Complexes of Organometallic Compounds. LII *. ^{119}Sn Mössbauer Isomer Shifts, Partial Atomic Charges on Tin, and Structure, in Triorganotin(IV) Halides

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We previously reported on the correlation occurring between ^{119}Sn Mössbauer isomer shifts, δ, and partial atomic charges on tin, Q_{Sn} (determined empirically by an orbital electronegativity equalization procedure using the CHELEQ program), for five-coordinated species R_3SnL (L = F, Cl, O–, pseudohalide) [1]. This result was interpreted in terms of additional evidence of the reliability of δ/Q_{Sn} correlations in the structural tin(IV) chemistry [1]. Continuing our researches in the field [1, 2], we have taken into account δ/Q_{Sn} data for homologous series R_3Snhal as a function of the nature of both R (Me, Et, Pr^n, Bu^n, Cyclohexyl = Cy, Ph) and halide (F, Cl, Br, I), and the results are reported in the present paper.

The compounds Alk_3SnF and –Cl here considered, and Ph_3SnF, are very probably solid state polymers with bridging halide and a trigonal bipyramidal (tbp) environment of the tin atoms [1]. Tetrahedral type structures have been instead detected at room temperature for Ph_3SnBr and Ph_3SnCl, and at low temperature for Ph_3SnCl, by X-ray diffractometry [3, 4]. Contrasting conclusions have been advanced concerning the configurations of R_3SnI and –Br derivatives at low temperatures from Mössbauer spectroscopic studies. In fact, quadrupole splitting data, ΔE, have been interpreted in terms of tbp structures for Alk_3SnI and –Br (Alk = Me, Et, Pr^n, Bu^n) where the intermolecular interaction would weaken for the higher alkyl derivatives, perhaps due to steric factors [5]. Analogous assumptions have been advanced for Cy_3SnI and –Br [6]. Moreover, Me_3SnI, Ph_3SnBr and Ph_3SnCl have been considered as both polymeric and monomeric solid state species, while Ph_3SnI seems definitely a tetrahedral monomer [5, 7–9].

In particular, as far as Ph_3SnCl is concerned, the occurrence of a tbp polymeric species has been assumed at 77 K on the basis of NQR spectroscopic data [4, 10], which, on the other hand, do not seem to be reproduceable [11]. Moreover, the near constancy of the parameters δ and ΔE of Ph_3SnCl at 80, 110 and 295 K has been taken as evidence of isostructurality (tetrahedral) for this compound in the above temperature range [12].

Lattice dynamics studies effected by temperature dependent Mössbauer spectroscopy indicated an essentially molecular structure for Me_3SnBr and Ph_3SnCl [13–15].

A structural trend from tbp to tetrahedral then appears to occur in R_3Snhal by increasing the chain length or the steric hindrance of the radical R, and parellel to the nature of hal in the sequence F, Cl, Br, I. These configurational changes would imply consistent variations in the magnitude of δ values along the series, and would be evidenced by δ/Q_{Sn} correlations. The latter have been then determined and are reported in Fig. 1.

To the purpose, literature data for δ values of Alk_3SnI and –Br, and Ph_3SnI, –Br and –Cl have been collected and are reported in Table I, while data for Alk_3SnF and –Cl, and Ph_3SnF are taken from ref. 1. The CHELEQ values of Q_{Sn}, also reported in Table I, have been calculated [36] on the basis of tbp structures, the bond orders of the equatorial SnC_3 skeleton being 1.00 and those of the apical (bridging) halide atoms 0.50, while formal charges are generally taken as 0.00 [1], analogously to the calculations of Q_{Sn} effected for Alk_3SnF and –Cl, and Ph_3SnF, previously reported [1]. On the

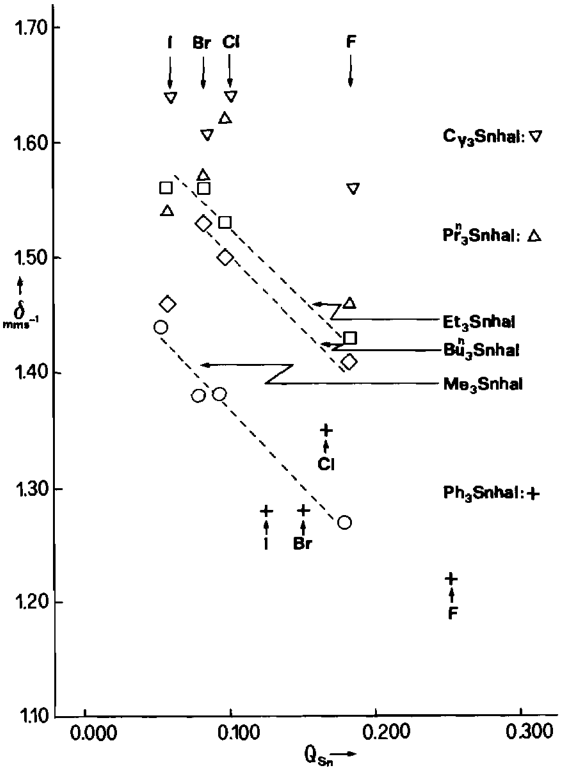

Fig. 1. Correlation δ/Q_{Sn} for R_3Snhal, see text. The values of δ are arithmetic averages of data in Table I and ref. 1.

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*Part LI is ref. 1.

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TABLE I. Atomic Charges (CHELEQ)[a] on Tin, Q_{Sn}, and ^{119}Sn Mössbauer Isomer Shifts, δ, of R_3SnI, R_3SnBr and Ph_3SnCl

Compound[b]	Q_{Sn}	δ^c (mm s^{-1})	References for δ
Me_3SnI	0.054	1.41; 1.49; 1.43; 1.42	16; 17, 18; 8; 9
Me_3SnBr	0.078	1.42; 1.30; 1.38; 1.38; 1.41; 1.30; 1.44	16; 19; 20; 21; 17, 18; 22; 11
Et_3SnI	0.058	1.57; 1.56; 1.55; 1.55	17; 23; 22; 24
Et_3SnBr	0.083	1.38; 1.55; 1.61; 1.57; 1.62; 1.60; 1.57	19; 21; 17; 23; 22; 24; 11
Pr^n_3SnI	0.058	1.59, 1.46; 1.57	17; 25; 26
Pr^n_3SnBr	0.083	1.39; 1.64; 1.67	21; 17; 22
Bu^n_3SnI	0.058	1.47; 1.39; 1.52	17; 22; 26
Bu^n_3SnBr	0.083	1.70; 1.53; 1.54; 1.33; 1.56	27; 21; 17; 22; 11
Ph_3SnI	0.120	1.41; 1.24; 1.19; 1.20; 1.34	28; 21; 17; 23; 9
Ph_3SnBr	0.151	1.23; 1.33; 1.20; 1.37	29; 21; 17; 23
Ph_3SnCl	0.167	1.38; 1.40; 1.28; 1.37; 1.34 1.28; 1.34; 1.37; 1.36; 1.31; 1.36; 1.33; 1.39	30; 31; 29; 32; 13; 33; 20; 28; 17; 23; 34; 11; 8
Cy_3SnI	0.061	1.64; 1.65	6; 35,
Cy_3SnBr	0.086	1.63; 1.58; 1.65	6; 11; 35

[a] See text. [b] Cy = Cyclohexyl. [c] Data generally measured at liquid N_2 temperature, and referred to room temperature SnO_3^{2-}, SnO_2. Whenever different standards were employed, data have been related to SnO_3^{2-} according to Mössbauer Effect References and Data Index.

other hand, it has been observed that these Q_{Sn} data for tbp structures differ very slightly from Q_{Sn} calculated for tetrahedral R_3SnI, –Br and –Cl (Q_{Sn}tbp–Q_{Sn}tet. $\leqslant 0.004$), as expected for the compounds here studied on the following basis: (i) the comparatively low orbital electronegativity CHELEQ parameters of I, Br, and also Cl [36]; (ii) the consequent near equivalence, with respect to the extent of the charge transferred from tin atoms, of two bridging halide atoms (in a special way I and Br) linked to tin with bond order 0.50 (in the tbp structures, *vide supra*) with one terminal halide linked with bond order 1.00 (in the tetrahedral structures). It then follows that the present approach does not discriminate between tbp and tetrahedral structures, for the compounds considered above, as far as their partial atomic charges are concerned; as a consequence, the eventual occurrence of a δ/Q_{Sn} correlation for homologous series of supposedly isostructural R_3Snhal species would be dictated only by the magnitude of the experimental parameters δ in the case of hal = I, Br, Cl.

Turning now to the δ/Q_{Sn} correlations reported in Fig. 1, an essentially linear relationship is observed to occur for the four data points of the Me_3Snhal series. An analogous result has been obtained earlier by correlating the δ values of these compounds with the ground state electronegativities (in Pauling and Mulliken units) of the ligand atoms and groups [37–39, 18]. This would suggest a common five-coordinated, polymeric structure, for these compounds. Assuming that any series of five-coordinated Alk_3Snhal compounds has to describe a straight line with a slope similar to that of the Me_3Snhal line, from the data in Fig. 1 it would be inferred that: (i) the iodide data points Et_3SnI, Pr_3^nSnI and Bu_3^nSnI seem to leave the respective correlations at an increasing extent as the alkyl chain lengthens; (ii) compounds Cy_3SnI and Cy_3SnBr seem to be out of the Cy_3SnF and –Cl line, although a correlation covering all four compounds, with a lower slope than for the methyl derivatives, could be assumed to hold.

One would be then inclined to assume that the δ/Q_{Sn} correlations of Fig. 1 indicate a general tbp configuration with the exception of the iodides and bromides listed under (i) and (ii). In fact, the scattering of the data points of Pr_3^nSnF, –Cl and –Br seem to be attributable to an abnormally high δ value of Pr_3^nSnCl, or alternatively to the inclusion of one very low δ value for Pr_3^nSnBr in the δ average, so that Pr_3^nSnBr could be perhaps assumed as a five-coordinate polymer according to the preceding discussion.

As far as the Ph_3Snhal series is concerned, it seems difficult to extract definite conclusions from the trend shown by the data points in Fig. 1. Anyway, if the slope rule given above for Alk_3Snhal compounds is assumed to hold also for Ph_3Snhal, it would seem that Ph_3SnF and –Cl are five-coordinated polymers while Ph_3SnBr and –I are monomeric species.

It seems to us that these structural suggestions, as extracted from the correlations of Fig. 1, are quite reasonable, being essentially in accordance with the more reliable results and assumptions from previous researches, perhaps except Ph_3SnCl, to which a possibly incorrect polymeric five-coordinated structure at 77 K would be assigned in the present context. The circumstance that the intermolecular bonds are weakened in the iodides, and perhaps in some bromides, by increasing the bulkiness of the organic radicals, seems logical and rational [5, 6]. Steric reason, in place of inductive [40], could be invoked for interpreting the general increase of δ, detected for the assumed five-coordinated species, in going from Me to Et, Pr^n, Cy (Bu^n being the exception in the present context), since the SnC_3 skeleton would be expected to be forced into a more planar configuration along the series when maintaining a bridged structure. This may be described as an effect of second order hybridization; it is known that in some instances tetrahedral species show a lesser δ value than, say, five-coordinate ones, which may be ascribed to changes in hydridization [5, 17].

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