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The Mössbauer Spectroscopy of Tin Halide Complexes with Organophosphorus Ligands

Sh.Sh.Bashkirov, I.Ya.Kuramshin, A.S.Khramov, and A.N.Pudovik

The Mössbauer parameters (the isomer shift δ, the quadrupole splitting ΔE, and the probability of recoilless absorption f') have been analysed for a large number (more than 200) of complexes of mono- and bi-dentate organophosphorus complexes with tetra-alkyltin and alkyltin halides. It is shown that the Mössbauer method can be used to determine the localisation centres of the donor-acceptor bond in complexes of organophosphorus compounds with tin tetrahalides and to determine the geometrical structures of the complexes. It has been observed that the quantities δ, ΔE, and f' for the compounds $[R'R''R'''P(Y)]_{2(1)}SnR_nX_{4-n}$ are definitely influenced by the nature of the substituents in the ligand and in the acceptor. This influence can be described with the aid of the reaction constants of the substituents σ^{ph} and σ^*.
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I. INTRODUCTION

The Mössbauer effect or nuclear gamma resonance (NGR) have been used recently on an extremely wide scale in a wide variety of fields of science and technology. Mössbauer spectroscopy has found the most extensive applications in chemistry: in physical chemistry, in the chemistry of coordination compounds, in nuclear chemistry, etc.[1]

The extensive and effective applications of Mössbauer spectroscopy in chemistry, particularly in the chemistry of organoelemental compounds, are due to the fact that the Mössbauer isotopes ^{57}Fe and ^{119}Sn have come to be most widely used in Mössbauer spectroscopy (these isotopes are relatively readily available and sources based on them are simple to prepare and to use in experiments). On the other hand, as a consequence of the enormous importance of iron- and tin-containing compounds in science and technology, the chemistry of these elements has been studied in extremely great detail. This happy coincidence led to the intensive employment of the Mössbauer effect for studies on organoelemental compounds.

The accumulation of extensive experimental data on Mössbauer spectroscopy during the last twenty years (the effect was discovered by Mössbauer in 1958[2]) entailed the appearance of a whole series of monographs and reviews in which the principles and applications of Mössbauer spectroscopy are described fairly completely[1,3,4]. However, unfortunately none of these publications deals with studies of the class of organoelemental compounds comprising the complexes of tin halides with organophosphorus ligands.

On the other hand, the interest in the coordination compounds of phosphorus is due to the fact that the wide variety of organoelemental compounds containing phosphorus and the unique set of their properties make these substances extremely valuable both for science and for practical purposes. Among organophosphorus compounds (OPC) and their complexes, effective medicinal substances have been found and many OPC are flotation agents, additives to oils, and plasticisers. Coordination compounds of the OPC have found applications in the preparation of materials in various fields (quantum electronics, microelectronics, etc.).

The most important Mössbauer parameters for chemistry are the isomer or chemical shift δ and the quadrupole splitting ΔE, the knowledge of which permits inferences to be drawn about the structure of the electronic valence shell and the geometrical structure of the immediate environment of the Mössbauer atom, about the nature of the chemical bond, etc. Yet another Mössbauer parameter—the probability of recoilless absorption f'—is also of undoubted interest; it permits the study of the dynamic properties of crystals, which depend on the masses of the atoms and on the force constants characterising the interaction between them.

The aim of the present review was to survey the available data on the Mössbauer spectroscopy of tin halide complexes with organophosphorus ligands and to examine the relation between the Mössbauer parameters, the reactivities, and the structures of the compounds. We do not deal with the experimental features of the Mössbauer spectroscopy of ^{119}Sn, which have been described fairly completely elsewhere[1,5-7].

In all cases the isomer shifts, the quadrupole splittings, and the resonance line widths (Γ) are quoted in terms of units of velocity (mm s^{-1}). The isomer shifts are given relative to SnO_2 at room temperature; if the shift is indicated in the original publication relative to another compound, the appropriate recalculation has been made. Since in virtually all studies the accuracy of the determinations of δ, ΔE, and Γ is stated to be in the range $\pm 0.03-0.05$ mm s^{-1}, we shall assume that the experimental error of the determination of these parameters is in this range. The accuracy of the determination is to within ± 0.03. The Mössbauer spectra of the compounds described below have been obtained in the region of liquid nitrogen temperatures (78–90 K) unless otherwise stated.

II. THE ISOMER SHIFT

1. The Influence of the Donor Atom

The isomer or chemical shift is the difference between the energies of the nuclear transitions in the absorbing and emitting nuclei. In the Mössbauer spectra this is manifested

by a shift of the absorption resonance line relative to the emission resonance line (Fig. 1).

In the general case the isomer shift is defined in the following way[1,3,4]:

$$\delta = \frac{4}{5}\pi e^2 z R^2 \frac{\Delta R}{R}\{|\psi(0)|_a^2 - |\psi(0)|_s^2\}, \quad (1)$$

where e is the electronic charge, z the nuclear charge, R the average charge radius of the nucleus, ΔR its change on transition from the ground to the excited state, and $|\psi(0)|_a^2$ and $|\psi(0)|_s^2$ are the electron densities at the nucleus in the absorber and the source respectively. Since the contribution of the inner shells in tin compounds is approximately constant[1,4], δ depends on the population of the valence shell of the Mössbauer atom. Furthermore, theoretical analysis[1,4,8] and numerous experimental results[9-12] showed that in the case of tin(IV) compounds one can neglect to a first approximation the population of the 5p states of the tin atom and the mutual shielding of the s electrons by the p and d electrons.

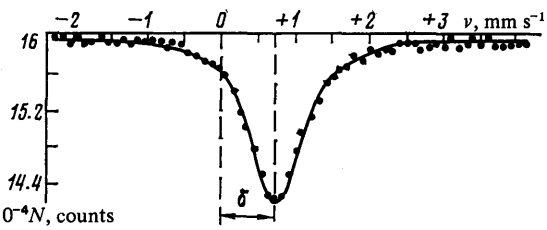


Figure 1. The Mössbauer spectrum of the complex $[(C_2H_5)_2P(S)S]_2SnCl_2$ at 85 K (continuous line—calculation).

Thus the state of the Mössbauer atom in various chemical compounds is determined primarily by the structure of the outer electronic valence shells and the main contribution to δ for tin-containing compounds comes from the difference $|\psi_{5s}(0)|_a^2 - |\psi_{5s}(0)|_s^2$. Consequently the relative change in the population of the valence 5s shells of the tin atom in a series of different absorbers (for a fixed source) can be inferred from the change in δ.

Since $\Delta R/R > 0$ for ^{119}Sn, one can claim unambiguously that, for tin-containing compounds, a large value of δ corresponds to a large population of the 5s shell of the tin atom. Thus if 100% covalent bonding is assumed in α-tin ($\delta = 2.1$ mm s^{-1}), i.e. that the population of the 5s orbital is 1.0–1.2 electrons[5,15,16], and a 50% ionic bond character is assumed for SnF_4 ($\delta = -0.25$ mm s^{-1}),[4] then evidently the closer the value of δ for any tin-containing compound to that for SnF_4, the smaller the population of the 5s shell of the tin atom in the given substance.

Thus the isomer shift permits inferences about the chemical environment of the Mössbauer atom in various compounds. Such analysis is particularly simple for the determination of the valence state of tin. Thus, for bivalent tin, the isomer shift relative to α-tin is greater than zero, while for quadrivalent tin it is less than zero[17]. If the shifts are considered relative to SnO_2 (a generally recognised standard in ^{119}Sn Mössbauer spectroscopy), then $\delta > 2.1$ mm s^{-1} for tin(II) and $\delta < 2.1$ mm s^{-1} for tin(IV). One must note that in certain complexes of the type $LSnCl_3$ the isomer shift ($\delta > 2.1$ mm s^{-1}) does not allow the estimation of the formal valence of tin[18].

Systematic treatment and analysis of the literature data[10-12,19-24] and the authors' own results[25-43], summarised in Tables 1–9, permits the claim that the values of δ for compounds of the type $L_3(L')SnX_4$ and the ratio of the isomer shifts of $L_2(L')SnBr_4$ (δ_{Br}) and $L_2(L')SnCl_4$ (δ_{Cl}) is determined in the first place by the nature of the immediate environment of the tin atom (Table 1) and this makes it possible to use Mössbauer spectroscopy for the determination of the localisation centres of the donor–acceptor bond in complexes of organophosphorus compounds with both tin chloride and tin bromide.

Table 1. The isomer shifts and quadrupole splittings in the Mössbauer spectra of tetra-alkyltin compounds, tetra-aryltin compounds, alkyltin halides, and aryltin halides with mono- and bi-dentate organophosphorus ligands $L_2(L')SnX_4$, $L_2SnR_nX_{4-n}$ ($n = 1,2$), and $LSnR_3Cl$ and of the organotin salts L_2SnX_2 at 78–90 K.[38,40]

No.	L(L′=5–8)	Acceptor	δ, mm s⁻¹		$\left(\frac{\delta_{Br}}{\delta_{Cl}}\right)_{av}$	ΔE, mm s⁻¹		ρ=ΔE/δ		Number of compounds	
			X=Cl	X=Br		X=Cl	X=Br	X=Cl	X=Br	X=Cl	X=Br
1	R′R″R‴P(O)	SnX_4^*	0.24–0.51	0.55–0.65	2.0	0.5–1.6 (*trans*); 0.5*** (*cis*)	0.6–1.11 (*trans*); 0.4 (*cis*)	1.6–3.1	1–1.9	56	22
	»	$SnRX_3$	0.80–1.15	1.00–1.05	1.36	1.99–2.36	2.02–2.31	⩽1.9	⩽1		
	»	SnR_2X_2	1.20–1.60	1.56	1.09	3.81–4.37	4.40	1.91–2.64	2.02–2.20	10	2
	»	SnR_3X	1.29–1.52	—	—	3.07–3.85	—	2.54–3.24	2.81	18	1
2	R′R″R‴P(S)	SnX_4	0.58–0.71	0.88–1.07	1.4	⩽0.50	⩽0.40	2.41–2.64	—	9	—
3	R′R″R‴P(Se)	SnX_4	0.73–0.82	—	—	⩽0.32	—	⩽0.95	⩽0.4	21	9
4	R′R″R‴P	SnX_4	0.56–0.91	0.83–1.13	1.3	⩽1.18	⩽1.13	⩽0.43	—	4	—
	»	$SnRX_3$	1.23	—	—	1.73	—	⩽1.5	⩽1.3	32	5
5	$R'_2P(CH_2)_{1(2)}R''_{2(1)}N$	SnX_4	0.50–0.70	—	—	⩽0.50	—	1.41	—	1	—
6	$R'_2P(O)(CH_2)_{1(2)}R''_{2(1)}N$	SnX_4	0.38–0.48	0.60–0.70	1.7	⩽0.50	⩽0.50	⩽1	—	3	—
7	$R'_2P(S)(CH_2)_{1(2)}R''_{2(1)}N$	SnX_4	0.45–0.52	—	—	⩽0.40	—	⩽1	⩽0.8	5	4
8	R'_3PNR''	SnX_4	0.29–0.36	—	—	0.0	—	0.8	—	3	—
9	R′R″P(O)O⁻	SnX_2^{**}	0.09–0.15	0.16–0.22	—	⩽0.32	0.50–0.63	0.0	—	3	—
10	R′R″P(S)S⁻	SnX_2	0.69–0.73	0.91	—	⩽0.38	0.0	0–10	3.1–4.1	7	2
								⩽0.53	0	3	1

* and ** For X = I, $\delta = 0.93$ and 0.40–0.45 mm s^{-1} respectively, $\Delta E = 0$ and 0.65–0.79 mm s^{-1}, and the number of compounds is unity.

*** For $[Cl_3P(O)]_2SnCl_4$, $\Delta E = 1.12$ mm s^{-1}.

The data in Table 1 show that there is a definite relation between δ and the electronegativity χ of the atoms surrounding the Mössbauer isotope, which makes it possible to determine the donor atom in ligands having two and more donor centres and to estimate the sequence in the variation of the isomer shift on passing from tin(IV) chloride to tin(IV) bromide complexes. This relation is described approximately by the following empirical equation[38]

$$\frac{\delta_{Br}}{\delta_{Cl}} = \alpha \frac{\chi_{Br} - \chi_{Sn}}{\chi_{Cl} - \chi_{Sn}} + \beta \frac{\chi_{Br} - \chi_{Sn}}{\chi_{Y} - \chi_{Sn}} , \qquad (2)$$

where α and β are coefficients and χ_Y is the electronegativity of the ligand donor atom.

Table 2. The Mössbauer parameters of complexes of tin(IV) chloride with phosphoryl compounds $[R'R''R'''P(O)]_2SnCl_4$ at 78–90 K.

No.	R′	R″	R‴	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	Refs.
1	CH_3	CH_3	CH_3	0.28	0.51	0.99	0.99	[75]
2	CH_3	CH_3	CH_3O	0.32	0.25	0.98	0.98	[74]
3	CH_3	CH_3	CH_3S	0.31	—	1.38	—	[25,32]
4	CH_3	CH_3	Cl	0.36	0.57	1.24	1.15	[74]
5	CH_3	CH_3	H	0.29	0.41	0.86	0.86	[96,97]
6	CH_3	Cl	Cl	0.87	0.50	1.66	—	[26]
7	CH_3	$(CH_3)_2N$	$(CH_3)_2N$	0.25	0.52	0.90	0.85	[31,36]
8	CH_3	C_6H_5	C_6H_5	0.31	0.68	0.92	0.89	[36,38]
9	C_6H_5	C_6H_5	C_6H_5	0.21	0.00	1.19	—	[24]
10	C_6H_5	C_6H_5	CH_3S	0.32	—	1.28	—	[25,34]
11	C_6H_5	C_6H_5	$C_6H_{16}S$	0.35	0.50	1.80	—	[25,36]
12	C_6H_5	C_6H_5	C_8H_7S	0.37	—	1.38	—	[25]
13	C_6H_5	Cl	Cl	0.46	0.78	1.05	1.05	[54]
14	C_6H_5	C_6H_5	Cl	0.34	0.46	1.22	1.22	[36,38]
15	C_6H_5	$(CH_3)_2N$	$(CH_3)_2N$	0.26	0.53	0.83	0.85	[31,36]
16	C_6H_5	C_6H_5	C_6H_5	0.36	—	0.95	—	[110]
17	C_6H_5O	C_6H_5O	$(C_6H_5)_2N$	0.38	0.64	0.96	0.94	[110]
18	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	CH_3S	0.37	—	1.28	—	[25,36]
19	$iso\text{-}C_3H_7$	$iso\text{-}C_3H_7$	CH_3S	0.32	0.83	2.02	—	[25,36]
20	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	0.24	—	1.15	—	[21,23]
	»	»	»	0.25	0.25	0.89	0.89	[74]
21	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	H	0.36	0.39	0.84	0.86	[110]
22	CH_3O	CH_3O	CH_3O	0.37	0.53	0.95	0.95	
23	CH_3O	CH_3O	CH_3	0.37	0.53	0.95	0.95	[109]
24	CH_3O	CH_3O	$(CH_3)_2N$	0.36	0.96	0.92	0.92	[31,36]
25	CH_3O	CH_3O	C_6H_5	0.31	0.49	0.84	0.84	[96,97]
26	CH_3O	CH_3O	$p\text{-}ClC_6H_4$	0.26	0.53	0.89	0.89	[96,97]
27	CH_3O	CH_3O	H	0.46	0.40	0.86	0.87	[110]
28	CH_3O	CH_3O	Cl	0.35	0.68	0.86	0.83	[110]
29	CH_3O	$(CH_3)_2N$	$(CH_3)_2N$	0.36	0.35	1.04	1.04	[36]
30	C_2H_5O	C_2H_5O	CH_3S	0.37	—	1.38	—	[25,34]
31	$n\text{-}C_3H_7O$	$n\text{-}C_3H_7O$	CH_3S	0.32	0.83	2.02	—	[25,36]
32	$iso\text{-}C_3H_7O$	$iso\text{-}C_3H_7O$	CH_3S	0.37	1.06	2.27	—	[25,34,36]
33	$n\text{-}C_4H_9O$	$n\text{-}C_4H_9O$	CH_3S	0.37	0.4	1.57	—	[25,34,26]
34	C_6H_5	C_6H_5	C_6H_5	0.27	0.51	0.82	0.84	[21,23]
35	C_6H_5	C_6H_5	$(CH_3)_2N$	0.27	0.77	0.80	0.80	[36]
36	C_6H_5	C_6H_5	Cl	0.37	0.78	0.96	0.96	[36]
	»	»	»	0.42	0.78	0.92	0.92	[110]
37	C_6H_5	C_6H_5	Br	0.35	0.68	0.85	0.87	[110]
38	C_6H_5	$(CH_3)_2N$	$(CH_3)_2N$	0.28	0.61	0.86	0.85	[31,36]
39	C_6H_5	Cl	Cl	0.46	1.60	1.10	1.10	[21,23]
	»	»	»	0.46	1.45	1.10	1.10	[26,35,36]
40	C_6H_5O	C_6H_5O	C_6H_5O	0.34	0.71	0.74	0.79	[21,23]
41	C_6H_5O	C_6H_5O	Cl	0.38	0.75	0.89	0.83	[21,23]
42	C_6H_5O	Cl	Cl	0.42	1.13	0.84	0.83	[21,23]
43	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	0.31	0.70	—	—	[10,23]
	»	»	»	0.33	0.69	0.91	0.90	[31,36,74]
	»	»	»	0.23	0.75	0.79	0.79	[96,97]
44	$(CH_3)_2N$	$(CH_3)_2N$	$p\text{-}CH_3OC_6H_4$	0.27	0.70	0.83	0.83	[36]
	»	»	»	0.28	0.63	0.93	0.93	[96,97]
45	$(CH_3)_2N$	$(CH_3)_2N$	$p\text{-}CH_3OC_6H_4$	0.28	0.63	0.93	0.93	[36]
46	$(CH_3)_2N$	$(CH_3)_2N$	$p\text{-}ClC_6H_4$	0.30	0.72	0.89	0.89	[36]
	»	»	»	0.295	0.72	0.89	0.89	[96,97]
47	$(CH_3)_2N$	$(CH_3)_2N$	H	0.38	—	1.15	—	[110]
48	$(CH_3)_2N$	$(CH_3)_2N$	CH_2Cl	0.45	0.79	0.91	0.87	[31,36]
49	Cl	Cl	Cl	0.51	1.12	0.88	0.99	[21,23]
50	Cl	Cl	$p\text{-}CH_3OC_6H_4$	0.41	0.98	0.96	0.96	[36]
	»	»	»	0.41	0.96	0.98	0.98	[96,97]
51	Cl	Cl	$p\text{-}ClC_6H_4$	0.42	0.97	0.88	0.88	[36]
52	Cl	Cl	CH_2Cl	0.45	1.12	0.91	0.92	[31]
53	Cl	Cl	C_6H_4S	0.44	1.51	1.00	1.00	[109]
54	$p\text{-}(CH_3)_2NC_6H_4$	$p\text{-}(CH_3)_2NC_6H_4$	$p\text{-}(CH_3)_2NC_6H_4$	0.28	0.52	0.90	0.90	[109]
55	Cl	Cl	C_5H_5N	0.35	0.45	0.81	0.81	[109]
56	CH_3	CH_3O	H	0.35	—	1.11	—	[110]
57	C_2H_5O	C_2H_5O	Cl	0.40	0.52	0.94	0.94	[110]
58	$n\text{-}C_4H_9O$	$n\text{-}C_4H_9O$	Cl	0.34	0.72	0.90	0.90	[110]
59	C_2H_5O	C_2H_5O	$(C_6H_5)_2N$	0.37	—	1.10	—	[110]
60	C_6H_5	C_6H_5	$(C_6H_5)_2P$	0.30	0.49	1.13	1.13	[110]

Note. For complexes 5, 25, 26, 43, 44, 46, and 50, the values of f'_{85} are respectively 0.31, 0.31, 0.15, 0.36, 0.23, 0.26, and 0.29.[96,97]

The data in Table 1 and Eqn.(2) suggest[38] that the complexes $[(C_5H_{10}N)P(S)]_2SnCl_4$ and $[(C_4H_8N)P(S)]_2SnCl_4$, whose isomer shifts are 0.49 and 0.43 mm s^{-1} respectively, are formed as a consequence of the electron-donating properties of the nitrogen atom and not the thiophosphoryl sulphur, as suggested by Carty and Sharma[23]. The above conclusion is confirmed by data obtained for similar systems in ^{35}Cl Mössbauer spectroscopic and vibrational spectroscopic studies[44].

Table 3. The Mössbauer parameters of complexes of tin(IV) bromide with phosphoryl compounds $[R'R''R'''P(O)]_2SnBr_4$ at 78–90 K.

No.	R′	R″	R‴	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	References
1	CH_3	CH_3	CH_3O	0.65	0.4	1.51	—	[26,27]
2	CH_3	CH_3	CH_3S	0.60	—	1.42	—	[25,26,34]
3	CH_3	CH_3	H	0.61	—	1.20	—	[110]
4	CH_3	CH_3	Cl	0.66	—	1.20	—	[26]
5	CH_3	C_6H_5	C_6H_5	0.62	0.37	0.83	0.83	[38]
6	CH_3	$(CH_3)_2N$	$(CH_3)_2N$	0.64	—	1.03	—	[31]
7	C_2H_5	C_2H_5	CH_3S	0.63	—	1.11	—	[25]
8	C_2H_5	$(CH_3)_2N$	$(CH_3)_2N$	0.64	0.36	1.07	1.07	[31]
9	CH_3O	CH_3O	C_6H_5	0.61	1.04	0.92	0.92	
10	C_2H_5O	C_2H_5O	$CH_2CH_2C_6H_4N$	0.76	0.50	1.03	1.03	[36,97,109]
11	C_6H_5	C_6H_5	$(CH_3)_2N$	0.54	0.71	0.80	0.80	[31]
12	C_6H_5	C_6H_5	Br	0.67	0.61	0.79	0.79	[110]
13	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	0.56	0.76	—	—	[23]
	»	»	»	0.57	0.805	0.92	0.92	[96,97]
14	$p\text{-}(CH_3)_2NC_6H_4$	$p\text{-}(CH_3)_2NC_6H_4$	$p\text{-}(CH_3)_2NC_6H_4$	0.56	0.52	0.91	0.91	[109]
15	C_2H_5	C_2H_5	C_2H_5	0.79	—	1.24	—	[24]
16	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	0.81	—	1.61	—	[24]
17	C_6H_5	C_6H_5	$(C_6H_5)_2N$	0.60	1.11	0.85	0.82	[110]
18	$n\text{-}C_3H_7$	C_6H_5	C_6H_5	0.64	0.05	1.45	—	[110]
19	C_6H_5	C_6H_5	Cl	0.67	—	0.86	—	[110]

Note. $f'_{85K} = 0.40$ for complex 13.[96,97]

Table 4. The Mössbauer parameters of complexes of alkyltin halides with phosphoryl compounds $[R'R''R'''P(O)]_2SnR_n \cdot Cl_{4-n}$ at 78–90 K.

No.	R′	R″	R‴	R	n	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	References
1	CH_3	CH_3	CH_3	CH_3	2	1.38	4.30	1.12	1.18	[26,28,74]
2	CH_3	CH_3	CH_3O	CH_3	1	0.90	2.20	1.20	1.25	[26,28,74]
3	CH_3	CH_3	CH_3O	CH_3	2	1.50	4.37	1.27	1.27	[26,28,74]
4	CH_3	CH_3	CH_3S	CH_3	2	1.45	4.20	1.20	1.20	[26]
5	CH_3	CH_3	Cl	CH_3	1	1.04	2.26	1.15	1.24	[26,28,74]
6	CH_3	CH_3	Cl	CH_3	2	1.58	4.10	1.06	1.28	[26,28,74]
7	CH_3	CH_3	Cl	C_2H_5	1	1.17	2.25	1.11	1.10	[26,28]
8	CH_3	CH_3	Cl	$n\text{-}C_4H_9$	1	1.06	2.30	1.23	1.32	[26,28]
9	C_2H_5	C_2H_5	CH_3S	CH_3	2	1.45	4.15	1.35	1.36	[26]
10	C_2H_5	C_2H_5	CH_3S	C_2H_5	1	1.10	2.10	1.25	1.25	[26]
11	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	CH_3S	CH_3	2	1.43	4.20	1.25	1.35	[26]
12	$iso\text{-}C_3H_7$	$iso\text{-}C_3H_7$	CH_3S	CH_3	2	1.56	4.05	1.19	1.19	[26]
13	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	CH_3	2	1.34	4.22	0.82	0.82	[74]
14	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	2	1.49	4.13	0.85	0.93	[20]
15	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	C_6H_5	2	1.20	3.81	0.95	1.01	[20]
16	C_2H_5O	C_2H_5O	CH_3S	CH_3	2	1.47	4.00	1.10	1.25	[26]
17	C_6H_5	C_6H_5	C_6H_5	$n\text{-}C_4H_9$	1	1.05	2.36	0.97	0.96	[20]
	»	»	»	»	1	1.10	2.32	—	—	[105,106]
18	C_6H_5	C_6H_5	C_6H_5	CH_3	2	1.37	4.30	1.15	1.02	[88]
19	C_6H_5	C_6H_5	C_6H_5	$n\text{-}C_4H_9$	2	1.62	4.11	0.97	1.03	[20]
20	C_6H_5	C_6H_5	C_6H_5	C_6H_5	1	0.80	2.01	1.19	1.38	[20]
21	C_6H_5	C_6H_5	C_6H_5	C_6H_5	2	1.25	3.98	0.97	1.00	[20]
22	C_6H_5	C_6H_5	$(CH_3)_2N$	CH_3	1	0.63	1.99	0.96	0.86	[96,97]
23	C_6H_5	C_6H_5	$(CH_3)_2N$	CH_3	2	1.26	3.95	0.80	0.80	
24	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	CH_3	1	0.89	2.35	—	—	[21]
25	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	CH_3	2	1.50	4.36	—	—	[21]
	»	»	»	»	»	1.32	4.28	1.27	1.06	[88]
	»	»	»	»	»	1.38	4.09	0.94	0.94	[96,97]

Note. The values of f'_{85K} have been determined for complexes 22 and 25 (0.29 and 0.38).[96,97]

In selecting the coefficients α and β in Eqn.(2), it was found that the optimum agreement between the calculated and experimental δ_{Br}/δ_{Cl} (Table 1) is observed when the ligands are subdivided into groups with similar electronegativities:

(a) the Allred–Rochow electronegativities[45,46]:

Y=O, N, Cl : α=2.61, β=—0.88;
Y=S, P, Br : α=1.69, β=—0.085;

(b) the Pauling electronegativities[45,47,48]:

Y=O, N, Cl : α=2.94, β=—0.85;
Y=S, P, Br : α=2.82, β=—0.055;

(c) the Mulliken electronegativities[23,49–51]:

Y=O, N, Cl : α=4.90, β=—2.89;
Y=S, P, Br : α=2.55, β=—0.48.

Table 5. The Mössbauer parameters of complexes of trialkyl-(aryl)tin chlorides $[R'R''R'''P(O)]SnR_3Cl$ at 78–90 K.

R′	R″	R‴	R	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	References
CH_3	CH_3	CH_3O	CH_3	1.38	3.65	1.20	1.10	[26,28]
CH_3	CH_3	Cl	CH_3	1.52	3.50	1.25	1.28	[26,28]
CH_3O	CH_3O	CH_3O	C_6H_5	1.31	3.18	—	—	[107]
C_6H_5	C_6H_5	C_6H_5	C_6H_5	1.29	3.14	—	—	[107]
C_6H_5O	C_6H_5O	C_6H_5O	C_6H_5	1.31	3.07	—	—	[107]
C_6H_5O	C_6H_5O	C_6H_5O	C_6H_5	1.30	3.15	—	—	[107]
C_6H_5	C_6H_5	C_6H_5	CH_3	1.45	3.49	—	—	[105,106]
$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	CH_3	1.44	3.52	—	—	[105,106]
$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	C_2H_5	1.43	3.47	0.77	0.77	[26]

Table 6. The Mössbauer parameters of complexes of tin tetrahalides with organophosphorus compounds containing tervalent phosphorus $[R'R''R'''P]_2SnX_4$ at 78–90 K.

No.	R′	R″	R‴	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	References
1	C_2H_5	C_2H_5	C_2H_5	0.87	0.95	0.52	0.54	[20,23]
2	C_2H_5	C_2H_5	n-C_3H_7S	0.82	0.91	0.97	0.97	[32]
	»	»	»	0.81	0.96	1.09	1.09	[96,97]
3	C_2H_5	C_2H_5	C_6H_5	0.88	0.99	0.74	0.71	[19]
4	C_2H_5	C_2H_5	Cl	0.75	0.49	0.89	0.89	[32]
	»	»	»	0.71	0.60	1.03	1.03	[96,97]
5	C_2H_5	C_2H_5	C_2H_5S	0.80	0.50	1.70	—	[26]
6	C_2H_5	n-C_3H_7	n-C_3H_7S	0.62	0.53	0.84	0.84	[32]
	»	»	»	0.63	0.57	0.91	0.91	[96,97]
7	C_2H_5	$(CH_3)_2N$	$(CH_3)_2N$	0.85	1.10	1.25	0.86	[31]
	»	»	»	0.85	1.02	1.03	1.03	[32]
8	C_2H_5	n-C_3H_7	Cl	0.70	0.57	0.97	0.97	[32]
9	C_2H_5	C_6H_5	Cl	0.57	0.46	0.84	0.84	
10	C_2H_5	C_6H_5	C_6H_5	0.63	0.46	0.83	0.86	[19]
11	C_2H_5O	C_2H_5O	$(C_2H_5)_2N$	0.64	0.4	1.30	—	[110]
12	n-C_3H_7	n-C_3H_7	n-C_3H_7	0.89	0.95	0.78	0.73	[19,23]
13	iso-C_3H_7	iso-C_3H_7	CH_3S	0.83	0.38	0.92	0.92	[32]
	»	»	»	0.83	0.37	1.04	1.04	[96,97]
14	n-C_4H_9	n-C_4H_9	n-C_4H_9	0.85	1.02	0.78	0.76	[19,23]
	»	»	»	0.85	1.17	1.28	1.06	[24]
	»	»	»	0.86	1.02	1.17	1.28	[31,34]
	»	»	»	0.87	1.07	0.97	0.97	[97]
15	CH_3O	CH_3O	CH_3O	0.63	0.54	1.01	1.01	[32,35]
16	n-C_3H_7S	n-C_3H_7S	n-C_3H_7S	0.66	0.52	0.86	0.86	[32]
	»	»	»	0.68	0.51	1.00	1.00	[96,97]
17	C_6H_5	C_6H_5	C_6H_5	0.75	—	0.81	—	[19,23]
	»	»	»	0.66	0.31	0.87	0.87	[97]
18	C_6H_5	C_6H_5	C_6H_5	0.95	—	—		[23]
	»	»	»	0.85		0.95		
19	C_6H_5	C_6H_5	CH_3	0.81	0.58	0.66	0.64	[19,23]
20	C_6H_5	C_6H_5	CH_3O	0.81	0.45	0.72	0.68	[19,23]
21	C_6H_5	C_6H_5	$C{=}CCH_3$	0.77	—	0.89	—	[19,23]
22	C_6H_5	C_6H_5	$(CH_3)_2N$	0.83	0.50	1.07	1.07	[32,108]
23	C_6H_5	C_6H_5	Cl	0.70	—	1.45	—	[26]
24	C_6H_5	C_6H_5	Cl	0.86	—	0.96	—	[38]
25	C_6H_5	C_6H_5	Br	0.89		0.92	—	[38]
26	C_6H_5	C_6H_5	$CH_2CH_2C_5H_4N$	0.69	—	0.97	—	[109]
27	C_6H_5	CH_3	CH_3	0.85	0.97	0.68	0.68	[10,23]
	»	»	»	0.91	1.18	1.24	1.12	[24]
28	C_6H_5	$(CH_3)_2N$	$(CH_3)_2N$	0.80	1.20	1.10	1.15	[31,36]
29	C_6H_5	C_6H_5	$(C_6H_5)_2N$	0.85	—	1.10	—	
30	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	0.74	0.59	0.90	0.90	[97]
	»	»	»	0.74	0.58	0.97	0.97	[32,38]
31	$(CH_3)_2N$	$(CH_3)_2N$	p-$CH_3OC_6H_4$	0.79	0.75	0.96	0.96	[34]
	»	»	»	0.79	0.70	0.96	0.96	[32]
32	$(CH_3)_2N$	$(CH_3)_2N$	p-ClC_6H_4	0.77	0.69	0.94	0.94	[32]
	»	»	»	0.77	0.72	0.94	0.89	[36]
33	$(CH_3)_2N$	Cl	Cl	0.56	0.4	1.45	—	[108]
34	CH_3	CH_3	C_2H_5	1.13	1.13	1.41	1.07	[24]
35	C_8H_{17}	C_8H_{17}	C_8H_{17}	0.72	1.08	0.94	1.17	[24]
36	C_8H_{17}	C_8H_{17}	C_8H_{17}	0.94	0.89	—	—	[24]

Note. X = Br in complexes 18, 24, 25, 34, and 35, while in the remaining cases X = Cl. f'_{85K} = 0.41, 0.31, 0.22, 0.21, 0.25, 0.25, 0.31, and 0.29 for complexes 2,4,6,13,14,16,17, and 30 respectively[96,97].

We may note that the correlations between the isomer shifts and the Mulliken group molecular electronegativities of the ligands (χ_L) in similar complexes has also been mentioned by Carty and Sharma[23]. The use of χ_L from their study[23] in Eqn.(2) instead of χ_Y also leads to satisfactory results.

Table 7. The Mössbauer parameters of complexes of tin tetrahalides with thio- and seleno-phosphoryl compounds $[R'R''R'''P(Y)]_2SnX_4$ at 78–90 K.

No.	R′	R″	R‴	X	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	References
1	CH_3	CH_3	CH_3O	Cl	0.65	—	1.10	—	[26,28,36]
2	CH_3	CH_3	CH_3O	Br	1.07	—	1.38	—	[26,28]
3	CH_3	CH_3	$(CH_3)_2N$	Cl	0.66	0.32	1.00	1.00	[36]
4	CH_3	CH_3	Cl	Cl	0.64	—	1.20	—	[26,28,36]
5	CH_3	$(CH_3)_2N$	$(CH_3)_2N$	Cl	0.67	—	0.92	—	[31]
6	CH_3	$(CH_3)_2N$	$(CH_3)_2N$	Br	0.86	0.31	0.99	0.99	[31]
7	CH_3	$(CH_3)_2N$	Cl	Cl	0.66	0.42	0.97	0.97	[31]
8	C_2H_5	C_2H_5	C_2H_5S	Cl	0.69	—	1.05	—	[26,36]
9	C_2H_5	C_2H_5	CH_3S	Cl	0.71	—	1.25	—	[25,26]
10	C_2H_5	C_2H_5	CH_3S	Br	0.88	—	1.27	—	[25,26]
11	C_2H_5	C_2H_5	n-C_3H_7S	Cl	0.60	—	1.20	—	[26]
12	C_2H_5	C_2H_5	$(CH_3)_2N$	Cl	0.66	—	1.10	—	[108]
13	C_2H_5	C_2H_5	$(CH_3)_2N$	Br	0.96	—	0.89	—	[108]
14	C_2H_5	C_2H_5	Cl	Cl	0.65	0.50	1.20	1.20	[35]
15	C_2H_5	$(CH_3)_2N$	$(CH_3)_2N$	Cl	0.66	0.32	0.91	0.91	[31,36]
16	C_2H_5	$(CH_3)_2N$	$(CH_3)_2N$	Br	0.94	—	1.15	—	[31]
17	C_2H_5	$(CH_3)_2N$	Cl	Cl	0.67	—	1.20	—	[36]
18	n-C_3H_7	n-C_3H_7	CH_3S	Cl	0.60	—	1.25	—	[25,26]
19	n-C_3H_7	n-C_3H_7	CH_3S	Br	0.99	0.4	1.56	—	[25,26]
20	n-C_4H_9	n-C_4H_9	n-C_4H_9	Cl	0.64	—	1.10	—	[31]
21	n-C_4H_9	n-C_4H_9	CH_3S	Br	0.88	—	1.36	—	[25,26]
22	C_6H_5	C_6H_5	$(CH_3)_2N$	Cl	0.60	0.3	1.28	—	[108]
23	C_6H_5	C_6H_5	$(CH_3)_2N$	Br	0.95	0.3	1.35	—	[108]
24	C_6H_5	C_6H_5	$CH_2CH_2C_5H_4N$	Cl	0.53	0.32	0.92	—	[109]
	»	»	»	Cl	0.53	—	1.00	—	[109]
25	C_6H_5	$(CH_3)_2N$	$(CH_3)_2N$	Cl	0.70	0.35	0.90	0.90	[31,36]
26	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	Cl	0.65	—	0.83	—	[31]
27	$(CH_3)_2N$	$(CH_3)_2N$	p-ClC_6H_4	Cl	0.62	0.39	1.08	1.01	[36]
	»	»	»	Cl	0.62	0.59	1.01	1.01	
28	C_2H_5	$(CH_3)_2N$	$(CH_3)_2N$	Cl	0.82	0.27	1.07	1.06	[31]
29	n-C_4H_9	n-C_4H_9	n-C_4H_9	Cl	0.74	0.32	0.93	0.93	[31]
30	C_6H_5	C_6H_5	$(CH_3)_2N$	Cl	0.75	—	0.93	—	[31]
31	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	Cl	0.73	—	1.18	—	[31]

Note. Y = Se for compounds 28–31, while in the remaining cases Y = S.

Table 8. The Mossbauer parameters of the salts $[R_2P(Y)Y]_2.SnX_2$ at 78–90 K.

No.	R	Y	X	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	f'_{85} K	References
1	CH_3	O	Cl	0.07	—	1.20	—	—	[26]
2	$\frac{1}{2}(CH_3)(CH_3O)$	O	Cl	0.02	—	1.43	—	—	[26]
3	C_2H_5	S	Cl	0.73	—	1.18	—	—	[26]
	»	S	Cl	0.76	—	0.92	—	0.37	[96,97]
4	n-C_3H_7	S	Cl	0.71	—	1.46	—	—	[26]
	»	S	Cl	0.72	0.38	1.03	1.03	0.36	[96,97]
5	n-C_4H_9	O	Cl	0.00	—	1.45	—	—	[26]
	»	O	Cl	0.03	0.32	0.92	0.92	0.57	[96,97]
6	CH_3O	O	Cl	0.04	—	1.42	—	—	[26]
7	C_6H_5	O	Cl	0.05	—	1.43	—	—	[26]
8	C_6H_{11}	O	Cl	0.66	—	1.27	—	—	[26]
9	C_6H_5	O	Br	0.16	0.5	1.70	—	—	[26]
	»	O	Br	0.18	0.63	0.81	0.81	0.52	[96,97]
10	C_2H_5O	O	Br	0.13	0.53	0.86	0.87	—	[54]
11	C_2H_5O	O	Cl	0.02	—	1.33	—	—	[54]
12	iso-C_3H_7O	S	Cl	0.72	0.21	0.85	0.85	—	[110]
13	iso-C_3H_7O	S	Br	0.91	—	0.95	—	—	[110]
14	C_6H_5	O	I	0.40	0.65	0.87	0.87	—	[110]

Together with the Mössbauer spectra of the molecular complexes of tin halides with organophosphorus compounds, Mananov et al.[26] investigated the Mössbauer spectra of the salt products $[R'R''P(Y)Y]_2SnX_2$ (Table 8). The similarity

of the values of δ for the complexes $[R'R''P(O)O_2]SnCl_2$ to those for SnO_2 and $BaSnO_3$ suggests that the immediate environment of the tin atom in these complexes is also octahedral[52,53]. This is possible for the polymeric structure $[R'R''P(O)O]_2SnCl_2$, which is in full agreement with data obtained for the above and similar compounds by vibrational spectroscopic methods[54].

2. The Effects of Substituents

Together with the influence of the immediate environment of the tin atom in the complexes $[R'R''R'''P(Y)]_{2(1)}SnR_nX_{4-n}$, on the isomer shift, the study of the influence of the substituents in R'R''R'''P(Y) and SnR_nX_{4-n} on the isomer shifts of the complexes $L_2SnR_nX_{4-n}$ and the estimation of the degree of their influence on the population of the 5s shell of the tin atom are also of undoubted interest. The tendency towards a linear dependence of δ on the sum of the constants of the substituents in the ligand and the acceptor was noted in our earlier studies[26,31,32,40-42,54] and by Khrapov et al.[55] and Ford and Sams[56].

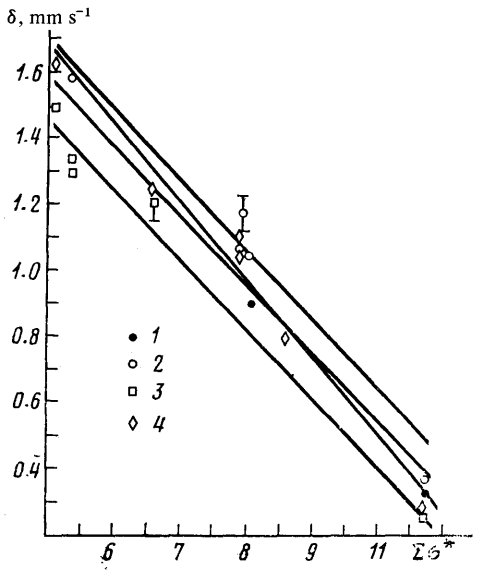


Figure 2. Relations between δ and $\Sigma\sigma^*_{R,Cl}$ for different complexes: 1) $[(CH_3)_2(CH_3O)P(O)]_2Sn(CH_3)_nCl_{4-n}$; 2) $[(CH_3)_2ClP(O)]_2SnR_nCl_{4-n}$ (R = CH_3, C_2H_5, or C_4H_9; 3) $[(n\text{-}C_4H_9)_3P(O)]_2SnR_nCl_{4-n}$ (R = CH_3, C_2H_5, or C_6H_5); 4) $[(C_6H_5)_3P(O)]_2SnR_nCl_{4-n}$ (R = C_4H_9 or C_6H_5).

Analysis of the dependence of δ on the sum of the Taft constants[57,58] of the substituents at the tin atom (Σσ*) leads to the following correlation equations† (Fig. 2):

$$[(CH_3)_2(CH_3O)P(O)]_2Sn(CH_3)_nX_{4-n}\ (n = 0, 1, 2;\ X = Cl, Br) \quad (3a)$$

$$\delta = -0.206\,\Sigma\sigma^* + 2.600\ (r = 0.984,\ S = 0.076,\ P \leqslant 0.0027,\ m = 4),$$

$$[(CH_3)_2ClP(O)]_2SnR_nX_{4-n}\ (n = 0, 1, 2;\ X = Cl, Br;\ R = CH_3, C_2H_5, C_4H_9) \quad (3b)$$

$$\delta = -0.213\,\Sigma\sigma^* + 2.770\ (r = 0.984,\ S = 0.0067,\ P < 0.0005,\ m = 7),$$

$$[(n\text{-}C_4H_9)_3P(O)]_2SnR_nCl_{4-n}\ (n = 0, 1, 2;\ R = CH_3, C_4H_9, C_6H_5) \quad (3c)$$

$$\delta = -0.210\,\Sigma\sigma^* + 2.501\ (r = 0.994,\ S = 0.057,\ P \leqslant 0.0008,\ m = 6),$$

$$[(C_6H_5)_3P(O)]_2SnR_nX_{4-n}\ (n = 0, 1, 2;\ X = Cl, Br;\ R = CH_3, C_4H_9, C_6H_5) \quad (3d)$$

$$\delta = -0.206\,\Sigma\sigma^* + 2.606\ (r = 0.972,\ S = 0.094,\ P < 0.0005,\ m = 8).$$

Evidently the coefficients representing the slopes in Eqns. (3a)–(3d) change insignificantly from series to series. This suggests that the Sn–Cl, Sn–Br, and Sn–C bonds make the main contribution to the population of the 5s valence shell of the tin atom in the complexes $[R'R''R'''P(O)]_{2(1)}\cdot SnR_nX_{4-n}$. This conclusion is consistent with those reached from the dependence of δ on χ[23,51] and with X-ray diffraction data[60].

The dependence of δ on Σσ* for the substituents at the tin atom and on the sum of the Kabachnik constants $(\Sigma\sigma^{ph})$[57,58] for the substituents at the phosphorus atom were examined by ourselves[40] to estimate the influence of the substituents at both tin and phosphorus atoms on the isomer shift in the Mössbauer spectra of the complexes $[R'R''R'''P(O)]_2SnR_nX_{4-n}$#:

$$\delta = -0.208\Sigma\sigma^* + 0.018\Sigma\sigma^{ph} + 2.635\ (r = 0.976,\ S = 0.095,\ P < 0.0005,\ m = 90). \quad (4)$$

Comparison of Eqns. (3) and (4) shows that allowance for the influence on δ by the nature of the substituents at the phosphorus atom together with that of the substituents at the tin atom does not introduce significant changes into the constant term and the coefficient of Σσ*.

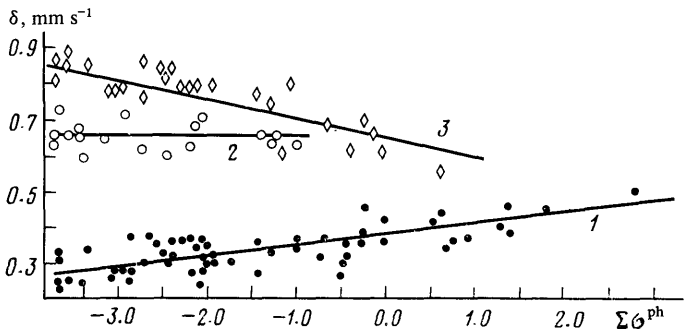


Figure 3. Relations between δ and $\Sigma\sigma^{ph}$ for the complexes $[R'R''R'''P(Y)]_2SnCl$: 1) Y = O; 2) Y = S; 3) Y = LEP.

Examination of the Mössbauer parameters of the complexes $[R'R''R'''P(Y)]_2SnCl_4$ shows that here too there is a tendency towards a linear variation of δ as a function of the sum of the constants of the substituents at the phosphorus atom[32,37,40,54] (Fig. 3):

$$[R'R''R'''P(O)]_2SnCl_4 \quad (5a)$$

$$\delta = 0.030\,\Sigma\sigma^{ph} + 0.381\ (r = 0.78,\ S = 0.039,\ P < 0.0005,\ m = 48),$$

† The two-parameter linear correlation equations have been obtained by the method of least squares[59]. Here and below the following notation has been adopted: r is the correlation coefficient, S the main error, P the level of significance, and m the number of experimental points.

Numerous correlation equations have been obtained by the Chebyshev method[61].

$$[R'R''R'''P(S)]_2SnCl_4 \quad (5b)$$
$$\delta = 0.66 \pm 0.06,$$
$$[R'R''R'''P]_2SnCl_4 \quad (5c)$$
$$\delta = 0.056\,\Sigma\sigma^{ph} + 0.646\,(r = 0.75, S = 0.061, P < 0.0005, m = 28),$$
$$[R'R''R'''P]_2SnR_nX_{4-n}\ (X = Cl, Br;\ n = 0.1;\ R = C_4H_9) \quad (5d)$$
$$\delta = -0.196\,\Sigma\sigma^* - 0.055\,\Sigma\sigma^{ph} + 2.768\,(r = 0.84,$$
$$S = 0.075,\ P < 0.0005,\ m = 32).$$

It is seen from Eqns.(5) that, as the nature of the donor centre varies from Y = O to Y = LEP (lone electron pair), the sign of the slope changes. In the reaction series investigated the sensitivity to the nature of the substituents at the phosphorus atom in the ligand decreases in the sequence $R'R''R'''P > R'R''R'''P(O) > R'R''R'''P(S)$. On the other hand, the sensitivity of the enthalpy of complex formation ΔH to the influence of the substituents decreases in the sequence $> R'R''R'''P(S) > R'R''R'''P > R'R''R'''P(O)$.[62,63] The observed difference can be due to small (in absolute magnitude) changes in ΔH in the series of complexes of thiophosphoryl compounds investigated by Mössbauer spectroscopy ($\Delta\Delta H \leq 5$ kcal mol^{-1}).[62,63]

Since the enthalpies of formation of the complexes increase as the "electron withdrawing" effect of the substituents at the phosphorus atom is reduced for all the $[R'R''R'''P(Y)]_2 \cdot SnX_4$ (Y = O, S, Se, or LEP) investigated[62,63], one of the possible causes of the difference between the values of ρ in Eqns.(4) and (5a) and in Eqns.(5c) and (5d) can apparently be an additional donor–acceptor interaction in $[R'R''R'''P]_2 \cdot SnX_4$ between the lone electron pair of the halogen atom in the acceptor molecule and the vacant d orbitals of the phosphorus atom of the ligand molecule[32,40,63]. With increase of the basicity of the phosphorus atom in $R'R''R'''P$, the strength of this interaction should increase, since the electron density transferred from the donor is concentrated at the halogen atoms[64,65], which leads to an increase of δ.

It is known[1,4,20,23,26,61] that tin halides are capable of forming trigonal-bipyramidal complexes as well as octahedral complexes. We therefore investigated[26,40] the influence of the substituents at the tin atom and of the organophosphorus ligand on δ in pentacoordinate complexes of tin halides. A correlation analysis of the isomer shifts in the Mössbauer spectra of the complexes $LSnR_3Cl$ (Table 5) as a function of the reaction constants of the substituents at the phosphorus and tin atoms was carried out for this purpose. The resulting correlation equations are

$$\delta = -0.076\,\Sigma\sigma^* + 1.648\,(r = 0.892, S = 0.036, P \leq 0.002, m = 8), \quad (6)$$
$$\delta = -0.093\,\Sigma\sigma^* + 0.020\,\Sigma\sigma^{ph} + 1.740\,(r = 0.919, S = 0.031, P < 0.0005,$$
$$m = 8). \quad (7)$$

It is seen from Eqns.(4), (5a), (6), and (7) that in the pentacoordinate compounds the sensitivity of the isomer shift to the nature of the substituents at the tin atom is much smaller than in the octahedral complexes, while the contribution of the organophosphorus ligand to δ remains virtually the same. We believe that the above finding is due to the fact that in the octahedral systems there is a relatively symmetrical distribution of ligands about the nucleus. On the other hand, in trigonal-bipyramidal complexes this symmetry breaks down in the axial plane (L–Sn–Cl), which apparently increases the sensitivity of δ to L.[40,60,67]

Thus the isomer shifts of the compounds $[R'R''R'''P(Y)]_{2(1)} \cdot SnR_nX_{4-n}$ are described satisfactorily in terms of the reaction constants of the substituents at the tin and phosphorus atoms. The correlation equations obtained can be used to predict the isomer shifts in the Mössbauer spectra of similar compounds and their other spectroscopic characteristics[23–44], to estimate the Taft and Kabachnik constants of the substituents in the ligand and acceptor, to determine the 5s valence shell populations of the tin atom in the complexes of tetra-alkyltin compounds and alkyltin halides with organophosphorus ligands, and to determine the coordination number of tin in the compounds investigated. Since the enthalpies of formation of the complexes $[R'R''R'''P(Y)]_{2(1)}SnR_nCl_{4-n}$, characterising the energies of the donor-acceptor interaction, are likewise linearly related to $\Sigma\sigma^*$ and $\Sigma\sigma^{ph}$,[62,63] Mössbauer spectroscopy can be used also to estimate the enthalpies of formation of the complexes of tetra-alkyltin compounds and alkyltin halides with $R'R''R'''P(Y)$.

Table 9. The Mössbauer parameters of complexes of tin tetrahalides with bidentate organophosphorus compounds $LSnX_4$ at 78–90 K.

No.	L	δ, mm s^{-1}	ΔE_Q, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	References
1	2,3-bis(diethylphosphono)butadiene	0.29	0.44	0.82	0.82	[96,97]
2	2,3-bis(diethylphosphono)butadiene	0.63	0.52	0.80	0.80	[96,97]
3	2,3-bis(diphenylphosphono)butadiene	0.35	0.66	—	—	[27]
4	2,3-bis(diphenylphosphono)butadiene	0.66	0.67	—	—	[27]
5	$(CH_3)_2P(S)P(CH_3)_2$	0.67	—	1.04	—	[28]
6	$(CH_3)_2P(S)(S)P(CH_3)_2$	0.70	—	1.13	—	[28]
7	*meso*-$CH_3C_2H_3P(S)(S)PCH_3C_2H_3$	0.70	—	1.10	—	[28]
8	racemate–$CH_3C_2H_3P(S)(S)PC_2H_3CH_3$	0.65	—	1.20	—	[28]
9	racemate–$CH_3C_2H_3P(S)(S)PC_2H_3CH_3$	0.67	—	0.99	—	[96,97]
10	$(CH_3O)_2P(O)(C_6H_5)_2$	0.42	—	1.30	—	[28]
11	$(C_6H_5)_2P(O)CH_2(C_6H_5)_2N$	0.38	0.45	0.83	0.83	[109]
12	$(C_6H_5)_2P(O)CH_2(C_6H_5)_2N$	0.60	0.45	0.99	0.99	[109]
13	$(C_6H_5)_2P(S)CH_2(C_6H_5)_2N$	0.52	0.44	0.84	0.84	[109]
14	$(C_6H_5)_2P(CH_2)(C_2H_5)_2N$	0.48	0.46	0.88	0.88	[109]
15	(α-pyridyl)P(O)Cl	0.35	—	1.00	—	[109]
16	$(C_6H_5)_2P(S)CH_2CH_2C_5H_4N$	0.45	—	1.00	—	[109]
17	$(C_6H_5)_2PCH_2CH_2C_5H_4N$	0.69	—	0.97	—	[109]
18	$(C_2H_5O)_2P(O)CH_2CH_2C_5H_4N$	0.43	—	1.08	—	[109]
		0.42	0.40	0.96	0.96	[96,97]
19	$(C_2H_5O)_2P(O)CH_2CH_2C_5H_4N$	0.70	0.46	0.96	0.96	[109]
20	$(C_6H_5)_2P(O)(O)P(C_6H_5)_2$	0.39	0.41	0.88	0.88	[110]
21	$(CH_3)_2P(O)(O)P(CH_3)_2$	0.28	0.41	0.88	0.88	[110]
22	$(C_6H_5)_2P(O)(O)P(C_6H_5)_2$	0.73	0.51	0.85	0.85	[110]
23	$(C_6H_5O)_2P(O)(O)P(C_6H_5O)_2$	0.37	0.60	0.94	0.94	[110]
24	$(CH_3)(C_6H_5)P(S)(S)P(C_6H_5)(CH_3)$	0.67	—	0.99	—	[96,97]

Note. X = Br in complexes 2,4,12,19, and 22, while in the remaining cases X = Cl. $f'_{85K} = 0.23$, 0.24, 0.22, 0.23, 0.21, and 0.22 for complexes 1,2,9,18, and 24 respectively.

III. THE QUADRUPOLE SPLITTING

1. The Influence of the Geometrical Structure of the Complexes

The electrical quadrupole interaction in the Mössbauer spectra is manifested by a fine structure whose components correspond to the gamma transitions between the split levels. For the ^{57}Fe and ^{119}Sn Mössbauer nuclei, where the spins of the excited and ground states are 3/2 and 1/2 respectively, this hyperfine structure appears in the spectrum in the form of a doublet. The appearance of the doublet is associated with the splitting of only the upper level into two states with spin projections $m_I = \pm 3/2$ and $m_I = \pm 1/2$, while the ground state with a spin of 1/2 is not split[1,4]. A typical Mössbauer spectrum with quadrupole splitting is presented in Fig.4.

The energy gap between the split sublevels (or the quadrupole splitting ΔE) can be represented as follows for ^{57}Fe and ^{119}Sn[1,4]:

$$\Delta E = -\frac{1}{2}e^2qQ\left(1 + \frac{1}{3}\eta^2\right)^{1/2}, \quad (8)$$

where Q is the quadrupole moment of the nucleus, characterising the deviation of the distribution of the averaged nuclear charge density in the state with $I = 3/2$ (for ^{57}Fe and ^{119}Sn) from spherical symmetry, $q = V_{zz}/e$ the electric field gradient (EFG) at the Mössbauer nucleus, $\eta = (V_{xx} - V_{yy})/V_{zz}$ the asymmetry parameter, and V_{xx}, V_{yy}, and V_{zz} are the principal components of the diagonalised EFG tensor chosen so that the condition $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$, for which the values of η are in the range $0 \leq \eta \leq 1$, holds.

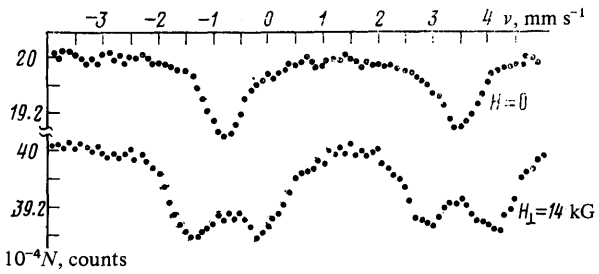


Figure 4. The Mössbauer spectra of $\{[(CH_3)_2N]_3P(O)\}_2 . Sn(CH_3)_2Cl_2$ for $H = 0$ and $H = 14$ kG.

The valence shell of the free tin atom has the structure $5s^25p^2$, but, since s electrons have the spherical symmetry (without taking shielding into account), they do not give rise to an electric field gradient at the nucleus and the EFG for ^{119}Sn depends on the distribution of p electrons. For different types of hybridisation, s and d electrons can contribute to the EFG,[1,4] but the nature of the p bond is decisive; consequently ΔE makes it possible to estimate the electron distribution in the valence p shell.

Like the isomer shift, the quadrupole splitting is a characteristic parameter for the determination of the valence state of the tin atom. In those cases where tin is in the bivalent state the absorption spectra have a doublet structure[1,4,17,68,69] ($\Delta E = 0.5-2.5$ mm s^{-1}) [with the exception of $SnCl_2$,[1,48] owing to the presence of unbalanced p electrons in tin(II) compounds giving rise to an EFG at the nucleus].

In compounds of quadrivalent tin there is a possibility of the formation of four (sp^3 hybridisation) or six (sp^3d^2 hybridisation) equivalent bonds, which ensure equal populations of the p_x, p_y, and p_z states and as a consequence the absence of a field gradient at the ^{119}Sn nucleus. On the other hand, the upper limit of the variation of ΔE for tin(IV) compounds can be greater than for bivalent tin compounds: $\Delta E = 0-5.4$ mm s^{-1}.[1,4,10-12,17-43,70] Table 1 presents the limits of the variation of the quadrupole splitting in the Mössbauer spectra of the complexes $[R'R''R'''P(Y)]_{2(1)} . SnR_nX_{4-n}$.

Analysis of the Mössbauer spectroscopic data in Tables 1–9, combined with data for the geometrical structures[10,26,60,67,71] and the enthalpies of formation[62,63] of the complexes $[R'R''R'''P(Y)]_2SnX_4$ and the complexes of organophosphorus compounds with alkyltin halides, shows that the following factors make the main contributions to the generation of the electric field gradient at the tin nucleus and hence to the quadrupole splitting ΔE for compounds of this type[42]: (1) the geometrical configuration of the complexes (*cis–trans* isomerism), (2) the spatial configuration of the organophosphorus ligand, (3) the electron-donating capacity of the atom Y in the P=Y group and the nature of the substituent R_nX_{4-n} atom.

We shall consider in greater detail the influence of each factor on the ΔE for the compounds investigated.

Analysis of the data in Table 1 shows that, for complexes of organophosphorus compounds with tin halides, the Mössbauer parameters of only the compounds formed as a result of the electron-donating properties of the oxygen of the phosphoryl group, namely $[R'R''R'''P(O)]_2SnX_4$, and of the phosphorus atom, namely $[R'R''R'''P]_2SnX_4$, are sensitive to structural isomerism. For the *trans*-complexes of phosphoryl compounds, the quadrupole splitting varies from 0.5 to 1.6 mm s^{-1}, while for the *cis*–compounds it is as a rule less than 0.5 mm s^{-1} [the *cis*-complexes of tin(IV) chloride with phosphoryl chloride and the dichlorides of phosphoric and phosphonic acid are an exception]. A change in the geometry of the complexes $[R'R''R'''P(O)]_2SnX_4$ from *trans* to *cis* entails a decrease of ΔE by a factor of two[72,73] (subject to the condition that the $\Sigma\sigma^{ph}$ and ΣE_S for the substituents in the ligand are approximately equal). This is illustrated fairly clearly by the Mössbauer spectra of the following complexes (Tables 2 and 3): *cis*-$[(C_4H_9O)_2(SCH_3)P(O)]_2SnCl_4$ ($\Delta E = 0.41$ mm s^{-1}), *trans*-$[(n\text{-}C_3H_7O)_2(SCH_3)P(O)]_2SnCl_4$ ($\Delta E = 0.83$ mm s^{-1}), *cis*-$[(C_6H_5)_2(CH_3)P(O)]_2SnBr_4$ ($\Delta E = 0.37$ mm s^{-1}), and *trans*-$[(C_6H_5)_2(CH_3)P(O)]_2SnCl_4$ ($\Delta E = 0.68$ mm s^{-1}).

For complexes with similar enthalpies of formation (with similar values of $\Sigma\sigma^{ph}$ for the substituents at the phosphorus atom), ΔE increases with increase of the bulk of the substituents at the phosphorus atom—for example, $\Delta E = 0.46$ mm s^{-1} for *trans*-$[(C_2H_5)_2ClP(O)]_2SnCl_4$, $\Delta E = 0.83$ mm s^{-1} for *trans*-$[(n\text{-}C_3H_7O)_2(SCH_3)P(O)]_2SnCl_4$, and $\Delta E = 1.06$ mm s^{-1} for *trans*-$[(iso\text{-}C_3H_7O)_2(SCH_3)P(O)]_2SnCl_4$ (Table 2), i.e. an increase of the bulk of the groups at the phosphorus atom in the ligands $R'R''R'''P(O)$ induces an EFG at the tin nuclei both as a result of the geometrical isomerism of the complexes and the steric effect[11,25,31].

The possibility of using the ΔE for the determination of the geometrical structure of complexes of tetra-alkyltin halides with phosphoryl compounds is also indicated by the finding that the structure of the complexes $[R'R''R'''P(O)]_2 . SnR_nX_{4-n}$ ($n = 0-2$) is described satisfactorily on the basis of the point charge model[22,74]. According to this model, the overall EFG (q) can be represented by the sum of the independent contributions of each ligand[75]. Since $\Delta E \propto q$, the principle of additivity can be extended also to the quadrupole splitting and can be regarded as the sum of the partial quadrupole splittings (*PQS*) of the ligands.

Table 10 presents the values of *PQS* for certain organophosphorus ligands in the complexes $L_2Sn(CH_3)_nCl_{4-n}$, which we calculated by the method proposed previously[75,76], and the ΔE for these complexes. The Table shows that in most cases there is a satisfactory agreement between the calculated and experimental ΔE.

The Mössbauer spectra of the complexes $[R'R''R'''P]_2SnCl_4$ having the *trans*-structure also exhibit quadrupole splitting (Tables 1 and 6). However, in the Mössbauer spectra of the $[R'R''R'''P]_2SnCl_4$ series ΔE diminishes with increase of the bulk of the ligands—for example, $\Delta E = 1.02$ mm s^{-1} for *trans*-$[(n\text{-}C_4H_9)_3P]_2SnCl_4$ and $\Delta E = 0.58$ mm s^{-1} for *trans*-$\{[(CH_3)_2N]_3P\}_2SnCl_4$ (see Table 6), while the opposite behaviour obtains for the complexes $[R'R''R'''P(O)]_2SnCl_4$. The observed difference in the influence of the steric effects of the substituents at the phosphorus atom on the ΔE for the complexes $[R'R''R'''P]_2SnCl_4$ and $[R'R''R'''P(O)]_2SnCl_4$ can also be explained by the additional intramolecular interaction in $[R'R''R'''P]_2SnCl_4$ due to the d orbitals of the phosphorus atom[32,63]. With increase of the bulk of the substituent at the phosphorus atom in $R'R''R'''P$, the strength of this interaction should decrease, which should lead to a decrease of ΔE.

In the Mössbauer spectra of the complexes formed as a result of the electron-donating properties of the S and Se atoms, the quadrupole splitting is small or altogether absent, although the complexes have the *trans*-structure (Tables 1 and 7). Together with geometrical and steric factors the nature of the substituents at the phosphorus and tin atoms in the ligand and acceptor respectively influence significantly the quadrupole splitting.

Table 10. The calculated (ΔE_t) and experimental (ΔE_e) quadrupole splittings for the complexes $L_2Sn(CH_3)_nX_{4-n}$.

No.	L	n	ΔE_e, mm s^{-1}	ΔE_t, mm s^{-1}
1	$(CH_3)_3P(O)$	0	0.51	+0.22
2	$(CH_3)_3P(O)$	2	4.30	+4.32
3	$(CH_3)_2(CH_3O)P(O)$	0	0.25	−0.56 (*trans*) ; +0.28 (*cis*)
4	$(CH_3)_2(CH_3O)P(O)$	0	0.40	+0.26
5	$(CH_3)_2(CH_3O)P(O)$	1	2.20	+2.37
6	$(CH_3)_2(CH_3O)P(O)$	2	4.37	+4.39
7	$(CH_3)_2ClP(O)$	0	0.57	−0.38 (*trans*) ; +0.19 (*cis*)
8	$(CH_3)_2ClP(O)$	0	0.35	−0.34
9	$(CH_3)_2ClP(O)$	1	2.26	+2.25
10	$(CH_3)_2ClP(O)$	2	4.10	+4.28
11	$[(CH_3)_2N]_3P(O)$	0	0.69	−0.52
12	$[(CH_3)_2N]_3P(O)$	0	0.93	−0.48
13	$[(CH_3)_2N]_3P(O)$	1	2.35	+2.34
14	$[(CH_3)_2N]_3P(O)$	2	4.36	+4.36
15	$(n\text{-}C_4H_9)_3P(O)$	0	0.25	+0.16
16	$(n\text{-}C_4H_9)_3P(O)$	0	0.00	+0.14
17	$(n\text{-}C_4H_9)_3P(O)$	2	4.15	+4.25

Note. X = Br in complexes 4,8,12, and 16, while in the remaining cases X = Cl. The *cis*-structure is characteristic of complexes 1 and 15, complexes 3 and 7 consist of mixtures of *cis*- and *trans*-isomers, while the *trans*-structure is characteristic of the remaining complexes[65,66]. The partial quadrupole splittings (PQS_L) for complexes 1,3,7,11, and 15 are respectively −0.10, −0.13, −0.085, −0.12,[22] and −0.07 mm s^{-1}. The values of PQS for CH_3, Cl, and Br are 1.03,[22] 0.01, and 0.00 mm s^{-1} respectively.

Before considering the nature of the influence of the electronic effects of the substituents at the phosphorus and tin atoms on ΔE, we should point out that, as a consequence of the large number of variables determining the ΔE for the compounds investigated, Herber's rule does not hold for the complexes $[R'R''R'''P(Y)]_2SnX_4$.[77] According to this rule, the ratio of the quadrupole splitting to the isomer shift $\rho = \Delta E/\delta$ is determined by the coordination number of tin. If $\rho < 1.8$, then the tin atom is tetracoordinated, while for $\rho > 2.1$ the environment of the tin atom is octahedral or trigonal-bipyramidal. The data summarised in Table 1 show that Herber's rule is valid only for the *trans*-complexes of organophosphorus compounds with tin tetrahalides formed due to the electron-donating properties of the phosphoryl oxygen.

2. Chemical Effects

Since, like the isomer effect, the quadrupole splitting characterises the electronic structure of the Mössbauer atom, it is natural to expect that[26,31,36,41,42,47,49,51,54,77-82] the electronegativity of the ligands and the electronic effects of the substituents in the ligand will exert a definite influence on ΔE.

Fig. 5 illustrates graphically the dependence of ΔE on $\Sigma\chi_{R,X}$ for the complexes $L_2Sn(CH_3)_nCl_{4-n}$. Evidently the quadrupole splitting increases with decrease of $\Sigma\chi_{R,X}$, i.e. the decrease of $\Sigma\chi_{R,X}$ for the substituents at the tin atom in the octahedral complexes $L_2Sn(CH_3)_nCl_{4-n}$ increases the asymmetry of the p electrons at the tin nucleus. The data for the trigonal-bipyramidal complexes $LSnR_3Cl$ deviate from the correlations presented in Fig. 5, which permits the use of ΔE together with δ for the determination of the coordination number of tin in compounds of this type[26,54].

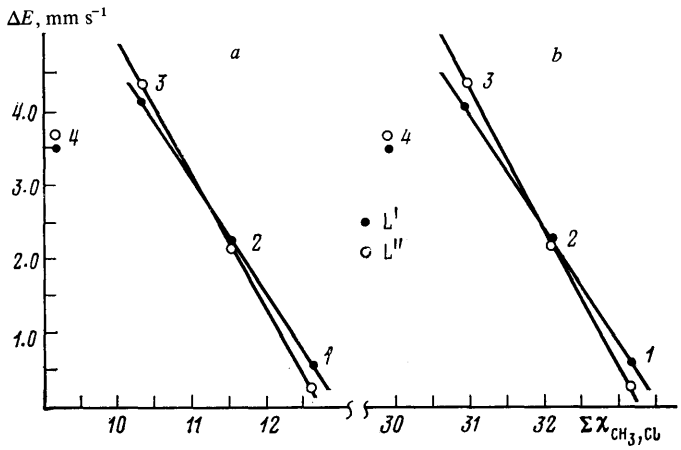


Figure 5. Relations between ΔE and $\Sigma\chi_{R,Cl}$ for the complexes $L_2Sn(CH_3)_nCl_{4-n}$, $n = 0,1,2$ [$L' = (CH_3)_2ClP(O)$; $L'' = (CH_3)_2(CH_3O)P(O)$, $n = 1$ (*1*), 1 (*2*), 2 (*3*), 3 (*4*)]; *a*) Pauling electronegativity; *b*) Mulliken electronegativity.

The influence of the substituents at the tin and phosphorus atoms on the quadrupole splitting can also be described with the aid of the substituent reaction constants σ^* and σ^{ph}.[26,31,41,42,54,78,80,83,84] The above analysis of the correlation between the ΔE and the constants $\Sigma\sigma^*$ and $\Sigma\sigma^{ph}$ shows that they are linear. The relations between the ΔE and the $\Sigma\sigma^*$ for the complexes $L_2SnR_nCl_{4-n}$ are as follows:

$[(CH_3)_2(CH_3O)P(O)]_2Sn(CH_3)_nCl_{4-n}$ ($n = 0, 1, 2$) (9a)

$\Delta E = -0.77\,\Sigma\sigma^* + 8.44$ ($r = 0.995$, $S = 0.17$, $P < 0.0025$, $m = 4$), $[(CH_3)_2ClP(O)]_2SnR_nCl_{4-n}$ ($n = 0, 1, 2$; $R = CH_3, C_2H_5, C_4H_9$) (9b)

$\Delta E = -0.71\,\Sigma\sigma^* + 7.94$ ($r = 0.992$, $S = 0.167$, $P < 0.0005$, $m = 6$), $[(n\text{-}C_4H_9)_3P(O)]_2SnR_nCl_{4-n}$ ($n = 0, 1, 2$; $R = CH_3, C_4H_9, C_6H_5$)

$\Delta E = -0.75\,\Sigma\sigma^* + 8.28$ ($r = 0.992$, $S = 0.24$, $P < 0.0005$, $m = 6$), (9c)

$[(C_6H_5)_3P(O)]_2SnR_nCl_{4-n}$ ($n = 0, 1, 2$; $R = C_4H_9, C_6H_5$) (9d)

$\Delta E = 0.69\,\Sigma\sigma^* + 7.91$ ($r = -0.970$, $S = 0.30$, $P < 0.001$, $m = 6$).

The results show that ΔE is more sensitive to the nature of the organophosphorus ligand than δ.[32]

Since ΔE and δ vary linearly with $\Sigma\sigma^*$, there is also a linear relation between these two Mössbauer parameters[1,4,26,41,42,54,82]:

$[(CH_3)_2(CH_3O)P(O)]_2Sn(CH_3)_nCl_{4-n}$ ($n = 0, 1, 2$), (10a)

$\delta = 0.28\,\Delta E + 0.27$ ($r = 0.997$, $S = 0.04$, $P < 0.0025$, $m = 4$), $[(CH_3)_2ClP(O)]_2SnR_nCl_{4-n}$ ($n = 0, 1, 2$; $R = CH_3, C_2H_5, C_4H_9$) (10b)

$\delta = 0.32\,\Delta E + 0.31$ ($r = 0.982$, $S = 0.08$, $P < 0.0005$, $m = 6$),

$$[(n\text{-}C_4H_9)_3P(O)]_2SnR_nCl_{4-n}\ (n = 0, 2;\ R = CH_3, C_4H_9, C_6H_5) \quad (10c)$$

$$\delta = 0.27\,\Delta E + 0.21\ (r = 0.990, S = 0.07, P < 0.0005, m = 6),$$

$$[(C_6H_5)_3P(O)]_2SnR_nCl_{4-n}\ (n = 0, 1, 2;\ R = C_4H_9, C_6H_5) \quad (10d)$$

$$\delta = 0.32\,\Delta E + 0.21\ (r = 0.943, S = 0.14, P < 0.0025, m = 6).$$

The tendency towards a linear variation of ΔE with $\Sigma\sigma^{ph}$ for the substituents at the phosphorus atom of the ligand has also been observed[36,42,54] for the complexes of tin tetrachloride with R'R"R'"P(Y). Fig.6 illustrates graphically the relations between the ΔE and the $\Sigma\sigma^{ph}$ for the *trans*-complexes $[R'R''R'''P(Y)]_2SnCl_4$ (Y = O or LEP). We may note that the hypothesis of Phillip et al.[10] that the quadrupole splitting for the tin(IV) bromide complexes should be greater than for the tin(IV) chloride complexes does not hold for the tin tetrahalide complexes of R'R"R'"P(Y). In the vast majority of cases the upper limit of the variation of ΔE for the bromides is much smaller than for the chlorides (Tables 1–3).

For the *trans*-complexes of phosphoryl compounds with substituents at the phosphorus atom such as C_2H_5, C_6H_5, and CH_3O the quantity ΔE is almost independent of the strength of the donor–acceptor interaction (Y=O) (see Fig.6*a*, lower straight line):

$$\Delta E = 0.50 \pm 0.10\ (m = 28). \quad (11a)$$

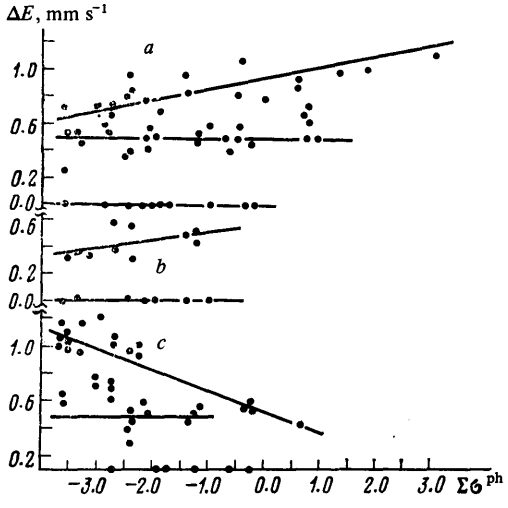


Figure 6. Relations between ΔE and $\Sigma\sigma^{ph}$ for the complexes $[R'R''R'''P(Y)]_2SnCl_4$: *a*) Y = O; *b*) Y = S; *c*) Y = LEP.

The absence of an influence by the nature of the substituents at the phosphorus atom on ΔE has been noted (see Fig.6c) also for certain complexes formed owing to the electron-donating properties of the phosphorus atom for Y=LEP:

$$\Delta E = 0.48 \pm 0.10\ (m = 17). \quad (11b)$$

On the other hand, for complexes containing the $(CH_3)_2N$, $(CH_3)_2CH$, and $(CH_3)_2CHO$ groups, ΔE varies approximately linearly with the $\Sigma\sigma^{ph}$ for the substituents at the phosphorus atom (Y=O):

$$\Delta E = 0.09\,\Sigma\sigma^{ph} + 0.95\ (r = 0.74, S = 0.15, P < 0.0005, m = 27). \quad (12)$$

On passing from the complexes of phosphoryl compounds to those of thiophosphoryl compounds and the complexes formed owing to the electron-donating properties of the phosphorus atom, the slope (Fig.6c) in the correlation equations for Y=LEP diminishes and then changes sign:

$$\Delta E = -0.15\,\Sigma\sigma^{ph} + 0.52\ (r = 0.87, S = 0.12, P < 0.0005, m = 21). \quad (13)$$

However, the behaviour of ΔE and of the isomer shift δ in the Mössbauer spectra of the $[R'R''R'''P(Y)]_2SnCl_4$ series investigated indicates in our view yet again an additional donor–acceptor interaction between the lone electron pair of the halogen atom in the acceptor molecule and the vacant *d* orbitals of the phosphorus atom in the ligand molecule in the complexes $[R'R''R'''P]_2SnCl_4$.[32,63] Comparison of the absolute slopes of the plots of ΔE against $\Sigma\sigma^{ph}$ for different series of complexes shows that the sensitivity of ΔE to the influence of the substituents in different classes of organic compounds is different and varies in the sequence R'R"R'"P > R'R"R'"P(O) > R'R"R'"P(S).

Correlation analysis of the ΔE for the Mössbauer spectra of the trigonal-bipyramidal complexes shows that here too there is a linear variation of the quadrupole splitting with $\Sigma\sigma^*$ and $\Sigma\sigma^{ph}$ and with the isomer shift[41,42]:

$$[R'R''P(O)]\,SnR_3Cl \quad (14a)$$

$$\Delta E = -0.205\,\Sigma\sigma^* + 4.087\ (r = 0.970, S = 0.047, P < 0.0005, m = 8),$$

$$\Delta E = -0.203\,\Sigma\sigma^* + 0.005\,\Sigma\sigma^{ph} + 4\,085\ (r = 0.972, S = 0.045, P < 0.0005, m = 8), \quad (14b)$$

$$\delta = 0.30\,\Delta E + 0.37\ (r = 0.730,\ S = 0.06, P < 0.05, m = 6). \quad (15)$$

We may note that the dependence of ΔE on $\Sigma\sigma^*$ agrees, as regards the sign of the slope, with the analogous relation for hexacoordinate compounds [Eqns.(9) and (14)], while the literature data[78,80,83,84] indicate the opposite tendency. On the other hand, the relations between δ and ΔE agree not only as regards sign but also as regards the slopes [see Eqns.(9) and (15)].

The above expressions do not take into account the sign of the EFG. It follows from theoretical and experimental studies[85–91] on other organotin compounds that the quadrupole splitting should be positive for the *trans*-octahedral complexes and negative for the pentacoordinate complexes. The results[42] of a study of the complexes of alkyltin halides with organophosphorus ligands agree with those published previously for the *trans*-octahedral compounds[85–91]. Thus Fig.4 presents the Mössbauer spectrum of the complex $\{[(CH_3)_2N]_3P(O)\}_2Sn(CH_3)_2Cl_2$ with and without superposition of an external magnetic field at right angles to the observation axis. It follows from the resulting spectrum, in conformity with the conclusions of earlier investigations[86,87,89], that the quadrupole splitting for the above compound is greater than zero and the electric field gradient is therefore negative.

IV. THE PROBABILITY OF THE MÖSSBAUER EFFECT

In the vast majority of studies where Mössbauer spectroscopy has been used to solve various problems of coordination and organoelemental compounds, only parameters such as δ and ΔE are discussed; on the other hand, the data for the probability of the recoil-less absorption of γ-quanta (f') available in the literature are extremely limited[1,4,51,92–94]. Two studies have been published on f' in the Mössbauer spectra of complexes of tin tetrahalides with organoelemental ligands[12,92]. The limited nature of the experimental data can be explained both by the complexity of the theoretical interpretation of the results and by certain experimental difficulties[1,4,6,7].

The probability of the Mössbauer effect depends on the dynamics of the crystal lattice, i.e. on its elastic properties, and a specific model of the crystal must be selected for an examination of the dependence of f' on the macroscopic parameters of the solid. It has been shown[1,92,94] that for organometallic compounds the most convenient model of the molecular crystal is one within the framework of which it is assumed that the probability of the Mössbauer effect can be formulated to a first approximation as $f' = f'_M f'_c$, where f'_M and f'_c are the probabilities that the intramolecular and intermolecular vibrations respectively will not be excited[1].

The atomic vibrations in the molecule occur in the high-frequency range; it can be assumed that f'_M is fairly large (~1) at a low temperature and depends only slightly on the latter. The quantity f'_c, described by the Debye model[1,92], depends greatly on the temperature and makes the main contribution to the temperature variation of f'. The probability of the Mössbauer effect then increases and its temperature dependence diminishes when stronger chemical bonds are formed between individual molecules; the formation of such bonds is usually coupled with an increase of the coordination number of tin[9,95].

Thus it is evident that f' makes it possible to infer the relative strengths of the intermolecular interactions and the coordination number of the Mössbauer atom; the principal consequence of the molecular crystal model is a linear dependence of $\ln f'$ on the temperature T in the high-temperature approximation ($T > \theta/2$, where θ is the characteristic temperature of the given crystal), because f'_c is an exponential function of T. Such a dependence of the intensity and area of the Mössbauer spectrum (which depend directly on f') was demonstrated previously for different organotin compounds[51, 92-94]. However, the authors[12] failed to observe a linear dependence of $\ln f'$ on T, which led them to the conclusion that the molecular crystal model is inapplicable to complexes of tin halides with organic ligands.

The results of our studies[96,97] on complexes of tin halides with organophosphorus ligands, presented in Tables 2–9, show that the probabilities of the Mössbauer effect for these systems lie within fairly broad limits: 0.15–0.58. Examination of the complexes of tin halides with mono- and bi-dentate ligands shows that the f' for these compounds are approximately the same.

The replacement of tin(IV) chloride as the acceptor by tin(IV) bromide also does not alter appreciably the probability of the Mössbauer effect, while other Mössbauer parameters (δ and ΔE) for the complexes $L_2(L')SnCl_4$ and $L_2(L')SnBr_4$ are significantly different. If the nature of the acceptor does not have an appreciable influence on f', then a tendency towards an increase of f' in the following sequence can be observed when the nature of the donor atom in the $[R'R''R'''P(Y)]_2SnX_4$ and $[R'R''P(Y)Y]_2SnX_2$ compounds investigated is altered: P : ≅ P=O > P=S (for R', R'', R''' = const.). The enthalpies of formation of the compounds vary in the same sequence[62,63].

It is noteworthy that the Mössbauer spectra of the complexes $[R'R''R'''P]_2SnCl_4$ exhibit a parallel variation of f' and ΔE, which is apparently also associated with the occurrence of an additional donor–acceptor interaction in these complexes. The highest value has been observed for the salts $[R_2P(O)O]_2SnX_2$. The probabilities of the recoil-less absorption for these substances are close to the values of f' for octahedral compounds such as SnO_2 and $BaSnO_3$.[98,99] Within the framework of the molecular crystal model, this can be accounted for by the considerable strengthening of the intermolecular bonds in such systems (compared with molecular crystals of the type L_2SnX_4) and we believe serves as additional confirmation of the octahedral structure of the given compounds[96,97].

In the case of the dithio-analogues $[R_2P(S)S]_2SnX_2$, having the octahedral bischelate structure, the probability of the Mössbauer effect is much smaller than for $R_2P(O)O]_2SnX_2$, which is apparently associated with the weaker donor–acceptor interaction in complexes formed via the thiophosphoryl sulphur[63,96,97,100,101] compared with the complexes formed via the phosphoryl oxygen.

We shall now consider the temperature variation of $\ln f'$ presented in Table 11 and in Fig. 7.[97] The data in Table 11 and Fig. 7 show that, in all the instances considered, a linear relation§ between $\ln f'(\ln c_A)$ and T holds with a satisfactory degree of reliability (a high level of significance), i.e. contrary to the data of Varnek et al.,[12] the molecular crystal model is applicable to the compounds $[R'R''R'''P(Y)]_2SnR_n \cdot X_{4-n}$ and $[R'R''P(Y)Y]_2SnX_2$, as well as other organotin compounds[9,50,92-94].

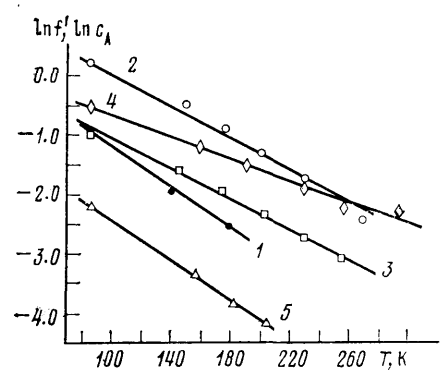


Figure 7. Temperature variation of $\ln f'$ and $\ln c_A$: 1) $\{[(CH_3)_2N]_3P(O)\}SnBr_4$; 2) $\{[(CH_3)_2N](C_6H_5)_2P(S)\}_2SnCl_4$; 3) $[(C_6H_5)_3P]_2SnCl_4$; 4) $[(n\text{-}C_4H_9)_2P(O)O]_2SnCl_4$; 5) $[(iso\text{-}C_3H_7O)_2P(S)S]_2SnCl_2$.

Table 11. The parameters of the correlations $\ln f' = 10^{-3}aT + b$ for the complexes[97].

No.	Compound	t, °C	m	$-a$	b	r	S	P	M
1	$\{[(CH_3)_2N]_3P(O)\}_2SnCl_4$	85—257	6	14.2	0.42	0.975	0.202	≤0.005	619
2	$\{[(CH_3)_2N]_3P(O)\}_2SnBr_4$	85—179	3	17.4	0.54	0.998	0.045	≤0.047	797
3	$[(C_6H_5)_2(CH_3)_2NP(O)]_2 \cdot Sn(CH_3)Cl_3$	85—266	7	16.4	0.48	0.969	0.251	<0.0005	734
4	$[(CH_3O)_3(C_6H_5)P(O)]_2SnCl_4$	85—248	6	17.4	0.60	0.962	0.291	≤0.009	633
5	$[(CH_3)_2N(C_6H_5)_2P(S)]_2SnCl_4$	85—268	6	14.9	1.66	0.994	0.099	<0.0005	783
6	$[(C_6H_5)_2ClP]_2SnCl_4$	90—232	5	27.5	3.64	0.953	0.415	≤0.013	762
7	$[(C_6H_5)_3P]_2SnCl_4$	85—253	6	12.8	0.19	0.994	0.079	<0.0005	785
8	$[(C_6H_5)_2ClP]_2SnCl_4$	85—265	7	15.7	0.46	0.974	0.283	<0.0005	510
9	$[(CH_3)_2N]_3P]_2SnCl_4$	85—235	6	14.1	0.165	0.980	0.137	<0.0005	587
10	$[(n\text{-}C_4H_9)_3P]_2SnCl_4$	85—212	5	22.5	0.65	0.982	0.206	≤0.01	665
11	DEPB.$SnBr_4$	85—229	4	21.1	0.685	0.965	0.300	≤0.04	765
12	$[(n\text{-}C_4H_9)_2P(O)O]_2SnCl_2$	85—292	6	9.05	0.21	0.988	0.096	<0.0005	658
13	$[(C_6H_5)_2P(O)O]_2SnBr_2$	85—296	8	9.26	0.29	0.947	0.205	<0.0005	713
14	$[(iso\text{-}C_3H_7O)_2P(S)S]_2SnCl_2$	85—205	4	17.8	1.38	0.995	0.085	<0.0005	616
15	$[(n\text{-}C_3H_7)_2P(S)S]_2SnCl_2$	85—229	5	20.1	0.67	0.989	0.154	≤0.0015	552
16	$[(C_2H_5)_2P(S)S]_2SnCl_2$	85—261	5	20.8	0.98	0.974	0.297	0.005	490

Note. M is the molecular weight and DEPB = 2,3-bis(diethylphosphono)butadiene. The relation $\ln c_A = 10^{-3}aT + b'$ is presented for compounds 5, 6, and 14.

§ Here c_A is the effective thickness of the absorber.

As mentioned above, according to this model one can write in terms of the high-temperature approximation[1,92]

$$\ln f' \propto \frac{3E_\gamma^2}{Mc^2} \cdot \frac{T}{k\theta^2}, \qquad (16)$$

where E_γ is the energy of the Mössbauer transition of the nucleus from the excited to the ground state, M the mass of the entire complex structural unit, c the velocity of light, k the Boltzmann constant, and θ the Debye temperature.

According to Eqn.(16), the slope of the $\ln f'(T)$ straight line is

$$a \cdot 10^{-3} = \frac{3E_\gamma^2}{Mc^2} \cdot \frac{1}{k\theta^2}. \qquad (17)$$

Hence it follows that, subject to the condition that the nature of the intermolecular bonds is the same ($\theta_M \cong$ const.), the coefficient representing the slope in the correlation equations should depend on the mass of the structural unit for different compounds. Such relations were observed previously for certain organotin compounds[102,103]. An analogous tendency towards a decrease of the absolute value of the slope with increasing mass may be noted also for certain complexes of tin halides with organophosphorus ligands (Table 11). This is manifested particularly clearly for the compounds $[R_2'P(S)S]_2SnCl_2$.

Comparison of the temperature variations of the $\ln f'$ for the tin(IV) chloride and bromide complexes shows that the probability of the Mössbauer effect for the bromides is more sensitive to temperature, since the corresponding slopes are greater in absolute magnitude than for the corresponding tin(IV) chloride compounds. The relatively small change of the slope as the nature of the acceptor is altered can be understood when account is taken of Eqn.(17). Consequently, despite the identical value of f' at 85 K, analysis of the temperature variations permits the conclusion that the tin(IV) bromide complexes have weaker chemical bonds. This conclusion is consistent with the results of studies by other methods[44,62,63]. The data presented show that, in contrast to f', the temperature variation of the probability of the Mössbauer effect is sensitive both to the nature of the ligand and to the nature of the halogen atom in the acceptor molecules. The sensitivity of the temperature variation of $\ln f'$ to the nature of the ligand varies in the following sequence: $R_2P(S)S^- \geq R'R''R'''P > R'R''R'''P(O) > R'R''P(O)O^-$ (Table 11).

Thus the study of the probability of the recoil-less absorption of gamma-quanta and its temperature variation for the complexes of tetra-alkyltin compounds and alkyltin halides with organophosphorus ligands yields interesting additional information about the properties and structures of these substances.

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Ul'yanov-Lenin Kazan State University