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Studies in Mössbauer Spectroscopy. II.[1] The Structures of Some Organotin Halides, and a Test of the Point-Charge Model

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Mössbauer spectroscopic data are presented for some organotin halides and their halide complexes. These data suggest that the halides R_3SnX *(*R = *alkyl) are strongly associated in the solid state, with five-coordinate tin atoms. The triphenyltin halides, apart from the fluoride, are less strongly associated. The dihalides,* R_2SnX_2*, are also associated, but the structures differ from that of* Me_2SnF_2*. The data are correlated with the point charge model, and it is shown that a parameter,* $[L]$*, may be ascribed to each ligand,* L*, which represents the contribution of* L *to the electric field gradient at the tin nucleus. Self-consistent, empirical values may be assigned to* $[L]$*. There is an approximately linear relationship between* $[L]$ *and the Taft inductive constant* σ_L^**.*

Introduction

The physical properties of organotin fluorides, *e.g.* their involatility and insolubility, are consistent with polymeric structures of the type found by X-ray crystallography for Me_3SnF[2] and Me_2SnF_2.[3] By contrast, the other halides are relatively low-melting, soluble compounds, which suggests that the association, if any, is markedly less than for the fluorides. The observation[4-6] that the halides Me_3SnX and Me_2SnX_2 (X = Cl, Br, I) show two infra-red active Sn–C stretching modes, the frequencies of which do not change when the solid compounds are dissolved, has often been interpreted in terms of monomeric, tetrahedral structures. However, Kriegsmann and Pischtschan found[5] that, for Me_3SnX (X = Cl, Br), the frequency of the Sn–X stretching mode increases from the solid compound to the melt to the solution in carbon disulphide. They also state that similar effects were found for $MeSnX_3$, which is confirmed by the data of Beattie and McQuillan,[6] which also show a similar variation for Me_2SnCl_2. These results suggest that these halides are associated in the solid state to some extent. By the same criterion, the phenyltin halides, Ph_3SnX (X = Cl, Br, I), do not seem to be associated.[7] We have previously suggested from Mössbauer data[8] that the halides Me_3SnX (X = F–I) may have similar structures and we now present further data for organotin halides and for some anionic halide complexes derived from them. The data are used to test the point-charge model.

Results and Discussion

COMPLEXES. The data for the organotin halide complexes are given in Table I, together with previously reported values.[9-11] The anion $[SnCl_5]^-$ is known to have trigonal bipyramidal geometry,[12] and the alkyl-substituted species would be expected to have similar structures with the substituents in the equatorial positions, as found[13] for $[Me_2SnCl_3]^-$ and suggested by the infra-red data (see experimental section). Infra-red evidence also shows that the methyl groups in $[Me_2SnX_4]^{2-}$ (X = F, Cl, Br)[6,14] are *trans*. The similarity in the Mössbauer data suggests that complexes of the same general formula have similar structures, in all the series studied. For the five-coordinate complexes $[R_nSnX_{5-n}]^-$ ($n = 0$–3), the isomer shift increases with increasing n, demonstrating the increasing electron density on the tin atom, although the values for the last two members in the series ($n = 2, 3$) are very similar. With the six-coordinate complexes $[R_mSnX_{6-m}]^{2-}$ ($m = 0$–2), the isomer shifts increase uniformly and do not show this « saturation » effect; this may be a result of the high isomer shifts which seem to be associated with *trans*–R_2SnX_4 structures.[15] In both series, the isomer shifts increase, as expected, with increasing atomic number of the halogen.

The quadrupole splitting data are consistent with the probable structures (see below). For the five-coordinate complexes, the splitting decreases with

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Table I. Mössbauer data for tin(IV) complexes.

Complex	δ(mm/s) [a, b]	Δ(mm/s) [b]	Γ_1(mm/s) [c]	Γ_2(mm/s) [c]	χ^2
$(Et_4N)[SnCl_5]$ [d]	0.59	0.77	1.02	0.89	366
$(Ph_3C)[SnCl_5]$ [e]	0.63	0.46	—	—	—
$(p.Tol\ Ph_2C)[SnCl_5]$ [e]	0.47	0.67	—	—	—
$(Ph_4As)[EtSnCl_4]$	1.18	1.82	0.94	0.69	610
$(Ph_4As)[Et_2SnCl_3]$	1.54	3.36	0.78	0.95	363
$(Et_4N)[Me_2SnCl_3]$	1.48	3.75	0.86	0.86	466
$(Et_4N)[Me_2SnCl_3]$ [f]	1.40	3.30	1.38	1.38	—
$(Ph_4As)[Me_2SnCl_3]$	1.42	3.50	0.80	0.98	338
$(Et_4N)[Ph_2SnCl_3]$ [f]	1.25	2.62	1.38	1.26	—
$(Et_4N)[Me_2SnBr_3]$	1.52	3.41	0.79	0.83	437
$(Et_4N)[Me_3SnCl_2]$	1.42	3.32	1.27	1.05	470
$(Et_4N)[Me_3SnCl_2]$ [f]	1.24	3.23	1.53	1.47	—
$(Ph_3PCH_2Ph)[Et_3SnCl_2]$	1.50	3.44	0.83	0.84	349
$(Me_4N)[Ph_3SnCl_2]$	1.32	3.00	0.83	0.88	359
$(Et_4N)[Me_3SnBr_2]$	1.43	3.45	0.81	0.86	373
$Cs_2[SnCl_6]$	0.52	—	0.90		423
$(Me_4N)_2[EtSnCl_5]$	1.10	1.93	0.80	0.80	287
$(Et_4N)_2[BuSnCl_5]$ [f]	1.07	1.86	1.20	1.20	—
$(PyH)_2[PhSnCl_5]$ [g]	1.10	1.92	—	—	—
$K_2[Me_2SnF_4]$	1.38	4.12	0.82	0.82	386
$K_2[Et_2SnF_4]$	1.45	4.44	1.10	1.03	465
$Cs_2[Me_2SnCl_4]$	1.63	4.32	0.94	0.87	431
$(PyH)_2[Me_2SnCl_4]$ [g]	1.59	4.32	—	—	—
$(Me_4N)_2[Et_2SnCl_4]$	1.64	3.99	0.78	0.83	820
$(PyH)_2[Ph_2SnCl_4]$ [g]	1.44	3.80	—	—	—
$Cs_2[Me_2SnBr_4]$	1.76	4.22	0.94	0.57	408

[a] Relative to SnO_2 at room temperature. [b] ±0.05 mm/s. [c] ±0.10 mm/s. [d] Ref. 1. [e] Ref. 11. [f] Ref. 10. [g] Ref. 9.

Table II. Mössbauer data for organotin halides.

Halide	δ(mm/s)	Δ(mm/s)	Γ_1(mm/s)	Γ_2(mm/s)	χ^2
Et_3SnF	1.41	3.82	0.86	0.86	354
Et_3SnCl	1.55	3.65	0.91	1.02	352
Et_3SnBr	1.57	3.28	0.97	0.95	397
Et_3SnI	1.56	2.95	0.92	0.88	377
Et_2SnCl_2	1.63	3.81	1.03	1.06	377
Et_2SnBr_2	1.70	3.27	0.86	0.76	412
Et_2SnI_2	1.72	2.97	0.81	1.03	399
$EtSnCl_3$	1.39	1.97	1.06	1.05	413
$EtSnBr_3$	1.49	1.85	0.93	0.60	386
Me_2SnCl_2	1.60	3.52	0.88	0.91	409
Me_2SnBr_2	1.60	3.30	0.85	0.95	378
Bu_3SnF	1.40	3.67	0.92	0.94	398
Bu_3SnCl	1.48	3.39	0.88	0.84	519
$(C_2H_3)_3SnCl$	1.34	3.29	0.82	0.74	543
$(C_2H_3)_2SnCl_2$	1.45	3.34	0.87	0.83	450
$C_2H_3SnCl_3$	1.22	1.86	0.90	0.80	413
Ph_3SnF	1.25	3.53	0.90	0.84	420
Ph_3SnCl	1.31	2.56	0.97	0.88	468
Ph_3SnBr	1.37	2.48	0.99	0.84	423
Ph_3SnI	1.20	2.25	1.29	1.24	429
Ph_2SnCl_2	1.38	2.90	1.24	1.01	547
Ph_2SnBr_2	1.43	2.54	1.03	0.81	877
Ph_2SnI_2	1.51	2.38	0.94	0.82	643
$PhSnCl_3$	1.22	1.84	0.84	0.85	393
$PhSnBr_3$	1.39	1.62	0.68	0.73	519

increasing atomic number of the halogen, following the decrease in polarity of the Sn–X bonds.[1] For the six-coordinate $[R_2SnX_4]^{2-}$ complexes the quadrupole splitting values do not vary systematically with change of the halogen. These values are rather larger than expected from the point-charge calculations[9] which suggest that $\Delta(R_2SnX_4^{2-}) = 2\Delta(RSnX_5^{2-})$.

The ratio $\rho = \Delta/\delta$ has often been used to diagnose empirically the coordination number of organotin compounds, it having been suggested[16] that four-coordinate compounds would give $\rho < 2.1$ and that larger values are asosciated with higher coordination numbers. Since the isomer shifts of organotin compounds lie in a very narrow range (*ca.* 1.0–1.5 mm/s), the most important factor in determining ρ is the quadrupole splitting. The point-charge treatment (see below and ref (1)) shows that Δ is determined by the geometrical distribution of the ligands and that high coordination numbers are not necessarily associated with large quadrupole splittings; this is illustrated by the data for $[SnCl_5]^-$ ($\rho = 0.7$–1.4) and $[EtSnCl_4]^-$ ($\rho = 1.5$).

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Halides. The Mössbauer data for the organotin halides are given in Table II. Agreement with other reported values is good.[10,17-19]

Monohalides. Trimethyltin fluoride is reported to give a quadrupole splitting of 3.8 mm/s,[17,18] which is consistent with the polymeric structure involving five-coordinate tin atoms.[2] The values for the other monofluorides are close to that for the trimethyl compound, suggesting that the structures are similar. For tri-alkyl derivatives, the values for the other halides are also high and decrease regularly with increasing atomic number of the halogen. It was suggested previously[1] that, for four four-coordinate tin compounds, quadrupole splitting greater than about 2.5 mm/s are unlikely, and the point-charge treatment given below suggests a probable value for monomeric organotin halides of about 1.9 mm/s. The observed values are significantly greater than this, and are very similar to those for the corresponding complexes $[R_3SnX_2]^-$. It seems likely that these halides are strongly associated, like the fluorides, with five-coordinate tin atoms, as suggested by the infra-red data.[5]

The observation of two infra-red active Sn–C stretching modes could be explained if the Sn ... Cl bridging bonds were longer than the terminal Sn–Cl bonds, so that the alkyl groups were no longer coplanar with tin atom. However, it seems unlikely that such a structure would result in quadrupole splitting values so similar to those of the anions. It has recently been shown by X-ray crystallography[20] that Me_3SnCl has a polymeric structure involving five-cordinate tin atoms but, in contrast to Me_3SnF, the –Sn–Cl–Sn–Cl– chains are bent at tin rather than at the halogen. The resulting loss of symmetry would account for the infra-red spectrum.

Of the triphenyltin derivatives, the fluoride has Mössbauer parameters similar to those for the trialkyltin fluorides, and presumably has a similar, strongly associated structure. The quadrupole splittings of the remaining triphenyltin halides are much lower than that of the fluoride and are also less than that of $[Ph_3SnCl_2]^-$. Even taking into account the observation[1] that quadrupole splittings for phenyltin compounds are usually lower than those for the corresponding alkyltin compounds, it seems unlikely that the triphenyltin halides are associated as strongly as their tri-alkyl analogues. The values are, however, still larger than would be expected for monomeric Ph_3SnX units, and it is probable that there is weak association, leading to distortion from tetrahedral configurations.

The diminished association in the phenyl compounds is probably caused by the steric effect of the phenyl group. It has been noted that the quadrupole splitting of the halides R_3SnX decreases as R increases in size from ethyl to iso-butyl.[18] This effect is even more marked for the corresponding neophyl derivatives, since $(neo)_3SnF$ has a quadrupole splitting of only 2.79 mm/s,[16] and is a low-melting, soluble compound, suggesting a considerable weakening of the solid state association. The other neophyltin halides have quadrupole splittings similar to those of the phenyl compounds.[16]

Dihalides. If the dihalides had structures similar to that[3] of Me_2SnF_2, quadrupole splitting values similar to those of the complex ions *trans*–$[R_2SnX_4]^{2-}$ would be expected. The observed values are lower than those for the complexes, but are still considerably greater than would be expected for monomeric species. Association must again occur, as shown also by the infra-red data,[6] but it is not possible to suggest a structure. A recent X-ray study[20] of Me_2SnCl_2 confirms its polymeric nature, the tin atoms having a very iregular six-coordinate configuration. The quadrupole splittings of the diphenyltin halides are lower than for the di-alkyl compounds, again suggesting a weaker, but definite, association.

Trihalides. The Mössbauer data alone are not sufficient to determine the state of association of compounds of the type $RSnX_3$, since the quadrupole splittings of all the likely structures would be similar. It is possible that the isomer shift would be more sensitive to coordination number, and we hope to be able to compare data for the solids and frozen solutions.

For a given value of n in any one series of halides R_nSnX_{4-n}, the isomer shift varies systematically with change of the halogen as expected. However, if X is kept constant and n varied, the isomer shifts do not follow the expected pattern, since $\delta(R_2SnX_2) > \delta(R_3SnX) > \delta(RSnX_3)$. While this ordeing may reflect nothing more than the differing degrees of association, it seems likely that it is an indication of the effect of structure on isomer shift mentioned earlier.[15]

Point-Charge Parameters. The point charge model provides a useful method of correlating quadrupole splittings with structures.[1,9] It is assumed that each ligand, L, makes a fixed contribution, [L], to the quadrupole splitting, regardless of the structure of the compound and the nature of the other ligands. The additivity of ligand contributions has been demonstrated for closely related *cis-trans* pairs of six-coordinate tin(IV) compounds[9] and also for some low-spin ferrous complexes.[21] A more detailed examination of the data for tin(IV) compounds is now possible.

A convenient series for comparison is that of the five-coordinate complexes, $[R_nSnX_{5-n}]^-$ $(n = 0\text{–}3)$, for which the point-charge expressions are given in Table III; the method of calculation is shown in the Appendix. There is no simple relationship between these expressions, which are complicated functions of both [R] and [X], and comparisons cannot be made unless numerical values are assigned to these parameters. One method of assigning such values is now outlined.

The average quadrupole splitting of the $[SnCl_5]^-$ complexes gives a value for [Cl] of 0.63 mm/s. A

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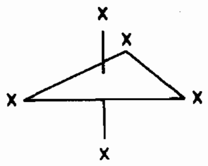
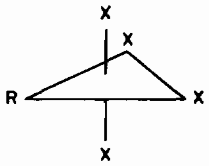
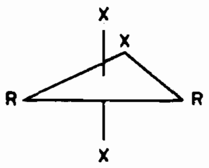
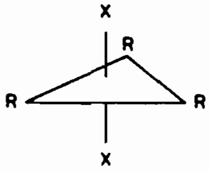
Table III. Point-charge treatment for $[R_nSnX_{5-n}]^-$

				
n	0	1	2	3
$V_{zz}(1+\eta^2/3)^{½}$	[X]	$\{7[X]^2-10[X][R]+4[R]^2\}^{½}$	$\{12[X]^2-18[X][R]+7[R]^2\}^{½}$	4[X]–3[R]
Δ_{calc} [a] (mm/s)	0.63	2.25 2.03 [b] 1.73 [c]	2.99 3.15 [d]	3.45
Δ_{obs}	0.46–0.77	1.82	3.30-3.75	3.23-3.74

[a] [Cl]=0.63 mm/s, [R]=–0.31 mm/s. [b] ClSnCl=110°. [c] ClSnCl=95°. [d] CSnC=140°.

Table IV. Point-charge parameters, [L], for various ligands.

Ligand L	Compound	Q.S. (mm/s)	Ref.	[L] (mm/s)
Cl	$(Et_4N)[SnCl_5]$	0.77	1	0.63
	$(Ph_3C)[SnCl_5]$	0.46	11	
	(*p*.tol $Ph_2C)[SnCl_5]$	0.67	11	
R	$(Et_4N)[Me_3SnCl_2]$	3.32		–0.31
		3.23	10	
	$(Ph_3PB_z)[Et_3SnCl_2]$	3.44		
	$[Me_3SnCl]_n$	3.41	17	
		3.47	18	
		3.41	19	
	$[Et_3SnCl]_n$	3.65		
		3.74	18	
F	$[Me_3SnF]_n$	3.86	17	0.73
		3.77	18	
	$[Et_3SnF]_n$	3.82		
		4.00	18	
Br	$(Et_4N)[Me_3SnBr_2]$	3.45		0.60
	$[Me_3SnBr]_n$	3.25	17	
		3.54	18	
		3.28	19	
	$[Et_3SnBr]_n$	3.28		
		3.27	18	
I	$[Me_3SnI]_n$	3.05	17	0.53
		3.15	18	
	$[Et_3SnI]_n$	2.95		
		3.13	18	
Ph	$[Ph_3SnF]_n$	3.53		–0.20
		3.62	18	
	$(Me_4N)[Ph_3SnCl_2]$	3.00		
C_2H_3	$[(C_2H_3)_3SnCl]_n$	3.29		–0.26
CF_3	Me_3SnCF_3	1.38	1	0.38
C_6F_5	$Me_3SnC_6F_5$	1.31	1	0.32
	$Me_2Sn(C_6F_5)_2$	1.50	1	
		1.48	19	
	$MeSn(C_6F_5)_3$	1.14	19	
C_6Cl_5	$Me_3SnC_6Cl_5$	1.09	1	0.24

value for R may be derived by combining the data for the complexes $[R_3SnCl_2]^-$ and the solid halides $[R_3SnCl]_n$, both of which contain five-coordinate tin. At this stage of the treatment, it is probably not worthwhile to distinguish between terminal and bridging chloride ligands. The quadrupole splitting values for the solid chlorides are a little higher (by *ca.* 0.2 mm/s) than those for the complexes, but this is probably due as much to the lowering of symmetry (non-linear Cl–Sn–Cl system, $\eta \neq 0$) as to differences in Cl–Sn bonding. The data for R = Me or Et give an average quadrupole splitting of 3.46 mm/s, from which, using [Cl]=0.63 mm/s, [R] = –0.31 mm/s. (Data for higher alkyl derivatives are not included because of the probable steric effect mentioned above). Using these values, the expected

Table V. Calculated and observed quadrupole splittings

Compound	Δ_{calc} (mm/s) [a]	Δ_{obs} (mm/s)	Ref.
$Ph_3SnC_6F_5$	1.04	0.90, 0.98	1, 19
$PhSn(C_6F_5)_3$	(—) 1.04	0.92	19
$Ph_2Sn(C_6F_5)_2$	1.20	1.11	19
$Me_3SnC_6H_5$	(—) 0.22	<0.4	17
$Ph_3SnC_6Cl_5$	0.88	0.84	1
$Ph_2Sn(C_6Cl_5)_2$	1.01	1.05,[b] 1.23	1
$R_2SnF_4^{2-}$	(—) 4.16	4.12, 4.32	
$R_2SnCl_4^{2-}$	(—) 3.73	3.99-4.32	9
$Ph_2SnCl_4^{2-}$	(—) 3.32	3.80	9
$EtSnCl_5^{2-}$	(—) 1.88	1.93	
$PhSnCl_5^{2-}$	(—) 1.66	1.92	9
R_3SnCl (monomeric)	1.88		
Ph_3SnCl (monomeric)	1.66		
R_2SnCl_2 (monomeric)	2.16		
Ph_2SnCl_2 (monomeric)	1.91		
$RSnCl_3$ (monomeric)	(—) 1.88		
Ph_3SnCl (polymeric)	3.12		
$RSnCl_3$ (polymeric)	(—) 1.88		

[a] The signs refer to the sign of V_{zz} (see text). [b] M. Cordey-Hayes, R.D.W. Kemmitt, R. D. Peacock, G. D. Rimmer, *J. Inorg. Nucl. Chem.*, *31*, 1515 (1969).

quadrupole splittings for $[RSnCl_4]^-$ and $[R_2SnCl_3]^-$ may be calculated (Table III). The values obtained are reasonably close to those observed, but the first is high and the second low. However, the C–Sn–C angle in $[Me_2SnCl_3]^-$ is not 120°, as assumed for the calculation, but is opened out to 140°.[13] The calculated quadrupole splitting is sensitive to this angle, rising when the larger value is used. A similar distortion, of opposite direction, might be expected for $[RSnCl_4]^-$, with the equatorial Cl–Sn–Cl angle closing to 95-110°. Allowing for this distortion again brings the calculated value closer to that observed.

The value of [R] may now be used with quadrupole splitting data for $[R_3SnX_2]^-$ and $[R_3'SnX]_n$ to obtain values for [F], [Br], [I], [Ph], and $[-CH{:}CH_2]$. Although the values of the point-charge parameters will probably be slightly dependent on the coordination number of the tin, an estimate of the values for $[C_6F_5]$, $[C_6Cl_5]$, and $[CF_3]$ may be obtained from data for four-coordinate compound. All these values, and the data used to derive them, are listed in Table IV. The consistency of the parameters may be checked by using them to calculate the expected quadrupole splitting for other compounds, as shown in Table V. For the four- and five-coordinate systems, agreement is good, *i.e.* within 0.1–0.2 mm/s. The calculated values for the six-coordinate systems are rather low, which may reflect the effect of coordination number. It has been suggested[1] that with increasing coordination number the Sn–X bonds become longer and more polar, which means that for an electronegative ligand [X] should increase with increasing coordination number. An independent check is not available for the four-coordinate compounds, but the value of $[CF_3]$ seems a little low.

The electric field gradient which produces the quadrupole splitting arises primarily from an imbalance in the polarity of the tin-ligand σ-bonds,[1] and it might be expected that the values of the point-charge parameters, [L], would be related to this polarity. It was shown previously[1] that there is a linear relationship between the quadrupole splitting of $[R_3SnX]_n$ (R = Me, Et; X = F, Cl, Br, I) and the Taft inductive constant σ_X^*. A similar relationship exists between [L] and σ_L^* (Figure 1).

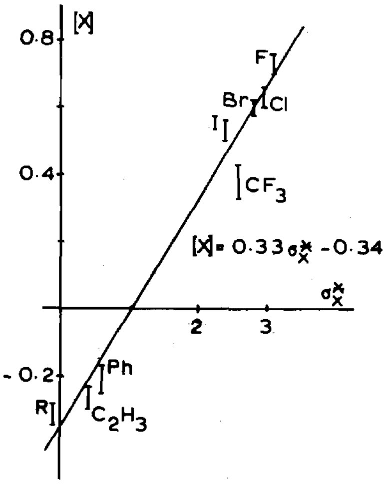


Figure 1. Plot of point-charge parameters, [X], *vs.* Taft's inductive constant, σ_x^*.

It should be emphasised that the [L] values calculated here are empirical numbers which can be manipulated, via the point-charge model, to reproduce observed quadrupole splitting values. The parallelism of [L] and σ_L^* suggests that there may be a more fundamental relationship which it is relevant to examine briefly. The electric field gradient arises from imbalances (*i.e.* non-cubic distributions) both of the charges on the ligands (and neighbouring ions) and of the valence-shell electrons.

$$\Delta = \tfrac{1}{2} e^2qQ(1+\eta^2/3)^{1/2}$$

$$eq = V_{zz} = -(\text{electric field gradient})$$

$$\eta = (V_{xx}-V_{yy})/V_{zz}$$

$$q = q_{lat}+q_{val} = \sum_L q_L(1-\gamma)(3\cos^2\theta-1)/r_L^3-\sum_i p_i(1-R)<(3\cos^2\theta-1)/r_i^3> \quad (1)$$

where

$-e$ is the charge on the electron;

eQ is the nuclear quadrupole moment;

q_L is the charge on ligand L with polar coordinates θ_L, r_L;

p_i is the population of the i-th valence-shell orbital;

$<(3\cos^2\theta-1)/r_i^3>$ is the expectation value for the i–th orbital, averaged over the electron coordinates θ_i, r_i;

γ, and R are Sternheimer shielding factors;

and the summations are taken over all ligands and all valence-shell orbitals.

In a neutral molecule, $\Sigma q_L = \Sigma p_i - 4$. Since the majority of ligands are more electronegative than tin, and will withdraw electron density from tin, q_{val} is better defined in terms of electron « holes ». If the valence-shell orbitals are redefined as hybrid orbitals (j), one directed towards each ligand, (1) may be rewritten

$$q = \sum_L q_L(1-\gamma)(3\cos^2\theta-1)/r_L^3 + \sum_j q_j(1-R) <(3\cos^2\theta-1)/r_j^3> \qquad (2)$$

and $q_j = -q_L$; q_{lat} and q_{val} thus differ in sign. A molecular orbital treatment[22a] shows that q_{val} follows the predictions of the point-charge model in the same way as q_{lat}, so that (2) may be rewritten

$$q = \Sigma\left[\frac{q_L(1-\gamma)}{r_L^3} + \frac{q_l(1-R)}{r_l^3}\right](3\cos^2\theta_L-1) \qquad (3)$$

where q_l/r_l^3 is an equivalent charge on the Sn–L bond axis, representing the electron « hole » density in the appropriate hybrid orbital, *i.e.*

$$q_l/r_l^3 = q_j<(3\cos^2\theta_j-1)/r_j^3>$$

θ_j now being defined relative to the appropriate bond axis. The magnitude of this term depends on the nature of L, so that

$$[L] = e\left[\frac{q_L(1-\gamma)}{r_L^3} + \frac{q_l(1-R)}{r_l^3}\right]$$

and

$$V_{zz} = \sum_L [L](3\cos^2\theta-1)$$

Since q_{lat} and q_{val} are opposite in sign, the sign of the electric field gradient will be determined by whichever has the larger (numerical) value. For iodine compounds, q_{val} is the major factor,[23] and this is probably true also for iron.[22b] Calculations suggest that, for tin, q_{val} will be more important than q_{lat} despite the difference in Sternheimer factors (γ = *ca.* -10; $0<R<1$).[24] This seems reasonable in view of the inverse cubic dependence of the q's on distance, the valence-shell electrons being, on average, closer to the tin nucleus than are the ligand electrons. In, say *trans*–R_2SnX_4, the valence shell of the tin atom will have more electron density concentrated in the z-direction (Sn–C) than in the x- and y-directions (Sn–X). Hence, q_{val} and V_{zz} would be negative, and this has recently been confirmed (assuming $Q<0$) by examination of the spectrum of $Cs_2[Me_2SnCl_4]$ in an applied magnetic field.[25]

The empirical parameters, [L], derived here embody contributions from both q_{val} and q_{lat}, although the latter would probably be significant only for electronegative ligands which become (relatively) highly charged with respect to tin. The large negative value of [R] is somewhat disconcerting, since Sn–C bonds would not be expected to be very polar. This value may simply reflect the arbitrary choice of the standard, [Cl], and equally satisfactory values may be obtained by scaling up the [L]-values, keeping the differences constant. Thus, a scale on which [R] = 0 mm/s and [F] = 1.03 mm/s gives calculated quadrupole splitting values similar to those in Table V, the major discrepancy being, of course, for $[SnX_5]^-$. An alternative means of deriving a scale would be to use the relationship[1] between $\Delta(R_3SnX)$ and σ_X^*. The slope of this line is about four times that of the line in Figure 1, as expected, and gives values for [R] of 0–0.15 mm/s depending on the selection of data used. Further measurements over a greater range of compounds are required to define the most satisfactory scale. It is, however, apparent that such a scale can be set up and used in the determination of structures. Even without correcting for the effect of coordination number on [L] values, a choice between the various possible forms, four-, five-, or six-coordinate, of organotin compounds can usually be made easily. Refinement of the scale should allow critical examination of the nature of tin-ligand bonds.

Experimental Section

The organotin halides and their complexes were made by literature methods;[13,26-36] the anions $Et_3SnCl_2^-$ and $EtSnCl_5^{2-}$ have not been reported previously. Diphenyltin dichloride was kindly supplied by Pure Chemicals Ltd. Satisfactory analyses were obtained for all products (Tables VI and VII).

The following infra-red bands wered recorded (cm^{-1}):

$(Et_4N)Me_3SnCl_2$	ν_{Sn-C} 534, vs, 510 vvw, sh, ν_{Sn-Cl} 338 mw
$(Et_4N)Me_3SnBr_2$	ν_{Sn-C} 538 vs, 507 vw
$(Me_4N)_2Et_2SnCl_4$	ν_{Sn-C} 520 s, ν_{Sn-Cl} 346 m

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Table VI. Analytical data for organotin halide complexes

Complex	Found (%) C	H	N	Hal	Calc. (%) C	H	N	Hal	Ref.[a]
$(Et_4N)[Me_3SnCl_2]$	36.1	8.3	4.1	19.3	36.2	8.0	3.9	19.4	—
$(Et_4N)[Me_3SnBr_2]$	29.4	6.2	3.4	35.3	29.1	6.4	3.1	35.2	26
$Cs_2[Me_2SnCl_4]$	4.5	1.1	—	25.6	4.3	1.1	—	25.5	13
$Cs_2[Me_2SnBr_4]$	3.4	0.9	—	43.2	3.3	0.8	—	43.4	13
$(Et_4N)[Me_2SnCl_3]$	31.0	6.9	3.9	27.3	31.2	6.8	3.6	27.6	13
$(Et_4N)[Me_2SnBr_3]$	23.3	5.2	2.7	46.5	23.2	5.0	2.7	46.3	13
$K_2[Me_2SnF_4]$	7.8	2.0	—	—	7.9	2.0	—	—	27
$(Ph_4As)[Me_2SnCl_3]$	49.0	4.1	—	16.4	48.9	4.1	—	16.6	28
$(Ph_3PCH_2Ph)[Et_3SnCl_2]$	59.0	6.1	—	11.0	59.1	5.9	—	11.3	—
$(Me_4N)[Et_2SnCl_4]$	30.5	7.2	5.8	30.5	30.8	7.3	6.0	30.4	26
$(Ph_4As)[Et_2SnCl_3]$	50.6	4.5	—	15.8	50.5	4.5	—	16.0	29
$(Ph_4As)[Et_2SnCl_4]$	46.5	3.8	—	21.0	46.4	3.7	—	21.0	29
$(Me_4N)_2[EtSnCl_5]$	25.2	5.8	5.6	37.2	25.4	6.1	5.9	37.5	—
$K_2[Et_2SnF_4]$	13.9	3.1	—	—	14.5	3.0	—	—	27
$(Me_4N)[Ph_3SnCl_2]$	53.3	5.6	2.8	14.1	53.4	5.5	2.8	14.4	30

[a] References are to preparative methods.

Table VII. Analytical data for organotin halides

Halide	Halogen (%) Found	Calc.	Other[a]	Ref.[b]
Et_3SnF	—	—	C = 32.0(32.0), H = 6.9(6.7)	27
Et_3SnCl	14.8	14.7		31
Et_3SnBr	28.2	28.0		31
Et_3SnI	37.8	38.1		31
Et_2SnCl_2	28.6	28.6		31
Et_2SnBr_2	47.6	47.5		31
Et_2SnI_2	58.7	59.0		32
$EtSnCl_3$	41.6	41.9		31
$EtSnBr_3$	61.7	61.9		31
Ph_3SnCl	9.2	9.2		31
Ph_3SnBr	18.6	18.7		33
Ph_3SnI	22.0	21.8	C = 45.6(45.3), H = 3.4(3.1)	34
Ph_2SnBr_2	37.1	36.9		31
Ph_2SnI_2	47.7	48.2		34
$PhSnCl_3$	35.0	35.2	C = 24.1(23.8), H = 1.6(1.6)	31
$PhSnBr_3$	54.9	55.1	C = 16.6(16.5), H = 1.3(1.2)	35
$(C_2H_3)_3SnCl$	—	—	C = 30.8(30.6), H = 3.9(3.8)	36
$(C_2H_3)_2SnCl_2$	—	—	C = 20.1(19.7), H = 2.3(2.5)	36
$C_2H_3SnCl_3$	—	—	C = 9.8(9.5), H = 1.4(1.2)	36

[a] Calculated values in brackets. [b] References refer to preparative methods.

The Mössbauer spectrometer and the method of computation have been described previously.[1] Typical spectra are shown in Figure 2. All spectra were measured with the samples at liquid nitrogen temperature and the source (Sn/Pd) at room temperature. Isomer shifts are quoted relative to an SnO_2 absorber, these spectra being computed as a single Lorentzian. A series of calibration spectra, run at intervals during this work, gave a standard deviation of 0.05 mm/s for the isomer shift and 0.10 mm/s for the line width.

Appendix

Point-Charge Calculations.[37] The electric field gradient (e.f.g.) is a traceless 3×3 tensor

$$\text{e.f.g.} = -\vec{\nabla} E = -\begin{vmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{vmatrix}$$

where

$$V_{ij} = \partial^2 V / \partial i \partial j$$
$$V_{xx} = \sum_L (3\sin^2\theta_L \cos^2\Phi_L - 1)\ [L]$$
$$V_{yy} = \sum_L (3\sin^2\theta_L \sin^2\Phi_L - 1)\ [L]$$
$$V_{zz} = \sum_L (3\cos^2\theta_L - 1)\ [L]$$
$$V_{xy} = V_{yx} = \sum_L (3\sin^2\theta_L \sin\Phi_L \cos\Phi_L)\ [L]$$
$$V_{xz} = V_{zx} = \sum_L (3\sin\theta_L \cos\theta_L \cos\Phi_L)\ [L]$$
$$V_{yz} = V_{zy} = \sum_L (3\sin\theta_L \cos\theta_L \sin\Phi_L)\ [L]$$

By convention the axes are chosen so that $|V_{zz}| \geqslant |V_{yy}| \geqslant |V_{xx}|$. By suitable choice of axes, the off-diagonal elements, X_{xy} etc., can usually be made to vanish. (Note — the z-axis does not always coincide with the highest-order symmetry axis). The e.f.g. tensor is traceless, *i.e.* $V_{xx}+V_{yy}+V_{zz} = 0$, so that only two parameters are required, usually chosen as V_{zz} and $\eta = (V_{xx}-V_{yy})/V_{zz}$, when $\Delta\ \alpha\ V_{zz}(1+\eta^2/3)$.

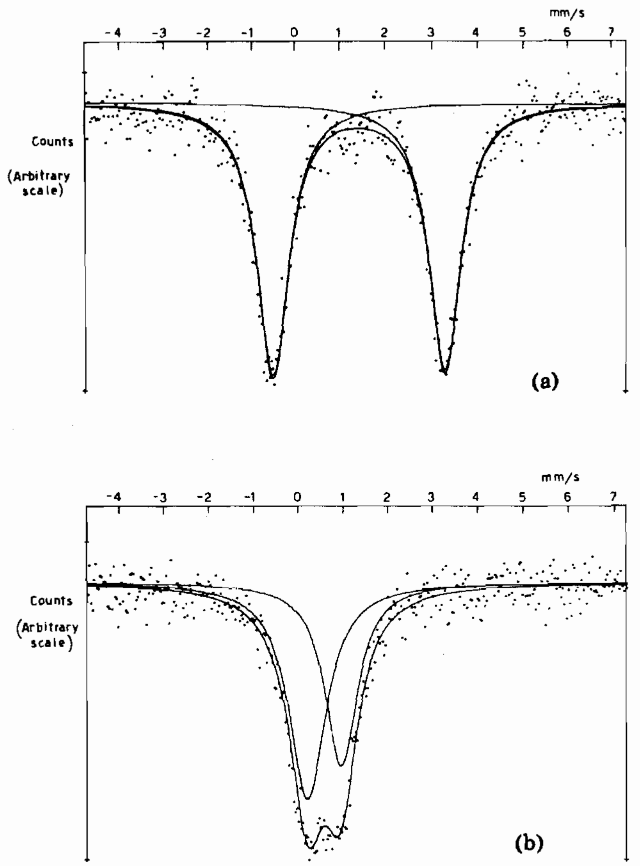

Figure 2. Mössbauer spectra for (a) Et_3SnF and (b) $(Et_4N)[SnCl_5]$. The continuous lines represent the computed spectra.

As an example, the case of an $RSnX_4$ structure will be treated, assuming 120° equatorial bond angles.

L = R		X_1	X_2	X_3	X_4
Φ_L	0	$2\pi/3$	$2\pi/3$	$\pi/2$	$\pi/2$
θ_L	0	π	0	$\pi/2$	$3\pi/2$

Hence,

$$V_{xx} = -[R] + \frac{5}{4}[X_1] + \frac{5}{4}[X_2] - [X_3] - [X_4]$$

Assuming all Sn–X to be equivalent,

$$X_{xx} = -[R] + \frac{1}{2}[X]$$

Similarly

$$V_{yy} = -[R] + 2[X]$$

$$V_{zz} = 2[R] - \frac{5}{2}[X]$$

$$V_{xy} = V_{xz} = V_{yz} = 0$$

$$\Delta \alpha \{V_{zz}^2 + \frac{1}{3}(V_{xx} - V_{yy})^2\}^{1/2}$$

$$\alpha \{4[R]^2 - 10[R][X] + 7[X]^2\}^{1/2}$$

The calculated relative values of Δ for various structures are:

$RSnX_3$	tetrahedral	$2[R]-2[X]$
R_3SnX	tetrahedral	$-2[R]+2[X]$
R_2SnX_2	tetrahedral	$1.15(2[R]-2[X])$ $(\eta = 1)$
SnX_5	trigonal bipyramid	$[X]$
$RSnX_4$	»	$\{4[R]^2-10[R][X]+7[X]^2\}^{1/2}$
R_2SnX_3	»	$\{7[R]^2-18[R][X]+12[X]^2\}^{1/2}$
R_3SnX_2	»	$-3[R]+4[X]$
R_2SnX_4 *cis*	octahedral	$-2[R]+2[X]$
R_2SnX_4 *trans*	octahedral	$4[R]-4[X]$

Acnowledgments. We are indebted to Mr. J.N.R. Ruddick for running the spectra of some of the complexes and to the Science Research Council for a studentship (to R.H.P.).

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