_3)_3\text{PbCl}$ and $\text{CH}_3\text{SnBr}_3$

In Table 1 the crystallographic data (lattice constants, space groups etc.) for  $(\text{CH}_3)_3\text{PbCl}$  and  $\text{CH}_3\text{SnBr}_3$  are given. The crystal structures were determined using the heavy-atom method (SHELX 86) [10]. Difference Fourier maps were calculated and the coordinates of atoms in  $(\text{CH}_3)_3\text{PbCl}$  and in  $\text{CH}_3\text{SnBr}_3$  could be determined. Because of the presence of heavy atoms, Pb in  $(\text{CH}_3)_3\text{PbCl}$  and Br in  $\text{CH}_3\text{SnBr}_3$ , the positions of the H-atoms in both compounds could

Table 2. Positional and thermal parameters of trimethyllead chloride,  $(\text{CH}_3)_3\text{PbCl}$ . The temperature factor is of the form:

$$T = \exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

The  $U_{ij}$  are given in  $(\text{pm})^2$ .

Atom	$x/a$	$y/b$	$z/c$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Pb	0.2978(1)	0.5	0.7485(1)	587(6)	853(7)	306(6)	-56(17)	21(4)	-31(16)
Cl	0.3025(8)	0.4447(9)	0.2440(13)	1389(93)	1219(64)	183(42)	110(48)	50(49)	-50(34)
C <sup>(1)</sup>	0.1250(22)	0.5150(80)	0.7231(75)	677(183)	1445(416)	1372(314)	431(407)	-224(222)	-477(536)
C <sup>(2)</sup>	0.4018(23)	0.3249(33)	0.7036(81)	630(196)	1058(217)	902(304)	767(179)	-354(202)	-622(213)
C <sup>(3)</sup>	0.3559(35)	0.6890(54)	0.8018(77)	853(337)	2888(601)	822(288)	-36(352)	586(242)	812(332)

Table 3. Positional and thermal parameters of methyltin tribromide, CH<sub>3</sub>SnBr<sub>3</sub>. For the temperature factor see Table 2.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Sn	0.5554(2)	0.2500(0)	0.4628(1)	538(7)	593(7)	529(7)	0	0(6)	0
Br <sup>(1)</sup>	0.7230(4)	0.2500(0)	0.6534(2)	811(14)	1065(16)	523(12)	0	83(11)	0
Br <sup>(2)</sup>	0.7074(3)	0.0593(2)	0.3599(2)	976(12)	714(9)	878(12)	−50(8)	−141(10)	−199(8)
C	0.2218(27)	0.2500(0)	0.4563(20)	458(92)	861(133)	970(169)	0	112(108)	0

Table 4. Interatomic distances and bond angles in trimethyllead chloride, (CH<sub>3</sub>)<sub>3</sub>PbCl.

Interatomic	<i>d</i> /pm	Interatomic	Angle/degree
Pb—Cl	276.4 (0.7)	Cl—Pb—C <sup>(1)</sup>	94.4 (1.1)
Pb...Cl'	281.4 *	Cl—Pb—C <sup>(2)</sup>	87.4 (1.2)
Pb—C <sup>(1)</sup>	221.3 (2.6)	Cl—Pb—C <sup>(3)</sup>	92.2 (1.2)
Pb—C <sup>(2)</sup>	219.0 (2.1)	C <sup>(1)</sup> —Pb—C <sup>(2)</sup>	130.6 (2.2)
Pb—C <sup>(3)</sup>	201.8 (5.3)	C <sup>(1)</sup> —Pb—C <sup>(3)</sup>	108.1 (2.3)
Cl...C <sup>(1)</sup>	367.1	C <sup>(2)</sup> —Pb—C <sup>(3)</sup>	121.1 (1.6)
Cl...C <sup>(2)</sup>	344.6		
Cl...C <sup>(3)</sup>	348.4	Cl—Pb...Cl'	157.4 (along <i>c</i> )
C <sup>(1)</sup> ...C <sup>(2)</sup>	400.0	Pb—Cl...Pb'	157.4 (along <i>c</i> )
C <sup>(1)</sup> ...C <sup>(3)</sup>	342.8	C <sup>(1)</sup> ...C <sup>(2)</sup> ...C <sup>(3)</sup>	52.9
C <sup>(2)</sup> ...C <sup>(3)</sup>	366.5	C <sup>(2)</sup> ...C <sup>(1)</sup> ...C <sup>(3)</sup>	58.5
Cl...C <sup>(1)'</sup>	356.5	C <sup>(1)</sup> ...C <sup>(3)</sup> ...C <sup>(2)</sup>	68.6
Cl...C <sup>(2)'</sup>	303.1		
Cl...C <sup>(3)'</sup>	393.1		

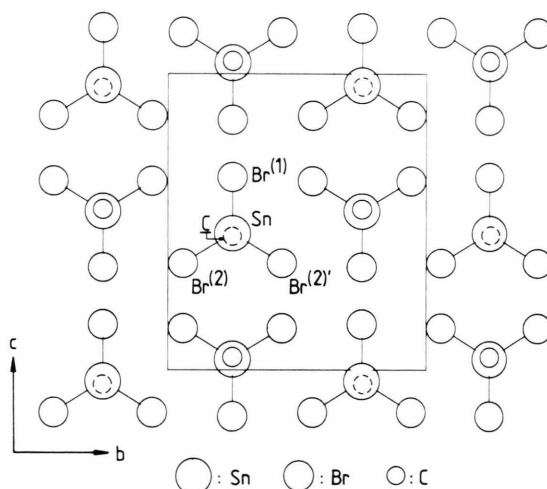
\* along *c*, it is shown explicitly in Figs. 1 and 6.

Table 5. Interatomic distances and bond angles in methyltin tribromide, CH<sub>3</sub>SnBr<sub>3</sub>.

Inter-atomic	<i>d</i> /pm	Interatomic	Angle/degree
Sn—Br <sup>(1)</sup>	244.0 (0.2)	C—Sn—Br <sup>(1)</sup>	118.2 (6)
Sn—Br <sup>(2)</sup>	245.4 (0.2)	C—Sn—Br <sup>(2)</sup>	112.4 (3)
Sn—C	214.7 (1.7)	Br <sup>(1)</sup> —Sn—Br <sup>(2)</sup>	104.8 (1)
		Br <sup>(2)</sup> —Sn—Br <sup>(2)'</sup>	102.7 (1)
C...Br <sup>(1)</sup>	393.8	C—Sn...C	177.0
C...Br <sup>(2)</sup>	382.7	Sn—C...Sn	177.0
Br <sup>(1)</sup> ...Br <sup>(2)</sup>	387.8	Br <sup>(1)</sup> ...Br <sup>(2)</sup> ...Br <sup>(2)'</sup>	60.4
Br <sup>(2)</sup> ...Br <sup>(2)'</sup>	383.4	Br <sup>(2)</sup> ...Br <sup>(1)</sup> ...Br <sup>(2)'</sup>	59.3
Sn...C	428.6 (along <i>a</i> )		
C...Br <sup>(1)</sup>	392.5 (along <i>a</i> )		
C...Br <sup>(2)</sup>	398.0 (along <i>a</i> )		
Sn...Sn	514.8		
Br <sup>(1)</sup> ...Br <sup>(2)</sup>	416.5 (along <i>b</i> )		

Table 6. Second moment *M*<sub>2</sub>(<sup>1</sup>H)-values for (CH<sub>3</sub>)<sub>3</sub>SnCl (in 10<sup>−8</sup> T<sup>2</sup>).

	<i>M</i> <sub>2</sub> (rigid lattice)	<i>M</i> <sub>2</sub> (rotating CH <sub>3</sub> )	<i>M</i> <sub>2</sub> (rotating CH <sub>3</sub> + C <sub>3</sub> -rotation)
intra-CH <sub>3</sub>	21.4	5.3	0
intramolecular	0.5	0.3	0
intermolecular	8.6	1.3	0.11
Total	30.5	6.9	0.11
Experiment	—	7.2	3.0

Fig. 2. Projection of the crystal structure of methyltin tribromide, CH<sub>3</sub>SnBr<sub>3</sub>, onto the *bc*-plane. The hydrogen atoms are not shown.

not be determined exactly. The other atomic parameters were refined by least squares cycles, and the final *R*-value was 0.0348 for (CH<sub>3</sub>)<sub>3</sub>PbCl and 0.0573 for CH<sub>3</sub>SnBr<sub>3</sub>. In Tables 2 and 3 the atomic coordinates and thermal parameters for (CH<sub>3</sub>)<sub>3</sub>PbCl and CH<sub>3</sub>SnBr<sub>3</sub> are listed, respectively. Interatomic distances and bond angles in (CH<sub>3</sub>)<sub>3</sub>PbCl and in CH<sub>3</sub>SnBr<sub>3</sub> are given in Tables 4 and 5, respectively. Figure 1 shows the projection of half of the unit cell (0 ≤ *x* ≤ 0.5) of (CH<sub>3</sub>)<sub>3</sub>PbCl onto the *bc*-plane, while Fig. 2 shows the projection of crystal structure of CH<sub>3</sub>SnBr<sub>3</sub> onto the *bc*-plane.

### Second Moment *M*<sub>2</sub>(<sup>1</sup>H)

The line widths Δ*B*(<sup>1</sup>H) and second moments *M*<sub>2</sub>(<sup>1</sup>H) for (CH<sub>3</sub>)<sub>3</sub>SnCl and (CH<sub>3</sub>)<sub>3</sub>PbCl are shown as functions of temperature in Figs. 3 and 4. In Tables 6 and 7 the *M*<sub>2</sub>(<sup>1</sup>H) values measured are summarized and compared with calculated values. *M*<sub>2</sub>(<sup>1</sup>H) for the polycrystalline samples was calculated using the well known van Vleck formalism [11, 12]:

$$M_2 = \frac{6}{5} I_i(I_i + 1) g_i^2 \beta_N^2 N_0^{-1} \sum_{i>j} r_{ij}^{-6}. \quad (1)$$

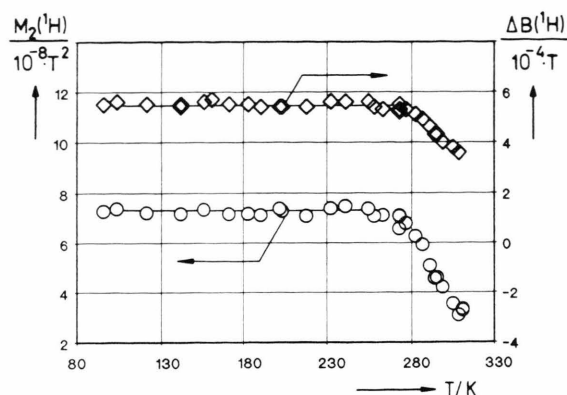


Fig. 3. Line width  $\Delta B(^1\text{H})$  and second moment  $M_2(^1\text{H})$  as function of temperature for trimethyltin chloride,  $(\text{CH}_3)_3\text{SnCl}$ .

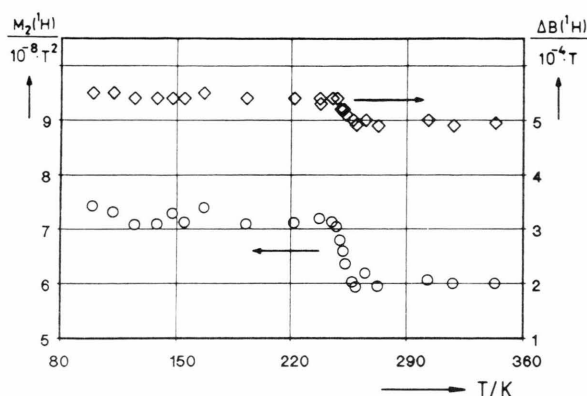


Fig. 4. Line width  $\Delta B(^1\text{H})$  and second moment  $M_2(^1\text{H})$  as function of temperature for trimethyllead chloride,  $(\text{CH}_3)_3\text{PbCl}$ .

Table 7. Second moment  $M_2(^1\text{H})$ -values for  $(\text{CH}_3)_3\text{PbCl}$  (in  $10^{-8} \text{ T}^2$ ).

	$M_2$ (rigid lattice)	$M_2$ (rotating $\text{CH}_3$ )	$M_2$ (rotating $\text{CH}_3$ + $\text{C}_3'$ -rotation)
intra- $\text{CH}_3$	21.4	5.3	0
intramolecular	0.75	0.14	0
intermolecular	10.49	1.26	0.1
Total	32.64	6.7	0.1
Experiment	—	(7.1 → 6.1)	—

Here  $I$  is the nuclear spin,  $g$  is the splitting factor,  $\beta_N$  is the nuclear magneton,  $N_0$  is the number of nuclei at resonance and  $r$  is the distance between interacting nuclei which are referred by indices  $i$  and  $j$ . In  $(\text{CH}_3)_3\text{SnCl}$  as well as in  $(\text{CH}_3)_3\text{PbCl}$  only dipolar interactions among  $^1\text{H}$ -nuclei were considered. The contributions to  $M_2$  from  $^{117,119}\text{Sn}-^1\text{H}$  interactions

in  $(\text{CH}_3)_3\text{SnCl}$  as well as from  $^{207}\text{Pb}-^1\text{H}$  interactions in  $(\text{CH}_3)_3\text{PbCl}$  are both small and unimportant within the experimental accuracy reached. They were neglected.

The crystal structure data of  $(\text{CH}_3)_3\text{SnCl}$  [13] and of  $(\text{CH}_3)_3\text{PbCl}$  (reported here) were used for the  $M_2(^1\text{H})$  calculations. The bond length  $d(\text{C}-\text{H})$  was fixed to 110 pm and the ideal tetrahedron symmetry of a  $\text{CH}_3$ -group with  $\angle(\text{H}-\text{C}-\text{H}) = 109.47^\circ$  was assumed.

## Discussion

### Trimethyltin Chloride, $(\text{CH}_3)_3\text{SnCl}$

The crystal structure of trimethyltin chloride has been studied at  $T = 138 \text{ K}$  by Lefferts *et al.* [13]. They have shown that  $(\text{CH}_3)_3\text{SnCl}$  crystallizes monoclinic, space group  $\text{C}_{2h}^6\text{-C2/c}$ , with 4 molecules in the unit cell. The three methyl groups of the molecule  $(\text{CH}_3)_3\text{SnCl}$  are crystallographically independent. The second moment  $M_2(^1\text{H})$  in trimethyltin chloride remains constant,  $M_2(^1\text{H}) = 7.2 \cdot 10^{-8} \text{ T}^2$ , from 95 K to 270 K. Above 272 K it decreases rather fast with increasing temperature and arrives finally at  $M_2(^1\text{H}) = 3.0 \cdot 10^{-8} \text{ T}^2$ , just below the melting point (312 K). In calculating  $M_2(^1\text{H})$ , three different situations must be distinguished, namely (a) the rigid lattice, without any motions (besides zero point vibrations), (b) rotating  $\text{CH}_3$ -groups, and (c) rotating  $\text{CH}_3$ -groups plus  $\text{C}_3'$ -rotation of the  $(\text{CH}_3)_3\text{Sn}$ -group about the  $\text{Sn}-\text{Cl}$  axis (in  $(\text{CH}_3)_3\text{PbCl}$  the  $\text{C}_3'$ -rotation of the  $(\text{CH}_3)_3\text{Pb}$ -group about the  $\text{Pb}-\text{Cl}$  axis). A fourth possible motional state, the overall tumbling of the molecule was not considered here. According to Gutowsky *et al.* [12] the intramethyl contribution to the total second moment for a rapidly reorientating  $\text{CH}_3$ -group reduces to 1/4 of the rigid lattice value.

The comparison between the experimental results and theoretically calculated  $M_2(^1\text{H})$  values in  $(\text{CH}_3)_3\text{SnCl}$  (see Table 6) shows that the methyl groups in  $(\text{CH}_3)_3\text{SnCl}$  are free rotating over the whole temperature range studied. The decrease of  $M_2(^1\text{H})$  above 272 K indicates the onset of a rotation of the  $(\text{CH}_3)_3\text{Sn}$ -group about the  $\text{Sn}-\text{Cl}$  axis in addition to the individual rotation of the  $\text{CH}_3$ -groups. The calculation gives for a free  $(\text{CH}_3)_3\text{Sn}$ -rotation plus rotating  $\text{CH}_3$  groups  $M_2(^1\text{H}) = 0.11 \cdot 10^{-8} \text{ T}^2$ . Measurements at the highest temperature reached give  $M_2(^1\text{H}) = 3.0 \cdot 10^{-8} \text{ T}^2$ . It means that the free rotation of the  $(\text{CH}_3)_3\text{Sn}$ -group is possible in the melt only.

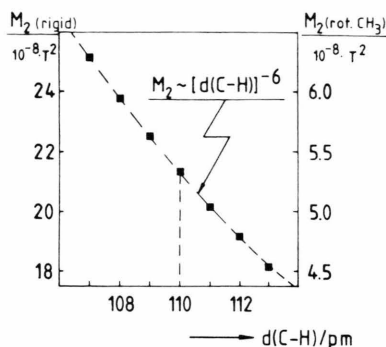


Fig. 5. The intra- $\text{CH}_3$  contribution to the second moment  $M_2(^1\text{H})$  for a rigid as well as a rotating methyl group as function of bond length  $d(\text{C}-\text{H})$ . The tetrahedron angle ( $109.47^\circ$ ) is assumed. It is:  $M_2(\text{rigid } \text{CH}_3) = 4 \cdot M_2(\text{rotating } \text{CH}_3)$  [12].

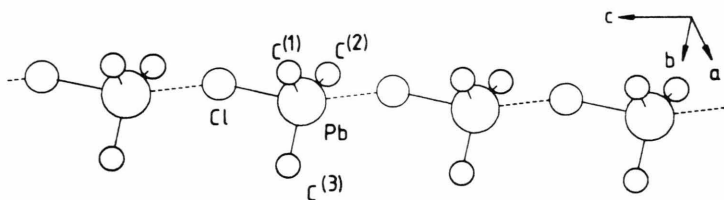


Fig. 6. Chain structure of  $(\text{CH}_3)_3\text{PbCl}$  along  $c$ -axis.

As seen in Table 6 there is a small difference between the calculated  $M_2(^1\text{H}) = 6.9 \cdot 10^{-8} \text{ T}^2$  and the experimental result,  $M_2(^1\text{H}) = 7.2 \cdot 10^{-8} \text{ T}^2$ , for  $(\text{CH}_3)_3\text{SnCl}$  with rotating  $\text{CH}_3$ -groups. A possible explanation for the discrepancy is the fixation of the ideal tetrahedron symmetry for the  $\text{CH}_3$ -groups and the fixed bond length  $d(\text{C}-\text{H}) = 110 \text{ pm}$ , we have applied. Equation (1) shows that the second moment  $M_2(^1\text{H})$  is a steep function of the distances between H-atoms, and it therefore depends on C-H bond lengths as  $M_2 \sim (r_{\text{H} \dots \text{H}})^{-6} \sim [d(\text{C}-\text{H})]^{-6}$ . Figure 5 illustrates the dependence of the intra-methyl group contribution to the second moment from the deviation of the assumed bond length by keeping the ideal tetrahedron angle ( $109.47^\circ$ ). Clearly, the intramethyl contribution to  $M_2(^1\text{H})$  increase slightly with shortening of C-H bond length, which corresponds to the reality.

#### Trimethyllead Chloride, $(\text{CH}_3)_3\text{PbCl}$ , Crystal Structure and Second Moment

Trimethyllead chloride,  $(\text{CH}_3)_3\text{PbCl}$ , crystallizes monoclinic, in a different space group compared with  $(\text{CH}_3)_3\text{SnCl}$ , namely  $\text{C}_2^3\text{-C2}$ , with 4 molecules in the unit cell. Figure 1 shows the projection of half of the unit cell ( $0 \leq x \leq 0.5$ ) of  $(\text{CH}_3)_3\text{PbCl}$  onto the  $bc$ -plane. The three carbon atoms  $\text{C}^{(n)}$ ,  $n = 1, 2$ , and 3 form a

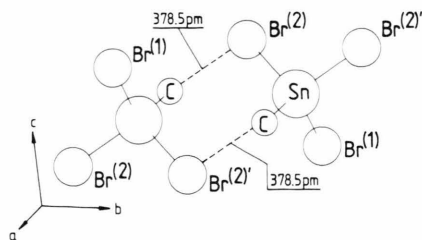
plane, which can be described by

$$0.6784x + 1.5417y - 5.399z + 3.0253 = 0. \quad (2)$$

$x$ ,  $y$ , and  $z$  in (2) are the coordinates of the  $\text{C}^{(n)}$  atoms in the unit cell. The distance between the Pb-atom and the  $\text{C}^{(1)}\text{C}^{(2)}\text{C}^{(3)}$ -plane is  $4.9 \text{ pm}$  only, which means that the three C-atoms and the Pb-atom are nearly coplanar as observed in case of  $(\text{CH}_3)_3\text{PbCH}_3\text{COO}$  [14]. The distances between the Pb-atom and the two next nearest Cl-atoms above and below the plane are almost equal,  $276.4 \text{ pm}$  and  $281.4 \text{ pm}$ , respectively. The Pb-Cl bond is nearly vertical to the  $\text{C}^{(1)}\text{C}^{(2)}\text{C}^{(3)}$ -plane; the angle between this bond and the normal of the plane is  $1.3^\circ$ . The Pb-atom in  $(\text{CH}_3)_3\text{PbCl}$  is five coordinated as found in some other trimethyllead compounds, i.e.  $(\text{CH}_3)_3\text{PbN}_3$  [15],  $(\text{CH}_3)_3\text{Pb}(\text{N}_2)\text{CO}_2\text{Et}$  [16], and  $(\text{CH}_3)_3\text{PbCH}_3\text{COO}$  [14]. Three equatorial methyl groups and two axial C-atoms form a distorted trigonal bipyramid around the Pb-atom. The  $(\text{CH}_3)_3\text{Pb}$ -groups pile up parallel with each other along the  $c$ -axis, connected through a Cl-atom in the middle. The angle  $\text{Pb}-\text{Cl} \cdots \text{Pb}$  is  $157.4^\circ$ , identical with the angle  $\text{Cl}-\text{Pb} \cdots \text{Cl}$ . Therefore zig-zag chains  $-\text{Cl} \cdots (\text{CH}_3)_3\text{Pb}-\text{Cl} \cdots (\text{CH}_3)_3\text{Pb}-\text{Cl} \cdots$  are formed along  $c$ -axis, just like in  $(\text{CH}_3)_3\text{SnCl}$  [13]. This is shown in Figure 6.

In Table 8 the bond lengths  $d(\text{Pb}-\text{C})$  in few trimethyllead compounds with known crystal struc-



Fig. 7. The pair of  $\text{CH}_3\text{SnBr}_3$  molecules.Table 8. Comparison of  $d(\text{Pb}-\text{C})$  in various trimethyllead compounds.

Compound	Pb-C <sup>(n)</sup>	$d(\text{Pb}-\text{C})/\text{pm}$	Ref.
$(\text{CH}_3)_3\text{PbCH}_3\text{COO}$	$n=1$	217.1 (2.9) 2x	[14]
	$n=2$	220.2 (3.5)	
$(\text{CH}_3)_3\text{PbN}_3$	$n=1$	223(2)	[15]
	$n=2$	220(1) 2x	
$(\text{CH}_3)_3\text{Pb}(\text{N}_2)\text{CO}_2\text{Et}$	$n=1$	220(3)	[16]
	$n=2$	221(3)	
	$n=3$	224(3)	
$(\text{CH}_3)_3\text{PbCl}$	$n=1$	221.3 (2.6)	*
	$n=2$	219.0 (2.1)	
	$n=3$	201.8 (5.3)	

\* this work.

ture are given. Two Pb-C bonds in  $(\text{CH}_3)_3\text{PbCl}$ ,  $d(\text{Pb}-\text{C}^{(n)})$ ,  $n=1$  and 2, are comparable with literature data. However, the third bond  $d(\text{Pb}-\text{C}^{(3)})$  is extremely short.

As seen in the INS study [1], one of the methyl groups shows a rather small tunnel splitting, which could not be resolved. This should be associated with  $\text{CH}_3^{(3)}$  with the shortest distance to Pb. The three crystallographical inequivalent methyl groups correspond well with the INS results [1]. The  $\text{CH}_3^{(1)}$  group with  $d(\text{Pb}-\text{C}^{(1)})=221.3$  pm can be associated with the tunnel energy  $h\nu_t=3.35$   $\mu\text{eV}$  while the  $\text{CH}_3^{(2)}$ -group with  $d(\text{Pb}-\text{C}^{(2)})=219.0$  pm corresponds with the tunnel splitting  $h\nu_t=1.72$   $\mu\text{eV}$ .

The structure determination results for  $(\text{CH}_3)_3\text{PbCl}$  here confirm the expectations from IR- and Raman studies [17]: a)  $(\text{CH}_3)_3\text{PbCl}$  has a chain structure with bridging Cl-atoms; b) the Pb-atom is five coordinated; and c) the  $(\text{CH}_3)_3\text{Pb}$ -group is nearly planar. The second moment  $M_2(^1\text{H})$  in  $(\text{CH}_3)_3\text{PbCl}$  was studied within the temperature range  $99 \leq T/\text{K} \leq 343$  (see Figure 4). From 343 K to 260 K the  $M_2(^1\text{H})$  is constant at  $6 \cdot 10^{-8} \text{ T}^2$ , and rising within 12 K to  $7.1 \cdot 10^{-8} \text{ T}^2$ . The calculated  $M_2$ -values according (1) are given in Table 7, together with the experimental results. The

ideal tetrahedron symmetry for the  $\text{CH}_3$ -group and  $d(\text{C}-\text{H})=110$  pm were assumed for the calculation. The interactions  $^{207}\text{Pb}-^1\text{H}$  were neglected. The comparison given in Table 7 shows that all methyl groups rotate freely at  $T=99$  K. Additional  $\text{C}'_3$ -rotation of  $(\text{CH}_3)_3\text{Pb}$ -groups does not arise even at 343 K. The origin of the decrease of  $M_2(^1\text{H})$  in the range  $248 < T/\text{K} < 260$  observed is, however, not understood. A differential thermal analysis (DTA) gives no indication of any phase transition in the range  $77 \leq T/\text{K} \leq 310$ . Compared with  $(\text{CH}_3)_3\text{SnCl}$ , the  $M_2(^1\text{H})$  in  $(\text{CH}_3)_3\text{PbCl}$  is a little smaller for the rotating methyl groups. The explanation should lie in the size of Pb-atom and therefore the increasing intramolecular methyl-methyl-distances.

#### *Methyltin Tribromide, $\text{CH}_3\text{SnBr}_3$ , Crystal Structure*

The methyltin tribromide crystallizes orthorhombic, space group  $\text{D}_{2h}^{16}-\text{Pnma}$ ,  $Z=4$ . In Fig. 2 the unit cell of  $\text{CH}_3\text{SnBr}_3$  is projected onto the  $bc$ -plane. The structure is a centrosymmetric one, so that two neighboring molecules can be considered as a pair. This is caused by the strong dipolar interaction between the  $\text{CH}_3\text{SnBr}_3$  molecules. There is a mirror plane through the molecule. All atoms in the molecule except  $\text{Br}^{(2)}$  lie in this plane, therefore two crystallographical inequivalent Br-atoms with the ratio 2:1 result. The two intramolecular  $d(\text{Sn}-\text{Br}^{(n)})$ ,  $n=1$  and 2, are nearly identical (see Table 5), so that three Br-atoms form a rather regular triangle. The angle between the Sn-C bond and the normal of  $\text{Br}^{(1)}\text{Br}^{(2)}\text{Br}^{(3)}$ -plane is  $3.7^\circ$  only. Consequently the  $\text{CH}_3\text{SnBr}_3$  molecule is a rather regular tetrahedron.

We wish to remark that  $\text{CH}_3\text{SnBr}_3$  could be refined in another orthorhombic, but acentric space group,  $\text{C}_{2v}^9-\text{Pan}2_1$ , too, which has been mentioned elsewhere [1]. The  $R$ -value is 5.73% for the centrosymmetric space group ( $\text{D}_{2h}^{16}-\text{Pnma}$ ) and 5.81% for acentric one ( $\text{C}_{2v}^9-\text{Pan}2_1$ ), respectively. The bond lengths and angles in both space groups differ barely only. The dominant difference between these two space groups is the molecular symmetry and the connected number of independent Br-atoms. For  $\text{D}_{2h}^{16}-\text{Pnma}$  there are two crystallographical inequivalent Br-atoms with the ratio 2:1, while for  $\text{C}_{2v}^9-\text{Pan}2_1$  all three Br-atoms in the molecule are independent. Petrosyan *et al.* have studied the  $^{81}\text{Br}$ -NQR at  $T=77$  K and have found two resonance frequencies (138.02 MHz and 148.34

MHz) with intensity ratio 1:2 [18]. The NQR results confirm that the space group  $\text{D}_{2h}^{16}\text{-Pnma}$  is the right one.

The only C-atom occupies the point position 4c, therefore all methyl groups are crystallographically identical. The INS study shows a well defined tunneling peak at  $h\nu_t = 0.75 \mu\text{eV}$ , and it was estimated to represent 50% of the methyl groups only. DTA-measurements within the temperature range  $77 \leq T/\text{K} \leq 310$  does not show any phase transitions. However, any changes in crystal structure under  $T = 77 \text{ K}$  can not be ruled out. A determination of the crystal structure at low temperature, i.e. at  $T = 10 \text{ K}$ , is necessary to explain this discrepancy.

The van-der-Waals radii of methyl group and Br-atom are 200 pm and 195 pm, respectively [19]. The intramolecular distances  $d(\text{Br} \cdots \text{Br}')$  as well as  $d(\text{Br} \cdots \text{C})$  are all shorter than the sum of the van-der-Waals radii (see Table 5). This indicates the overlap between the Br-atoms and between methyl group and Br-atom. Remarkable is the small distance between the C- and  $\text{Br}^{(2)}$ -atom, namely  $d(\text{Br}^{(2)} \cdots \text{C}) = 378.5 \text{ pm}$  (see Figure 7). The overlap here is rather large.

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