

# Crystal Structure of Bis(trimethyltin) Selenate Dihydrate and Rotational Tunnelling of the Methyl Groups

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Rotational tunnelling and librations of methyl groups in bis(trimethyltin) selenate dihydrate,  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$ , have been studied at low temperature using inelastic neutron scattering (INS) technique. Three tunnel transitions at 1.31  $\mu\text{eV}$ , 3.47  $\mu\text{eV}$ , and 21.0  $\mu\text{eV}$  of equal intensity were recorded. In the energy range of phonons a broad, slightly structured intensity distribution is observed. An attempt is made to identify and assign librational modes. The crystal structure of the title compound was determined by single crystal X-ray diffraction.  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$  crystallizes orthorhombic, space group  $\text{D}_{2h}^{14}$ -Pbcn with 4 molecules in the unit cell. The lattice constants at room temperature are  $a = 1142.9(3)$  pm,  $b = 1304.6(4)$  pm, and  $c = 1084.6(3)$  pm. According to the molecular symmetry, the two " $(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})$ " units in molecule are crystallographically equivalent, but the three methyl groups bound to one Sn-atom are inequivalent. This result coincides well with the observation of three tunnel transitions in INS. A comparison with the related compound, bis(trimethyltin) sulfate dihydrate, is presented. The existence of hydrogen bonding and the role of intermolecular interactions on rotational tunnelling are discussed.

## Introduction

Rotation is a fundamental motion in nature. Because of the simple structure and symmetry, methyl groups in organic and metallorganic compounds provide a suitable object for the study of rotational dynamics in solids.

In the high temperature limit the methyl group can be treated as a classical one-dimensional rotator whose rotational dynamics is driven by thermal excitation of the lattice. At low temperatures the methyl group rotation has to be described in the frame of quantum mechanics [1]. In a single particle model the librational ground state would be splitted into two tunnelling sublevels. The theoretical treatment is simple. A quantitative description was already given at the beginning of the seventies [2]. Recently a variety of organic and metallorganic compounds containing methyl groups have been investigated using high-resolution inelastic neutron scattering (INS) technique amongst other spectroscopic methods [3–6].

Rotational tunnelling is determined by the strength and symmetry of the rotational potential, which is produced by intra- and intermolecular interactions, in other words by the nature of the chemical bond  $\text{H}_3\text{C}-\text{X}$  and the molecular packing. Thus the tunnel splitting is very sensitive to any changes of the environment. Without a detailed knowledge of the molecular and crystal structure the explanation of the rotational tunnelling may be incomplete and sometimes misleading [7].

We have reported the rotational tunnelling of methyl groups and the crystal structure of bis(trimethyltin) sulfate dihydrate,  $[(\text{CH}_3)_3\text{Sn}]_2\text{SO}_4 \cdot 2 \text{H}_2\text{O}$  [8]. The two tunnelling transitions observed by INS were at variance with the three crystallographically inequivalent methyl groups in the molecule. This discrepancy led us to extend our investigation to the related compound bis(trimethyltin) selenate dihydrate,  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$ . The results of the INS-study and the crystal structure analysis are reported and discussed here.

## Experimental

Bis(trimethyltin) selenate dihydrate,  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$ , was synthesized by a procedure analogous to that used for the preparation of bis(trimethyltin) sul-

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Table 1. Experimental conditions for the crystal structure determination and crystal structure data of bis(trimethyltin) selenate dihydrate,  $[(CH_3)_3Sn]_2SeO_4 \cdot 2 H_2O$ .

Crystal habitus, size	plate, $(0.25 \cdot 0.3 \cdot 0.6) \text{ mm}^3$
Diffractionmeter	Stoe-Siemens AED-2
Wavelength/pm	71.073 (MoK $\alpha$ )
Monochromator	Graphite (002)
$T/K$	298
Absorption coefficient $\mu/\text{m}^{-1}$	5061
Scan	$2 \cdot \theta/\omega$
$(\sin \theta/\lambda)_{\text{max}}/\text{pm}$	0.006497
Number of measured reflexions	3568
Symmetry independent reflexions	1807
Reflexions considered $[F_0 \geq 2\sigma(F_0)]$	1711
Number of free parameters	85
$F(000)$	959.95
$R(F)$	0.0307
$R_w(F)$	0.0278
Lattice constants	$a/\text{pm}$ 1142.9(3) $b/\text{pm}$ 1304.6(4) $c/\text{pm}$ 1084.6(3)
Volume of the unit cell $V \cdot 10^{-6}/(\text{pm})^3$	1617.17
Space group	$D_{2h}^{14}$ -Pbcn
Formula units per unit cell	$Z = 4$
$\rho_{\text{calc}}/\text{Mg m}^{-3}$	2.081 ( $T = 298 \text{ K}$ )
$\rho_{\text{pykn}}/\text{Mg m}^{-3}$	2.07 ( $T = 299 \text{ K}$ )
Point position in $D_{2h}^{14}$ -Pbcn:	
Se in 4c:	$0, y, \frac{1}{4}; \frac{1}{2}, \frac{1}{2} + y, \frac{1}{4}; 0, \bar{y}, \frac{3}{4}; \frac{1}{2}, \frac{1}{2} - y, \frac{3}{4}$
All other atoms in 8d:	$x, y, z; \frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z; \frac{1}{2} + x, \frac{1}{2} - y, \bar{z}; \bar{x}, y, \frac{1}{2} - z; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} + y, z; x, \bar{y}, \frac{1}{2} + z$

fate dihydrate [8]. Silver selenate was synthesized at first by reaction of aqueous solutions of silver nitrate and magnesium selenate. To an aqueous solution of trimethyltin bromide,  $(CH_3)_3SnBr$ , the stoichiometric amount of silver selenate is added. After complete precipitation of silver bromide the solution is concentrated by the evaporation of the solvent,  $H_2O$ . The title compound crystallizes in form of colourless, transparent orthorhombic prisms. The crystals obtained were used in both, X-ray diffraction and INS experiments.

#### Crystal Structure Analysis

The crystal structure of bis(trimethyltin) selenate dihydrate, was studied in detail using single-crystal technique at 298 K. In Table 1 the experimental con-

ditions are listed together with the crystallographic data (lattice constants, space group etc.).

#### Inelastic Neutron Scattering Experiments

In order to cover a reasonable wide energy range, the INS measurements were carried out with two spectrometers at the Institut Laue-Langevin, Grenoble: the backscattering spectrometer IN 10 covering an energy range  $|E| \leq 14.6 \mu\text{eV}$  and the time-of-flight (TOF) spectrometer IN 5 used in a narrow energy range  $|E| \leq 50 \mu\text{eV}$ . The energy resolutions full width at half maximum were  $\delta E = 0.4 \mu\text{eV}$  for IN 10 and  $\delta E = 5 \mu\text{eV}$  for IN 5, respectively.

The density of state (DOS) was measured with the thermal TOF spectrometer SV 22 at the DIDO reactor, Kernforschungsanlage Jülich. An incident neutron energy  $E = 35 \text{ meV}$  was used, yielding an elastic energy resolution  $\delta E = 1.8 \text{ meV}$ .

## Results

#### Crystal Structure

In Table 1 the crystallographic data (lattice constants, space group etc.) for  $[(CH_3)_3Sn]_2SeO_4 \cdot 2 H_2O$  are given. The crystal structure was determined using the heavy-atom method (SHELX86). Difference Fourier maps were calculated, and the coordinates of all atoms could be determined. The carbon-hydrogen bond distance was fixed at 108.0 pm and the oxygen-hydrogen bond distance in  $H_2O$  was fixed at 96.0 pm. The atomic parameters were refined by least squares cycles, and the final  $R$ -value was reduced to 0.0307.

In Table 2 the relative atomic coordinates and the thermal parameters for  $[(CH_3)_3Sn]_2SeO_4 \cdot 2 H_2O$  are listed. Intramolecular (intraionic) bond distances and bond angles are given in Table 3. Figures 1 and 2 show the "molecule"  $[(CH_3)_3Sn]_2SeO_4 \cdot 2 H_2O$  and the projection of the crystal structure along  $[001]^*$ , respectively.

#### Inelastic Neutron Scattering Spectroscopy

In Figs. 3a and 3b the high-resolution INS spectra of bis(trimethyltin) selenate dihydrate measured at a

\* We wish to remark that the projection of the crystal structure of bis(trimethyltin) sulfate dihydrate along  $[001]$  (Fig. 2 in [8]) has to be shifted by  $1/2b$  in the  $y$ -direction to correspond with the atom positions given in Table 2 [8].

Table 2. Positional and thermal parameters of bis(trimethyltin) selenate dihydrate,  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$ . 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	$x/a$	$y/b$	$z/c$	$U_{11}, U$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Sn	0.2488	0.3182	0.3233	406(2)	403(2)	336(2)	−112(1)	−22(1)	35(1)
Se	0	0.1692	0.25	269(3)	269(2)	309(3)	0	−2(2)	0
O <sup>(1)</sup>	0.1102(2)	0.2421(2)	0.2097(3)	477(19)	626(21)	409(16)	−282(16)	−65(14)	71(14)
O <sup>(2)</sup>	0.0330(2)	0.1015(2)	0.3703(3)	543(20)	472(16)	402(16)	178(14)	105(14)	137(14)
O <sub>w</sub> <sup>(3)</sup>	0.4024(4)	0.4043(3)	0.4164(3)	939(27)	702(23)	528(20)	−558(22)	−329(20)	214(18)
C <sup>(1)</sup>	0.2779(5)	0.4145(4)	0.1699(4)	787(37)	611(32)	444(29)	−311(26)	−122(24)	151(23)
C <sup>(2)</sup>	0.3438(5)	0.1812(4)	0.3463(5)	555(34)	616(35)	785(37)	31(23)	−56(28)	40(28)
C <sup>(3)</sup>	0.1328(5)	0.3649(5)	0.4637(5)	763(42)	915(43)	700(37)	−123(33)	213(32)	−279(32)
H <sup>(C<sup>(1)</sup>, 1)</sup>	0.3408(5)	0.4754(4)	0.1826(4)	600					
H <sup>(C<sup>(1)</sup>, 2)</sup>	0.1954(5)	0.4466(4)	0.1403(4)	600					
H <sup>(C<sup>(1)</sup>, 3)</sup>	0.3096(5)	0.3619(4)	0.1006(4)	600					
H <sup>(C<sup>(2)</sup>, 1)</sup>	0.2949(5)	0.1138(4)	0.3200(5)	600					
H <sup>(C<sup>(2)</sup>, 2)</sup>	0.3589(5)	0.1801(4)	0.4446(5)	600					
H <sup>(C<sup>(2)</sup>, 3)</sup>	0.4267(5)	0.1819(4)	0.2985(5)	600					
H <sup>(C<sup>(3)</sup>, 1)</sup>	0.0494(5)	0.3272(5)	0.4519(5)	600					
H <sup>(C<sup>(3)</sup>, 2)</sup>	0.1187(5)	0.4446(5)	0.4861(5)	600					
H <sup>(C<sup>(3)</sup>, 3)</sup>	0.1806(5)	0.3284(5)	0.5375(5)	600					
H <sup>(O<sub>w</sub><sup>(3)</sup>, 1)</sup>	0.4414(31)	0.4636(24)	0.3816(38)	600					
H <sup>(O<sub>w</sub><sup>(3)</sup>, 2)</sup>	0.4083(39)	0.4169(34)	0.5039(12)	600					

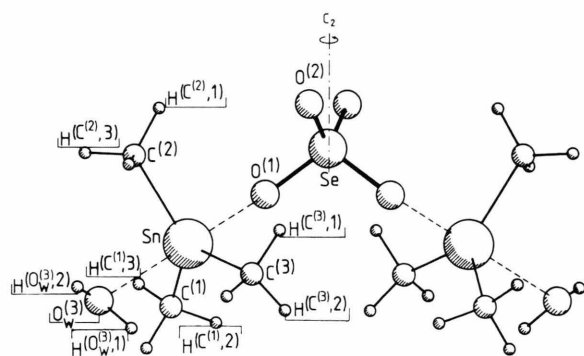


Fig. 1. Molecular unit of bis(trimethyltin) selenate dihydrate,  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$ .

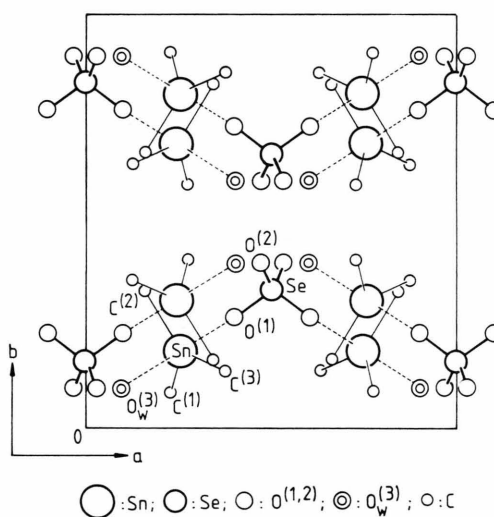


Fig. 2. Projection of the crystal structure of bis(trimethyltin) selenate dihydrate,  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$ , along  $[001]$ . The hydrogen atoms are not shown.

sample temperature of 5 K with IN 10 and IN 5, respectively, are given. Two tunnelling transitions at  $E_{\text{TUN}}^{\text{I}} = 1.31 \mu\text{eV}$  and  $E_{\text{TUN}}^{\text{II}} = 3.47 \mu\text{eV}$  were recorded by IN 10 (Figure 3a). A further tunnelling peak at  $E_{\text{TUN}}^{\text{III}} = 21.0 \mu\text{eV}$  was observed in the extended energy range using IN 5 (Figure 3b).

Fits using resolution functions to describe the observed transition lines show that the total inelastic intensity measured by IN 10 (Fig. 3a) corresponds to 2/3 of the whole inelastic intensity and that the two inelastic lines have equal intensity. The intensity of the

third line measured by IN 5 (Fig. 3b) cannot be compared directly with the  $1.31 \mu\text{eV}$  and  $3.47 \mu\text{eV}$  lines because of the different instruments, but the same arguments as above show that the tunnel peak here represents the residual methyl group in the molecule.

Table 3. Intra- and intermolecular(ionic) bond distances and bond angles of bis(trimethyltin) selenate dihydrate,  $[(CH_3)_3Sn]_2SeO_4 \cdot 2H_2O$ .

Intramolecular $d/\text{pm}$ (intraionic)	Intramolecular (intraionic)	Angle/ degree	
Sn...O <sup>(1)</sup>	223.9(3)	O <sup>(1)</sup> ...Sn...O <sub>w</sub> <sup>(3)</sup>	172.4(1)
Sn...O <sub>w</sub> <sup>(3)</sup>	231.6(3)	O <sup>(1)</sup> ...Sn...C <sup>(1)</sup>	86.6(1)
Sn-C <sup>(1)</sup>	211.2(4)	O <sup>(1)</sup> ...Sn...C <sup>(2)</sup>	93.1(2)
Sn-C <sup>(2)</sup>	210.6(5)	O <sup>(1)</sup> ...Sn...C <sup>(3)</sup>	94.7(2)
Sn-C <sup>(3)</sup>	210.8(5)	O <sub>w</sub> <sup>(3)</sup> ...Sn-C <sup>(1)</sup>	86.3(2)
Se-O <sup>(1)</sup>	163.8(3)	O <sub>w</sub> <sup>(3)</sup> ...Sn-C <sup>(2)</sup>	88.2(2)
Se-O <sup>(2)</sup>	162.1(3)	O <sub>w</sub> <sup>(3)</sup> ...Sn-C <sup>(3)</sup>	91.2(2)
C-H	108.0	C <sup>(1)</sup> -Sn-C <sup>(2)</sup>	121.1(2)
O <sub>w</sub> <sup>(3)</sup> -H(O <sub>w</sub> <sup>(3)</sup> , 1)	97.0(6)	C <sup>(1)</sup> -Sn-C <sup>(3)</sup>	119.7(3)
O <sub>w</sub> <sup>(3)</sup> -H(O <sub>w</sub> <sup>(3)</sup> , 2)	96.5(5)	C <sup>(2)</sup> -Sn-C <sup>(3)</sup>	119.0(3)
		O <sup>(1)</sup> -Se-O <sup>(1)'</sup>	109.0(2)
O <sub>w</sub> <sup>(3)</sup> ...C <sup>(1)</sup>	303.2	O <sup>(1)</sup> -Se-O <sup>(2)</sup>	110.7(1)
O <sub>w</sub> <sup>(3)</sup> ...C <sup>(2)</sup>	308.2	O <sup>(2)</sup> -Se-O <sup>(2)'</sup>	113.9(2)
O <sub>w</sub> <sup>(3)</sup> ...C <sup>(3)</sup>	316.5	Se-O <sup>(1)</sup> ...Sn	130.9(2)
O <sup>(1)</sup> ...C <sup>(1)</sup>	298.6	H <sup>(C<sup>(1)</sup>, 1)</sup> ...C <sup>(1)</sup> -Sn	116.2(1)
O <sup>(1)</sup> ...C <sup>(2)</sup>	315.5	H <sup>(C<sup>(1)</sup>, 2)</sup> ...C <sup>(1)</sup> -Sn	109.1(2)
O <sup>(1)</sup> ...C <sup>(3)</sup>	319.8	H <sup>(C<sup>(1)</sup>, 3)</sup> ...C <sup>(1)</sup> -Sn	102.9(2)
C <sup>(1)</sup> ...C <sup>(2)</sup>	367.3	H <sup>(C<sup>(2)</sup>, 1)</sup> ...C <sup>(2)</sup> -Sn	113.2(2)
C <sup>(1)</sup> ...C <sup>(3)</sup>	365.0	H <sup>(C<sup>(2)</sup>, 2)</sup> ...C <sup>(2)</sup> -Sn	102.1(2)
C <sup>(2)</sup> ...C <sup>(3)</sup>	363.0	H <sup>(C<sup>(2)</sup>, 3)</sup> ...C <sup>(2)</sup> -Sn	112.9(2)
H(O <sub>w</sub> <sup>(3)</sup> , 1)...H(O <sub>w</sub> <sup>(3)</sup> , 2)	150.8	H <sup>(C<sup>(3)</sup>, 1)</sup> ...C <sup>(3)</sup> -Sn	109.7(2)
O <sup>(2)</sup> ...H(O <sub>w</sub> <sup>(3)</sup> , 1)	182.7	H <sup>(C<sup>(3)</sup>, 2)</sup> ...C <sup>(3)</sup> -Sn	122.3(2)
O <sup>(2)'</sup> ...H(O <sub>w</sub> <sup>(3)</sup> , 2)	198.8	H <sup>(C<sup>(3)</sup>, 3)</sup> ...C <sup>(3)</sup> -Sn	95.2(2)
O <sub>w</sub> <sup>(3)</sup> ...O <sup>(2)</sup>	272.2	H-C-H	109.5
O <sub>w</sub> <sup>(3)</sup> ...O <sup>(2)'</sup>	275.4	H(O <sub>w</sub> <sup>(3)</sup> , 1)-O <sub>w</sub> <sup>(3)</sup> -Sn	124.5(2.7)
		H(O <sub>w</sub> <sup>(3)</sup> , 2)-O <sub>w</sub> <sup>(3)</sup> -Sn	124.4(2.7)
		H(O <sub>w</sub> <sup>(3)</sup> , 1)-O <sub>w</sub> <sup>(3)</sup> -H(O <sub>w</sub> <sup>(3)</sup> , 2)	102.4(3.8)
		O <sub>w</sub> <sup>(3)</sup> -H(O <sub>w</sub> <sup>(3)</sup> , 1)...O <sup>(2)</sup>	152.0
		O <sub>w</sub> <sup>(3)</sup> -H(O <sub>w</sub> <sup>(3)</sup> , 2)...O <sup>(2)'</sup>	134.8
		O <sup>(2)</sup> -O <sub>w</sub> <sup>(3)</sup> -O <sup>(2)'</sup>	91.9

Table 4. Peak positions of bis(trimethyltin) selenate dihydrate,  $[(CH_3)_3Sn]_2SeO_4 \cdot 2H_2O$ , in the meV range and proposed assignments (P = Phonon, L = Libration).

Measured $E/meV$	Assignment	Measured $E/meV$	Assignment
8.75	L	17.59	P
12.72	L	19.49	P
13.86	L	23.03	P

Thus we have observed all tunnel transitions present in the titel compound. The three inelastic peaks indicate the existence of three types of methyl groups with equal occurrence.

The density of state (DOS) is shown in Figure 4. The spectrum represents the sum over all detectors arranged at scattering angles between 20° and 130°. In Table 4 the energetic positions of the peaks observed at 15 K are listed together with the proposed assign-

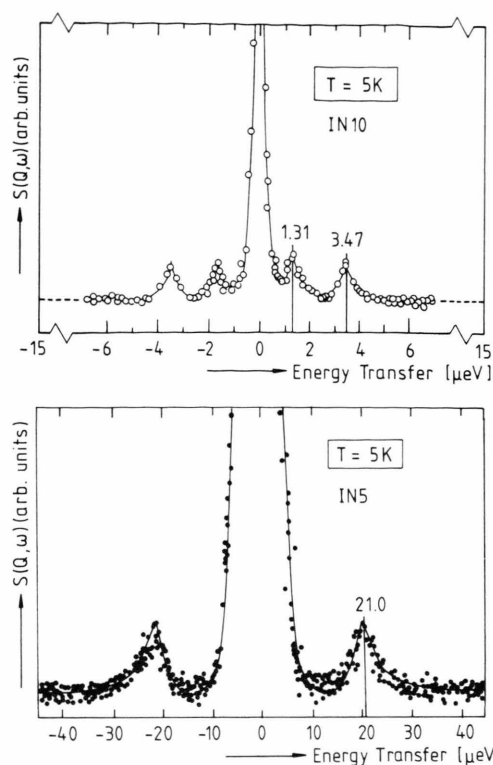


Fig. 3. High-resolution INS-spectrum of bis(trimethyltin) selenate dihydrate,  $[(CH_3)_3Sn]_2SeO_4 \cdot 2H_2O$ . Plotted is the intensity  $S(Q, \omega)$  as a function of energy transfer.

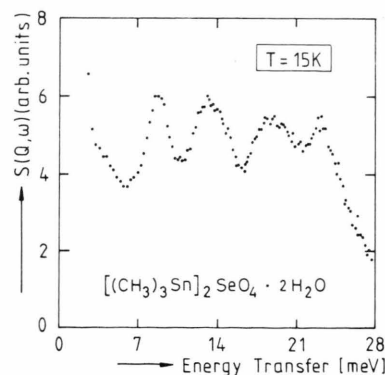


Fig. 4. Inelastic neutron scattering spectrum of bis(trimethyltin) selenate dihydrate,  $[(CH_3)_3Sn]_2SeO_4 \cdot 2H_2O$ , taken in the meV range at the indicated sample temperature. Spectrometer: SV 22. Energy resolution:  $\delta E = 1.8$  meV.

ments, which are based on the different temperature dependences of librations and lattice phonons [7]. Additionally, the spectrum was compared with those found for the isostructural bis(trimethyltin) sulfate dihydrate [8].

Table 5. Observed tunnel splittings  $\hbar\omega_0$  and librational energies  $E_{01}$ . Calculated activation energies  $E_A$  and the mixed three- and sixfold rotational potential. I, II, and III denote the three types of crystallographically different methyl groups in  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$ .

	$\frac{\hbar\omega_0}{\mu\text{eV}}$	$\frac{E_{01}}{\text{meV}}$	$\frac{V_3}{\text{kJ mol}^{-1}}$	$\frac{V_6}{\text{kJ mol}^{-1}}$	$k$	$\frac{E_A}{\text{kJ mol}^{-1}}$
$\text{CH}_3$ (I)	21.0	8.75	1.35	0.34	0	2.4
$\text{CH}_3$ (II)	3.47	12.72	2.01	0.18	0	3.5
$\text{CH}_3$ (III)	1.31	13.86	2.53	0.28	0	4.5

The observed librational and tunnelling energies can be explained in a single particle picture [1] as solutions of the rotational Schrödinger equation

$$\hat{H}_R \Psi_i = E_i \Psi_i, \quad \hat{H}_R = -B \frac{\partial^2}{\partial \Phi^2} + V(\Phi). \quad (1)$$

Here  $B = \hbar^2/2I = 0.6475 \text{ meV}$  ( $\cong 0.0625 \text{ kJ mol}^{-1} \cong 9.84 \cdot 10^{11} \text{ s}^{-1}$ ) is called the rotational constant of the methyl group with the momentum of inertia  $I = 5.3 \cdot 10^{-47} \text{ kg m}^2$ , and  $V(\Phi)$  is the rotational potential, usually described by the first two terms of a Fourier expansion

$$V(\Phi) = V_3/2 \cdot [1 + (-1)^k \cos 3\Phi] + V_6/2 \cdot [1 + (-1)^k \cos 6\Phi]. \quad (2)$$

It is a major problem to assign the tunnel and librational transitions correctly in systems containing inequivalent  $\text{CH}_3$ -groups [7]. On the basis of the general experience that the deviation from a pure  $\cos 3\Phi$  potential is small [3], we assign the largest tunnel splitting to the lowest librational mode and continue in this order.

Then we can derive the three- and sixfold contributions  $V_3$  and  $V_6$  of the corresponding rotational potentials, (2), and activation energies for the three rotators  $\text{CH}_3$ (I),  $\text{CH}_3$ (II), and  $\text{CH}_3$ (III) using the tabulated solutions of the Mathieu equation [2]. The results are listed together with the measured librational and tunnelling energies in Table 5.

## Discussion

The crystal structure determination shows unequivocally that the title compound, bis(trimethyltin) selenate dihydrate,  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$ , is isostructural with the corresponding sulfate compounds,

$[(\text{CH}_3)_3\text{Sn}]_2\text{SO}_4 \cdot 2 \text{H}_2\text{O}$  [8]. Both compounds crystallize orthorhombic, space group  $\text{D}_{2h}^{14}\text{-Pbcn}$ , with  $Z = 4$  formula units in the unit cell. The existence of the proposed coordination [9], two  $\text{H}_2\text{O}$  attached to each molecule as well as a trigonal bipyramidal environment of the tin atoms with three equatorial methyl groups and two axial oxygen atoms, one donated by the selenate ion and the another by the  $\text{H}_2\text{O}$  molecule [9], is confirmed by the present work (see Figs. 1 and 2). As for bis(trimethyltin) sulfate dihydrate, there is a twofold axis through the central atom of the  $\text{XO}_4^{2-}$  anion, here  $\text{X} = \text{Se}$ . Consequently, the two “ $(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})$ ” units in the molecule are crystallographically equivalent. According to the molecular symmetry, the three methyl groups bound to each tin atom are crystallographically inequivalent.

The structure data given in Table 3 show that the trigonal bipyramid,  $\text{O}^{(1)} \dots [(\text{CH}_3)_3\text{Sn}] \dots \text{O}_w^{(3)}$ , is quite regular. For the distances between tin and oxygen atoms we find 223.9 pm and 231.6 pm (224 pm and 236 pm in the sulfate compound). The angle  $\text{O}^{(1)} \dots \text{Sn} \dots \text{O}_w^{(3)}$  in this way is  $172.4^\circ$ , deviating by  $7.6^\circ$  from  $180^\circ$ . Also the angles  $\text{O}^{(1)} \dots \text{Sn} - \text{C}^{(n)}$  ( $n = 1, 2, 3$ ) and  $\text{O}_w^{(3)} \dots \text{Sn} - \text{C}^{(n)}$  ( $n = 1, 2, 3$ ) are in the average  $90^\circ \pm 5^\circ$  for both compounds.

An interesting point in the crystal structure of  $[(\text{CH}_3)_3\text{Sn}]_2\text{XO}_4 \cdot 2 \text{H}_2\text{O}$ ,  $\text{X} = \text{S}$  and  $\text{Se}$ , is the intermolecular (interionic) interaction in these solids. It was observed [10], that  $\text{H}_2\text{O}$  can be removed from the solid compounds under extreme conditions only (heating under vacuum). The anhydrous product is rather unstable and rehydrates on air quite rapidly [9]. In Fig. 5 the crystal structure of  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$  is projected along [100] onto the plane (bc). In this projection the hydrogen bonds are shown. The molecules  $\text{H}_2\text{O}$  connect via hydrogen bonds  $\text{SeO}_4^{2-}$  ions, and thereby chains  $(\dots \text{SeO}_4(2 \text{H}_2\text{O})\text{SeO}_4(2 \text{H}_2\text{O})\dots)$  are formed, running



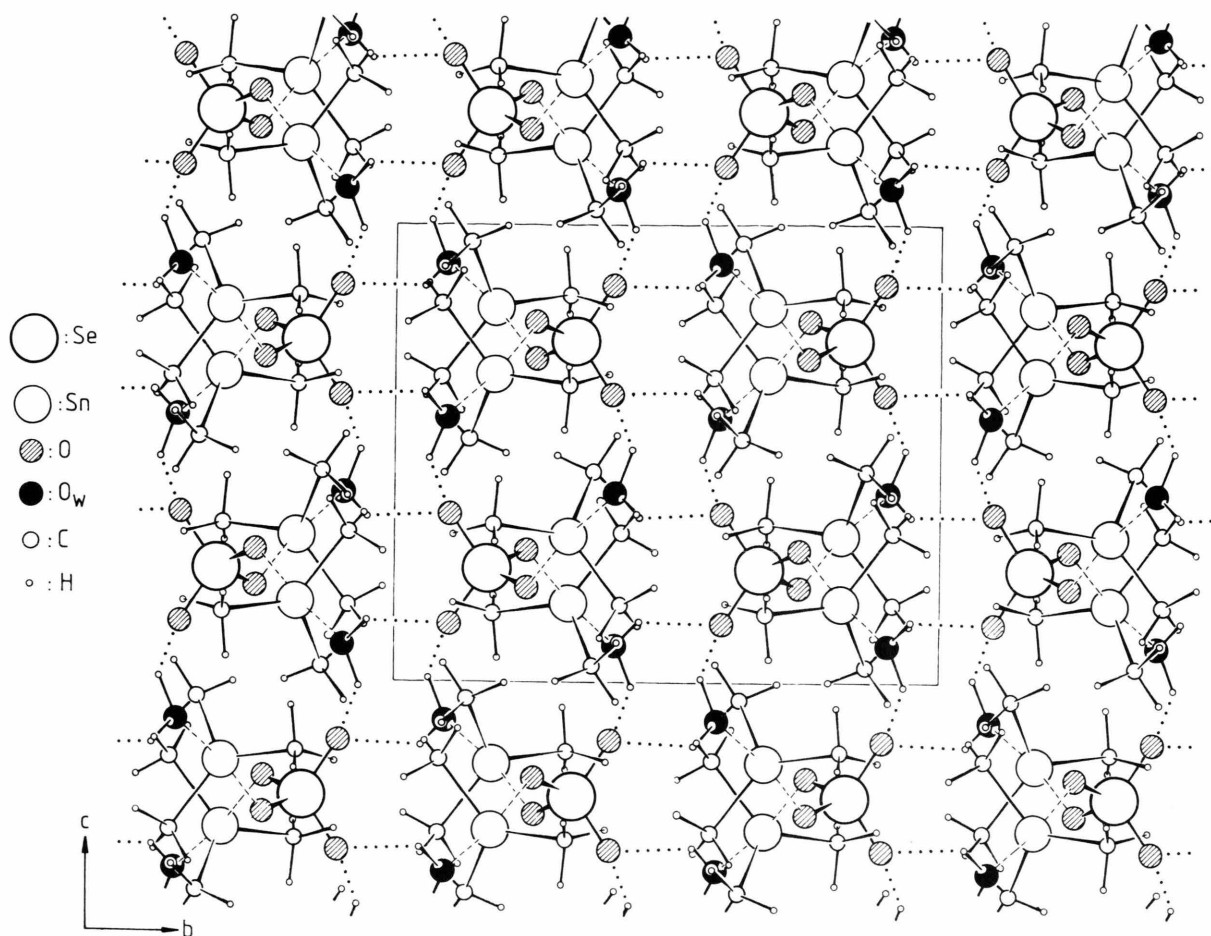


Fig. 5. Projection of the crystal structure of bis(trimethyltin) selenate dihydrate,  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$ , along  $[100]$ .  $\cdots$  hydrogen bonds,  $---$  coordinative bonds.

along the  $c$ -axis at  $y = 0$  and  $y = 0.5$ , respectively. The parallelograms  $\text{O}^{(2)} \dots \text{O}_w \dots \text{O}^{(2)'} \dots \text{O}_w'$  are centered at  $(1/2, 1/2, 1/2)$ ,  $(0, 0, 0)$ ,  $(1/2, 1/2, 0)$ , and  $(0, 0, 1/2)$ .

The hydrogen bonds are unsymmetrical, and this finding is supported by chemical reasoning [11] and by the distances  $\text{O}_w \dots \text{O}^{(2)}$ ,  $d(\text{O}_w \dots \text{O}^{(2)})$  being 272 pm and 275 pm, respectively, see Table 3. The projection of the crystal structure along  $[001]$ , given in Fig. 2, shows, that the chains of hydrogen bonds are running into the paper plain, their axes being  $[001]$  and  $[221]$ . As pointed out, the  $[(\text{CH}_3)_3\text{Sn}]^\oplus$  ions are coordinated with  $\text{O}_w$  and  $\text{O}^{(1)}$  of the  $\text{SeO}_4^{2-}$  ions in a quite regular trigonal bipyramid. The coordinative bondings and the Coulomb interactions lead, together with the hydrogen bonds, to a stable network.

To connect the crystal structure with the results of the INS is not an easy task. The crystal structure was determined at 298 K. Going down to 4 K, the lattice constants will change – most probably they will shrink – in an anisotropic manner. We assume that the intramolecular bonds (static bond lengths) are not affected by the lattice constants change. The three carbon-tin bond lengths are slightly different in both compounds, the sulfate and the selenate. In the present selenate compound we find:  $\text{Sn}-\text{C}^{(1)}$ : 211.2(4) pm,  $\text{Sn}-\text{C}^{(2)}$ : 210.6(5) pm, and  $\text{Sn}-\text{C}^{(3)}$ : 210.8(5) pm. A simple approach to connect a certain methyl group to a certain tunnel splitting is, that the largest tunnel splitting belongs to the methyl group which has the largest carbon-tin bond length. This means here, the

splitting  $\hbar\omega_0 = 21.0 \mu\text{eV}$  corresponds to the group  $\text{H}_3\text{C}^{(1)}$ . Consequently  $\hbar\omega_0 = 3.47 \mu\text{eV}$  with  $\text{H}_3\text{C}^{(3)}$  and  $\hbar\omega_0 = 1.37 \mu\text{eV}$  with  $\text{H}_3\text{C}^{(2)}$ .

This model, which is a rather crude one, completely neglects the overlap of the carbon-tin bond lengths within the limits of error and the different potential wells in which the three methyl rotors are embedded. On the basis of an identical potential shape for the three methyl groups, the large differences in the tunnel splittings cannot at all be understood.

The above model, taking only the intramolecular bond lengths into account to interpret the INS spectra, may be satisfactory as long as it is confined to the selenate and the sulfate compound separately.

However, comparison (Table 6) of the Sn—C bond lengths as well as the tunnel splittings of bis(trimethyltin) selenate dihydrate with those of bis(trimethyltin) sulfate dihydrate yields some anomaly which might be worthwhile discussing.

Within a model which considers intramolecular interactions only, the rotational potential strength should be related to the intramolecular distances. Since both compounds discussed here are isostructural, the relative values of bond distances determined at room temperature will most probably be maintained down to 4 K. As shown in Table 6, the carbon-tin bond lengths, Sn—C<sup>(*n*)</sup> with *n* = 1, 2, and 3 in the selenate compound are slightly shorter than those in the sulfate compound. Therefore one expects the stronger rotational potentials, i.e. the smaller tunnel splitting for the selenate compound, in contradiction with the present observation. There must be other important interactions, neglected in the above simple model.

At room temperature the unit cell of the selenate compound is more than 4.5% larger than the one of the sulfate compound ( $1617.17 \cdot 10^6 \text{ pm}^3$  compared to  $1542.66 \cdot 10^6 \text{ pm}^3$ ). In the order of magnitude this difference should be preserved down to 4 K.

From the crystal structure analysis of both compounds it is seen that the substitution of sulfur by selenium causes an expansion of the whole unit  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2\text{H}_2\text{O}$  and an increasing of Sn...Sn distance within the molecule. The intermolecular Sn...Sn distances in the selenate compound are all larger than those in the sulfate one, see Table 7 and Figure 6. Whereas the carbon-tin bond lengths within the ion  $[(\text{CH}_3)_3\text{Sn}]^\oplus$  decrease slightly by going from the sulfate to the selenate compound, the carbon-carbon distances between different  $[(\text{CH}_3)_3\text{Sn}]^\oplus$  become longer because of the substitution  $\text{S} \rightarrow \text{Se}$ . The

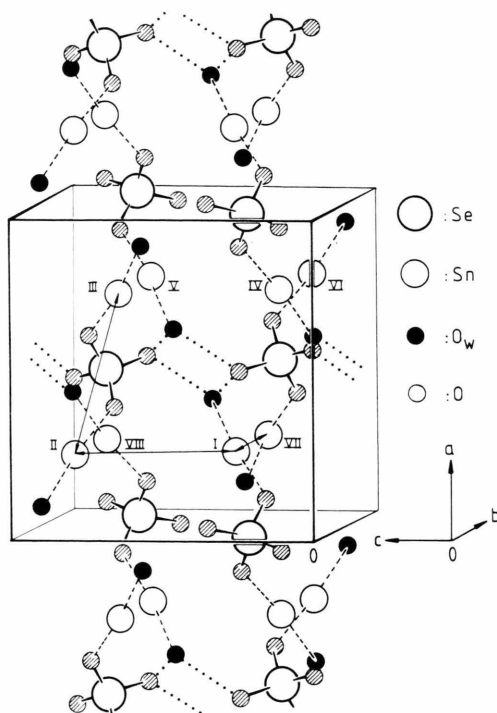


Fig. 6. Sketch of the crystal structure (without carbon and hydrogen atoms). The interionic bonds (— — — for coordinative bonds and ····· for hydrogen bonds) are shown. Additionally the frame of the Sn...Sn distances is marked, see also Table 7. All Sn atoms in the unit cell are crystallographically equivalent. The numbers (I–VIII) of the Sn atom show the individual point positions resulting from the symmetry operations.

Table 6. Comparison of Sn—C bond lengths and tunnel splittings in bis(trimethyltin) selenate dihydrate (this work) and in bis(trimethyltin) sulfate dihydrate [8].

	Sn—C / pm	$\hbar\omega_0 / \mu\text{eV}$
$[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2\text{H}_2\text{O}$	211.2(5)	21.0
	210.8(5)	3.47
	210.6(5)	1.31
$[(\text{CH}_3)_3\text{Sn}]_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$	212.6(5)	11.36
	211.4(5) }	1.10
	210.8(5) }	

Table 7. Comparison of the relevant distances,  $d(\text{Sn} \dots \text{Sn})$  in the unit cell of  $[(\text{CH}_3)_3\text{Sn}]_2\text{XO}_4 \cdot 2\text{H}_2\text{O}$ , X = Se and S. The numbers (I–VIII) indicate the individual point positions of Sn atoms resulting by different symmetry operations, see Figure 6.

	X = Se <i>d</i> / pm	X = S <i>d</i> / pm	$\Delta d$ / pm
$\text{Sn}^{\text{I}} \dots \text{Sn}^{\text{II}}$	570.76	561.79	8.97
$\text{Sn}^{\text{I}} \dots \text{Sn}^{\text{VII}}$	652.31	634.78	17.53
$\text{Sn}^{\text{II}} \dots \text{Sn}^{\text{III}}$	590.52	571.92	18.60

packing of the particles of  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$  is less dense than that of the sulfate compound, especially along the axes *a* and *b*. The increasing inter-spaces therefore reduce the interactions between neighbouring molecules and thus the strength of the rotational potential of methyl groups measured by the tunnel splitting if the intermolecular interaction is equally relevant as the intramolecular interactions. These results show that the intermolecular interactions play an important role in the tunnelling mechanism of the trimethyl tin salts we have studied. Similar conclusions were obtained in an experiment on  $(\text{CH}_3)_4\text{Sn}$ , where the intermolecular interaction was reduced by incorporating the molecules in a rare gas matrix [12].

We now qualitatively understand the apparent discrepancy between the presence of two tunnelling transitions with relative intensities 2:1 observed in the INS-experiment and three crystallographically independent methyl groups found in the crystal structure analysis of  $[(\text{CH}_3)_3\text{Sn}]_2\text{SO}_4 \cdot 2 \text{H}_2\text{O}$  [8]. Because of the strong intermolecular interactions in  $[(\text{CH}_3)_3\text{Sn}]_2\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ , resulting from the compact molecular packing, the three methyl groups feel rather strong intermolecular rotational potentials, and consequently their tunnel splitting are rather weak. Two of three methyl groups are forced to take alike rotational potentials and therefore show similar tunnel splittings.

The crystal structure determinations of both compounds  $[(\text{CH}_3)_3\text{Sn}]_2\text{XO}_4 \cdot 2 \text{H}_2\text{O}$ , X = S and Se, show that the averages of thermal parameters,  $\bar{U} = (U_{11} + U_{22} + U_{33})/3$ , in the selenate compounds are larger than those in the sulfate compound (Table 2, and Table 2 in [8]). This indicates stronger thermal vibrations of the atoms in the lattice of  $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4 \cdot 2 \text{H}_2\text{O}$  and a higher degree of freedom of motion. In consequence, the intermolecular interactions are weaker.

The influence of the intra- and intermolecular interactions on rotational tunnelling is certainly more complicated than covered here by discussion of the intramolecular bond lengths and the intermolecular

distances. A more quantitative analysis is beyond the scope of this paper. At least it would require a crystal structure determination at 4 K by neutron diffraction.

## Conclusion

The present investigation shows the importance of two informations for a deeper understanding of rotational tunnelling of methyl groups.

Firstly, a detailed information about the crystal structure taken at low temperatures is necessary for a reliable interpretation of INS-results. The high-resolution INS tunnel spectra can provide the number of different tunnel transitions within the resolution limit directly. In combination with the crystal structure analysis information becomes available whether different tunnel peaks are caused by crystallographically inequivalent methyl groups or whether they originate in other effects, e.g. the coupling of tunnel rotators [13]. A correlation of the tunnel splitting with intermolecular and intramolecular distances yields a higher level of understanding of the experimental observations [8, 14, 15].

Secondly it is found that beside the intramolecular interactions the intermolecular ones must be considered in the discussion of rotational potentials. Our above investigation shows that a suitable choice of related compounds or the investigation of isotopic compounds [14] yields data sets whose consistent description demonstrates the role of intermolecular interactions in rotational tunnelling.

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