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Studies in Mössbauer Spectroscopy. III.[1] An Analysis of the Isomer Shifts of Substituted Organotin(IV) Compounds

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The isomer shift in organotin(IV) compounds is examined as a function of the polarity, number, and disposition of the tin-ligand bonds. In compounds of the type R_3SnX and, to a lesser extent, R_2SnX_2 the isomer shift is insensitive to the nature of the ligand X, owing to changes in electronic shielding. The coordination number has no observable effect. Stereochemistry plays an important rôle, and the isomer shifts of di-alkyl and di-aryl compounds increase with increasing C–Sn–C bond angle, reflecting increasing involvement of s*-orbitals in the bonding.*

Introduction

Mössbauer spectra of chemical compounds are characterised by two major parameters, the isomer shift and the quadrupole splitting. For tin(IV) compounds it is now established that the quadrupol splitting is due to imbalance in the electron distribution of the tin valence-shell,[2] caused by differences in the polarity of the σ-bonds between the tin atom and its ligands.[3,4] The isomer shift is a measure of the total electron density at the tin nucleus, and calculation shows that this depends primarily on the valence-shell population, the contribution of the inner shells being virtually constant.[5] Current interpretations have focussed attention on the polarity of the tin-ligand bonds and the coordination number.

Herber and Cheng[6] and Donaldson and his co-workers[7] find that in the series $SnX_4Y_2^{2-}$, SnX_4, $SnX_4(oxinH)_2$, $SnX_2(oxin)_2$, and $SnX_2(sal)_2$ (X, Y = Cl, Br, I; oxinH = 8-hydroxyquinoline; sal = salicylate) the isomer shift is a linear function both of the Pauling electronegativity of the halogen and of the number of halogen atoms bound to the tin. For the complexes $SnX_4Y_2^{2-}$, the use of a revised scale of Mulliken electronegativities[8] allows the fluoro-complexes to be included, but apparently shows a much greater dependence of isomer shift on halogen-electronegativity for SnX_4 than for $SnX_4Y_2^{2-}$. This difference is, however, due more to the selection of isomer shift data than to the differing electronegativity scales, since Clausen and Good[8] find rather lower values for the iodo-complexes and have used a high value for SnI_4. In Figure 1, both sets of data are compared to a common set[9] for SnX_4. It is seen that, for complexes in which all the tin-ligand bonds are of relatively high polarity, a reasonable correlation exists between isomer shift and electronegativity, and that a decrease in coordination number leads to an increase in isomer shift.

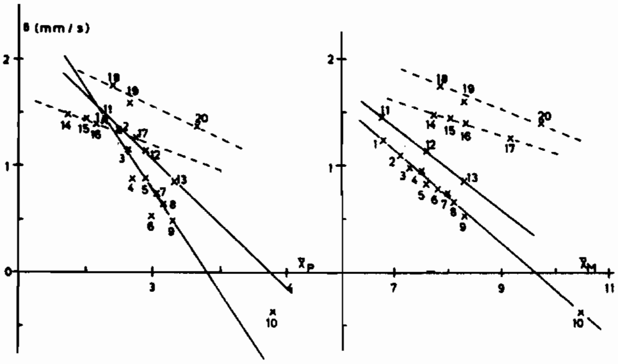

Figure 1. Isomer shift *vs* average electronegativity. (a) Data of Herber and Cheng[6] (points 1-9), Pauling scale, 2.2 assumed for methyl group (points 14-20); (b) Data of Clausen and Good[7] (points 1-10), Mulliken scale, 8.3 assumed for methyl group (points 14-20). Key: 1 SnI_6^{2-}, 2 $SnBr_2I_4^{2-}$, 3 $SnCl_2I_4^{2-}$, 4 $SnBr_4I_2^{2-}$, 5 $SnBr_6^{2-}$, 6 $SnCl_4I_2^{2-}$, 7 $SnCl_2Br_4^{2-}$, 8 $SnCl_4Br_2^{2-}$, 9 $SnCl_6^{2-}$, 10 SnF_6^{2-}, 11 SnI_4, 12 $SnBr_4$, 13 $SnCl_4$, 14 Me_3SnI, 15 Me_3SnBr, 16 Me_3SnCl, 17 Me_3SnF, 18 $Me_2SnBr_4^{2-}$, 19 $Me_2SnCl_4^{2-}$, 20 $Me_2SnF_4^{2-}$.

The data for $SnX_2(oxin)_2$ were extrapolated to yield an effective Pauling electronegativity of about 2.2 for the alkyl groups in $R_2Sn(oxin)_2$.[7] However, neither this value nor any other will allow data for alkyltin halide complexes to be fitted to the correlations of Figure 1, since the slope of the line for $Me_2SnX_4^{2-}$ is much less than that for $SnX_4Y_2^{2-}$. A decrease in coordination number and an increase in the number of alkyl groups leads to a lowering of the isomer shift, as shown by the line for $[Me_3SnX]_n$; both these

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trends conflict with the above correlations. It is thus evident that, in systems in which there is a large disparity between the polarities of the various tin-ligand bonds, factors other than the polarity and number of these bonds are affecting the isomer shift. It is the purpose of this Paper to examine these factors.

Discussion

The Nature of the Ligands. As shown in Figure 1, the isomer shifts of organotin halide systems are less sensitive to the nature of the halogen than might be expected. In the neutral halides, R_nSnX_{4-n}, there is a distinct increase in the isomer shift from the fluoride to the chloride (of 0.1-0.2 mm/s), but in the majority of cases the values for corresponding chlorides, bromides, and iodides are similar and show no systematic trends (Table I). (Comparisons must be made only within isostructural series since, as the discussion below shows, changes of structure may affect the isomer shift. We have also tried, wherever possible, to compare values from a single laboratory.) This lack of sensitivity has been attributed to the greater covalency (*i.e.* *s*-character) of the Sn–C bonds than the Sn–X bonds.[10] This would presumably account also for the quite distinct changes in isomer shift which occur when slight variations are made in the electronegativity of the organic groups, *e.g.* $R = Ph < Me < Et$.

Table I. Isomer shifts (mm/s) in organotin compounds.

Et_3SnF	1.47, 1.41 [a,b]		
Et_3SnCl	1.61, 1.55 [a,b]	Et_2SnCl_2	1.63 [b]
Et_3SnBr	1.61, 1.57 [a,b]	Et_2SnBr_2	1.70 [b]
Et_3SnI	1.57, 1.56 [a,b]	Et_2SnI_2	1.72 [b]
Me_3SnF	1.24, 1.28 [a,c]		
Me_3SnCl	1.40, 1.42 [a,c]	Me_2SnCl_2	1.60 [b]
Me_3SnBr	1.41, 1.49 [a,c]	Me_2SnBr_2	1.60 [b]
Me_3SnI	1.48, 1.49 [a,c]		
Ph_3SnF	1.18, 1.25 [a,b]		
Ph_3SnCl	1.36, 1.31 [a,b]	Ph_2SnCl_2	1.38 [b]
Ph_3SnBr	1.20, 1.37 [a,b]	Ph_2SnBr_2	1.43 [b]
Ph_3SnI	1.19, 1.20 [a,b]	Ph_2SnI_2	1.51 [b]
$(Ph_3Sn)_2O$	1.08 [d]		
$(Ph_3Sn)_2S$	1.22 [d]		
$Et_2SnCl_3^-$	1.54 [b]	$Et_3SnCl_2^-$	1.50 [b]
$Me_2SnCl_3^-$	1.48, 1.40 [b,e]	$Me_3SnCl_2^-$	1.42, 1.24 [b,e]
$Me_2SnBr_3^-$	1.52 [b]	$Me_3SnBr_2^-$	1.43 [b]
$Ph_2SnCl_3^-$	1.25 [b]	$Ph_3SnCl_2^-$	1.32 [b]
$Et_2SnF_4^{2-}$	1.45 [b]		
$Et_2SnCl_4^{2-}$	1.64 [b]		
$Me_2SnCl_4^{2-}$	1.38 [b]		
$Me_2SnCl_4^{2-}$	1.63, 1.59 [b,f]		
$Me_2SnBr_4^{2-}$	1.76 [b]		

[a] Ref. 28. [b] Ref. 1. [c] M. Cordey-Hayes, R.D. Peacock, and M. Vucelic, *J. Inorg. Nucl. Chem.*, *29*, 1117 (1967). [d] R. H. Herber, H.A. Stöckler, and W.T. Reichle, *J. Chem. Phys.*, *42*, 2447 (1965). [e] N.W.G. Debye, E. Rosenberg, and J.J. Zuckerman, *J. Amer. Chem. Soc.*, *90*, 3234 (1968). [f] Ref. 19.

Successive replacement of electronegative ligands by alkyl or aryl groups would be expected, on the bond-polarity argument, to lead to a continuous increase in the isomer shift. Such increases are found in the early stages of substitution, *e.g.* in the series $SnCl_6^{2-} < EtSnCl_5^{2-} < Et_2SnCl_4^{2-}$, $SnCl_5^- < EtSnCl_4^- < Et_2SnCl_3^-$, and $Sn(C_6F_5)_4 < MeSn(C_6F_5)_3 < Me_2Sn(C_6F_5)_2$ (Table II). Further substitution may arrest the decrease ($R_nSn(C_6F_5)_{4-n}$, $n = 2, 3, 4$) or even reverse it ($R_nSnX_{5-n}^-$, $n = 2, 3$). In four-coordinate compounds, R_3SnY, the isomer shift is quite insensitive to the nature of Y, although quadrupole splitting data demonstrate clearly varying degrees of polarity in the Sn–Y bonds (Table III); the isomer shifts are all equal, within experimental error, to that of R_4Sn.

Table II. Isomer shifts (mm/s) as a function of number of organic groups.

n =	0	1	2	3	4	Ref.
$Et_nSnCl_{6-n}^{2-}$	0.52	1.10	1.64	—	—	1
$Et_nSnCl_{5-n}^-$	0.59	1.18	1.54	1.50	—	1
$Me_nSn(C_6F_5)_{4-n}$	1.04	1.19	1.25	1.27	1.21	1 [a]
$Ph_nSn(C_6F_5)_{4-n}$	1.04	1.16	1.22	1.25	1.22	[a]

[a] H.A. Stöckler and H. Sano, *Trans. Farad. Soc.*, *64*, 577 (1968).

Table III. Mössbauer data (mm/s) for four-coordinate compounds of the type R_3SnX (from Ref. 3).

	δ	Δ
Me_4Sn	1.29	0
$Me_3SnC_6Cl_5$	1.32	1.09
$Me_3SnC\equiv CPh$	1.23	1.17
$Me_3SnCCl=CCl_2$	1.31	1.24
$Me_3SnC_6F_5$	1.27	1.31
Me_3SnCF_3	1.31	1.38
Ph_4Sn	1.27	0
$Ph_3SnCH=CH_2$	1.28	0
$Ph_3SnC_6Cl_5$	1.27	0.84
$Ph_3SnC_6F_5$	1.31	0.90
Bu_4Sn	1.30	0
$(Bu_3Sn)_2O$	1.29	1.56

The replacement of an organic group in R_4Sn by a more electronegative group might be expected to induce rehybridisation at the tin atom, concentrating *s*-character in the Sn–C bonds.[11] Although there is some evidence that the Sn–C bonds shorten with progressive substitution, the bond angles hardly change,[12] which suggests that rehybridisation is relatively unimportant. However, the substitution should increase the positive charge on the tin atom, which will result in a deshielding and contraction of the 5*s*-orbital, *i.e.* an increase in the effective nuclear charge. In terms of the electron density at the tin nucleus, this effect could compensate for the loss of some 5*s*-electron density to the electronegative ligand. There is a parallel here with n.m.r. coupling constants,[13] which also depend on the *s*-electron density at the nucleus. It has been shown[14] that, for the Fermi contact term, the effective nuclear charge is more important than the

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Table IV. Mössbauer data (mm/s) for organotin dithiocarbamates (from Ref. 23).

cis	δ	Δ	*trans*	δ	Δ	δ(δ)
$Ph_2Sn(S_2CNPh_2)_2$	1.19	1.69	$Me_2Sn(S_2CNPh_2)_2$	1.54	3.20	0.35
			$Bu_2Sn(S_2CNPh_2)_2$	1.72	3.21	0.53
$Ph_2Sn(S_2CNEt_2)_2$	1.17	1.76	$Me_2Sn(S_2CNEt_2)_2$	1.57	3.14	0.38
$Ph_2Sn(S_2CN(CH_2)_4)_2$	1.17	1.68	$Me_2Sn(S_2CN(CH_2)_4)_2$	1.59	2.85	0.42
			$Bu_2Sn(S_2CN(CH_2)_4)_2$	1.53	3.06	0.36
$Ph_2Sn(S_2CNBz_2)_2$	1.08	1.66	$Bu_2Sn(S_2CNBz_2)_2$	1.69	3.38	0.58

Table V. Isomer shifts (mm/s) for compounds of the type R_2SnX_4

		δ		δ	δ(δ)
1.	$Ph_2Sn(oxin)_2$	0.83	$Bu_2Sn(oxin)_2$	1.10	0.27 [a]
2.			$Pr_2Sn(oxin)_2$	1.02	0.19 [a]
3.	$Ph_2Sn(oxin)_2$	0.72	$Bu_2Sn(oxin)_2$	0.93	0.21 [b]
4.	$Ph_2Sn(NCS)_2$	1.45	$Bu_2Sn(NCS)_2$	1.54	0.09 [b]
5.	$(PyH)_2Ph_2SnCl_4$	1.44	$(PyH)_2Me_2SnCl_4$	1.59	0.15 [a]
6.	$Ph_2Sn(NCS)_2bipy$	0.82	$Bu_2Sn(NCS)_2bipy$	1.43	0.61 [b]
7.	$Ph_2Sn(NCS)_2phen$	0.82	$Bu_2Sn(NCS)_2phen$	1.42	0.60 [b]

[a] Ref. 19. [b] Ref. 21.

s-character of the bonds. It was possible to rationalise a wide range of $^{13}C-H$ coupling constant values on this basis without invoking, as is more usual, changes in hybridisation. Consistently with the present suggestion, the coupling constants $J(^{119}Sn-CH_3)$ of a variety of Me_3SnY compounds ($Y = Cl$, Br, I, CF_3, $OSnMe_3$, $SSnMe_3$, H, NMe_2, $SnMe_3$) cover a very narrow range (54.0-60.3 Hz).[15,16] The relative constancy of the J-values reflects the constancy of $|\psi_{5s}(0)|^2$ demonstrated by the isomer shifts.

Coordination Number. The coordination of additional ligands to the halides, SnX_4, leads to a decrease in the isomer shift,[2,17,18] which has been attributed to the increasing polarity of the lengthening Sn–X bonds,[2] and to increased shielding by participation of 5*d*-orbitals.[18] It has also been shown that, for mixed halide-oxinate or -salicylate complexes, change in cordination number has a greater effect on the isomer shift than changes in the ligands.[7]

In organotin systems, however, there do not seem to be any changes in isomer shift which are due solely to a change in coordination number, except possibly the small decrease from $EtSnCl_4^-$ to $EtSnCl_5^{2-}$ (0.08 mm/s). In the pairs $R_2SnX_3^-$, $R_2SnX_4^{2-}$ there is usually an increase in isomer shift of 0.1-0.2 mm/s, which can probably be attributed to stereochemical changes as discussed below.

Stereochemistry. A factor which does not seem to have been considered previously is the possible effect of the geometrical structure of a complex on its isomer shift. A good test would be to examine pairs of *cis-trans* isomers in the series R_2SnX_4 ($X =$ electronegative ligands), since the coordination number and bond polarities may be kept constant. Although no strict *cis-trans* pairs have been reported, an impression may be gained by using data for complexes in which X is an O- or N-donor ligand or Cl. The quadrupole splittings[19-22] show that the Sn–X bond polarities do not vary widely in this group, but the *cis* compounds have isomer shifts in the range 0.77-1.10 mm/s (average 0.86±0.13 mm/s*) while the *trans* derivatives cover the range 1.18-1.70 mm/s (average 1.44±0.17 mm/s). This difference is certainly significant. More direct comparison can be made in the series of dithiocarbamate complexes, $R_2Sn(S_2CNR_2')_2$ (R = Me, Bu, Ph), for which the quadrupole splittings show that the phenyl derivatives have *cis* geometry and the alkyl derivatives are *trans* (Table IV).[23] The average isomer shift of the *cis* compounds is 1.15±0.05 mm/s and that of the *trans* compounds is 1.61±0.08 mm/s; the average difference between corresponding pairs, δ(δ), is 0.44±0.10 mm/s. Part of this difference must be due to the difference in polarity of the phenyl-tin and alkyl-tin bonds, but this effect is not large enough to account for the whole of the difference. Thus, Table V shows data for pairs of compounds (1-5) which differ only in that two phenyl groups are replaced by two alkyl groups, the configurations being the same. The differences in isomer shifts are in the range 0.09-0.27 mm/s (average 0.18±0.07 mm/s). These values should be contrasted with those for the pairs 6 and 7 and the dithiocarbamate complexes, where the phenyl derivative is *cis* and the alkyl compound *trans*. In these cases, δ(δ) covers the range 0.35-0.61 mm/s (average 0.52±0.12 mm/s). The change in isomer shift is clearly as much due to the change in geometry as to that in the ligands. (In this treatment the difference between the isomer shifts of methyl compounds and the higher alkyl derivatives has been ignored. The conclusions are unaffected when this difference is taken into account.)

The difference in isomer shift between the *cis* and *trans* forms must presumably reflect a difference in the distribution of electrons between the 5*s*- and 5*p*-orbitals of the tin atom (and possibly of the 5*d*-orbitals also; however, as these are probably of high energy and relatively diffuse, they will be ignored). The valence-shell electron density of the tin atom will

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be concentrated in the relatively non-polar Sn–C bonds, and the isomer shift trends can be rationalised on a simple molecular orbital argument. In the *trans*–R_2SnX_4 case, with ideal D_{4h} symmetry, the Sn–C bond orbitals transform as A_{1g} and A_{2u}. These molecular orbitals therefore involve the 5*s* (A_{1g}) and 5p_z (A_{2u}) orbitals of the tin atom. In the *cis* case (C_{2v} symmetry) the orbital representations are A_1 and B_2. The B_2 orbital again involves only a single tin orbital (5p_y), but the 5*s*- and 5p_z-orbitals have A_1 symmetry. It is therefore reasonable to suppose that there will be more 5*s*-character in the Sn–C bonds of the *trans* isomer than of the *cis* form. On this basis, other non-linear R_2SnX_n systems should also have isomer shifts lower than those of *trans*–R_2SnX_4, as found for $R_2SnX_3^-$ (X = Cl, Br; δ = 1.38-1.54 mm/s). (The change in coordination number has been shown above to have a negligeible effect on the isomer shift.)

Although there is no general relationship between molecular orbital treatments and hybridisation, it is interesting that the isomer shifts increase with increasing C–Sn–C bond angle, corresponding, on the hybridisation treatment, to increasing *s*-character. The *s*-character in a pair of equivalent hybrids at an angle θ is $\cos\theta/(1-\cos\theta)$.[24] In the only cases where X-ray data are available, *viz.* *cis*–$Me_2Sn(oxin)_2$ and the anion in $[Me_2SnCl(terpy)][Me_2SnCl_3]$, the bond angles are 111° and 140° respectively.[25,26] The series is thus:

	cis-R_2SnX_4	$R_2SnCl_3^-$	*trans*-R_2SnCl_4
C–Sn–C angle	90-111°	120-140°	180°
% *s*-character	0-25	33-42	50
δ (mm/s)	0.77-1.10	1.38-1.54	1.44-1,63

The change in isomer shifts between *cis* and *trans* systems is again parallelled by the n.m.r. coupling constants: 71.2 Hz for $Me_2Sn(oxin)_2$ and 82.5-106.0 Hz for a range of *trans*–Me_2Sn systems.[27]

For R_3Sn derivatives it has been noted that the isomer shifts for $[R_3SnX]_n$ and $R_3SnX_2^-$ (X = halogen) are often larger (by 0.1-0.2 mm/s) than those of R_4Sn or monomeric R_3SnY (Y = C_6F_5, etc.). This difference has been atributed to electron delocalisation (deshielding) effects associated with the change in hybridisation.[28] However, this result also follows the change in *s*-character, which is *ca.* 25% per Sn–C bond for the four-coordinate systems and 33% for the five-coordinate case. Indeed, there seems to be a rough correlation between the isomer shift and the total *s*-character of the Sn–C bonds, the latter being defined as the product of the number bonds with the *s*-character per bond. This correlation would only be expected to apply when the Sn–X bonds are very polar.

We do not, of course, mean to imply that the whole of the 5*s*-electron density is concentrated in the Sn–C bonds. If this were so, the isomer shifts would be independent of the nature of X, whereas small changes may be observed, *e.g.* from X = F to X = Cl. Also the observed changes in isomer shift indicate relatively small changes in *s*-electron density. Using the Lees-Flinn estimate,[5] the total range of isomer shifts discussed corresponds to a change in 5*s*-population of only about one-third of an electron in a total population of about 0.6 electrons. Nevertheless, the observed trends in isomer shift parallel those predicted on a hybridisation basis, and it is clear that, in mixed-ligand systems, a simple correlation between isomer shifts and the nature of the ligands cannot be made. It will probably not be possible, therefore, to set up a partial isomer shift scale, as has been done for iron complexes,[29] unless detailed account is taken of structural factors.

The largest isomer shifts in organotin systems (excluding the metal-metal bonded compounds, which are also thought to involve large *s*-characters[30]) are found in *trans*–R_2SnX_4 systems, and it is interesting to note that other phenomena are also connected with mutually *trans* pairs of soft ligands, *e.g.* the trans-effect and *trans*-influence and the strong coupling of nuclear spins. It is probable that these effects are transmitted *via* the *s*-orbitals of the metal atom in the same way as suggested here.

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