

## VARIABLE TEMPERATURE $^{119m}\text{Sn}$ MÖSSBAUER STUDIES OF $\text{Ph}_3\text{SnSCH}_2\text{CH}_2\text{COOSnPh}_3$ AND $\text{Bu}_3\text{SnSCH}_2\text{CH}_2\text{COOSnBu}_3$

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### Summary

Variable temperature  $^{119m}\text{Sn}$  Mössbauer data are presented for two organotin compounds which each contain 4- and 5-coordinate tin sites. The absorption line areas of each site have been determined and the Debye model of solids has been used to fit the experimental data. The Debye temperature associated with each site has been determined, and compared with other data.

### Introduction

This paper presents the results of a series of variable temperature  $^{119m}\text{Sn}$  Mössbauer experiments of two compounds:

(A): (3-Mercaptopropionate)bis(triphenyltin(IV)),  $\text{Ph}_3\text{SnSCH}_2\text{CH}_2\text{COOSnPh}_3$   
 and

(B): (3-Mercaptopropionate)bis(tributyltin(IV)),  $\text{Bu}_3\text{SnSCH}_2\text{CH}_2\text{COOSnBu}_3$ .

This work is an extension of our previous study of triorganotin derivatives of amino acids [1].

These are solid state polymers and the structure of A is shown in Fig. 1. The equivalent trimethyl compound has been investigated previously and the Mössbauer lattice dynamics reported [2]. These materials are of particular interest for studying the Mössbauer absorption since they contain 4- and 5-coordinate tin sites. It has been reported that there exists no simple functional dependence of the recoilless free fraction upon the coordination number of the Mössbauer atom [3]. These solid state polymers allow the Mössbauer absorption line areas to be determined for the 4-coordinate and 5-coordinate sites within a repeating molecular unit, and their respective variation with temperature determined.

### Experimental

Thin Mössbauer samples were packed into Perspex discs and cooled using a continuous flow cryostat and helium exchange gas. For temperatures above 80 K

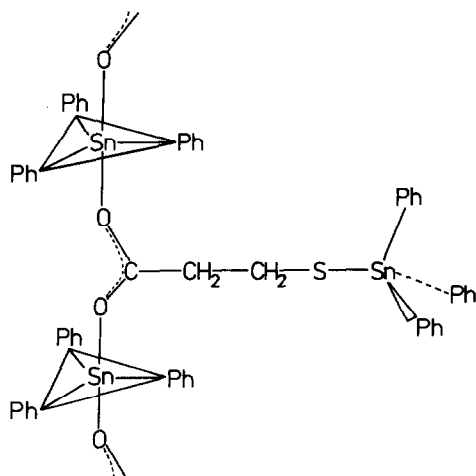


Fig. 1. The structure of  $\text{Ph}_3\text{SnSCH}_2\text{CH}_2\text{COOSnPh}_3$  (A).

liquid nitrogen coolant was used, and for temperatures below 80 K liquid helium was used. The Mössbauer spectra were recorded using constant acceleration Mössbauer spectrometers with a 15 mCi  $^{119\text{m}}\text{Sn}$  barium stannate source. The Mössbauer parameters were obtained from computer least-squares fits to the spectra using Lorentzian line shapes.

### Theory

The Mössbauer absorption line area is related to the Mössbauer thickness  $t$  by the expression [4]:

$$A(t) \propto \frac{t}{2} \exp\left\{\frac{-t}{2}\right\} \left[ I_0\left\{\frac{t}{2}\right\} + I_1\left\{\frac{t}{2}\right\} \right] \quad (1)$$

where  $I_0$  and  $I_1$  are the zeroth and first order Bessel functions. The Mössbauer thickness  $t$  is given by

$$t = n f_a \sigma_0 \quad (2)$$

for a single line. Where hyperfine splittings, such as the quadrupole interaction, result in multiple absorption lines, we must consider an effective reduced thickness for each resolved absorption line,  $t_i = \beta_i t$

$$\text{where } \sum_{i=1}^n t_i = \sum_{i=1}^n \beta_i t = t \quad (3)$$

The small  $t$  expansion of eq. 1 is

$$A(t) \propto t(1 - 0.25t + 0.0625t^2 + \dots) \quad (4)$$

Thus for small  $t$ , the absorption line area is proportional to the absorber recoil-free fraction  $f_a$ . The temperature dependence of the recoil-free fraction is given from the Debye model of solids by an expression of the form:

$$f_a(T) = \exp - \frac{3E_R}{2k_B\theta_D} \left[ 1 + 4 \left\{ \frac{T}{\theta_D} \right\}^2 \int_0^{\theta_D/T} \frac{x dx}{(e^x - 1)} \right] \quad (5)$$

where  $E_R = E_\gamma^2/2M_{\text{eff}}c^2$  and  $\theta_D$  is the Debye temperature. In the high temperature limit ( $T > \theta_D$ ) the integral goes to  $\theta_D/T$  and hence:

$$f_a(T) = \exp\left[-\frac{3E_R}{2k_B\theta_D} - \frac{6E_RT}{k_B\theta_D^2}\right] \quad (6)$$

Thus for an ideal monatomic isotropic cubic solid, the slope of the  $\ln f_a(T)$  vs. temperature graph would be given by

$$\frac{d(\ln f_a(T))}{dT} = -\frac{6E_R}{k_B\theta_D^2} \quad (7)$$

and hence

$$\frac{d(\ln A)}{dT} = \frac{-3E_\gamma^2}{(M_{\text{eff}}c^2)k_B\theta_D^2} \quad (8)$$

Equation 8 in general contains two unknowns, namely the Debye temperature and the effective mass,  $M_{\text{eff}}$ , of the absorbing atom.

## Results and discussion

The Mössbauer hyperfine parameters for the two samples are shown in Table 1, and a typical spectrum of  $\text{Ph}_3\text{SnSCH}_2\text{CH}_2\text{COOSnPh}_3$  recorded at 100 K is shown in Fig. 2. The recoil-free fraction for this sample was sufficiently large to allow good quality spectra to be recorded over the temperature range 80–200 K at 20 K intervals. The tributyltin compound, however, had a significantly smaller recoil-free fraction and it was necessary to cover the temperature range 20–140 K to obtain equivalent sets of data. Four spectra recorded in the temperature range 20–80 K are shown in Fig. 3. In all spectra, the solid line represents the least-squares computer fit to the data using two pairs of Lorentzian lines. The normalised areas were determined in the usual way using the fitted line widths and depths of the quadrupole pairs. For each spectrum the total normalised absorption area and the individual areas were calculated.

The results for the triphenyltin compound are shown in Table 2 and for the tributyl analogue in Table 3. The natural logarithm plots of the area vs. temperature are shown in Figs. 4 and 5. In both cases, the total area and the individual doublet

TABLE 1  
 $^{119\text{m}}\text{Sn}$  MÖSSBAUER PARAMETERS MEASURED AT 80 K

	Isomer shift $\delta$ ( $\text{mm s}^{-1}$ ) $\pm 0.02$	Quadrupole splitting $\Delta$ ( $\text{mm s}^{-1}$ ) $\pm 0.02$	Full width at half max $\Gamma$ ( $\text{mm s}^{-1}$ ) $\pm 0.02$
$\text{Bu}_3\text{SnSCH}_2\text{CH}_2\text{COOSnBu}_3$ (i)	1.47	3.62	1.09
(ii)	1.46	1.76	1.11
$\text{Ph}_3\text{SnSCH}_2\text{CH}_2\text{COOSnPh}_3$ (i)	1.35	3.49	0.99
(ii)	1.35	1.32	1.03

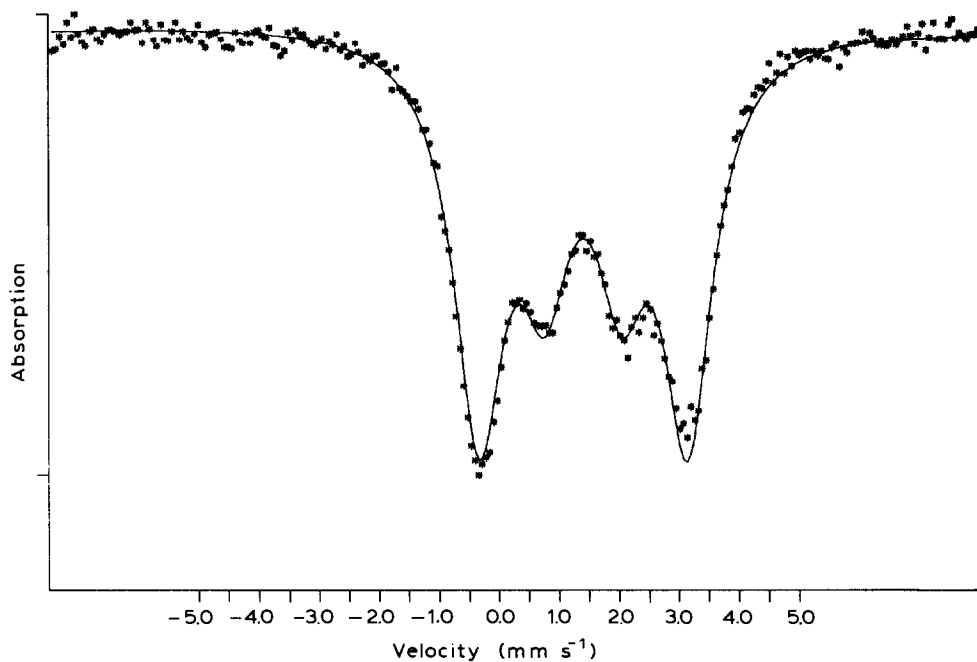


Fig. 2.  $^{119}\text{mSn}$  Mössbauer spectrum of  $\text{Ph}_3\text{SnSCH}_2\text{CH}_2\text{COOSnPh}_3$  (A) at 100 K.

areas have been plotted. In each case line (I) corresponds to the 5-coordinate Sn–O site while line (II) corresponds to the 4-coordinate Sn–S site. There was no significant deviation from linearity over the observed temperature range. The interpretation of these results using the simple Debye model of solids requires the effective vibrating mass to be specified. While it is apparent that the complex structure of the solid state polymer is far from the model on which the Debye theory is based, it appears that this continuum model may be applied if the Debye temperature is treated as a parameter. However, too much physical significance should not be attached to the value obtained.

The Debye approximation to the Debye-Waller factor assumes that the mean square displacement of an atom is isotropic, whereas in general, and certainly in the example presented here, the mean square displacement of the tin atom is anisotropic [5]. Nevertheless the smaller the value of the Debye temperature the larger is the value of the mean square displacement of the atom. If the effective vibrating mass (EVM) is taken to be the unit formation mass then the Debye temperatures for the two tin sites can be determined from the measured gradients. The results are shown in Table 4. The different Debye temperatures for the two tin sites indicates the different vibrational properties of the 5-coordinate Sn–O site and the 4-coordinate Sn–S site. Since the determined Debye temperatures are comparable to the lowest observation temperatures, the use of the high temperature limit ( $T > \theta_D$ ) may not be fully justified. Using a least-squares computer fitting method, the data for the individual line areas was fitted using the exact evaluation of eq. 5 with  $\theta_D$  as a variable. The values obtained for the Debye temperatures by this method were all in close agreement with those obtained using the high temperature limit. The values for

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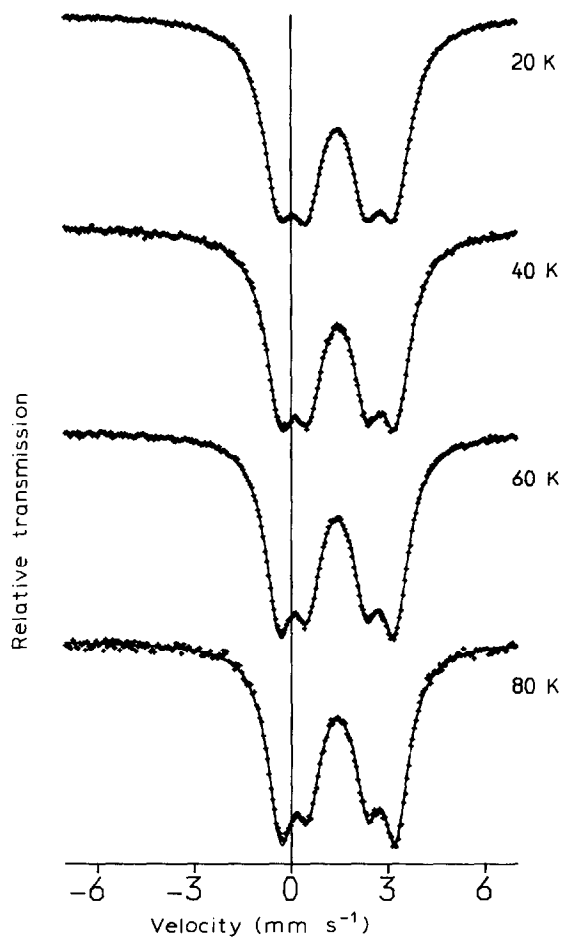


Fig. 3.  $^{119m}\text{Sn}$  Mössbauer spectra of  $\text{Bu}_3\text{SnSCH}_2\text{CH}_2\text{COOSnBu}_3$  (B) in the temperature range 20–80 K.

TABLE 2

VARIABLE TEMPERATURE  $^{119m}\text{Sn}$  MÖSSBAUER DATA FOR  $\text{Ph}_3\text{SnSCH}_2\text{CH}_2\text{COOSnPh}_3$

Temperature (K)	Total area ( $A$ )	$\ln A$	Individual areas ( $A'$ )	$\ln A'$
80	277.1	5.62	111.6	4.71
			165.6	5.11
100	169.7	5.13	63.6	4.15
			106.1	4.66
120	101.5	4.62	33.7	3.52
			67.8	4.22
140	77.0	4.34	27.8	3.32
			49.2	3.90
160	43.5	3.77	13.6	2.61
			29.9	3.40
180	25.9	3.25	7.6	2.03
			18.3	2.91
200	16.3	2.79	3.71	1.31
			12.6	2.53

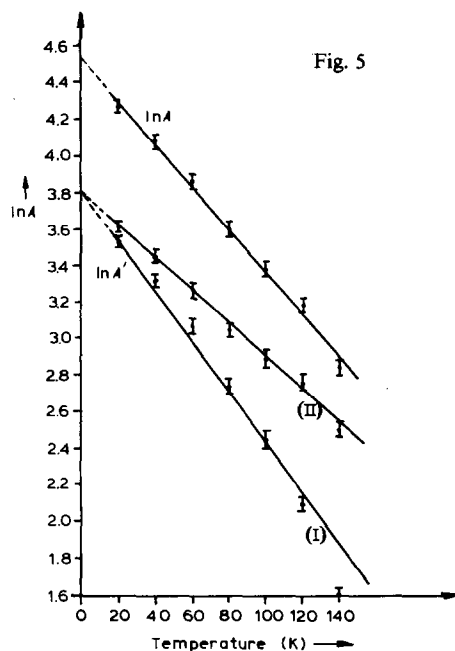
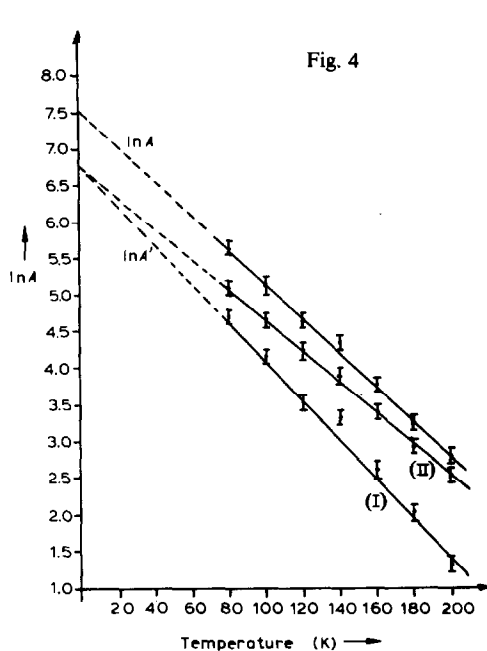


Fig. 4. Temperature dependence of the areas under the inner and outer pair of resonance maxima of  $\text{Ph}_3\text{SnSCH}_2\text{CH}_2\text{COOSnPh}_3$ ;  $\ln A$  is the total Lorentzian area under the resonance peaks;  $\ln A'$  represents the temperature dependence of the individual areas due to the inner (I) and outer (II) resonance peaks.

Fig. 5. Temperature dependence of the areas under the inner and outer pair of resonance maxima of  $\text{Bu}_3\text{SnSCH}_2\text{CH}_2\text{COOSnBu}_3$ ;  $\ln A$  is the total Lorentzian area under the resonance peaks;  $\ln A'$  represents the temperature dependence of the individual areas due to the inner (I) and outer (II) resonance peaks.

TABLE 3

VARIABLE TEMPERATURE  $^{119\text{m}}\text{Sn}$  MÖSSBAUER DATA FOR  $\text{Bu}_3\text{SnSCH}_2\text{CH}_2\text{COOSnBu}_3$

Temperature (K)	Total area (A)	$\ln A$	Individual areas (A')	$\ln A'$
20	71.4	4.27	34.3 37.1	3.53 3.61
40	59.1	4.08	27.7 31.4	3.32 3.45
60	47.4	3.86	21.4 26.0	3.06 3.26
80	35.8	3.58	15.51 20.31	2.74 3.01
100	29.4	3.38	11.45 17.92	2.44 2.89
120	24.0	3.18	8.18 15.9	2.10 2.76
140	17.1	2.84	4.96 12.1	1.60 2.50

TABLE 4  
EVM MODEL

	Gradient	$M_{eff} \theta_D^2$	$\theta_D$ (K)
Ph <sub>3</sub> SnSCH <sub>2</sub> CH <sub>2</sub> COOSnPh <sub>3</sub> $M_{eff} = 804$ u	$G_1 = -2.1 \times 10^{-2}$	$1.01 \times 10^6$	35.5
	$G_2 = -2.6 \times 10^{-2}$	$0.81 \times 10^6$	31.7
Bu <sub>3</sub> SnSCH <sub>2</sub> CH <sub>2</sub> COOSnBu <sub>3</sub> $M_{eff} = 684$ u	$G_1 = -0.90 \times 10^{-2}$	$2.38 \times 10^6$	59.1
	$G_2 = -1.3 \times 10^{-2}$	$1.65 \times 10^6$	49.1

the Debye temperatures determined from this study compare similarly with the values obtained by Barbieri et al. [2] for the trimethyltin compound. Also using the effective vibrating mass to be the formula mass Barbieri and his workers obtained Sn-O site  $\theta_D = 59.6$ , and Sn-S site  $\theta_D = 50.8$ . Thus we see that the Debye temperatures of the trimethyl and tributyl compounds are very similar, while the triphenyl compound is significantly smaller, indicating an increased vibrational amplitude of the tin atom.

This work illustrates the sensitivity of Mössbauer absorption line area upon the vibrational properties of the tin site, and thus upon the coordination.

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