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Mössbauer Spectroscopy of Mono-organotin(IV) Derivatives

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Summary

The Mössbauer parameters isomer shift, δ, and quadrupole splitting, ΔE, of mono-organotin compounds insofar investigated have been collected and tabulated. It is demonstrated that isomer shifts consistently depend on ligand electronegativities and coordination numbers, from which it is deduced that RSn^{IV} behave much more as Sn^{IV} rather than R_2Sn^{IV} and R_3Sn^{IV} derivatives. The changes of δ for RSn^{IV} are then interpreted by hypotheses analogous to those advanced for Sn^{IV} and its adducts and complexes. It is also inferred that in RSn^{IV} compounds there is a consistent s-character in all tin–ligand atom bonds. The rationalization of ΔE values is carried out for several series of RSn^{IV} derivatives by calculations according to the point-charge model and additive partial electric field gradients. It is observed that self-consistent partial quadrupole splitting values occur in tetrahedral compounds of Sn^{IV}, RSn^{IV}, R_2Sn^{IV} and R_3Sn^{IV}. The possibility of assigning true structures by comparison of calculated and experimental ΔE for octahedral RSn^{IV} derivatives, where structural isomers are predictable, is explored. The point-charge model is also employed in discussing the partial quadrupole splittings of a series of five-coordinate species, and in searching for a relationship between ΔE of five and seven-coordinate organotin(IV) compounds.

TABLE I. Mössbauer Parameters[a] (mm s^{-1}) of $RSnX_3$ Compounds, their Adducts and Complexes.

Code No.	Compound[b]	δ[c]	$\lvert\Delta E\rvert$[d]	Advanced or probable structure (idealized)	Ref.
1	$MeSnF_3$	0.76	3.24	Polymeric, octahedral	(8)
2	$MeSnCl_2F$	1.08	2.69	Polymeric, trigonal bipyramidal	(8)
3	$MeSnCl_3$	1.32;1.36	1.94;2.07	Polymeric, octahedral	(9)
4	$MeSnBr_3$	1.36–1.44	1.75–1.94	Polymeric, octahedral	(9, 10)
5	$EtSnCl_3$	1.64	1.77;1.97	Polymeric, octahedral?	(11, 12)
6	$EtSnBr_3$	–	1.85	Polymeric, octahedral?	(11)
7	$(CH_2{=}CH)SnCl_3$	–	1.86	Polymeric, octahedral?	(11)
8	$n\text{-}BuSnCl_3$	1.31–1.70	1.83–3.40	Polymeric, octahedral?	(13–16)
9	$n\text{-}BuSn(OH)_2Cl$	0.74	2.02	Polymeric, octahedral?	(17)
10	$n\text{-}BuSn(NCS)_3$	1.43	1.46	Polymeric, octahedral?	(18)
11	$n\text{-}BuSn(OMe)_3$	0.64	1.52	Tetrahedral?	(19)
12	$n\text{-}BuSn(OSiPh_3)_3$	0.82	1.39	Tetrahedral?	(17)
13	$PhSnCl_3$	1.10–1.47	1.75–1.84	Polymeric, octahedral?	(10, 11, 13, 16, 17, 20)
14	$PhSnBr_3$	–	1.62	Polymeric, octahedral?	(11)
15	$PhSn(NMe_2)_3$	1.06	0	Tetrahedral	(21)
16	$MeSnH_3$	1.24	0	Tetrahedral	(22)
17	$i\text{-}PrSnH_3$	1.43	0	Tetrahedral	(22)
18	$n\text{-}BuSnH_3$	1.44	0	Tetrahedral	(22)
19	$PhSnH_3$	1.40	0	Tetrahedral	(22)
20	$MeCl_2SnMn(CO)_5$	1.62–1.66	2.56–2.62	Tetrahedral	(23–25)
21	$MeBr_2SnMn(CO)_5$	1.69	2.51	Tetrahedral	(25)
22	$PhCl_2SnFe(CO)_2\pi\text{-}C_5H_5$	1.58;1.70	2.56;2.84	Tetrahedral	(23, 26)
23	$PhBr_2SnFe(CO)_2\pi\text{-}C_5H_5$	1.73	2.65	Tetrahedral	(27)
24	$Ph(OSOPh)_2SnMn(CO)_5$	1.60	3.06	Octahedral?	(26)

TABLE I. (Cont.)

Code No.	Compound[b]	δ[c]	$\lvert\Delta E\rvert$[d]	Advanced or probable structure (idealized)	Ref.
25	$\mathrm{PhCl_2SnMn(CO)_5}$	1.63–1.74	2.36–2.52	Tetrahedral	(25, 27, 28)
26	$\mathrm{PhBr_2SnMn(CO)_5}$	1.75–1.80	2.63–2.68	Tetrahedral	(25, 27, 28)
27	$\mathrm{PhI_2SnMn(CO)_5}$	1.80	2.19	Tetrahedral	(28)
28	$\mathrm{MeClSn(Co(CO)_4)_2}$	1.74	2.38	Tetrahedral	(29)
29	$\mathrm{PhClSn(Co(CO)_4)_2}$	1.70	1.88	Tetrahedral	(29)
30	$\mathrm{PhClSnCo(CO)_4Co(CO)_3Ph_3P}$	1.67	2.00	Tetrahedral	(29)
31	$\mathrm{PhSn(Fe(CO)_2\pi\text{-}C_5H_5)_3}$	2.00	0	Tetrahedral	(30)
32	$\mathrm{PhSn(Re(CO)_5)_3}$	1.75	0	Tetrahedral·	(31)
33	$\mathrm{PhSn(Co(CO)_4)_3}$	–	1.28	Tetrahedral	(32)
34	$\mathrm{MeSn(Mn(CO)_5)_3}$	1.83	0.95	Tetrahedral	(33)
35	$\mathrm{MeSn(Co(CO)_4)_3}$	1.79	1.29	Tetrahedral	(29)
36	$\mathrm{(AlkSnS_{1.5})_4}$[e]	1.38–1.42	1.37–1.49	Tetrahedral	(19)
37	$\mathrm{(PhSnS_{1.5})_4}$	1.34	1.17	Tetrahedral	(19)
38	$\mathrm{(n\text{-}BuCl_2Sn)_2S}$	1.36	2.07	Tetrahedral	(17)
39	$\mathrm{n\text{-}BuCl_2SnSSnCln\text{-}Bu_2}$ inner	1.30	2.30	Tetrahedral	(17, 34)
	outer	1.49	3.31	Tetrahedral?	
40	$\mathrm{(MeSn(O)OH)_n}$	0.40	1.29	Tetrahedral, polymeric	(19)
41	$\mathrm{(AlkSn(O)OH)_n}$[f]	0.65–0.76	1.52–1.80	Tetrahedral, polymeric	(11, 19, 35)
42	$\mathrm{(PhSn(O)OH)_n}$	0.78	1.83	Tetrahedral, polymeric	(19)
43	$\mathrm{(PhSn(OCOCMe_3)O)_n}$	0.59	2.00	Trigonal bipyramidal, polymeric	(36)
44	$\mathrm{(PhSn(OCOCCl_3)O)_n}$	0.72	2.33	Trigonal bipyramidal, polymeric	(36)
45	$\mathrm{(PhSn(OCOCF_3)O)_n}$	0.66	2.64	Trigonal bipyramidal, polymeric	(36)
46	$\mathrm{(n\text{-}BuSn(OCOMe)O)_n}$	0.70	2.26	Trigonal bipyramidal, polymeric	(17)
47	$\mathrm{(PhSn(OCO(CH_2)_8CH{=}CH_2)O)_n}$	0.57	2.31	Trigonal bipyramidal, polymeric ·	(35)
48	$\mathrm{(PhSn(OCO(CH_2)_{16}CH_3)O)_n}$	0.56	2.32	Trigonal bipyramidal, polymeric	(35)
49	$\mathrm{n\text{-}BuSn(OCOC(Me){=}CH_2)_3}$	1.40	4.25	?	(17)
50	$\mathrm{AlkSn(OCH_2CH_2)_3N}$[e]	0.70–1.20	1.64–2.00	Trigonal bipyramidal	(19, 37)
51	$\mathrm{PhSn(OCH_2CH_2)_3N}$	0.43; 0.94	1.18; 1.66	Trigonal bipyramidal	(19, 37)
52	RSnCl Trid[g]	0.82–1.06	1.89–2.24	Trigonal bipyramidal	(38)
53	$\mathrm{(Ph_4As)(EtSnCl_4)}$	1.18	1.82	Trigonal bipyramidal	(39)
54	$\mathrm{(Me_4N)_2(EtSnCl_5)}$	0.96; 1.10	1.93; 1.94	Octahedral	(40)
55	$\mathrm{(Et_4N)_2(n\text{-}BuSnCl_5)}$	1.07; 1.12	1.86	Octahedral	(13, 15)
56	$\mathrm{(PyH)_2(PhSnCl_5)}$	1.10	1.92	Octahedral	(2)
57	$\mathrm{(Et_4N)_2(n\text{-}BuSnCl_3Br_2)}$	1.20	1.85	I–III	(15)
58	$\mathrm{n\text{-}BuSnCl_3\cdot 2Ph_3PO}$	1.05; 1.10	2.32; 2.36	I–III	(15, 41)
59	$\mathrm{n\text{-}BuSnCl_3\cdot 2DMA}$	1.10	2.22	I–III	(15)
60	$\mathrm{n\text{-}BuSnCl_3\cdot 2Py}$	0.91	1.86	I–III	(15)
61	$\mathrm{n\text{-}BuSnCl_3\cdot 2DMSO}$	0.94	1.73	I–III	(15)
62	$\mathrm{n\text{-}BuSnCl_3\cdot 2PyO}$	1.02	2.00	I–III	(15)
63	$\mathrm{n\text{-}BuSnCl_3\cdot 2Ph_3AsO}$	0.90	1.81	I–III	(41)
64	$\mathrm{n\text{-}BuSnCl_3\cdot 2Ph_3P}$	1.23	1.73	II, III	(41)
65	$\mathrm{PhSnCl_3\cdot 2Ph_3PO}$	0.80	2.01	I–III	(41)
66	$\mathrm{PhSnCl_3\cdot 2Pip}$	0.87	1.70	I–III	(42)
67	$\mathrm{PhSnCl_3\cdot 2\beta Pic}$	0.91	1.40	I–III	(42)
68	$\mathrm{PhSnCl_3\cdot 2Isoquin}$	0.89	1.51	I–III	(42)
69	$\mathrm{PhSnCl_3\cdot 4Morph}$	0.53	1.54	I–V	(42)
70	$\mathrm{n\text{-}PrSnCl_3\cdot 2Pip}$	0.76	1.99	I–III	(42)
71	$\mathrm{n\text{-}PrSnCl_3\cdot 2\beta\text{-}Pic}$	0.88	1.87	I–III	(42)
72	$\mathrm{n\text{-}PrSnCl_3\cdot 2Isoquin}$	0.92	1.89	I–III	(42)
73	$\mathrm{n\text{-}PrSnCl_3\cdot 4Morph}$	0.75	1.75	I–V	(42)
74	$\mathrm{n\text{-}PrSnCl_3\cdot 4\gamma\text{-}Pic}$	0.92	1.82	I–V	(42)
75	$\mathrm{MeSnCl_3\cdot 2L}$[h]	0.80–1.21	1.68–2.50	I–III	(9)

TABLE I. (Cont.)

Code No.	Compound[b]	δ[c]	$\lvert\Delta E\rvert$[d]	Advanced or probable structure (idealized)	Ref.
76	$MeSnBr_3 \cdot 2L$[h]	0.93–1.39	1.74–2.48	I–III	(9)
77	$MeSnCl_3 \cdot H_2Acen$	0.91	2.25	I(polymeric)	(43)
78	$MeSnCl_3 \cdot H_2Salen$	0.86	1.97	I(polymeric)	(44)
79	$n\text{-}OctSnCl_3 \cdot H_2Salen$	0.95	1.84	I(polymeric)	(44)
80	$PhSnCl_3 \cdot H_2Salen$	0.81	1.68	I(polymeric)	(44)
81	$MeSnCl_3 \cdot NiSalen$	0.90	1.63	II,III	(45)
82	$PhSnCl_3 \cdot NiSalen$	0.86	1.38	II, III	(45)
83	$n\text{-}BuSnCl_3 \cdot Bipy$	0.87; 1.01	1.62; 1.65	II, III	(15, 16)
84	$PhSnCl_3 \cdot Bipy$	0.87	1.50	II, III	(16)
85	$n\text{-}BuSnCl_3 \cdot o\text{-}Phen$	0.91; 1.03	1.60; 1.67	II, III	(15, 16)
86	$PhSnCl_3 \cdot o\text{-}Phen$	0.87	1.48	II, III	(16)
87	$n\text{-}BuSn(NCS)_3 \cdot Bipy$	0.84	1.75	II, III	(16)
88	$PhSn(NCS)_3 \cdot Bipy$	0.58	1.55	II, III	(16)
89	$n\text{-}BuSn(NCS)_3 \cdot o\text{-}Phen$	0.77	1.80	II, III	(16)
90	$PhSn(NCS)_3 \cdot o\text{-}Phen$	0.57	1.56	II, III	(16)
91	$n\text{-}BuSnCl_3 \cdot 8AQ$	1.02	1.88	II, III	(16)
91a	$[n\text{-}BuSnCl_2Terpy]_2[n\text{-}BuSnCl_5]$	1.07	1.94	I, III	(13)
91b	$[n\text{-}BuSnCl_2Terpy]X$[i]	0.92; 1.09	1.74; 1.76	I, III	(13)
92	$n\text{-}BuSnClOx_2$	0.78–0.84	1.65–1.71	IV, V	(15, 16, 46)
93	$n\text{-}BuSn(NCS)Ox_2$	0.76	1.73	IV, V	(16)
94	$PhSnClOx_2$	0.66; 0.68	1.48	IV, V	(16, 46)
95	$PhSn(NCS)Ox_2$	0.58	1.57	IV, V	(16)
96	$MeSnCl\ Trop_2$	0.53	1.70	IV, V	(47)
97	$n\text{-}BuSnCl(2SPyO)_2$	1.09	1.72	IV, V	(16)
98	$PhSnCl(2SPyO)_2$	0.95	1.52	IV, V	(16)
99	$MeSnhal(SSCNAlk_2)_2$[l]	1.07–1.19	1.71–1.83	IV, V	(48, 49)
100	$n\text{-}BuSnhal(SSCNAlk_2)_2$[l]	1.19–1.33	1.66–1.80	IV, V	(48, 49)
101	$PhSnhal(SSCNAlk_2)_2$[l]	1.06–1.15	1.56–1.70	IV, V	(48, 49)
102	$MeSn(NCS)(SSCNMe_2)_2$	0.99	1.87	IV, V	(48)
103	$PhSn(NCS)(SSCNMe_2)_2$	0.94	1.64	IV, V	(48)
104	$MeSn(SSCNAlk_2)_3$[l]	1.16; 1.19	1.95; 1.97	Pentagonal bipyramidal	(48)
105	$n\text{-}BuSn(SSCNAlk_2)_3$[l]	1.26; 1,28	1.90; 1.94	Pentagonal bipyramidal	(48)
106	$PhSn(SSCNAlk_2)_3$[l]	1.12; 1.16	1.81; 1.84	Pentagonal bipyramidal	(48)
107	$n\text{-}BuSnOx_3$	0.68; 0.69	1.70; 1.82	Pentagonal bipyramidal	(15, 46)
108	$MeSnTrop_3CH_3OH$	0.57	2.00	Pentagonal bipyramidal	(47)
109	$n\text{-}BuSnTrop_3$	0.66	2.11	Pentagonal bipyramidal	(47)
110	$PhSnTrop_3$	0.49	1.91	Pentagonal bipyramidal	(47)
111	$PhSnClDB$	0.56	2.12	IV, V	(50)
112	$(n\text{-}BuSn(OCOCH_2SH)(OCOCH_2S))_n$	1.31	2.67	6-coord.	(51)
113	$MeSn(SC_{12}H_{25})_3$	1.47	1.16	Tetrahedral	(66)
114	$AlkSn(SCH_2COOR)_3$[m]	1.43–1.61	1.45–1.74	5-coord.	(66)
115	$MeSn(SCH_2COOC_8H_{17})Cl_2$	1.23	2.31	5-coord.	(66)
116	$MeSn(SCH_2COOC_8H_{17})_2Cl$	1.28	2.32	5-coord.	(66)
117	$AlkSn(SCH_2COOR)_3$[m]	1.33–1.42	2.34–2.35	6-coord.	(66)

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[a] Mainly at liquid N_2 temperature. When in the literature appear two values of a parameter for a given compound they are reported in the table separated by(;), while in the cases of more than two data the extreme values are reported separated by(–). [b] Symbols: H_2trid: 4-(2-benzothiazolinyl)2-pentanone, H_2AAT; 2-(*o*-hydroxyphenyl)benzothiazoline, H_2SAT; 3-(*o*-hydroxyphenylamino)crotonophenone, H_2BAH; N-(2-hydroxyphenyl)salicylaldimine, H_2SAH;DMA,N,N-dimethylacetamide; DMSO, dimethylsulfoxide; Py, pyridine; PyO, pyridine N-oxide; Pip, piperidine; β-Pic, β-picoline; γ-Pic, γ-picoline; Isoquin, Isoquinoline; Morph, morpholine; H_2Acen, N,N′ethylenebis(acetylacetoneimine); H_2Salen, N,N′ethylenebis(salicylideneimine); NiSalen, N,N′ethylenebis(salicylideneiminato)Ni^{II}; Bipy, α,α'bipyridyl; *o*-Phen, *o*-phenanthroline; 8AQ, 8-aminoquinoline; Terpy, terpyridine; Ox, 8-hydroxyquinoline; Trop, tropolonato; 2SPyO, 2-pyridinethiol 1-oxide; DB=diacetylbis(benzoylhydrazone). [c] Isomer shift, with respect to $BaSnO_3$ or SnO_2. [d] Quadrupole splitting. [e] Alk = Me, Et, n-Bu, n-Oct. [f] Alk = Et, n-Bu, n-Oct. [g] R = Me, n-Oct, Ph; [h] Adducts presumably present in frozen solutions, the donor solvent, L being: diethylether, dimetoxyethane, tetrahydrofurane, dioxane, acetone, dimethylformamide, dimethylsulfoxide, tetramethylethylenediamine, hexamethylphosphoric triamide, pyridine. [i] $X = BPh_4^-, ClO_4^-$. [l] Alk = Me, Et; hal = Cl, Br, I. [m] Alk = Me, n-Bu; R = CH_3, C_8H_{17}, $CH_2C_6H_5$.

1. Introduction

The present review deals with Mössbauer spectroscopic studies on mono-organotin(IV) salts and related adducts and complexes, where the tin(IV) atom exhibits coordination numbers four to seven. The Mössbauer parameters isomer shift, δ^1, and quadrupole splitting, ΔE^1, of the derivatives so far investigated are collected in Table I. The rationalization of δ values in terms of the nature of the coordinated basic atoms, of the coordination number and of the structure is attempted, and it is observed that the first two factors essentially determine the order of δ magnitudes. The relationships between ΔE of RSn^{IV} derivatives and those of corresponding R_3Sn^{IV}, R_2Sn^{IV} and Sn^{IV} compounds, inferred from calculations according to the point-charge model formalism[2–6], are reviewed, and new calculated data are reported.

Excellent reviews appeared on Mössbauer spectroscopy of tin(IV) and organotin(IV) compounds (see for example Ref. 3, 6, 7), but parameters of mono-organotin(IV) were not specifically discussed before.

2. Discussion

A. Isomer Shift

The parameter isomer shift is expressed by Equation (1):

$$\delta = \frac{4\pi}{5} Ze^2 R^2 \left(\frac{\Delta R}{R}\right) \left(|\psi_o|_a^2 - |\psi_o|_s^2\right) \qquad (1)$$

where Z is the atomic number, e the electronic charge, R the charge radius of the nucleus, ΔR the difference of nuclear radii in the excited and ground states, and $|\psi_o|^2$ are s-electron densities at the absorber and source nuclei[1]; R_{ex} being larger than R_g for ^{119m}Sn, increases of δ reflect increasing s-electron densities.[1,3,6]

The isomer shift values of Table I are visualized in Figure 1, plotted *vs.* the average Pauling electronegativity of the bound atoms (other than C). It must be borne in mind that this correlation is merely indicative of general trends, since valence state electronegativities of the coordinated atoms had to be calculated and used in order to get a correct relationship with δ^{52}; on the other hand, the best correlation would be perhaps that between δ and the charge on the Mössbauer nucleus, as obtained from electron binding energies (by ESCA spectra).[53]

The data of Figure 1 suggest the following observations:

a) The δ values show a rough dependence from the electronegativity of the atoms bonded to tin(IV), there being an approximate tendency to the increase of δ with the diminution of the average electronegativity.

b) In general, but with many exceptions, it seems that the increase of the coordination number causes a decrease of δ. For a given χ value, in fact, δ usually decreases from four to seven coordinated Sn^{IV}.

c) Values of δ for Ph derivatives are often (but not always) lesser than those of corresponding Alk compounds, as it would be expected in terms of the respective inductive effects of the organic radicals.

It clearly appears that the behaviour of RSn^{IV} derivatives essentially corresponds to that of $Snhal_4$ and their adducts and complexes, consistently differing from R_2Sn^{IV} and R_3Sn^{IV} compounds.[3,6] For the latter, in fact, δ are in general practically independent from coordination number and basicity of the ligands, which was interpreted in terms of re-hybridization increasing the s-character of Sn–C bonds, and of deshielding and contraction of 5s tin(IV) orbitals.[3,6] The trends reported in a) and b) may be instead interpreted by the same arguments advanced for $Snhal_4$ and $Snhal_2 \cdot 2L^{3,6}$; in particular, the decrease of δ upon increasing coordination number may be explained by the increasing polarity of Sn–hal bonds as well as by the higher degree of deshielding of 5s electrons due to the electronic charge donated to 5d Sn orbitals.[3,6] These interpretations have been expecially given in the case of $RSnhal_3$ and related adducts studied in frozen solutions.[9] On the other hand, it was demonstrated that the neat solids $RSnhal_3$ are polymeric compounds containing six-coordinated tin(IV),[54] and the fact that their δ values are constantly the highest for a given χ_{av} (Figure 1) cannot be easily interpreted in this context. One would be inclined to assume that bridging halides increase consistently their electronegativity, thus causing a more efficient deshielding of 5s electrons on the hypothesis that the hal–Sn bonds involve a considerable amount of d-orbital character, but this is contrasted by the fact that other RSn^{IV} polymeric species (with bridging oxygen, Table I and Figure 1) behave in a regular way, and that the rough dependence of δ from χ_{av} (Figure 1) strongly suggests a noticeable percentage of s-character in all RSn^{IV}–ligand atom bonds.

The latter is indeed the most interesting deduction we may extract from the discussed trend of RSn^{IV} δ values, which renders the bonding situation in mono-organotin(IV) derivatives essentially different from that in R_2Sn^{IV} and R_3Sn^{IV} compounds, where it is very likely that s-character is essentially concentrated in Sn–C bonds, and Sn–ligand atom links are mainly made up by p and d Sn orbitals.[3]

The changes of δ within individual series of R_nSn^{IV} compounds with a given ligand and its analogous have been extensively discussed in the original papers (see Ref. of Table I), to whom the reader is addressed. In particular, the isomer shifts of compounds with tin–metal bonds have been interpreted in terms of the s-character of this bond[6,27–29]; a similar hypothesis has been also advanced in explaining the changes of δ

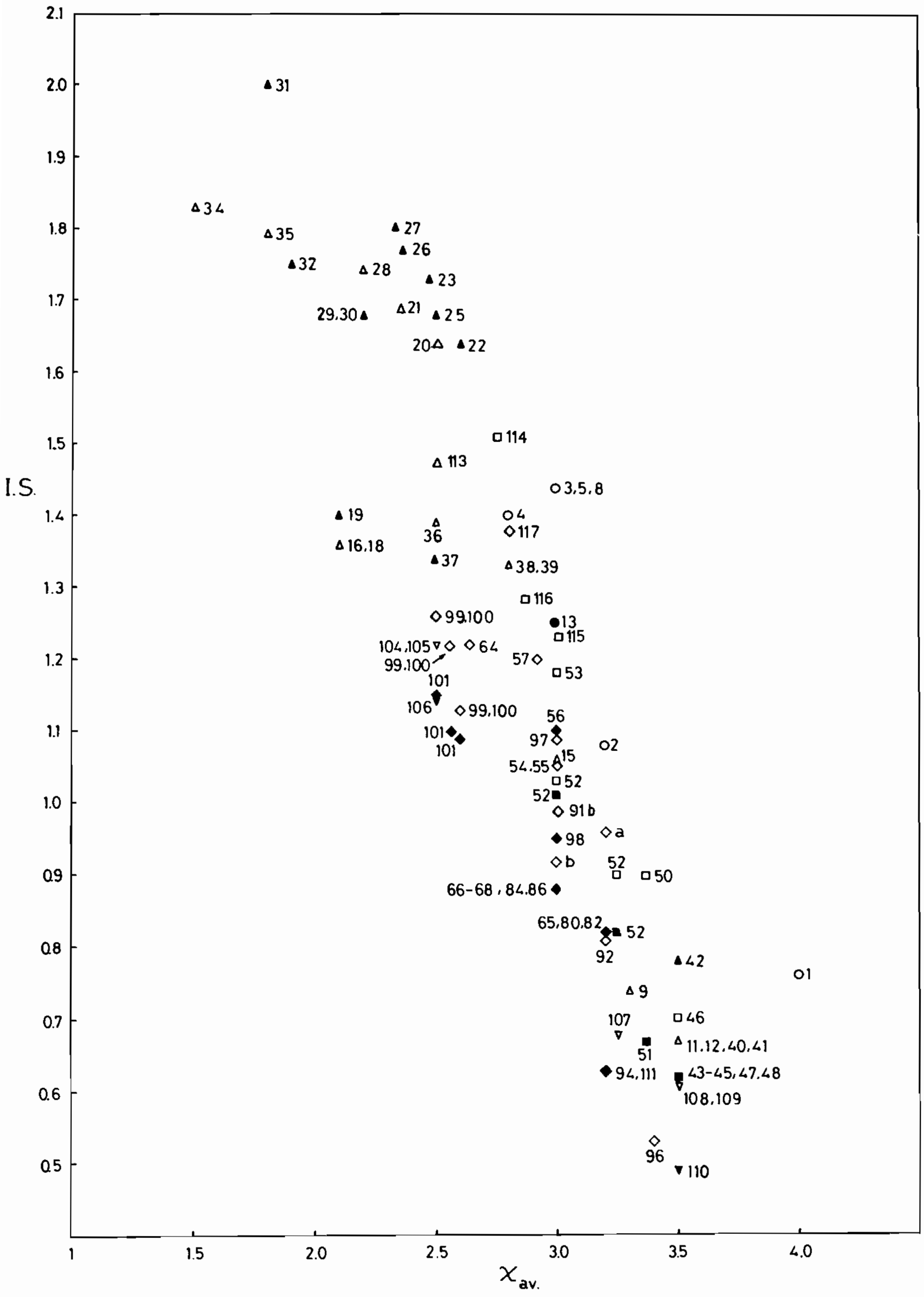

Figure 1. Isomer shifts *vs.* average Pauling electronegativities of ligand atoms (other than C). Code Nos. as in Table I. a: Nos. 58, 61–63, 77–79, 81. b: Nos. 60, 70–72, 83, 85, 91. Different points with equal code Nos. refer to complexes with partly different donor atoms (*e.g.*, halide). Symbols are as follows (open, R = Alk; full, R = Ph): R Snhal$_3$: ○. Compounds with: 4-coordinate Sn^{IV}: △; 5-coord. Sn^{IV}: □; 6-coord. Sn^{IV}: ◇; 7-coord. Sn^{IV}: ▽.

from six to seven coordinated Sn^{IV} in the series of tropolone, oxine and diorgano-dithiocarbamate derivatives[47,48], although interpretations based on the relative electronegativities of the bound atoms as well as on deshielding effects have been proposed by other authors for the oxine series.[15,46]

B. Quadrupole Splitting

The interaction of the nuclear quadrupole moment with the electric field gradient at the nucleus itself is given by the Equation[1]:

$$|\Delta E| = 1/2\, e^2 |QV_{zz}| \left(1 + \frac{\eta^2}{3}\right)^{1/2} \qquad (2)$$

where Q is the nuclear quadrupole moment, V_{zz} the principal component of the electric field gradient tensor and $\eta = \frac{V_{xx}-V_{yy}}{V_{zz}}$ the asymmetry parameter.[1,5] Predictions of ΔE as function of coordination number, structure and nature of the ligands may be effected by the point charge model (which corresponds to the crystal field approach of representing the basic ligand atoms as point charges arranged around the central ion according to the stereochemistry of the complex) and the approximation of treating the total electric field gradient (e.f.g.) as made up of additive independent contributions by each donating charge (partial electric field gradients).[2–6,11,39] For a given structure, the components of the e.f.g., $V_{\alpha\alpha}$, are calculated as angular functions with respect to a system of coordinate axes, and the tensor is diagonalized as to get vanishing off-diagonal components.[5,6] The expressions for V_{xx}, V_{yy} and V_{zz} are then inserted in Eq. (2), obtaining the corresponding ΔE equation, which is used either for determining the partial e.f.g. due to the particular ligand atom K in that geometry (in partial quadrupole splitting, p.q.s., units, *i.e., 1/2 e^2Q* [K] mm s^{-1}; this is extracted employing in Eq. (2) the experimental ΔE, with its correct sign, of the estimator compound(s)) and for calculating predicted ΔE (by inserting the appropriate 1/2 e^2Q [K] values in the particular ΔE equation); these procedures and implications were widely discussed elsewhere, and $V_{\alpha\alpha}$ and ΔE equations were reported.[2–6,11,23,27,29,39,40,44,50,55–59]

It is evident that the main interest of a chemist, when dealing with the ΔE of a particular compound, is immediately focussed on predicting its configuration. This was effected for very many tetrahedral Sn^{IV} derivatives, including compounds with tin-metal bonds (Y_nSnM_{4-n}, M being the coordinated metal atom and Y halide ions and organic radicals); in the latter series it has been demonstrated that 1/2 e^2Q [K] terms are internally consistent, *i.e., they apply equally well to Sn^{IV}, RSn^{IV}, R_2Sn^{IV} and R_3Sn^{IV} compounds* (which is consistent with the observation that p.q.s. values are peculiar for a given ligand in a given geometry[4]), so that calculated ΔE for RSn^{IV} containing species fit reasonably well to experimental values.[6,23,26,27,29,60] Deviations from predicted values were attributed to distortions of the actual configuration, whose nature was inferred also by determined, and estimated, signs of ΔE and values of η.[4,6,23,24,26–29,60]

Mono-organotin(IV) halides and pseudohalides form a series of (ideally) octahedral compounds, *i.e.*, adducts $RSnX_3 \cdot 2L$ and $RSnX_3 \cdot L_2$, as well as complexes $RSnX_5^{2-}$ and $RSnX \cdot (L_2)_2$; besides, there are examples of $RSnX_2 \cdot L_3$ and $RSnX \cdot L_4$ species (Table I; L_n are mono- and multidentate ligands). The p.q.s. values $1/2\, e^2|Q|([Alk]–[Cl])$ and $1/2\, e^2|Q|([Ph]–[Cl])$ coincide in the anions $RSnCl_5^{2-}$ and in octahedral R_2Sn^{IV} compounds[4], which could suggest the suitability of p.q.s. extracted from R_2Sn^{IV} compounds in calculating ΔE for RSn^{IV} derivatives in corresponding configurations. The latter, on the other hand, may in principle appear as structural isomers, according to the idealized configurations I–V (see Table I for attributions). It is then interesting in these cases to check if the point-charge formalism and the additive e.f.g. approximation give the right answer to the structural questions. The related calculations of ΔE have been effected for compounds 58, 60, 61, 63, 65–67, 70, 71, $RSnX_3 \cdot 2L$ type; 83–90, $RSnX_3 \cdot L_2$; and 97, 98, $RSnX (L_2)_2$ (Code Nos. refer to Table I), employing p.q.s. obtained from corresponding complexes of R_2Sn^{IV} (Ref. 6, Tables 27 and 24, and Discussion in the text; Tables II and III, this work). We completed the available data by calculating further ligand p.q.s.'s (Table II), subsequently used to get the estimated ΔE values reported in Table III.

Before discussing the calculated ΔE data for RSn^{IV} compounds, it is opportune to take into account some implications of the ΔE equations pertaining to the individual structures I to V,[6,44,56–59] Y = hal, in order to facilitate the interpretation of data in the Tables II and III, this work, and 26–27, Ref. 6. The results are governed by the p.q.s. values of ligands other than C. In fact, for $1/2\, e^2 Q([L]–[hal]) = 0$, for each structure it comes $\Delta E = 2([R]–[Cl])$, *i.e.*, +2.06 for alkyl and +1.90 for phenyl derivatives respectively. In the cases where $1/2\, e^2 Q([L]–[hal]) <\sim \pm 0.1$, calculated ΔE for I and II essentially coincide, since the ΔE equation for I, *mer*-hal_3 and *trans*-L_2, tends to that for II, *fac*-hal_3 and *cis*-L_2 ($\Delta E = 2([R]–[hal])–2([L]–[hal])$); it is then expected to possibly discriminate between I and II only for p.q.s. of L sensibly different from that of hal. Calculations of ΔE for structures III give in any case values differing from those for I and II; in particular, for small ([L]–[hal]), $\Delta E_{III} > \Delta E_{I,II}$ when $1/2\, e^2 Q([L]–[hal])$ is positive, and $\Delta E_{III} < \Delta E_{I,II}$ in the opposite case. The equations for the structures IV and V are expected to yield in any context sufficiently differing values.

In our opinion, the discussion of the calculated ΔE values in Tables III, this work, and 27, Ref. 6, may

TABLE II. Partial Quadrupole Splitting Parameters[a] for Ligands Coordinated to Sn^{IV} in Octahedral Structures.

Code No.	Estimator(s)	ΔE_{exp}[b]	Ref.	Structure	Ligand	p.q.s.[c]
1	$n\text{-}Pr_2SnCl_2 \cdot 2L$[d]	(+)4.07[e]	(42)	VI, VII	d	+0.02(5)
2	$Ph_2SnCl_2 \cdot 2Isoquin$	(+)3.70	(42)	VI, VII	Isoquin	+0.05(5)
3	$n\text{-}Bu_2SnCl_2 \cdot 2Ph_3PO$	(+)4.11	(41)	VI, VII	Ph_3PO	+0.01
4	$n\text{-}Bu_2SnCl_2 \cdot 2Ph_3AsO$	(+)4.04	(41)	VI, VII	Ph_3AsO	+0.04
5	$R_2Snhal_2 \cdot H_2Acen$	(+)4.35[e] (+)3.62[f]	(43)	VI	H_2Acen	−0.05
6	$Alk_2SnCl_2 \cdot H_2Salen$	(+)4.27[e]	(44)	VI	H_2Salen	−0.07
7	$Ph_2SnCl_2 \cdot H_2Salen$	(+)3.89	(44)	VI	H_2Salen	−0.04
8	$Me_2SnCl_2 \cdot NiSalen$	(+)4.06	(45)	VII	NiSalen/2	+0.05
9	$Ph_2SnCl_2 \cdot NiSalen$	(+)3.76	(45)	VII	NiSalen/2	+0.05
10	$[Me_2SnClTerpy]X$	(+)3.54	(13)	X	Terpy/3	+0.19
11	$[Ph_2SnClTerpy]X$	(+)3.12	(13)	X	Terpy/3	+0.23
12	Alk_2SnOx_2	(−)2.00[e]	(17)	VIII	Ox/2	+0.03
13	Ph_2SnOx_2	(−)1.64[e]	(17)	VIII	Ox/2	+0.13
14	$n\text{-}Bu_2Sn(2SPyO)_2$	(+)3.20	(61)	IX	2SPyO/2	+0.23
15	$Ph_2Sn(2SPyO)_2$	(−)1.45	(61)	VIII	2SPyO/2	+0.22(5)
16	$n\text{-}Bu_2SnTrop_2$	(+)3.68	(47)	IX	Trop/2	+0.11
17	$Ph_2SnTrop_2$	(−)1.88	(47)	VIII	Trop/2	+0.01
18	Ph_2SnDB	(+)3.40	(50)	IX	DB/4	+0.10

[a] 1/2 $e^2Q([K]-[hal])$, mm s^{-1}; calculations were effected by point-charge equations from Refs. 6, 44, 56, 57–59, using the p.q.s. ([Alk]–[hal]) = +1.03, ([Ph]–[hal]) = +0.95[4] mm s^{-1}. Symbols as in footnote of Table I. Other p.q.s. from Ref.(4): Py, +0.10; PyO, +0.08; DMSO, −0.01; Bipy/2, +0.08; *o*-Phen/2, +0.04. [b] Signs are attributed according to point-charge model[2–6, 11, 39] predictions, as well as to literature data[40, 42, 55] for compounds listed in the Table and compounds having related configurations. Negative signs (No. 12, 13, 15, 17) are point-charge predictions for *cis*-R_2 regular octahedral species, irrespective of changes of sign due to distortions[40]. [c] Weighed averages: No. 1 and 2, +0.028(5); No. 6 and 7, −0.06; No. 10 and 11, +0.21; No. 12 and 13, +0.05; No. 16 and 17, +0.06. [d] L = Pip, β-Pic, γ-Pic, Isoquin. [e] Average values. [f] R = Ph.

be effected following two different approaches: a) consider the comparison between experimental and calculated ΔE of RSn^{IV} compounds as a test of the internal consistency of ΔE in R_2Sn^{IV} and RSn^{IV} derivatives, or b) assume that a particular p.q.s. concerning a given ligand in an octahedral structure holds for any n in R_nSn^{IV},[4] so that structures are attributed in view of the best accordance between experimental and calculated ΔE.

According to approach a), since ligands in adducts $RSnY_3 \cdot 2L$ and $RSnY_3 \cdot L_2$ of Tables III, this work, and 27 of Ref. 6, show p.q.s. particularly similar to those of halides (Tables II, this work, and 26, Ref. 6), calculated ΔE had to be mutually similar for each possible structure (I–III); besides, an acceptable agreement with experimental data (within 0.4 mm s^{-1}[4]) would show the internal consistency of p.q.s. and ΔE values in R_2Sn^{IV} and RSn^{IV} complexes of the same ligands, no choice being feasible between the possible structural isomers. This is generally the case for the adducts $RSnY_3 \cdot 2L$, L being a monodentate ligand, and complexes Nos. 92–96 (see Table III, and Table 27 of Ref. 6). It is instead observed that all adducts $RSnY_3 \cdot L_2$ (L_2 being a bidentate neutral ligand; No 81–90, Table I) have experimental ΔE always sensibly lower than the calculated values, the difference being sometimes larger than the maximum accepted[4] for structure III, and also for II in the case of compound 82. This would suggest that the internal consistency of p.q.s. and ΔE fails for these octahedral $RSnY_3 \cdot L_2$ and $R_2SnY_2 \cdot L_2$ adducts, the contribution of L_2, Y and R to the e.f.g. being lesser in RSn^{IV} with respect to R_2Sn^{IV}. It is difficult to assess the reason for this behaviour in the present context, although hypotheses based on larger distortions of $RSnY_3 \cdot L_2$ species with respect to $R_2SnY_2 \cdot L_2$ could be advanced.

The reliability of approach a), which we favour, is demonstrated by some inconsistencies encountered by application of the criterion b). While it is not possible to assign any structure with reasonable certainty for adducts with monodentate ligands listed within Nos. 58–80 of Table I, one would be inclined to assume structure II for the adducts $RSnY_3 \cdot L_2$, Nos. 81–90, on the basis of the closer similarity between calculated and experimental ΔE; this contrasts with dipole moment data for α,α'bipyridyl and *o*-phenanthroline adducts, Nos. 83–90, for which the *mer*-Y_3 structure III is strongly suggested.[16] Besides, the *cis*-PhCl structure V had to be assumed for PhClSnDB, No. 101, where the tetradentate ligand would adopt an unsound non-planar configuration. The best illustration of the

TABLE III. Point-Charge Calculations of Quadrupole Splittings[a] for RSn^{IV} Octahedral Species.

Code No.[b]	Compounds	ΔE_{exp}	Structure	ΔE_{calcd}	Code No.[b]	Compounds	ΔE_{exp}	Structure	ΔE_{calcd}
62[c]	$n\text{-}BuSnCl_3 \cdot 2PyO$	2.00	I	+1.92	91b	$[n\text{-}BuSnClTerpy]X$	1.75	I[d]	+2.09
			II	+1.90				II[d]	+1.47
			III	+2.14					
70–72	$n\text{-}PrSnCl_3 \cdot 2L$	1.91[c]	I	+2.00	92	$n\text{-}BuSnClOx_2$	1.65–1.71	IV	+1.86
			II	+2.00				V	+2.00
			III	+2.08					
66–68	$PhSnCl_3 \cdot 2L$	1.54[c]	I	+1.84	93	$n\text{-}BuSn(NCS)Ox_2$	1.73	IV	+1.72
			II	+1.84				V	+2.08
			III	+1.92					
77	$MeSnCl_3 \cdot H_2Acen$	2.25	I	+2.16	94	$PhSnClOx_2$	1.48	IV	+1.70
			II	+2.16				V	+1.84
			III	+2.10					
78–79	$AlkSnCl_3 \cdot H_2Salen$	1.90[c]	I	+2.18	95	$PhSn(NCS)Ox_2$	1.57	IV	+1.56
			II	+2.18				V	+1.92
			III	+2.00					
80	$PhSnCl_3 \cdot H_2Salen$	1.68	I	+2.02	96	$MeSnClTrop_2$	1.70	IV	+1.82
			II	+2.02				V	+2.00
			III	+1.84					
81	$MeSnCl_3 \cdot NiSalen$	1.63	II	+2.01	89	$n\text{-}BuSn(NCS)_3 \cdot o\text{-}Phen$	1.80	II	+1.98[e]
			III	+2.08				III	+2.32
82	$PhSnCl_3 \cdot NiSalen$	1.38	II	+1.85	90	$PhSn(NCS)_3 \cdot o\text{-}Phen$	1.56	II	+1.82[e]
			III	+1.92				III	+2.16
60	$n\text{-}BuSnCl_3 \cdot 2Py$	1.86	I	+1.89[e]	83	$n\text{-}BuSnCl_3 \cdot Bipy$	1.63[c]	II	+1.90[e]
			II	+1.86				III	+2.14
			III	+2.16					
61	$n\text{-}BuSnCl_3 \cdot 2DMSO$	1.73	I	+2.08[e]	84	$PhSnCl_3 \cdot Bipy$	1.50	II	+1.74[e]
			II	+2.08				III	+1.98
			III	+2.05					
58	$n\text{-}BuSnCl_3 \cdot 2Ph_3PO$	2.34[c]	I	+2.04[e]	85	$n\text{-}BuSnCl_3 \cdot o\text{-}Phen$	1.64	II	+1.98[e]
			II	+2.04				III	+2.10
			III	+2.07					
63	$n\text{-}BuSnCl_3 \cdot 2Ph_3AsO$	1.81	I	+1.98[e]	86	$PhSnCl_3 \cdot o\text{-}Phen$	1.48	II	+1.82[e]
			II	+1.98				III	+1.94
			III	+2.10					
65	$PhSnCl_3 \cdot 2Ph_3PO$	2.01	I	+1.88[e]	97	$n\text{-}BuSnCl(2SPyO)_2$	1.72	IV	+1.15[e]
			II	+1.88				V	+1.70
			III	+1.91					
87	$n\text{-}BuSn(NCS)_3 \cdot Bipy$	1.75	II	+1.90[e]	98	$PhSnCl(2SPyO)_2$	1.52	IV	+0.99[e]
			III	+2.36				V	+1.70
88	$PhSn(NCS)_3 \cdot Bipy$	1.55	II	+1.74[e]	111	$PhSnClDB$	2.12	IV	+1.50
			III	+2.20				V	+1.80

[a] Carried out by point-charge Eqns. from Refs. 6, 44, 56, 57 and p.q.s. of Table II. [b] Code numbers refer to Table I. [c] Average value. [d] Y = N (of Terpy), L = Cl. [e] See also Table 27 and text, Ref. 6.

danger of extracting wrong conclusions from approach b) is demonstrated by recent calculations on diorganodithiocarbamates,[57] which have been extensively studied till the present time (see Refs. 6, 17 and Refs. in Table I, compounds Nos. 99–106) The p.q.s. $1/2\, e^2Q([S]-[hal])$ show self-consistent values (within 0.2 mm s^{-1} [4]) in the series $Alk_2Sn(S_2CNR_2)_2$ (+0.26 mm s^{-1}, *trans*-Alk_2, structure IX), $Ph_2Sn(S_2CNR_2)_2$ (+0.10, *cis*-Ph_2, VIII), $RhalSn(S_2CNR'_2)_2$ (+0.07, *trans*-Rhal, IV), from which the indicated configurations were advanced as actual.[57] On the other hand, by taking ΔE_{exp} of compounds $Alk_2Sn(S_2CNR_2)_2$, *trans*-Alk_2, as estimators of the p.q.s. $[S_2CNR_2/2]$, and inserting the calculated value, +0.26 mm s^{-1}, into the ΔE equations for Ph_2Sn^{IV} and $RhalSn^{IV}$ complexes in the various configurations, the best accordance is found for *cis*-Ph_2, VIII (which is consistent with the X-ray crystal and molecular structure of that compound) and *cis*-Rhal, V, configurations, the latter being at variance with the conclusions above. This although the considerable difference between the contributions to e.f.g. due to S and hal donor atoms

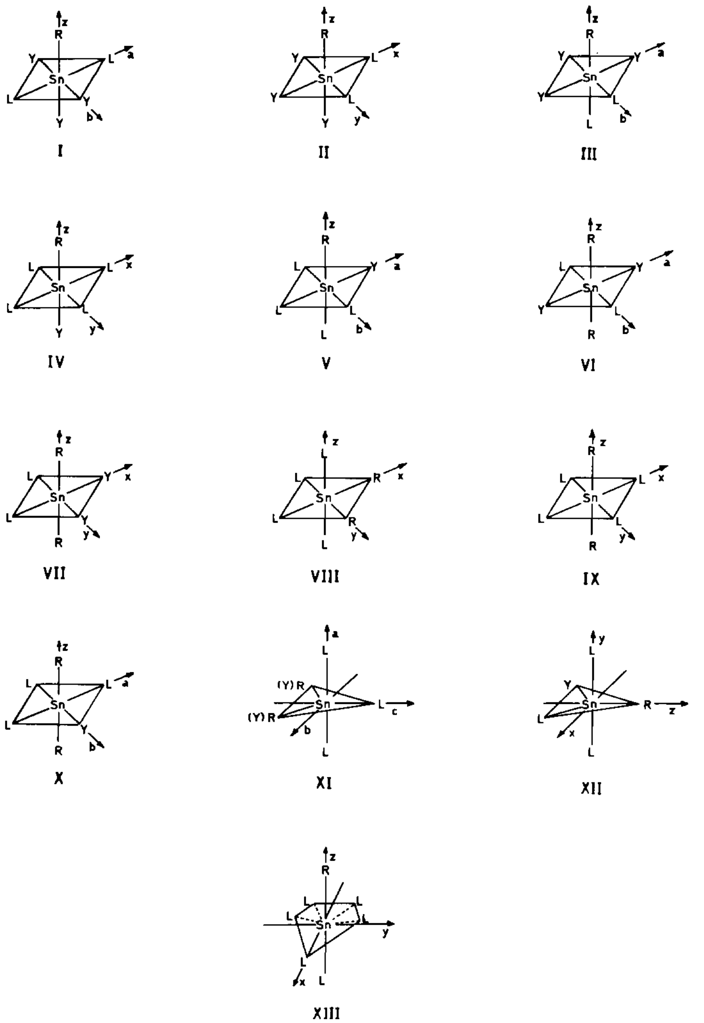

Figure 2. Possible structures for organotin(IV) derivatives. L = organic ligand donor atom, Y = halide or pseudo halide (unless otherwise stated, see text), R = organic radical. The choice of axes respects the rule $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. The assignment of a, b, c is function of p.q.s. of L and Y.

obviously favours the differentiation of ΔE calculated with the proper expressions for the various configurations as well as the choice of the true structure, as demonstrated in the cases of $RClSn(2SPyO)_2$, Nos. 97 and 98, to which *cis*-RCl configurations, V, have been attributed, in consonance with dipole moment studies.[6,16]

The cases of five-coordinate species deserve a special discussion. It has been reported that the point-charge model and the additive approximation, as employed earlier[3,11,39], are not applicable in calculations concerning five-coordinated species, where the metal orbitals to be employed in forming the bond orbitals display two different sets.[4] In few words, the point-charge ΔE equations for these geometries are not amenable to a simple difference, with equal numerical coefficients, between the e.f.g. contributions by organic and halide ligands, so that the latter had to be known as an absolute numerical value, and this possibility is contrasted.[4] Besides, the p.q.s. value [Cl] which was extracted from ΔE of $SnCl_5^-$[39] was questioned since, on the basis of a molecular orbital treatment, its meaning would be the difference between the contribution to the e.f.g. due to axial and equatorial Cl^- ligands.[4] On the other hand, it was observed that, from a practical point of view, the use of this formalism and related point-charge equations,[6,3,11,39,57–59] which correspond in some respects to the "ligand only splitting" case treated by Travis,[5] give excellent answers by using $1/2\, e^2Q[Cl] = -0.63$ mm s^{-1} [57,62], according to the sign of ΔE for $SnCl_5^-$ proposed by Bancroft.[63] In the case of diorganodithiocarbamates, the value of $1/2\,e^2Q$ [S] for 5-coordinate species, based on this treatment, corresponds to the p.q.s. extracted from 6-coordinate compounds.[57]

In this context the experimental ΔE of a series of complexes R_2Sntrid, RClSntrid and hal_2Sntrid, where $trid^{2-}$ are dianions of tridentate ligands with ONO and SNO donor atoms,[38,62,64] have been inserted in the appropriate point-charge equations[62], extracting the generally self-consistent values reported in Table IV and referred to the configurations XI and XII; this implies that the contributions to the e.f.g. due to the various ligands in these structures reasonably agree for hal_2Sn^{IV}, $RClSn^{IV}$ and R_2Sn^{IV} derivatives. The deviations observed in the cases of R_2Sntrid may be due to molecular distortions as well as to the possible occurrence of structures other than XI; indeed, the latter cannot be *a priori* excluded for any of these compounds (a change to coordination number six via intermolecular association in the solid state cannot be ruled out, and structural X-ray studies seem quite urgent in this field).

Attempts to correlate p.q.s. $1/2\,e^2Q[K]$ from five-coordinate structures to values obtained from seven-coordinate, pentagonal bipyramidal (XIII), configurations were also carried out using the ΔE equations pertaining to the species considered.[57,59,62] This gave very good results in diorganodithiocarbamate series, where the p.q.s. of a coordinated S atom, [S], was -0.49 mm s^{-1} (average) and -0.46 mm s^{-1} respectively for the species $R_2ClSnS_2CNR_2$ and $Me_3SnS_2CNMe_2$ considered to be five-coordinate[57], and -0.44 mm s^{-1}, -0.47 mm s^{-1} for the seven-coordinate compounds $AlkSn(S_2CNR_2)_3$ and $PhSn(S_2CNR_2)_3$ respectively.[57] Anyhow, the approach does not work in the case of the oxinates. In fact, assuming the average value $|\Delta E|_{exp} = 3.07$ mm s^{-1} for the five-coordinate series $Alk_2SnhalOx$[46], and employing the ΔE point-charge equation reported elsewhere[57], the p.q.s. value $[Ox/2] = -0.67$ mm s^{-1} is obtained, while for $Ph_2SnClOx$, $|\Delta E|_{exp} = 2.40$ mm s^{-1}[65], this procedure gives $[Ox/2] = -0.45$ mm s^{-1}. Insertion of these p.q.s., as well as of $1/2\,e^2Q[Alk] = +0.31$ mm s^{-1}[57], into the ΔE equation for XIII($= 2[R]-3[L]$[59]), gives estimated $\Delta E = +2.63$ and $+1.97$ mm s^{-1} respectively, the first of which being at great variance with $|\Delta E|_{exp}$ of *n*-$BuSnOx_3$, No. 107 (+1.76, av.).

TABLE IV. Partial Quadrupole Splittings $1/2e^2Q$[trid/3], mm s^{-1}, for Complexes Cl_2Sntrid and R_2Sntrid (XI), and RClSntrid(XII).[a]

Compound[c]	ΔE_{exp}[b]	[trid/3]
hal_2SnBAH[d]	0.77	−0.68
hal_2SnSAH[d]	0.73	−0.66
hal_2SnSAT[d]	0.82	−0.69
Br_2SnAAT	0.62	−0.63
Me_2SnBAH,−SAH	3.18	−0.68
Me_2SnSAT,−AAT	2.41	−0.46
Ph_2SnBAH,−SAH,−SAT,−AAT	2.14	−0.47
MeClSnBAH,−SAH	2.21	−0.61
MeClSnSAT,−AAT	2.04	−0.55
PhClSnBAH,−SAH,−SAT	1.99	−0.61

[a] Point-charge eqns. from Refs. 6, 39, 58, 59, 61. P.q.s. employed in the calculations: [Cl] = −0.63[62], [Alk] = + 0.31, [Ph] = + 0.20 mm s^{-1}[61]. [b] Average values from Refs. 38, 61, 63. [c] Symbols in footnote of Table I. [d] hal = Cl, Br.

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