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Complexes of Organometallic Compounds. LI*. The Correlation between ^{119}Sn Mössbauer Isomer Shifts and Partial Atomic Charges on Tin in R_3SnL Compounds

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Abstract

The ^{119}Sn Mössbauer isomer shift parameters, δ, of compounds R_3SnL (R = AlK, Ph; L = F, Cl, OH, OR′, CN, NCS, NCO, N_3) have been correlated to partial atomic charges on tin Q_{Sn}, calculated according to a valence state electronegativity equalization procedure carried out by the CHELEQ program. A unique δ/Q_{Sn} correlation has been obtained for all the five-coordinated R_3SnL species by using average δ parameters for the AlK_3Sn^{IV} derivatives.

Introduction

In the context of our research work on the correlation of δ parameters with calculated partial atomic charges on tin, Q_{Sn}, in homologous series of six- and five-coordinated R_nSn^{IV} (n = 1–3) and Sn^{IV} adducts and complexes [1], it seemed advisable to determine correlations δ/Q_{Sn} CHELEQ [1, 2] for the series R_3SnL, L being F, Cl, OH, OR′, CN, NCS, NCO, N_3, in order to get further information on the reliability of our method of rationalizing δ data through Q_{Sn} charges as a function of the molecular structures of the compounds under study. The results obtained are reported and discussed in the present paper.

Valence Bond Structures and Calculation of Partial Charges

A number of compounds R_3SnL considered here are solid state polymers, where the metal atom is five coordinated, with equatorial SnC_3 skeletons and axially bridging L atoms or groups, according *e.g.* to the result of X-ray diffractometric studies [3]. Consequently, we employed the valence bond structure of Fig. 1, and the related values of bond orders and formal charges (caption to Fig. 1), in the calculation of Q_{Sn} CHELEQ partial charges through an orbital electronegativity equalization procedure by the CHELEQ program [1, 2]. In this way it was expected to generate a linear correlation relative to isostructural polymeric species from which the possible molecular terms would be excluded. It is worthwhile to recall that the significance and implications of the valence bond structure of Fig. 1, which has been successfully employed in calculating Q_{Sn} data for series or R_3SnL_2 and R_3SnLL' five-coordinated species, have been discussed earlier [1c].

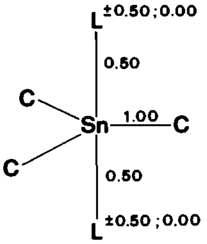

Fig. 1. Valence bond structure and input values of bond orders and formal charges, assumed for the calculation of CHELEQ partial atomic charges for R_3SnL compounds. The formal charges of the equatorial carbon atoms are taken as 0.00, while those of the axial bridging atoms L are as follows: $hal^{0.0}$; $O^{0.0}$ (of OH, OR); $^{-0.5}C{\equiv}N^{+0.5}$; $^{+0.5}N{\equiv}C{-}S^{-0.5}$; $^{-0.5}N{=}C{=}O^{+0.5}$; $>N^{0.0}$ (of $>N{=}N^{+1.0}{=}N^{-1.0}$, α,α-bonding to Sn, see text.

The input data of bond orders and formal charges for atoms and bonds in the molecules, other than those in Fig. 1, have been assigned as usual [2]. Moreover, the resonance structure N≡C–S has been selected for the solid state polymers R_3SnNCS, mainly on the basis of the angle SnNC in the trimethyl derivative, ~173°, which would imply a sp hybridization of N although the real structure is intermediate between N≡C–S and N=C=S [3g,m]. In the case of R_3SnNCO compounds, the structure N=C=O comes from the CN bond length, typical of a double bond [3n]. The structure of bridging cyanide has been arbitrarily taken as C≡N, with alternating Sn–C and Sn–N axial bonds (see legend to Fig. 1); CN

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*Part L: Ref. [1a].

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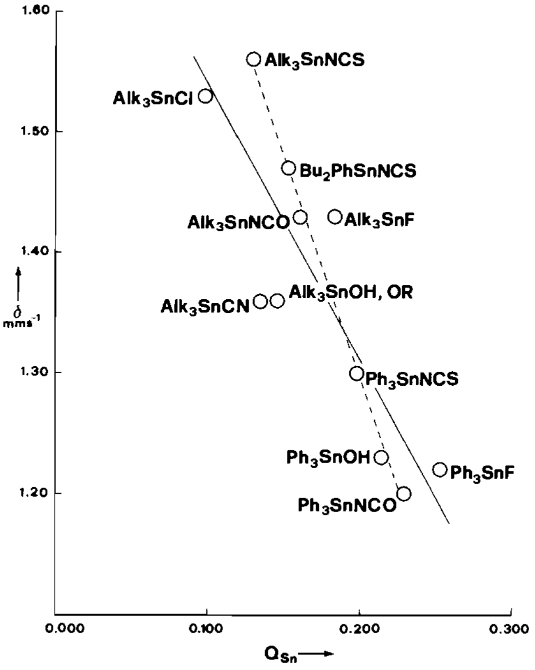

Fig. 2. The correlation δ/Q_{Sn} for compounds $(R_3SnL)_n$, structure as in Fig. 1 and caption. Arithmetic averages are taken for δ and Q_{Sn} from data listed in Table I. Full line is the least-squares fit of data points, $\delta = 1.77-2.28Q_{Sn}$ (correlation coefficient $r = 0.865$). Alk means alkyl, cyclohexyl, benzyl. The dotted line graphically indicates the excellent correlation of the R_3SnNCS, R_3SnNCO data points.

groups are in fact disordered in crystals of AlK$_3$SnCN so that the only information obtainable concerns the possible bridging of R_3Sn^{IV} moieties by CN groups [3e]. Lastly, azide groups seem to be intermediate between the resonance extremes $N^{-1}-N^{+1}\equiv N^{\circ}$ and $N^{\circ}=N^{+1}=N^{-1}$ when acting as α,α-N bridging [3h]; we have employed here the latter one since the use of the first structure yields negative Q_{Sn}, inconsistent with the data range shown by the species $(R_3SnL)_n$.

When computing Q_{Sn} for $(R_3SnL)_n$, three repeating units were considered and the charge obtained for the central tin atom was selected.

The Q_{Sn} values thus obtained are reported in Table I, where literature δ values of each compound are also tabulated. The correlation δ/Q_{Sn} obtained with these data is shown in Fig. 2.

Discussion

In order to correctly interpret the trends shown by the δ/Q_{Sn} correlation obtained for R_3SnL compounds, it seems advisable to briefly comment on the information available on their structures.

From X-ray diffractometry it results that Me_3SnF is a solid state polymer with halogen bridges [3c], as Me_3SnCl at 135 K [3a]; the intermolecular contact distance Sn···Cl in Cy_3SnCl at room temperature [3b] is consistently shorter than the sum of the Sn and Cl van der Waals radii [39], which would suggest a polymeric structure. Five coordination of tin atoms has been established for the solid state polymers R_3SnOH [3d,l], Me_3SnOMe [3i], AlK$_3$SnCN [3e,f], R_3SnNCS [3g,m], Ph_3SnNCO [3n] and Me_3SnN_3 [3h].

As far as structural spectroscopic (mainly Mössbauer) investigations are concerned, contrasting views have been reported for structures at 77 K of several R_3Sn hal derivatives, while generally suggesting five-coordinated polymeric structures for the other classes of compounds investigated here. In any case, from ΔE parameters as well as their point-charge model rationalization, AlK$_3$SnF and –Cl (AlK = Me, Et, Pr^n, Bu^n and Cy) and Ph_3SnF have been assumed to have $(R_3Snhal)_n$ structures [35, 40].

Information on the extent of the intermolecular interactions in several compounds investigated here has been also extracted from lattice dynamics studies through temperature-dependent Mössbauer spectroscopy. The magnitude of the respective parameters of intermolecular force constant, $\theta_D{}^2M$ (θ_D being the Debye temperature and M the molecular mass), of Me_3SnCl suggests a molecular structure in the whole temperature range examined, while data of Me_3- and Ph_3SnF are consistent with the occurrence of uni-dimensional polymers [41]. Functions $\langle x^2\rangle$ (T), where $\langle x^2\rangle$ is the mean square displacement of ^{119}Sn pertaining to Me_3SnF, –Cl as well as to Ph_3SnF, are consistent with monomers and uni-dimensional polymers [42]. The slope of lines $d\ln A/dT = d\ln f_a/dT$ (A is the total area under the resonant peaks, and f_a is the absorber recoil free fraction) ranges from -1.75×10^{-2} to -1.41×10^{-2} for Me_3SnF [43, 16]. Small (negative) slopes $d\ln A/dT$ in the range above have been associated to polymeric solids [44]. Moreover, the lattice dynamics parameter $\theta_D{}^2$ M and the $\langle x^2\rangle$ (T) function of Me_3SnCN and –OH, as well as the slopes $d\ln A/dT = -2.11 \times 10^{-2}$ for Me_3SnNCO and -1.41×10^{-2} for Me_3SnN_3, essentially indicate the occurrence of uni-dimensional polymers [41, 42]*.

Turning now to the δ/Q_{Sn} correlation, the respective data points are plotted in Fig. 2, except those pertaining to AlK$_3$SnN$_3$ and Ph_3SnN_3, clearly irregular in their δ values (Table I: $\delta Ph_3 \gg \delta Me_3$), and that of $(Me_3Sn)_2(OH)N_3$. In view of the circumstance that Q_{Sn} coincide for AlK$_3$SnOH and –OR compounds, a single point has been calculated,

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*For footnote, see p. 116.

TABLE I. Partial Charges on Tin, Q_{Sn} (CHELEQ), and ^{119}Sn Mössbauer Isomer Shifts, δ, for $(R_3SnL)_n$.

Compound[a]	Q_{Sn}	δ[b]	Refs.
Me$_3$SnCl	0.094	1.37; 1.40; 1.36; 1.12; 1.41; 1.44; 1.34; 1.43; 1.40; 1.43; 1.51	4: 5; 6; 7; 8; 9; 10; 11; 12; 13; 14; 15
Me$_3$SnF	0.179	1.18; 1.21; 1.23; 1.24; 1.35; 1.31; 1.36; 1.27	5; 6; 10; 12; 14; 16; 17; 18
Me$_3$SnOH	0.140	1.07; 1.12; 1.08; 1.09; 1.20; 1.20; 1.23	5; 6; 15; 19; 20; 21; 22
Me$_3$SnCN	0.131	1.36; 1.39; 1.21; 1.29	23; 12; 24; 15
Me$_3$SnNCS	0.125	1.40; 1.36; 1.40	12; 15; 19
Me$_3$SnNCO	0.156	1.36	25
Me$_3$SnN$_3$	0.149	1.24; 1.43	5; 26
(Me$_3$Sn)$_2$(OH)N$_3$	0.145	1.29	21
Et$_3$SnCl	0.098	1.61; 1.30; 1.55; 1.62; 1.57	12; 15; 27; 14; 28
Et$_3$SnF	0.183	1.47; 1.35; 1.41; 1.47; 1.46	12; 15; 27; 14; 17
Et$_3$SnOH	0.145	1.35; 1.30	29; 20
Et$_3$SnOMe	0.145	1.41	30
Et$_3$SnOPh	0.147	1.42	31
Et$_3$SnCN	0.135	1.41; 1.29; 1.46	12; 15; 32
Et$_3$SnNCS	0.129	1.57	12
Et$_3$SnNCO	0.160	1.46	25
Et$_3$SnN$_3$	0.153	1.24	26
Pr$_3{}^n$SnCl	0.098	1.62; 1.62	12; 14
Pr$_3{}^n$SnF	0.183	1.44; 1.47; 1.47	12; 14; 17
Pr$_3{}^n$SnOH	0.145	1.34	20
Pr$_3{}^n$SnOMe	0.145	1.40	15
Pr$_3{}^n$SnNCO	0.160	1.48	25
Pr$_3{}^n$SnN$_3$	0.153	1.21	26
Bu$_3{}^n$SnCl	0.098	1.65; 1.58; 1.36; 1.53; 1.38	29; 33; 7; 12; 14
Bu$_3{}^n$SnF	0.183	1.37; 1.48; 1.31; 1.47	12; 15; 14; 17
Bu$_3{}^n$SnOH	0.145	1.37	20
Bu$_3{}^n$SnOMe	0.145	1.38	34
Bu$_3{}^n$SnOPh	0.147	1.42	34
Bu$_3{}^n$SnCN	0.135	1.37	12
Bu$_3{}^n$SnNCS	0.129	1.60	12
Bu$_3{}^n$SnNCO	0.160	1.36	25
Bu$_3{}^n$SnN$_3$	0.153	1.26	26
Cy$_3$SnCl	0.102	1.64	35
Cy$_3$SnF	0.186	1.56	35
Cy$_3$SnOH	0.148	1.40; 1.46	35; 22
Cy$_3$SnNCS	0.136	1.68	35
(PhCH$_2$)$_3$SnNCO	0.164	1.51	25
Bu$_2{}^n$PhSnNCS	0.152	1.47	36
Ph$_3$SnF	0.252	1.22; 1.17; 1.18; 1.25; 1.25; 1.18; 1.32	4; 5; 12; 15; 27; 19; 17
Ph$_3$SnOH	0.214	1.35; 1.18; 1.16; 1.21; 1.26; 1.24	37; 5; 23; 12; 20; 38

(continued overleaf)

TABLE I. *(continued)*

Compound[a]	Q_{Sn}	δ[b]	Refs.
Ph_3SnNCS	0.198	1.35; 1.45	12; 38
Ph_3SnNCO	0.229	1.30; 1.10	25; 38
Ph_3SnN_3	0.222	1.40	5

[a] Assumed to have the structure of Fig. 1. Formal charges of the atoms bound to Sn, and the resonance structures assumed for the pseudohalide ligands, are in the caption to Fig. 1, and commented in the text. Cy = Cyclohexyl. [b] mm s^{-1}, at liquid N_2 temperature, with respect to R. T. SnO_2 or $BaSnO_3$. Data referred to different standards have been treated according to reports in *Möss. Effect Refs. and Data J.*

comprehensive of both series. For all trialkyltin derivatives, average parameters have been employed [1c], giving the same weight to (mean) δ values of any individual AlK_3Sn^{IV} derivative irrespective of the number of δ values available for each term. A unique relationship is obtained, whose correlation coefficient is reasonably good (legend to Fig. 2). In particular, a very satisfactory correlation occurs for the sub-series R_3SnNCS–R_3SnNCO (Fig. 2), which is only partially due to the choice of the N≡C–S resonance structure (to which Q_{Sn} data of Table I refer); in fact, the use of the form N=C=S shifts CHELEQ Q_{Sn} values by only about 0.01 to less positive values, leaving the correlation practically unchanged.

It may be concluded that the present work further demonstrates the applicability of the correlation between ^{119}Sn Mössbauer isomer shifts and partial atomic charges on tin for the purpose of structural assignments in homologous series of compounds. In fact, it seems to us that the structural suggestions, extracted from the correlations of Fig. 2, are quite reasonable, being essentially in accordance with the more reliable results and assumptions from previous researches.

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[*] Literature data $\mathrm{d}\log_{10}A/\mathrm{d}T$ have been here recalculated as $\mathrm{d}\ln A/\mathrm{d}T$. It has been claimed [45] that 'the reporting of the temperature dependence of Mössbauer resonance areas is in a confused state', and that many measurements preceding more recent quotations [46] have to be repeated, since reported slopes $\mathrm{d}\ln A/\mathrm{d}T$ are too large. In reality, the only apparent inconsistency in the literature values in fact refer to the use of different bases in the logarithmic expression of functions $A(T)$, and this may be easily avoided by recalculating *e.g* decimal log data into natural logs. On the other hand, there are several misprints in Ref. [45], where the following correct literature quotation, for example, had to be reported for Me_3SnF: $\ln f(T) = -1.75 \times 10^{2}T - 59.5T$ [47] (in turn, in Ref. [47] the misprint consists in reporting 10^{2} in place of 10^{-2}). The $\mathrm{d}\ln A/\mathrm{d}T$ value of Me_3Sn NCO has been calculated here from $A(T)$ data of Ref. [25], the correlation coefficient being 0.997, while the value for Me_3SnN_3 is taken as that of Me_3SnF [16, 26].

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