Room Temperature Tin-119 Mössbauer Spectra of Unassociated Tin Compounds

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Room-temperature ^{119}Sn Mössbauer spectra have been obtained for Ph_3SnCl, Me_2SnCl_2, $[Ph_3SnMn(CO)_5]$, $Ph_3Sn(bzbz)$, Ph_4Sn, $[Me_4N][Ph_3SnCl_2]$, $Me_2Sn(acac)_2$, $[\{Fe(CO)_2(cp)\}_2SnCl_2]$, and $[\{Me_2Sn(OH)NO_3\}_2]$ (acac and bzbz are the anions of acetylacetone and dibenzoylmethane). *X*-Ray crystal structures for all compounds except $[Me_4N][Ph_3SnCl_2]$ show no evidence for strongly associated polymeric structures. Because the magnitude of the Mössbauer effect is surprisingly large (*ca.* 1% absorption) in some cases, the observation of a room-temperature ^{119}Sn spectrum can no longer be taken by itself as strong evidence for a polymeric structure. The quadrupole splittings indicate that Ph_3SnCl remains four-co-ordinate from 80 to 295 K, while Me_2SnCl_2 becomes more weakly associated over the same temperature range. From the Goldanskii-Karyagin asymmetry in the room temperature spectrum of *trans*-$Me_2Sn(acac)_2$, the difference in mean square amplitudes parallel and perendicular to the Me–Sn–Me axis, $< X_{\|}^2 > - < X_{\perp}^2 > = 2.8 \pm 0.6 \times 10^{-18}$ cm^2, is in good agreement with the crystallographic value of 2.92×10^{-18} cm^2.

On the basis of a number of studies of the ^{119}Sn Mössbauer effect [1-4] it has been widely accepted that the observation of a room-temperature ^{119}Sn Mössbauer effect in an organometallic tin compound is a sufficient criterion for assigning a polymeric structure to that compound.[5-7] A detailed search of the literature indicates, however, that a room-temperature spectrum for at least one unassociated compound, Ph_4Sn, must have been obtained.[2,8] The absence of a room temperature spectrum does not indicate a non-polymeric structure, as a number of known polymeric tin compounds have been found to exhibit no detectable room-temperature effect.[9-11] In a study of thirty compounds, Poller *et al.*[4] measured the ratio (*R*) of the room-temperature effect to that at

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liquid-nitrogen temperature. Among these compounds, the only ones to exhibit finite *R* values ($\geqslant 0.03$) were those that were considered to be polymeric on the basis of other techniques.

We became interested in obtaining the room-temperature spectrum of Ph_3SnCl because of its central importance in the development of additivity models for quadrupole splittings. Some workers assigned associated trigonal bipyramidal structures to Ph_3SnCl and related compounds from early Mössbauer data.[12,13] More recently, Clark *et al.*[14] assigned a four-co-ordinate structure to Ph_3SnCl, and this stereochemistry was confirmed by a room-temperature single-crystal *X*-ray diffraction study.[15] However, all Mössbauer spectra had been taken at liquid-nitrogen temperatures, and Bokii *et al.* noted that the ^{35}Cl n.q.r. spectra of Ph_3SnCl observed at 77 K[16] and 303 K[17] were significantly different. They speculated that at liquid-nitrogen temperatures, Ph_3SnCl may exist as a polymeric solid with five-co-ordination about the tin. It became important then to obtain a Mössbauer spectrum at room temperature to confirm whether a substantial structural change occurred between liquid nitrogen and room temperatures.

After the observation of a room-temperature spectrum for Ph_3SnCl, we looked at other ^{119}Sn compounds which were known not to have polymeric structures. It soon became apparent that some of these gave easily observable room-temperature spectra. Here we report these spectra and show the usefulness of the quadrupole splittings for structural studies. In addition, the Goldanskii-Karyagin asymmetry at room temperature can be used to calculate the anisotropy of the thermal motion of the tin atom which can then be compared directly with *X*-ray crystallographic thermal ellipsoids.

Mössbauer parameters (in mm s^{-1}) at 110 and 295 K †

	110 K		295 K			
Compound	C.s. ± 0.02	Q.s. ± 0.02	C.s.	Q.s.	No. of spectra	R_{110} *
Ph_3SnCl	1.32	2.54	1.21 ± 0.08	2.46 ± 0.08	7	0.02 ± 0.01
Me_2SnCl_2	1.52	3.57	1.47 ± 0.03	3.37 ± 0.03	3	0.13 ± 0.01
$[Ph_3SnMn(CO)_5]$	1.35	0.41	1.23 ± 0.04	Not resolved	2	0.03 ± 0.01
$Ph_3Sn(bzbz)$ [a]	1.13	2.25	1.00 ± 0.15	2.20 ± 0.15	2	0.05 ± 0.01
Ph_4Sn	1.21	0	1.13 ± 0.04	0	1	0.09 ± 0.01
$[Me_4H][Ph_3SnCl_2]$	1.22	3.00	1.25 ± 0.10	3.00 ± 0.10	2	0.09 ± 0.01
$Me_2Sn(acac)_2$ [a]	1.16	3.93	1.08 ± 0.07	3.81 ± 0.07	3	0.10 ± 0.01
$[\{Fe(CO)_2(cp)\}_2SnCl_2]$	1.92	2.40	1.91 ± 0.02	2.36 ± 0.02	2	0.16 ± 0.02
$[\{Me_2Sn(OH)NO_3\}_2]$	1.28	3.67	1.24 ± 0.02	3.66 ± 0.02	1	0.19 ± 0.02

* R_{110} is the ratio of the total normalized area at 295 K to the total normalized area at 110 K. † All line widths are 1.10 ± 0.0 mm s^{-1}.

[a] bzbz and acac are the anions of dibenzoylmethane and acetylacetone respectively.

EXPERIMENTAL

All compounds were obtained commercially or were prepared by well established procedures. They were characterized by m.p.s., i.r. spectra and their well established Mössbauer spectra. Mössbauer spectra were obtained using a 5 mCi $BaSnO_3$ source at room temperature and a newly constructed drive system, analogous to that reported previously.[18] Absorbers contained 0.20 ± 0.05 mg ^{119}Sn per cm^2 in a Perspex–aluminium holder. Both room-temperature and liquid-nitrogen spectra were obtained with the absorber holder in a Cu block covered by a thin Styrofoam lid. With the Cu block dipping into liquid N_2, the measured temperature at the sample was 110 K ± 5K. Velocity calibration and spectral fitting were carried out as described previously.[19,20]

For the spectra of $Me_2Sn(acac)_2$ (acac, see footnote to Table), 200 mesh powder was used without compacting to ensure little or no orientation effects.

RESULTS

The room-temperature spectra for Ph_3SnCl and $[Cl_2Sn\{Fe(CO)_2(cp)\}_2]$ are shown in Figure 1. The Mössbauer parameters as well as the *R* value (ratio of normalized areas at the two temperatures) are given in the Table. All spectra had at least 1×10^6 baseline counts. For compounds such as $[\{Fe(CO)_2(cp)\}_2SnCl_2]$ and $[\{Me_2Sn(OH)NO_3\}_2]$, the room-temperature spectra gave close to 1% absorptions and were apparent within one hour. For others such as Ph_3SnCl, the absorption was *ca.* 0.1% and a number of spectra had to be averaged to achieve reasonable errors. The total room-temperature spectrum is shown in the Figure. Snedecor's *F* test[21] was used to check the consistency of the internal and external estimates of the variance of the quadrupole splittings measured in the separate room temperature spectra. The derived value of *Z* was 0.82 giving rise to an *F* value well within the 5% significance limit.

Our liquid-nitrogen spectra give parameters in good agreement with those previously reported for Ph_3SnCl, Me_2SnCl_2, Ph_4Sn, $[Me_4N][Ph_3SnCl_2]$, $[\{Fe(CO)_2(cp)\}_2SnCl_2]$, $Me_2Sn(acac)_2$,[5] and $[Ph_3Sn(bzbz)]$ (bzbz, see footnote to

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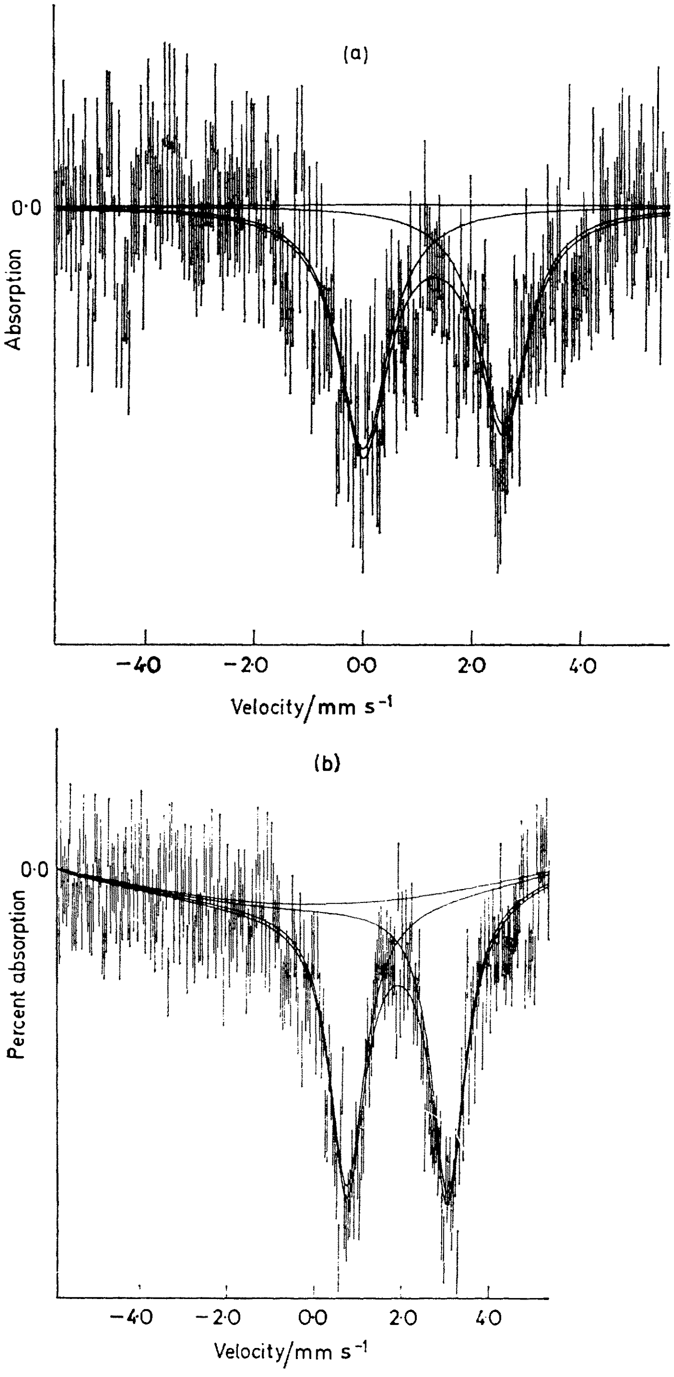
Table).[22] The room temperature quadrupole splittings (q.s.) and centre shifts (c.s.) are generally slightly smaller than those at liquid-nitrogen temperature, although there is a marked decrease of 0.20 mm s^{-1} in the q.s. of Me_2SnCl_2 from 110 to 295 K.



Room temperature spectra of (*a*) Ph_3SnCl accumulated from seven separate spectra and (*b*) $[\{Fe(CO)_2(cp)\}_2SnCl_2]$

The $Me_2Sn(acac)_2$ spectra were markedly asymmetric, giving an area ratio of 0.85 ± 0.01 at 110 K, and 0.72 ± 0.02 at 295 K. The former value is in very good agreement with that quoted by Herber at 110 K.[23] The room temperature spectrum for $Me_2Sn(acac)_2$ is easily obtained, further emphasizing the fact that everyone including Herber [23] and ourselves [19] strongly believed that spectra could not be obtained at room temperature.

DISCUSSION

The structures of all compounds, except that of the $[Ph_3SnCl_2]^-$ species, are known from *X*-ray diffraction results. Ph_4Sn,[24] Ph_3SnCl,[15] $[\{Fe(CO)_2(cp)\}_2SnCl_2]$,[25] and $[Ph_3SnMn(CO)_5]$ [26] are known to contain four-co-ordinate Sn, with no evidence for association. Similarly, $Ph_3Sn(bzbz)$ [22] and $Me_2Sn(acac)_2$ [27] are known to contain five- and six-co-ordinate Sn respectively with no association. The $[Ph_3SnCl_2]^-$ moiety almost certainly contains five-co-ordinate Sn, and $[\{Me_2Sn(OH)NO_3\}_2]$ [28] is known to be a dimer with Sn being five-co-ordinate. There has been some dispute about the co-ordination of Sn in Me_2SnCl_2 from *X*-ray results [29,30] but the large Mössbauer quadrupole splitting of Me_2SnCl_2 relative to Ph_2SnCl_2 indicates some weak association in Me_2SnCl_2 at liquid-nitrogen temperatures.[31]

For all compounds, except Me_2SnCl_2, there is a small ($\leqslant 0.12$ mm s^{-1}) decrease in quadrupole splitting on going from 110 to 295 K. This small decrease is expected due to the small increase in bond lengths at the higher temperature. In particular, the close similarity of the c.s. and q.s. for Ph_3SnCl at 80,[5] 110, and 295 K strongly indicates that the essential features of the structures and bonding of Ph_3SnCl over the range of temperatures 80 to 295 K are the same. Gross alterations, such as a change in co-ordination number, would result in a more appreciable change in both parameters.[5] It seems likely from our study that the differences in Cl n.q.r. frequencies at 77 and 303 K [16,17] are not due to a gross structural change as suggested by Bokii.[15] Thus Ph_3SnCl appears to be unambiguously four-co-ordinate at both high and low temperatures, and is a very suitable compound for the basis of the partial quadrupole splitting approach.[14]

Conversely, the quadrupole splitting for Me_2SnCl_2 decreases substantially (0.20 mm s^{-1}) indicating that there are probably changes in the structure other than the usual changes in bond length. The quadrupole splitting of 3.37 mm s^{-1} is not far off the expected 3.15 mm s^{-1} predicted for tetrahedral Me_2SnCl_2 ($\text{p.q.s}_{Me} = -1.37$ mm s^{-1}; $\text{p.q.s}_{Cl} = 0$ mm s^{-1}).[14] We thus suggest that the weak association at liquid-nitrogen temperature becomes substantially weaker at room temperature. A crystal structure of Me_2SnCl_2 at liquid

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nitrogen temperature, and a detailed Mössbauer temperature study of the quadrupole splitting of weakly associated compounds, would now be very interesting.

As in previous studies of the magnitude of the Mössbauer effect [1-3] there does not appear to be any correlation of our R value with the co-ordination number or type of atom bonded to the Sn. Although the magnitude of F can almost double from 110 to 80 K,[23] it is apparent that for unassociated compounds R_{80} ($A_{80\,\mathrm{K}}/A_{295\,\mathrm{K}}$) can still be $\geqslant 0.1$, and that room temperature spectra can be easily obtained for many unassociated compounds. Although it is undoubtedly true that polymeric structures generally give larger room-temperature effects than unassociated compounds, our results indicate that much more caution is needed when assigning structures from room-temperature observations. In particular, our results suggest that an R_{80} of less than 0.1 cannot be taken as good evidence either for or against association without other structural information. Our results also indicate that intramolecular bonding is more important in determining both F and the Goldanskii asymmetry than previously assumed.

Finally, it is possible for high symmetry compounds such as *trans*-$Me_2Sn(acac)_2$[27] to use the Goldanskii-Karyagin asymmetry at room temperature to derive the difference in mean-square vibrational amplitudes of the Sn atom parallel and perpendicular to the Z e.f.g. axes (in this case the CH_3–Sn–CH_3 axis).[23,19] This difference is vibrational amplitudes can then be compared directly with the crystallographically derived difference.

The area ratio (A) of the 3/2 and 1/2 lines can be expressed as follows:[32]

$$A = I_{3/2}/I_{1/2} = \frac{\int_0^1 (1 + \mu^2)e^{-\epsilon\mu^2}\mathrm{d}\mu}{\int_0^1 (^5/_3 - \mu^2)e^{-\epsilon\mu^2}\mathrm{d}\mu}$$

where $\varepsilon = \langle X_{\parallel}^2\rangle - \langle X_{\perp}^2\rangle$
and $\mu = \cos\theta$

Using $A = 0.72 \pm 0.02$ and the known positive e^2qQ for $Me_2Sn(acac)_2$,[5] numerical solutions to the above equation give $\varepsilon = 4.1 \pm 0.8$. Taking $E_\gamma = 23.9$ keV, this leads to $\langle X_{\parallel}^2\rangle - \langle X_{\perp}^2\rangle = 2.8\ (\pm 0.6) \times 10^{-18}$ cm^2, in good agreement with the value of 2.92×10^{-18} cm^2 calculated from the X-ray diffraction data of Miller and Schlemper [27] making the assumption that the arithmetic mean of axis 1 and axis 2 could be used for $\langle X_{\perp}^2\rangle$. For such a large Goldanskii asymmetry, ε is very sensitive to small changes in A, and this leads to the large standard deviation in $\langle X_{\parallel}^2\rangle - \langle X_{\perp}^2\rangle$. Unless A can be obtained with great accuracy (and this is difficult to do with the room-temperature spectra), the Mössbauer determination of $\langle X_{\parallel}^2\rangle - \langle X_{\perp}^2\rangle$ will have a large uncertainty.

We are grateful to N.R.C. for financial support and the award of a scholarship to K. D. B.

[4/2177 *Received*, 22*nd October*, 1974]

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