Temperature Dependence of the Mössbauer Recoil-free Fraction as a Probe of the Lattice Structure of Tin Compounds

By PHILIP G. HARRISON,* ROBIN C. PHILLIPS, and EDWARD W. THORNTON
(*Department of Chemistry, University of Nottingham, University Park, Nottingham* NG7 2RD)

Summary The temperature coefficient of the Mössbauer recoil-free fraction is a useful guide to the nature of the lattice structure of tin compounds.

DURING the past decade, Mössbauer spectroscopy has emerged as a particularly useful structural technique in tin chemistry. However, by far the majority of the accumulated data refer to the application of isomer shift and quadrupole splitting measurements to the solution of structure and bonding problems within the first co-ordination sphere of the metal atom. By measuring the variation with temperature of the recoil-free fraction, a measure of the number of nuclei undergoing recoil-less γ-ray resonance, Mössbauer spectroscopy may also be applied to the investigation of the lattice structure of tin-containing materials.

Since for a thin absorber the recoil-free fraction, $f(T)$, is directly related to the area under the resonance curve, $A(T)$, of a Mössbauer spectrum, the temperature variation of $f(T)$ may be followed by evaluating the experimentally more accessible parameter, $A(T)$. We have collected resonance area data for the compounds listed in the Table, and semilogarithmic plots of the resonance areas (normalised to 77 K) against temperature were found to be linear in the temperature range $77 \leqslant T \leqslant 150$ K, as expected

TABLE. Recoil-free fraction temperature coefficients.

Compound	$a \times 10^2/\mathrm{K}^{-1}$	Valance state	Comment on Lattice Structure
$Me_3SnONPhCOPh$ (**1**)	1·74$_5$	IV	Crystals composed of monomeric molecules (*X*-ray)[a]
$Ph_3SnONPhCOPh$ (**2**)	1·85	IV	,,[b]
$Me_3SnO_3SPh{\cdot}H_2O$ (**3**)	1·71	IV	Adjacent molecules weakly linked by H-bonds to form a 1-D infinite chain (*X*-ray)[c]
$Me_3SnO_2CC_5H_4N\text{-}2{\cdot}H_2O$ (**4**)	1·27	IV	Adjacent molecules linked by a 3-D network of H-bonds (*X*-ray)[d]
$Me_3SnONC_6H_{10}$ (**5**)	0·97	IV	1-D co-ordinate chain polymer (*X*-ray)[e]
$Et_3SnONC_6H_{10}$ (**6**)	1·16	IV	
$Pr^n{}_3SnONC_6H_{10}$ (**7**)	1·43	IV	
$Ph_3SnONC_6H_{10}$ (**8**)	1·82$_5$	IV	
$Me_2Sn(ONMeCOMe)_2$ (**9**)	1·85	IV	Crystals composed of monomeric molecules (*X*-ray)[f]
$Me_2Sn(ONHCOMe)_2$ (**10**)	0·92	IV	Adjacent molecules linked by H-bonds (*X*-ray)[g]
$ClMe_2SnSnMe_2Cl$ (**11**)	1·93	IV	
Me_2SnO (**12**)	0·87	IV	Polymeric
$[Sn^{IV}Sn^{II}(O_2CC_6H_4NO_2\text{-}o)_4O{\cdot}thf]_2$[i] (**13**)			
(a) Sn^{IV}	1·30	IV	Crystals composed of tetranuclear cluster molecules (*X*-ray)[h]
(b) Sn^{II}	1·70	II	
$Sn(O_2CH)_2$ (**14**)	0·84	II	2-D Sheet polymer (*X*-ray)[j]
SnO (**15**)	0·23	II	Ionic lattice (*X*-ray)[k]
$SnCl_2$ (**16**)	0·92	II	$PbCl_2$-type lattice (*X*-ray)[l]
$Sn(C_5H_5)_2$ (**17**)	3·13	II	

[a] P. G. Harrison, K. Molloy, and E. W. Thornton, unpublished results. [b] P. G. Harrison and T. J. King, *J.C.S. Dalton*, 1974, 2298. [c] P. G. Harrison, R. C. Phillips, and J. A. Richards, *J. Organometallic Chem.*, 1976, **114**, 47. [d] P. G. Harrison and R. C. Phillips, unpublished results; R. C. Phillips, Ph.D. Thesis, University of Nottingham, 1976. [e] P. F. R. Ewings, P. G. Harrison, T. J. King, R. C. Phillips, and J. A. Richards, *J.C.S. Dalton*, 1975, 1950. [f] P. G. Harrison, T. J. King, and J. A. Richards, *J.C.S. Dalton*, 1975, 826. [g] P. G. Harrison, T. J. King, and R. C. Phillips, *J.C.S. Dalton*, 1976, 2317. [h] Ref. 4. [i] thf = Tetrahydrofuran. [j] P. G. Harrison and E. W. Thornton, unpublished results. [k] W. J. Moore and L. Pauling, *J. Amer. Chem. Soc.*, 1941, **63**, 1392. [l] J. M. van den Berg, *Acta Cryst.*, 1961, **14**, 1002.

according to the Debye model of solids in the high temperature limit. The temperature coefficients of the recoil-free fraction (a/K^{-1}†) derived therefrom are also listed in the Table, together with other available data concerning the solid-state structure for the materials.

From a comparison with those compounds of known structure, it is apparent that those organotin(IV) compounds which have lattices consisting of non-interacting monomeric molecules [(**1**), (**2**), and (**9**)] have temperature coefficients of *ca.* $1{\cdot}8 \times 10^{-2}\ \mathrm{K}^{-1}$, irrespective of the co-ordination number at tin. Weak intermolecular interactions, such as the hydrogen-bonding between adjacent $Me_3SnO_3SPh{\cdot}H_2O$ molecules (**3**) reduces the value of a slightly (to $1{\cdot}71 \times 10^{-2}\ \mathrm{K}^{-1}$), whilst a more complex system of hydrogen bonds as in $Me_3SnO_2CC_5H_4N\text{-}2{\cdot}H_2O$ (**4**) causes a larger reduction (to $1{\cdot}27 \times 10^{-2}\ \mathrm{K}^{-1}$), reflecting the increasing rigidity of the lattice. Strongly hydrogen-bonded lattices such as (**10**), and one-, two-, and three-dimensional polymeric lattices [*e.g.* (**5**), (**14**), and (**12**), respectively] exhibit temperature coefficients of *ca.* $0{\cdot}9 \times 10^{-2}\ \mathrm{K}^{-1}$, as does tin(II) chloride (**16**), which possesses the $PbCl_2$-type lattice. Tin(II) oxide (**15**) exhibits the lowest temperature coefficient of all the compounds measured, $0{\cdot}23 \times 10^{-2}\ \mathrm{K}^{-1}$, consistent with its tightly packed ionic lattice.

Using these data, we can thus infer that $Ph_3SnONC_6H_{10}$ (**8**) ($a = 1{\cdot}825 \times 10^{-2}$) is unassociated, and that the ethyl and n-propyl homologues [(**6**) and (**7**), respectively] with a values of $1{\cdot}16 \times 10^{-2}$ and $1{\cdot}43 \times 10^{-2}\ \mathrm{K}^{-1}$, respectively, have structures intermediate between the one-dimensional co-ordinate polymeric structure determined for the methyl homologue (**5**) and the monomeric phenyl derivative (**8**), demonstrating the weakening of the co-ordinate interaction as the steric bulk of the organic groups bonded to tin increases. The high value for 1,2-dichloro-1,1,2,2-tetramethylditin (**11**) ($1{\cdot}93 \times 10^{-2}\ \mathrm{K}^{-1}$) is also indicative of the absence of significant intermolecular interaction for this compound in the solid. Dicyclopentadienyltin(II) (**17**) exhibits the highest temperature coefficient recorded ($3{\cdot}13 \times 10^{-2}\ \mathrm{K}^{-1}$), being higher than that reported for bis(propane-1,3-dionato)tin(II) ($2{\cdot}8 \times 10^{-2}\ \mathrm{K}^{-1}$),[1] which is most probably isostructural with bis(1-phenylpropane-1,3-dionato)tin(II).[2] Such values of a are clearly consistent with the presence of non-interacting monomeric units in the solid for these materials [*cf.* the structure of dicyclopentadienyl-lead(II) in the solid[3]].

The values of a for the two types of tin atom in the mixed-valence carboxylate (**13**) are interesting. Crystals of the compound consist of tetranuclear clusters with the Sn^{IV} atoms tightly bound in an octahedral arrangement, and the Sn^{II} atoms enjoying pseudo-pentagonal bipyramidal co-ordination.[4] The temperature coefficient values of $1{\cdot}30 \times 10^{-2}\ \mathrm{K}^{-1}$ for the Sn^{IV} atoms and $1{\cdot}70 \times 10^{-2}\ \mathrm{K}^{-1}$ for the Sn^{II} atoms thus reflect the oligomeric constitution of the material, as well as the relative strengths of binding of the two tin atoms within the macromolecule ($Sn^{IV} > Sn^{II}$).

We thank the S.R.C. for support.

(*Received, 30th May* 1977; *Com.* 532.)

---

† $a = -\,\mathrm{d}\,[\ln A(T)/A(77)]/\mathrm{d}T$.

[1] R. H. Herber and A. E. Smelkinson, *Inorg. Chem.*, 1977, **16**, 953.
[2] P. F. R. Ewings, P. G. Harrison, and T. J. King, *J.C.S. Dalton*, 1977, 1455.
[3] C. Pannatoni, G. Bombieri, and U. Croatto, *Acta Cryst.*, 1966, **21**, 823.
[4] P. F. R. Ewings, P. G. Harrison, A. Morris, and T. J. King, *J.C.S. Dalton*, 1976, 1602.