Molecular Dynamics of Adducts of Organotin(IV) and Tin(IV) Chlorides with *NN'*-Ethylenebis(salicylideneimine) studied by Temperature-dependent Mössbauer Spectroscopy

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Lattice dynamics studies have been carried out on the solid-state polymers $(SnR_nCl_{4-n}\cdot H_2salen)_x$ (H_2salen = *NN'*-ethylenebis(salicylideneimine); $n = 2$, R = Me or Ph; $n = 1$, R = Me, Bu^n, n-octyl, or Ph; $n = 0$), as well as on the monomeric complex $SnMe_2$(salen), by temperature-dependent Mössbauer spectroscopy. The functions ln $A(T)$, ln $f_a(T)$, and $\langle x^2\rangle(T)$ are linear for adducts with $n = 0$—2 and R = Me or Ph, but are perceptibly non-linear for the remaining compounds, suggesting motional anharmonicity of ^{119}Sn atoms in the latter. Compounds characterized by linear functions form two distinct homologous series ($n = 2$, $n = 0$ or 1) where a general decrease of the parameters θ_D and $\bar{\nu}_D$ takes place in parallel to an increase of the vibrating mass. The results are discussed in relation to the vibrating mass model, and to previous investigations. The characteristics of the anharmonic derivatives are tentatively interpreted in terms of progressive structural changes to form monomers.

We have previously investigated, by temperature-dependent ^{119}Sn Mössbauer spectroscopy, the solid-state polymers $SnRCl_3\cdot$pyz (R = Me, Bu^n, n-octyl, Ph, or Cl; pyz = pyrazine) and $SnRCl_3\cdot$dppe [R = Me or Ph; dppe = 1,2-bis(diphenylphosphino)ethane], and observed that the slopes d ln$A$/dT, where A is the total area under the resonant peaks, increase with increasing molecular mass within each homologous series.[1,2] This effect was attributed to a steady diminution of the Debye temperature, θ_D, as well as of the Debye cut-off frequency, ν_D, in parallel to the increase of mass (taken as the effective vibrating mass).[2] In fact, the calculation of these parameters (from the slopes, see Experimental section) shows that, for $SnRCl_3\cdot$pyz, θ_D continuously decreases from 100.1 to 70.9 K, and $\bar{\nu}_D$ from 70.2 to 49.2 cm^{-1}, on going from R = Me to n-octyl; analogously, in the case of $SnRCl_3\cdot$dppe, θ_D = 49.2 and 46.4 K and $\bar{\nu}_D$ = 34.2 and 32.2 cm^{-1}, for R = Me and Ph, respectively. A similar trend is also detected when vibrating masses differing from the molecular weights[2] are selected (*e.g.* M of $SnRCl_3$ or $SnCl_4$). It was suggested[2] that a given member of the homologous series, characterized by a substantially different solid-state structure, could be identified by its θ_D and $\bar{\nu}_D$ values, since these would not fit the correlation above.

These results seem to be important in the context of employing temperature-dependent Mössbauer spectroscopy to study the interaction of tin compounds with biological molecules. There is growing interest in the role of tin in biochemical processes, and conventional Mössbauer spectroscopy has been successfully employed to examine this.[3] Mössbauer structural investigations on organotin(IV) derivatives of adenine, adenosine, and glycylglycine have recently been published,[4] and interesting temperature-dependent Mössbauer studies have been carried out on tin(II)–crown ether derivatives.[5] The $SnRCl_3\cdot$pyz adducts can be considered to be representatives of systems where tin(IV) atoms are inserted into a polymer backbone and co-ordinated by heterocyclic nitrogens embedded in a bulky molecule, *e.g.* they could mimic systems where tin is bound to the nitrogen bases of nucleic acids. If the correlation between the molecular mass (or the effective vibrating mass) and the Debye parameters, observed for $SnRCl_3\cdot$pyz, were to hold generally in homologous systems, it could be an additional powerful tool in structural work.

Other relevant studies carried out on individual tin-containing solid-state polymers concern thiol sulphur[6-8] and quinone oxygen[9] as donor atoms in the bulky bridging moiety. Considering the wide occurrence of OH groups in biological molecules, we have investigated the lattice dynamics of model systems characterized by donation to tin by three-co-ordinated OH oxygens, and report the results for the homologous series formed by 1 : 1 adducts of tin(IV) derivatives with the ligand *NN'*-ethylenebis(salicylideneimine), $SnR_nCl_{4-n}\cdot H_2$salen (R = Me or Ph, $n = 2$; R = Me, Bu^n, n-octyl or Ph, $n = 1$; $n = 0$). These compounds are very probably solid-state polymers where the ligand acts as a bis(unidentate) unit bridging tin(IV) atoms through OH oxygens[10,11] (Figure 1).

EXPERIMENTAL

The compounds were prepared according to the literature.[10] Organotin derivatives were a gift from Schering A.G., Bergkamen.

Mössbauer spectra were recorded independently in both our laboratories, in duplicate or even triplicate runs, using $Ca^{119}SnO_3$ sources (10 mCi; R.C., Amersham) at room temperature, with constant acceleration and triangular waveform; the apparatus and techniques were as described elsewhere.[1,2,10,12] Temperature-dependent spectra were determined on Oxford equipment, or by using an insert-T.C.-cryostat arrangement from A.E.R.E. Harwell (MVTIN 200, CTC 200). Temperatures were constant within ±0.5° during the accumulation of each spectrum. Data reduction was effected by our usual computer programs,[1,2,10,12] fitting experimental lines to Lorentzian lineshapes. The experimental functions $A(T)$ (A being the total area under the resonant peaks) are available on request, including sets employed in calculating absolute recoil-free fractions, f_a^{abs}, and related parameters (see text and Table). At least seven data points were determined for each compound, about twice this amount being available in the majority of cases. Sample thicknesses were generally in the range 0.49—0.51 (mg ^{119}Sn) cm^{-2}, except for the $SnMe_2Cl_2$ derivative (0.83). Measurements were usually carried out between 77.3 and *ca.* 170 K (see Figure 2).

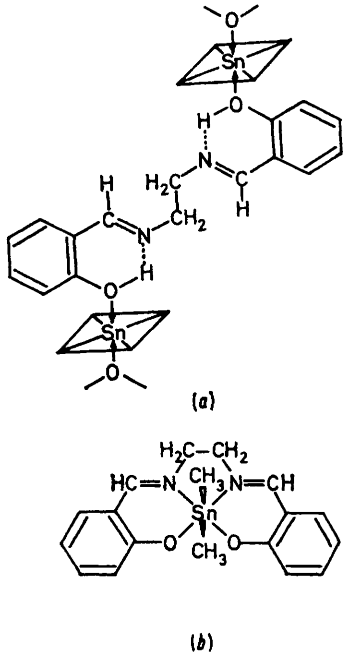

FIGURE 1 Idealized configurations of $(SnR_nCl_{4-n}\cdot H_2salen)_x$ (*a*) and $SnMe_2(salen)$ (*b*) in the solid state

The monomeric complex '*trans*' -$SnMe_2(salen)$ [13] (Figure 1) has been reinvestigated for comparison purposes.

Experimental plots of $\ln(A_T/A_{77.3})$ *vs.* T (normalization being effected in order to compare data obtained in independent runs on samples from different batches, using two sets of instruments), not shown here, gave linear correlations with the exception of compounds (6)—(8) (see Table) for which a perceptible curvature was observed.

The $A(T)$ data were treated as usual in lattice dynamics studies; the procedures used here are now briefly sketched. In the Debye approximation, the absorber recoil-free fraction f_a, in the high T limit ($\geqslant \theta_D/2$), is expressed as in equation (1),[14] where E_γ is the energy of the Mössbauer

$$f_a = \exp(-3E_\gamma^2 T/Mc^2 k\theta_D^2) \qquad (1)$$

transition, M is the effective vibrating mass of the Mössbauer atom, k is the Boltzmann constant, and θ_D the Debye temperature. From the relationship between A and f_a,[15] for a 'thin' absorber one obtains [8] equation (2).

$$\frac{d\ln A_{tot}}{dT} = \frac{d\ln f_a}{dT} = \frac{-3E_\gamma^2}{Mc^2 k\theta_D^2} \qquad (2)$$

Experimental $d\ln A_{tot}/dT$ slopes are employed to get 'relative' [16] values of $f_a(T)$, *i.e.* f_a^{rel}, using equation (1), from which mean-square displacements of the Mössbauer nucleus, $\langle x^2\rangle(T)$, are calculated [7,14] using equation (3),

$$f_a = \exp(-K^2\langle x^2\rangle) \qquad (3)$$

where K is the wavevector of γ-rays. Debye temperatures, assumed to be independent of T (which in principle would not be the case in the high T range [14]), are calculated from equation (2), and Debye cut-off frequencies ν_D from equation (4),[14] h being the Planck constant.

$$\nu_D = k\theta_D/h \qquad (4)$$

In addition to the known limitations of the above procedure, our data also suffer from the fact that absorber samples are not 'thin', the product $\sigma_0 N$ being greater than unity [14] (σ_0 = resonant absorption cross section of ^{119}Sn, N = number of absorber resonant atoms per cm^2).

In the case of compounds showing non-linear ln $A_{tot}(T)$ functions, and in some other instances for comparison purposes, 'absolute' values of f_a, *i.e.* f_a^{abs}, were obtained as follows. Recoil-free fractions of sources, f_s, were calculated from spectra at liquid-nitrogen temperature of white metallic β-Sn, 0.1 mm thick, fitted to Lorentzian lineshapes. Effective absorber thicknesses, t_i, were determined from equation (5) [7,17] where Γ_{Nat} is ^{119}Sn natural linewidth and

$$t_i = (\pi/2)\Gamma_{Nat} N\sigma_0 f_a \qquad (5)$$

published f_a data were used.[18] From t_i, assuming a Lorentzian resonant absorption, the value of the corresponding saturation function $L(t_i)$ [17] was extrapolated from tabulated data,[19] and f_s obtained from relation (6).[7,17]

$$f_s = \frac{A}{(\pi/2)\Gamma_{Nat} L(t_i)} \qquad (6)$$

Essentially the reverse of this procedure was employed to determine f_a^{abs} of H_2salen adducts. Saturation functions $L(t_{1,2})$ were calculated from the areas $A_{1,2}$ corresponding to each peak of the doublet, using equation (6). From $L(t_{1,2})$, $t_{1,2}$ was obtained by interpolation,[17] and then f_a^{abs} was calculated from equation (7).[7] Reliable values of f_a^{abs}

$$f_a^{abs} = \frac{t_1 + t_2}{(\pi/2)\,\Gamma_{Nat}\sigma_0 N} \qquad (7)$$

are obtained by this procedure, which involves a ratio of areas, measured under the same conditions and with the same instrumentation, and implies eventual cancellation of experimental errors. From $f_a^{abs}(T)$, sets of $\langle x^2\rangle(T)$, $\theta_D(T)$, and $\nu_D(T)$ values are calculated using equations (3), (1), and (4), assuming that (3) holds in the case of non-Debye solids.

Parameters determined by these procedures are given in the Table; the functions $f_a(T)$ and $\langle x^2\rangle(T)$ are shown in Figure 2.

DISCUSSION

The absence of breaks in the functions $A(T)$ rules out any phase transition in the T range investigated. This is supported by the virtual invariance of parameters δ and ΔE (Table; the data essentially agree with previous values [10,13]).

The functions $\ln f_a(T)$ are clearly linear for compounds (1)—(5) and are smoothly curved for (6)—(8) (Figure 2); *cf.* ln $A(T)$. The data pertaining to the last compounds have been tentatively treated under the constraint of linearity, in view of the acceptable magnitudes of the correlation coefficients (Table). The lines ln $f_a^{rel}(T)$ obviously extrapolate to unity [equation (1)], while ln

$f_a^{abs}(T)$ in some instances do not (Figure 2), as previously observed.[16] Whenever both f_a^{rel} and f_a^{abs} are available for a given compound, differences at the same T are within *ca.* 0.01 for (1), (2), and (5),[16] while larger (*ca.* 0.03) for (6) and (7) (Figure 2); the slopes d ln$f_a^{rel, abs}$/dT are essentially coincident, and correspond to d ln A/dT data in the Table, only for compounds (1), (2), and (5). Lastly, Debye temperatures, θ_D, and cut-off frequencies, $\tilde{\nu}_D$, extracted from area slopes and f_a^{abs}, respectively, agree within 1.8—2.4% for (1), (2), and (5), but deviate by up to 4.3—5.0% for (6) and (7) (Table). These results suggest that the assumption of linearity of ln $A(T)$ for (6) and (7) is a gross approximation, so that only f_a^{abs} and related functions can be considered for these two compounds.

Parameters of 1 : 1 adducts of tin(IV) derivatives with H_2salen

Compound	H_2salen adduct of	M	10^2 d ln A/dT [a] K^{-1}	θ_D [b] K	$\tilde{\nu}_D$ [b] cm^{-1}	$\delta_{av.}$ [c] mm s^{-1}	$\Delta E_{av.}$ [d] mm s^{-1}
(1)	$SnMe_2Cl_2$	487.98	−1.353 (0.998)	56.8 (55.8 ± 0.3	39.4 (38.8 ± 0.2)	1.327 ± 0.003	3.979 ± 0.009
(2)	$SnPh_2Cl_2$	612.12	−1.268 (0.995)	52.4 (53.2 ± 0.2)	36.4 (36.9 ± 0.1)	1.233 ± 0.002	3.838 ± 0.008
(3)	$SnMeCl_3$	508.40	−1.629 (1.000)	50.7	35.2	0.751 ± 0.005	1.920 ± 0.006
(4)	$SnCl_4$	528.82	−1.648 (0.999)	49.4	34.3	0.340 ± 0.012 [e]	0.000
(5)	$SnPhCl_3$	570.47	−1.936 (0.995)	43.9 (43.1 ± 0.4)	30.5 (29.9 ± 0.3)	0.777 ± 0.005	1.671 ± 0.009
(6)	$SnBu^nCl_3$	550.48	−2.048 (0.993) [f]	43.5 [f] (45.7 ± 0.1)	30.2 [f] (31.7 ± 0.1)	0.905 ± 0.005	1.839 ± 0.006
(7)	$Sn(C_8H_{17})Cl_3$	606.59	−1.757 (0.993) [f]	44.7 [f] (46.4 ± 0.1)	31.1 [f] (32.2 ± 0.1)	0.910 ± 0.003	1.858 ± 0.006
	$salen^{2-}$ complex of						
(8)	$SnMe_2^{2+}$	415.06	−1.690 (0.997) [f]	55.1	38.3 [f]	1.162 ± 0.004	3.491 ± 0.011

[a] A = Total area under the resonant peaks, in mm s^{-1}; all data points, in the T interval shown in Figure 2, were employed in the least-squares determination of the slopes for each compound. Correlation coefficients are given in parentheses (see Experimental section). [b] Debye temperature, θ_D, and cut-off frequency, $\tilde{\nu}_D$, calculated for a given compound through the slope d ln A/dT (first value) and f_a^{abs} (value in parentheses), assuming the molecular mass of the adduct to be the effective vibrating mass. Data from f_a^{abs} are quoted with standard errors. [c] Isomer shift with respect to $CaSnO_3$ (room temperature) averaged over the whole T range (Figure 2) with standard error. [d] Nuclear quadrupole splitting, details as in footnote *c*. [e] Shows a steady decrease with T. [f] Approximate data pertaining to linearly constrained ln $A(T)$ functions, strictly valid only for the whole experimental T range of Figure 2.

The temperature dependence of the mean-square

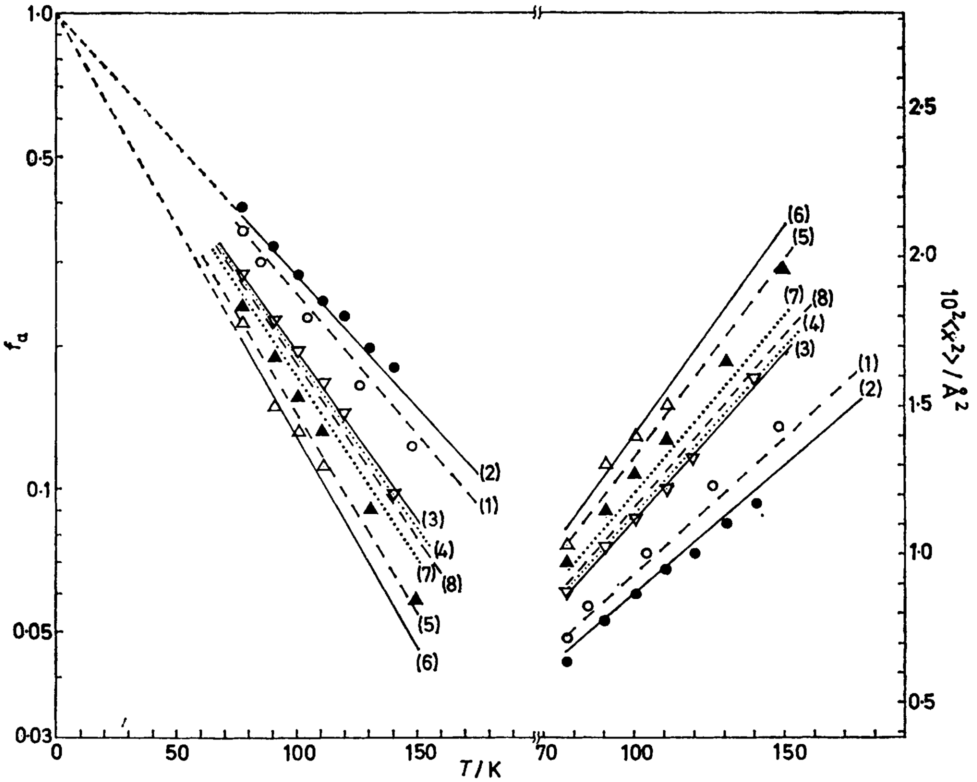

FIGURE 2 Recoil-free fraction of absorber ^{119}Sn nuclei, f_a, and mean-square displacements of ^{119}Sn, $\langle x^2\rangle$, as functions of T, for H_2salen adducts (1)—(8). Lines are $f_a^{rel}(T)$ and $\langle x^2\rangle$ (T) functions obtained from slopes d ln A/dT, while data points are f_a^{abs} and related $\langle x^2\rangle$ values (see text) and refer to compounds (1) (○), (2) (●), (5) (△), (6) (▲), and (7) (▽)

displacements of ^{119}Sn atoms yield $\langle x^2\rangle(T)$ functions (Figure 2) lying typically in the zone of tin-containing monomers and one-dimensional polymers, the $SnPh_2Cl_2$ derivative being approximately at the borderline with multi-dimensional polymers.[20] This is in accord with the previously determined or proposed one-dimensional polymeric structures of our adducts [10,11] (see also Introduction).

Turning now to the relationship between molecular mass and lattice parameters, from the data in the Table and Figure 2 it appears that compounds (1)—(5) may be subdivided into two classes: (*i*) the adducts of SnR_2Cl_2, (1) and (2), where an increase of molecular mass (taken as the effective vibrating mass [21]), leads to decreasing $d \ln A/dT$ and $\langle x^2\rangle(T)$, while $f_a(T)$ increases; (*ii*) the adducts of $SnRCl_3$ (R = Me or Ph) and $SnCl_4$ (3)—(5), where the opposite trend occurs. Nevertheless, within both classes the parameters θ_D and $\tilde{\nu}_D$ constantly decrease on increasing the vibrating mass, whatever value is chosen for the latter, *e.g.* M of the adduct (Table) or of the organometallic and metal derivative.[21,22]

These trends in Debye parameters agree perfectly with previous observations on $SnRCl_3$·pyz and $SnRCl_3$·dppe (see Introduction). It is also worth examining preceding reports on the Debye–Waller–Mössbauer factors, f, of members of homologous series of diorganotin(IV) oxides. It appears that f values of SnR_2O, measured at 77 K, decrease with increasing molecular mass in the series R = C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, but the reverse holds true tor R = CH_3, C_6H_5, C_6H_4Cl, C_6H_4Br, C_6H_4I.[23,24] Using tabulated f data,[23] we have calculated the following Debye parameters at 77 K for the above four dialkyltin oxides, from ethyl to octyl respectively, taking the molecular mass as the effective vibrating mass: $\theta_D = 77.0$, 61.0, 52.3, and 44.4 K; $\tilde{\nu}_D = 49.7$, 39.4, 33.8, and 28.7 cm^{-1}. For the second series, calculations have been made assuming that af' values reported in ref. 24 are linearly proportional to true f data, and evidence has been obtained for a steady decrease of both θ_D and $\tilde{\nu}_D$ with increasing molecular mass. Sets of data for SnR_2O are then fully consistent with those discussed above.

The physical significance of the correlation between the vibrating mass and θ_D, $\tilde{\nu}_D$ is straightforward. The same crystal lattice is assumed to occur throughout each homologous series. For example, on the basis of intermolecular couplings, in the case of SnR_nCl_{4-n}·H_2salen, one can consider that differences between SnR_2Cl_2 and $SnRCl_3$, $SnCl_4$ adducts may arise from the Sn orbitals employed in accepting oxygen doublets, *i.e.* mainly 5*p* in the first cases (*sp* Sn hybrids being involved in C–Sn–C bonds) and containing a considerable 5*s* contribution in the second.[25] Assuming the effective vibrating mass model,[21] the members of a given series would differ only in the masses of the vibrating hard spheres, *e.g.* in the masses of the repeating units of the polymer backbones. An increase of the vibrating mass is reasonably expected to provoke a decrease of $\tilde{\nu}_D$, and θ_D; the latter effect would reflect the decrease in intermolecular interactions.[26]

The lattice dynamics of the adducts of $SnBu^nCl_3$ and $Sn(C_8H_{17})Cl_3$, (6) and (7), are compared with polymers (3)—(5) on the one hand and with the monomer (8) on the other (Figure 1). As discussed above, the temperature-dependent lattice parameters of (6) and (7) have to be considered as non-linear; the same may be true of (8), due to analogies between the $A(T)$ functions (Experimental section and ref. 13). This implies motional anharmonicity of ^{119}Sn atoms in compounds (6)—(8); on the other hand, anharmonicity has been detected in polymeric [5] as well as in monomeric [27] solid-state species, so that the occurrence of this effect in different compounds cannot be taken as definite evidence of corresponding structures.

In the temperature range explored here, the $f_a^{abs}(T)$ data, and derived $\langle x^2\rangle(T)$, θ_D, and $\tilde{\nu}_D$, of the $SnBu^nCl_3$ adduct (6) are in accord with the systematic mass–lattice parameters of compounds (3)—(5), while the data for the $Sn(C_8H_{17})Cl_3$ adduct (7) are definitely different (Table and Figure 2). This could be qualitatively interpreted by assuming the occurrence of gradual changes in the lattices of (6) and (7) (more pronounced) with respect to (3)—(5). Speculating on the trends in lattice parameters and functions of (6)—(8) (Table and Figure 2), it could be argued that an increase of mass in the repeating units $SnRCl_3$·H_2salen weakens the intermolecular forces in such a way as to change the polymers, especially (7), to monomers.

In conclusion, we believe that the present work demonstrates the usefulness of investigations of lattice dynamics, by means of temperature-dependent Mössbauer spectroscopy, to the study of the solid-state nature of homologous series of compounds. In particular, the possible use of the previously observed correlation between vibrating masses and θ_D,$\tilde{\nu}_D$ in predicting structural similarities has substantially been confirmed for adducts SnR_nCl_{4-n}·H_2salen. Further work on other series of compounds of this type is needed in order to test the extent of applicability of the relationship.

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