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The Far Infra-red Spectra and Bonding of some Five and Six Coordinate Complex Tin Ions

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Far infra-red spectra of several five- and six- coordinate organotin complex ions have been recorded in the tin-ligand stretching region, and stereochemistries assigned where possible. The trialkyltin moiety in a five-coordinate environment is universally trigonal planar. The methyl groups of the $Me_2SnX_3^-$, $X = Cl$, Br, anions occupy similar cis *equatorial positions. The organic residues in octahedral dialkyltin complexes are, with very few exceptions, mutually* trans. *As the coordination number at tin increases, the tin-carbon bonds have increasing s-character, and the dominance of the Fermi contact term of the nmr coupling constant is confirmed by the shortening of the tin-methyl bond as $^2J(^{119}Sn{-}C{-}^1H)$ increases.*

Introduction

The vibrational spectra of four-cordinate alkyltin halides, $R_{4-n}SnX_n$, and five- and six-coordinate complexes derived from them has aroused much interest.[1-7] In the present paper we report the far infra-red spectra of some five- and six-coordinate organohalogenotin complex anions. In addition, we have studied the corresponding infra-red spectra of eleven tin complex cations containing terpyridyl as a ligand.

Experimental Section

The anionic tin complexes were prepared by mixing the appropriate tin halide and tetraethyl(butyl)ammonium halide in the desired molar ratio in either ethanol or dichloromethane. Analytical figures for new complexes are given in Table I. We thank Dr. E. Rosenberg for the gift of the terpyridyl complexes.

Infra-red spectra were recorded as nujol mulls using Beckman IR11 and Perkin-Elmer 457 instruments. Nmr spectra were recorded using a Varian HA-100 spectrometer at 33.5°.

Results

The data for the five- and six-coordinate tin complexes is given in Table II.

Five-coordinate complexes of the type MX_3Y_2 may assume either of the two trigonal bipyramidal arrangements, A and B, of D_{3h} and C_{2v} symmetry respectively.**

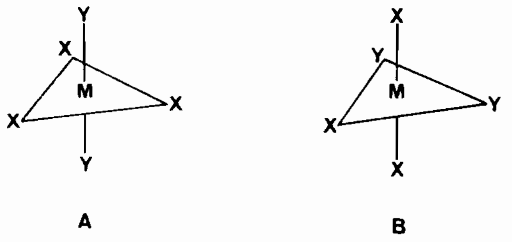

Figure 1. Possible geometries for MX_3Y_2.

Group theoretical predictions for the normal stretching modes for these configurations are summarized in Table III. Thus it is apparent that the anions $Me_3SnX_2^-$, $X = Cl$, Br, I, with only one tin-carbon and one tin-halogen stretching frequency, have the *trans* structure A. The fluoro anion, $Me_2SnF_3^-$, also has structure A, but with *trans* methyl groups.[5] The trichloro- and tribromodimethyltin anions, on the other hand, show both symmetric and antisymmetric tin-carbon and three tin-halogen stretching frequencies, and therefore possess the *cis* configuration B.

The spectrum of the diphenyltrichlorotin anion is worthy of comment. Previous investigators[3,6,8] have assigned bands at ca. 450 cm^{-1} and 260-200 cm^{-1} to ν(Sn–Ph) symmetric and antisymmetric. These bands are more properly[9,10] described as the y- and t-modes of Whiffen's notation[11] (Figure 2). The y-mode is largely a ring deformation (ocurring at 450vs in $Ph_2SnCl_3^-$), whereas the t-mode describes what is for the most part the Sn–Ph stretching vibration, for which two bands (219s and 228vs in $Ph_2SnCl_3^-$) are

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** A trigonal bipyramidal isomer of C_s symmetry is also possible which predicts the same number of infra-red active bands as the C_{2v} isomer [ν(M—X): 2A′ + A″; ν(M—Y): 2A′]. Although these may bb distinguished by observation of skeletal bending modes, this isomer is not included in the discussion for reasons which become apparent later. Square pyramidal geometries are also possible, but energetically less probable.

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Table I. Analytical Data on the New Complex Ions.

Complex	Found C	Found H	Found N	Required C	Required H	Required N
$Et_4N^+Me_3SnBr_2^-$	29.37	6.18	2.94	29.12	6.39	3.09
$Bu_4N^+Me_3SnI_2^-$	35.21	6.60	2.01	34.59	6.82	2.12
$2Et_4N^+Me_2SnBr_4^{2-}$	29.08	6.37	3.99	29.68	6.32	3.84
$2Bu_4N^+Me_2SnI_4^{2-}$	36.79	7.62	2.21	35.8	6.8	2.45[a]
$2Et_4N^+MeSnBr_5^{2-}$	25.98	5.79	2.99	25.73	5.42	3.54
$2Et_4N^+MeSnCl_3Br_2^{2-}$	31.12	6.58	3.94	30.93	6.52	4.24
$2Bu_4N^+MeSnCl_3I_2^{2-}$	40.94	7.80	2.83	40.52	7.67	2.86
$2Et_4N^+MeSnBr_3Cl_2^{2-}$	28.54	6.29	3.35	28.98	6.10	3.98
$2Bu_4N^+MeSnBr_3I_2^{2-}$	37.06	7.01	2.60	36.64	7.64	2.52
$2Et_4N^+MeSnCl_4I^{2-}$ [b]	30.45	5.57	4.09	31.35	5.10	4.29

[a] Found, I, 45.17%. Required, I, 44.51%. [b] From $MeSnI_3$ and $Et_4N^+Cl^-$ in dichloromethane.

Table II. Far Infrared Spectra of Five- and Six-coordinate Anions.

Anion	νSn—C	νSn—Cl	νSn—Br	νSn—I
$Me_3SnCl_2^-$ [a]	552vs	227s		
$Me_3SnBr_2^-$ [a]	555vs		140m	
$Me_3SnI_2^-$	553vs			134m
$Me_2SnF_3^-$ [a]	553w	592s [b]		
$Me_2SnCl_3^-$	573m 518m	313s, 256s sh, 242vs br		
$Me_2SnBr_3^-$ [c]	567m 512m		228s sh, 218s	
$Ph_2SnCl_3^-$	229vs 218s	332vs, 281s, 242vs		
$Me_2SnCl_4^{2-}$ [c,d]	580m	227s		
$Me_2SnBr_4^{2-}$	572m		220s	
$Me_2SnI_4^{2-}$	559m			186m
$MeSnCl_5^{2-}$	534m	318s, 258vs, 215m		
$BuSnCl_5^{2-}$	560m 539m	305s, 250vs, 235vs		
$MeSnCl_3Br_2^{2-}$	530m	312s, 294s, 267s	210m, 160s	
$MeSnCl_3I_2^{2-}$	530w	328s, 297vs, 267m sh		187m sh, 163s
$MeSnBr_5^{2-}$	524m		212m, 191m, 160s br	
$MeSnBr_3Cl_2^{2-}$	528m	306s, 248s	209m, 188s sh, 160s br	
$MeSnCl_4I^{2-}$	534m	307s, 261w		163s

[a] Data taken from ref. 5. [b] ν_{Sn-F}. [c] Data taken from ref. 2. [d] Ref. 22 reports the following infra-red data:

	ν_{Sn-C}	ν_{Sn-Cl}
$Et_4N^+\ Me_3SnCl_2^-$	534vs, 510vw sh	338mw
$Et_4N^+\ Me_3SnBr_2^-$	538vs, 507vw	
$(Me_4N^+)_2\ Et_2SnCl_4^-$	520s	346m

It is obvious from this data [cf. ref. 4:

	ν_{Sn-C}	ν_{Sn-Cl}
Me_3SnCl	542s, 513w	331vs
Me_3SnBr	539s, 511m	
Et_2SnCl_2	531, 497	359, 352sh]

that these samples contained considerable amounts of uncomplexed organotin halide.

Table III. Normal Stretching Modes for *cis* and *trans* MX_3Y_2. [a]

	symmetry point group	$\nu_{(M-X)}$	$\nu_{(M-Y)}$
cis-MX_3Y_2	C_{2v}	$2A_1+B_2$ (italic)	A_1+B_1 (italic)
trans-MX_3Y_2	D_{3h}	$A_1'+E'$	$A_1'+A_2'$

[a] Infra-red active species are italicised.

Table IV. Normal Stretching Modes for *cis* and *trans* MX_4Y_2. [a]

	symmetry point group	$\nu_{(M-X)}$	$\nu_{(M-Y)}$
cis-MX_4Y_2	C_{2v}	$2A_1+B_1+B_2$	A_1+B_1
trans-MX_4Y_2	D_{4h}	$A_{1g}+B_{1g}+E_u$	$A_{1g}+A_{2u}$

[a] Infra-red active species are italicised.

expected for an anion of C_{2v} symmetry. In a reassignment of the far infra-red spectrum of the anion $Ph_3SnCl_2^-$, the corresponding modes occur at 460, 450 cm^{-1} and 270 cm^{-1} respectively, a band at 190 cm^{-1} being assigned to the Sn—Cl_2 antisymmetric stretching mode (A_2'').[6]

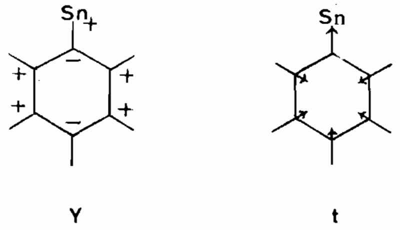

Figure 2. y- and t-modes of vibration of $C_6H_5Sn\leqslant$ (after Whiffen [11]).

Complexes of the type MX_4Y_2 may also have either the *cis* or *trans* configurations, and the group theoretical predictions for these are noted in Table IV. Exhibiting only one tin-carbon and one tin-halogen stretching mode, the dimethyltetrahalogenotin dianions, $Me_2SnX_4^{2-}$, X = Cl, Br, I, have, therefore, a structure in which the two methyl groups are mutually *trans*. Similar conclusions based on infra-red and Raman work have been reached by Hobbs and Tobias for the complexes $K_2[Me_2SnF_4]$, $Cs_2[Me_2SnCl_4]$, $Cs_2[Me_2SnBr_4]$ and $(Et_4N)_2[Me_2Sn(NCS)_4]$.[7] Good agreement between this data and that reported here was found, except that $\nu_{as}(Sn{-}Br_4)$ appears to be missing from the spectra of $Cs_2[Me_2SnBr_4]_2$.[7]

The methylpentahalogenotin dianions, as expected, have a single tin-carbon stretching frequency. The $BuSnCl_5^{2-}$ anion, however, has two tin-carbon stretching frequencies due to *trans-gauche* isomerism in the alkyl chain.[12] For an octahedral arrangement of one alkyl group and five halogens around the central tin atom, group theory predicts that three tin-halogen stretching frequencies ($2A_1 + E$) will be infra-red active. The three anions studied, $MeSnCl_5^{2-}$, $BuSnCl_5^{2-}$, exhibit three tin-halogen bands, indicating that the $SnCl_5$ framework of these anions does not differ significantly from square pyramidal. For the mixed methylpentahalogeno anions, the low symmetry of possible isomers does not allow predictions concerning stereochemistry, the same number of infra-red or Raman active bands being predicted for each isomer. The mixed anions studied, however, did exhibit the expected number of tin-ligand stretching vibrations.

The infra-red data for the anion $MeSnCl_4I^{2-}$ fit the low number of bands predicted by the C_{4v} symmetrical arrangement shown in Fig. 3. The bands at 307s and 261w cm^{-1} may be assigned to the expected tin chlorine vibrations of A_1 and E symmetry respectively.

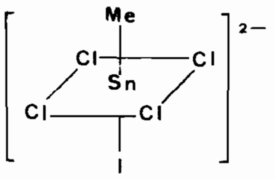

Figure 3. The proposed stereochemical configuration of the $MeSnCl_4I^{2-}$ anion.

The identical vibrations of the $MeSnCl_5^{2-}$ anion (also of C_{4v} symmetry) occur at 318s and 258vs. The difference in the intenstities of the E modes for the two complexes may be reconciled qualitatively on steric grounds. The A_1 symmetric breathing mode of the $Sn{-}Cl_4$ moiety (Fig. 4) would only be affected to a small degree by the replacement of a chlorine by an iodine in the axial position. The change in dipole moment for this vibration in the two vibration in the two vibrations is therefore similar, and both bands are of strong intensity. However, the presence of a large iodine atom might be expected to seriously reduce the amplitude of the E vibration, hence reducing the intensity of the corresponding band in the spectrum of the $MeSnCl_4I^{2-}$ anion.

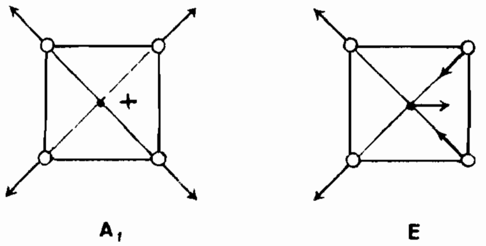

Figure 4. The A_1 and E modes of vibration of the $Sn{-}Cl_4$ moiety of $MeSnCl_5^{2-}$ and $MeSnCl_4I^{2-}$ anions.

The $Me_2SnX_2 \rightarrow$ *cis*-$Me_2SnX_3^- \rightarrow$ *trans*-$Me_2SnX_4^{2-}$ transformations have mechanistic implications. To obtain the *cis* configuration of II (Fig. 5) the anion X^- may approach along either of the routes A or B. *Trans*–$Me_2SnX_4^{2-}$ can only be formed, however, if the second X^- ion approaches the *cis*-$Me_2Sn_3^-$ *anion* along pathway C. This would seem reasonable in view of the large C–Sn–C bond angle (140°) of the *cis*–$Me_2SnCl_3^-$ anion.[13]

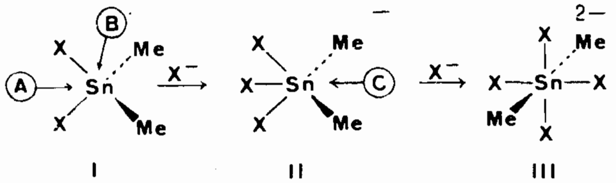

Figure 5. Mechanisms of the $Me_2SnX_2 \rightarrow$ *cis*-$Me_2SnX_3^- \rightarrow$ *trans*-$Me_2SnX_4^{2-}$ transformations.

Low frequency infra-red data for terpyridyl-containing tin complex ions are listed in Table V. The complex nature of the spectra, due to the large number of terpyridyl bands, makes assignments of stretching modes difficult. Extra bands in the tin-carbon stretching region of the methyltin cations are possibly due to there being more than one formula unit per unit cell, as been demonstrated for $[Me_2SnterCl]^+[Me_2SnCl_3]^-$.[13] The broad linewdith of the tin-carbon stretching frequency of the $[BuSnterCl]^+$ cation is most probably due to unresolved *trans-gauche* isomerism.

Discussion of the Results

It is apparent from an examination of the available data for five- and six-coordinate organotin complexes, the preferred geometries are, respectively, trigonal bipyramidal with *cis* (equatorial) organic moieties and octahedral with a *trans* arrangement of organic groups, seemingly independent of any charge carried by the complex.

Trialkyltin halides form neutral complexes with a variety of monodentate oxygen and nitrogen Lewis

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Table V. Low Frequency Infra-red Spectra of Terpyridyl Adducts of Organotin Halides.

Complex	νSn—C																			
$2[MeSnterCl_2]^+[MeSnCl_5^{2-}]$	578s br, 545s, 530s	508s		441s	412s	390w		322s	304vs sh	295vs	288vs sh	267s						165vs		
$[MeSnterCl_2]^+BPh_4^-$	557m, 539s	508s	478vw	445m sh	420w sh	390vw	355vw	311m			275w sh		268w	227w	202m					
$[BuSnterCl_2]^+BPh_4^-$	560m br	505s		442m	415w	386vw	385vw	301s			284m		265w	228vw	201m					
$[Me_2SnterCl]^+[Me_2SnCl_3]^-$	582m, 560s, 525m sh	509s		432m	411w		363vw	331s	312w	280vw	242s						182m	164s	152s	149s
$[Me_2SnterCl]^+I^-$	575s, 560s, 530m	511s		431m	411m		359vw	331m	312w	279w	242s			231w		193s	180s	161s br		
$[Me_2SnterBr]^+[Me_2SnBr_3]^-$	586m, 576m, 519m			438m	420w			310w	279w					232w	*205m*	*191s*	*173s*	*166s*		
$[Me_2SnterI]^+[Me_2SnI_3]^-$	589m, 562m, 526vw	511w		434m	415m			323w	274w						*203m*	*189m sh*		*183m*		
$2[SnterCl_3]^+[SnCl_6]^-$		510s			403w			*345m*	*331m sh*	*314s br*					206vw			165s		
$[Ph_2SnterCl]^+[Ph_2SnCl_3]^-$		510m	451vs	440s sh	417m		357vw	329s	*313m sh*	*285s*	246vs			225vs*	210s*					
$[Ph_2SnterCl]^+BPh_4^-$		505s		432m	415w			312vw		290w	*261m*		242m	234w*	228w*	205w				
$[Ph_2SnterCl]^+ClO_4^-$		511s	472s	431m	418w		360vw	318w		290m	*271m*			234m*	219*					

* Tin-carbon (aryl) stretching modes? Bands thought to be mainly associated with tin-halogen stretching modes are italicised.

bases, $R_3SnX \cdot L$,[1,14] and anionic complexes with halides, $Ph_3SnCl_2^-$.[3]

Similar cationic complexes containing the $[R_3Sn \cdot 2L]^+$ moiety are known where L = NH_3[15], DMSO, DMF, DMA or H_2O[16] All are thought to possess a planar trigonal arrangement of organic groups with mutually *trans* electronegative atoms.

From the far infra-red data, we propose a similar disposition of methyl groups and halogens in the $Me_3SnX_2^-$ anions, consistent with the previous stereochemical suggestions on the basis of the Mössbauer spectra of $R_3SnCl_2^-$ anions and solid (5–coordinate) triorganotin halides.[17,18]

The five cordinate anions, $R_2SnX_3^-$, R = Me, Ph; X = Cl, Br, are also considered to be trigonal bipyramidal with *cis* equatorial position. This has been confirmed by structural analysis for the $Me_2SnCl_3^-$ anion.[13] The dimethyltrifluorotin monoanion, $Me_2SnF_3^-$, on the other hand, possesses *trans* methyl groups.[5]

Octahedral cationic[13,19], neutral[2,4,19,20] and anionic[2] complexes containing two organic residues and four electronegative ligands possess a mutually *trans* geometry for the tin-carbon bonds, with few exceptions.

In this context, the magnitude of the ^{191m}Sn Mössbauer quadrupole splitting,, Q, is a useful parameter. Point charge calculations[17,21,22] for octahedral SnX_4Y_2 systems predict that the Q for the *trans* isomer will be twice that of the *cis* isomer. The ^{119m}Sn Mössbauer stereochemical predictions are summarised in Table VI. The *cis* nature of dimethyltin-8-hydroxyquinolate has been confirmed by an X-ray crystal structure analysis,[23] whilst (polymeric) dimethyltin difluoride consists of an infinite planar network of tin and bridging fluorine atoms with *trans* methyl groups above and below the plane.[26]

In contrast, for octahedral neutral[1,2,5,27,28] and anionic[29] complexes of tin in which all bonds are to electronegative, potentially π–bonding, atoms, it appears that *cis* stereochemistrv is preferred, except when steric restrictions are placed on the system.[27,30] This behaviour was explained by the ability of *cis* ligands to π–donate into different t_{2g} orbitals, and hence preferentially stabilise the *cis* complex.[29]

Table VI. Stereochemistry of Octahedral R_2SnX_4 species based on ^{119m}Sn Mössbauer Quadrupole Splittings.

cis	*trans*
$Ph_2Sn(NCS)_2 \cdot$ bipy [25]	$R_2Sn(NCS)_2 \cdot$ bipy [25]
$Ph_2Sn(NCS)_2 \cdot$ phen [25]	$R_2Sn(NCS)_2 \cdot$ phen [25]
$R_2Snoxin_2$ [21]	$R_2SnX_4^{2-}$ [21]
$Ph_2Snoxin_2$ [21]	$R_2SnX_2 \cdot$ bipy [21,24]
$Ph_2Snacac_2$[21]	$R_2SnX_2 \cdot$ phen [21,24]
$Ph_2Sn[S_2CNR_2']$ [22]	$Me_2Snacac_2$ [21]
	$R_2Sn[S_2CNR_2']_2$ [22]

R,R′ = alkyl; x = halogen; bipy = 2,2′-bipyridyl; phen = 1,10-phenanthroline; acac = acetylacetonate.

Examination of Table VI shows that *trans* geometry is preferred[13] except by (a) the dialkyltinbis(8-hydroxyquinolates) and (b) derivatives with a di*phenyl*tin moiety. The configuration of the latter may be rationalised if the phenyl group is classed as a potentially π–bonding ligand.[32,33]

Examination of the available structural and nuclear magnetic resonance data provides a rationalisation of the *cis vs. trans* possibilities for the alkyltin derivatives.

Given a fixed amount of tin 5s character to distribute among available bonds, an increase in coordination number, 4⟶5⟶6, should increase the tin-ligand bond length as the percentage d character increases and the s character per bond falls. This is exemplified by the series $SnCl_4$, $SnCl_5^-$, $SnCl_6^{2-}$, in which the tin-chlorine bond length increases in the order 2.30Å,[34] 2.37Å,[35] 2.39-2.45Å (depending on the cation).[20] Consistent with this the ^{119m}Sn Mössbauer isomer shift decreases as 5s electron density is withdrawn from the tin nucleus.[17] Listed in Table VII are the available structural data for alkyltin compounds.

As the cordination number at tin increases, contrary to expectation, there is a progressive decrease in the tin carbon bond length, accompanied by an increase in the tin chlorine bond length. This may be interpreted as a preferential redistribution of available tin 5s character in bonds to electropositive carbon at the

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Table VII.

Compound	Coordination Number at tin.	d(Sn—C) Å	d(Sn—Cl) Å
Me_3SnCl [a]	4	2.19	2.37
$Me_3SnMn(CO)_5$ [b]	4	2.13	
$Me_{10}Sn_4Ru_2(CO)_6$ [c]	4	2.14 ($SnMe_3$) 2.16 ($SnMe_2$)	
Me_2SnCl_2 [a*]	4		2.34
$Me_2Sn[Fe(CO)_2cp]_2$ [d]	4	2.19	
$Me_4Sn_3Fe_4(CO)_{16}$ [e]	4	2.22	
$MeSnCl_3$ [a]	4		2.32
$MeSnH_3$ [a]	4	2.14	
$(MeSnS_{3/2})_4$ [f]	4	2.1	
$IPh_2Sn—(CH_2)_4SnPh_2I$ [g]	4	2.14 (Sn—alkyl) 2.15 (Sn—aryl)	
$ClSn[Mn(CO)_5]_3$ [h]	4		2.43
$Cl_2Sn[\pi—cpFe(CO)_2]_2$ [i]	4		2.43
$(\pi-C_8H_{12})IrSnCl_3$	4		2.39
$Me_3SnCl \cdot py$ [k]	5	2.15	2.42
Me_3SnF [l]	5	2.10	
Me_3SnNCS [m]	5	2.13	
Me_3SnCN [n]	5	2.16	
$Me_2SnCl_3^-$ [o]	5	2.11	2.32, 2.54
$MeCl_2SnW(Cl)(CO)_3(MeSCH_2CH_2SMe)$ [p]	5	2.12	2.38, 2.39, 2.96
$MeCl_2SnMo(Cl)(CO)_3bipy$ [q]	5	2.12	2.36, 2.43, 2.80
tarns-Me_2SnF_2 [r]	6	2.08	
trans-$Me_2SnCl_2 \cdot 2DMSO$ [s]	6	2.06	2.51
trans-$Me_2SnCl_2 \cdot 2pyNO$ [t]	6	2.22	2.58
trans-$Me_2SnterCl^+$ [o]	6	2.07	2.65
trans-$Me_2Sn(NO_3)_2$ [u]	6	1.99	
cis-Me_2SnOx_2 [v]	6	2.16	

[a] Ref. 34. [b] R.F. Bryan, *J. Chem. Soc.* (A), 696 (1968). [c] S.F. Watkins, *ibid.*, 1552 (1969). [d] B.P. Bir'yukov, *et al., Chem. Commun.*, 159 (1968). [e] R.M. Sweet, C.J. Frichiet, Jr., and R.A. Schunn, *Inorg. Chem.*, 6, 749 (1967). [f] C. Dörfelt, A. Janeck, D. Kobelt, E.F. Paulus and H. Scherer, *J. Organometal. Chem.*, *14*, P22 (1968). [g] V. Cody and E.R. Corey, *ibid.*, *19*, 359 (1969). [h] J.H. Tsai, J.J. Flynn, and J.P. Boer, *Chem. Commun.*, 702 (1967). [i] J.E. O'Connor and E.R. Corey, *Inorg. Chem.*, 6, 968 (1967), [j] P. Porta, H.M. Powell, R.J. Mawby, and L.M. Venanzi, *J. Chem. Soc.* (A), 455 (1967). [k] R. Hulme, *ibid.*, 1524 (1963). [l] H.C. Clark, R.J. O'Brien, and J. Trotter, *ibid.*, 2332 (1964). [m] R.A. Forder and G.M. Sheldrick, *Chem. Commun.*, 1125 (1969). [n] *E.*O. Schlemper and D. Britton, *Inorg. Chem.*, 5, 507 (1966). [o] Ref. 13. [p] M. Elder and D. Hall, *Inorg. Cem.*, *8*, 1273 (1969). [q] *Idem, ibid.*, *8*, 1268 (1969). [r] *E.*O. Schlemper and W.C. Hamilton, *ibid.*, 5, 995 (1966). [s] Ref. 18. [t] E.A. Blom, B.R. Penfold, and W.T. Robinson, *J. Chem. Soc.* (A), 913 (1969). [u] J. Hilton, Ph.D. Thesis, Univ. of Nottingham, (1964). [v] Ref. 26.
* Gas phase parameters. A recent X-ray crystal structure analysis shows that the solid phase structure shows considerable distortion from tetrahedral to octahedral, because of intermolecular association. Solid phase parameters: d(Sn—C), 2.21Å; d(Sn—Cl), 2.40Å; d(Sn ... Cl), 3.54Å. (A.G. Davies, H.J. Milledge, D.C. Puxley and P.J. Smith, *J. Chem. Soc.* (A), 2862 (1970))

Table VIII. Nmr $^2J(^{119}Sn—C—^1H)$ Coupling Constants. (Hz).

Compound	Solvent	$^2J(^{119}Sn—C—^1H)$
Me_4Sn [a]		54.0
Me_3SnCl [b]	$CHCl_3$	58.5
Me_2SnCl_2 [b]	$CHCl_3$	70
$MeSnCl_3$ [b]	$CHCl_3$	98
$Me_3SnCl \cdot DMSO$ [c]	DMSO	69.2
$Me_3SnCl \cdot py$ [c]	py	67.0
$Me_3SnCl_2^-$ [d]	$CHCl_3$	70.5
$Me_2SnCl_3^-$ [d]	$CHCl_3$	88.9
$Me_2SnCl_2 \cdot 2DMSO$ [e]	DMSO	113
$Me_2SnCl_2 \cdot 2DMSO$ [e]	$CHCl_3$	86
$Me_2SnCl_2 \cdot 2pyNO$ [e]	CH_2Cl_2	93
Me_2SnOX_2 [f]	$CDCl_3$	71.2
$Me_2SnterCl^+$ [d]	$PhNO_2$	94.6
$Me_2SnCl_4^{2-}$ [d]	$CHCl_3$	90.5
$Me_2Sn(NO_3)_2$ [f]	H_2O	108.7
$MeSnCl_3$ [a]	D_2O	127.5

[a] J.R. Holmes and H.D. Kaesz, *J. Amer. Chem. Soc.*, *83*, 3903 (1961). [b] E.V. Vanden Berghe and G.P. Van der Kelen, *J. Organometal. Chem.*, 6, 515 (1966). [c] T.F. Bulles and R.S. Drago, *J. Amer. Chem. Soc.*, *88*, 5730 (1966) [d] This work. [e] V.G. Kumar Das and W. Kitching, *J. Organometal Chem.*, *13*, 523 (1968). [f] Ref. 19.

expense of the bonds to electronegative atoms, in accordance with the predictions of isovalent hybrization.[36]

The nmr $^2J(^{119}Sn—C—^1H)$ coupling constant is also a guide, via the Fermi contact mechanism, to the s electron distribution along the tin-carbon axes. From Table VII, it can be seen that the coupling constant parallels the tin-methyl bond length, lending credance to dominance of the Fermi contact term in this case. The tin-ligand bond lengths are parallelled in the vibrational spectra; the tin-carbon stretching frequency moving to higher frequencies, and very low tin-halogen frequencies being observed for the $Me_2SnX_4^{2-}$, $Me_3SnX_2^-$, and $Me_2SnX_3^-$ (axial) anions.

The $Me_2SnX_3^-$, X = Cl, Br, anions appear to be exceptional, having *cis* equatorial methyl groups. Tin-119m isomer shifts for these are almost identical to the values for the corresponding $Me_3SnX_2^-$ anions indicating no gross changes in the total s-electron density at the tin nucleus.[17] However, $^2J(^{119}Sn—C—^1H)$ values for the chlorides indicate a relative increase in the s-character of the tin-carbon bonds of $Me_2SnCl_3^-$, which is also apparent from the increased C—Sn—C bond angle.[13]

It is interesting to note that Me_2SnOx_2, the sole example of *cis*-methyl octahedral stereochemistry for which structural data are available, has a considerably

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(36) Bent H., *Chem. Rev.*, *61*, 275 (1961).

higher tin-carbon bond length and a lower $^2J(^{119}Sn-C-^1H)$ than the *trans* cases, demonstrating the inefficiency of distribution of s-electron density to *cis* tin-carbon bonds. The bis pyridine *N*–oxide complex of dimethyl dichloride is truly anomalous. Although it possesses *trans* geometry, the tin-carbon bond length for the similar dimethyl sulphoxide complex. This is very long, but $^2J(^{119}Sn-C-^1H)$ is higher than that behaviour may, in part at least, be due to non-bonding repulsions between tin and oxygen atoms, since the Sn . . . O distance is very short (3.01 Å).

It appears, therefore, that there is good evidence that, on increase in coordination number in organotin derivatives, there is a tendency for available tin 5s electron density to concentrate in bonds to carbon at the expense of bonds to more electronegative atoms. For octahedral dialkyltin derivatives, this is more efficiently accomplished by forming bonds to carbon which are predominantly sp in character, hence the observed *trans* geometry. Trigonal bipyramidal trialkyltin derivatives form bonds to carbon which have largely sp^2 hybrid character, hence *cis* equatorial geometry. In the $Me_2SnX_3^-$, X = Cl, Br, anions an equatorial $(sp)^2$ site is occupied by a chlorine atom.