

Group 4 Organometallic Compounds. Part 8.† Preparation and Mössbauer Spectra of Five- and Six-co-ordinate Di- and Tri-organotin Compounds containing Mixed Phenyl and Butyl Groups on Tin

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Mössbauer spectroscopic data and preparative details are reported for a range of $[\text{Sn}^{\text{IV}}\text{BuPh}]$, $[\text{Sn}^{\text{IV}}\text{Bu}_2\text{Ph}]$, and $[\text{Sn}^{\text{IV}}\text{BuPh}_2]$ compounds. The stereochemical preferences of the butyl and phenyl groups in octahedral and trigonal-bipyramidal co-ordination in these mixed-ligand complexes, relative to their symmetrical analogues, have been examined on the additivity model, with comparison between theory and experiment based on our previously reported data on ligand partial quadrupole splittings. For the derivatives of the two triorganotins, trends in centre shift (c.s.) and quadrupole splitting (q.s.) parameters are reported, which are consistent with the additivity model. An approximate inverse correlation has been noted between q.s. and element-oxygen stretching frequency in comparing complexes of $[\text{SnBu}_x\text{Ph}_{3-x}]$ ($x = 0, 1, \text{ or } 2$) with PPh_3O and AsPh_3O .

THE additivity treatment of electric field gradients has allowed detailed analysis of the quadrupole splittings of a wide range of five- and six-co-ordinate organotin(IV) compounds.¹⁻⁴ In particular, the molecular-orbital approximation introduced by Clark *et al.*¹ provides the basis for having different partial quadrupole splitting (p.q.s.) assignments for the same ligand in different structural types. Thus, apical (tba) and equatorial (tbe) ligands in trigonal-bipyramidal co-ordination have different p.q.s. values⁴ which differ also from their values in tetrahedral (tet) and octahedral (oct) co-ordination. Based on these p.q.s. values, which are defined relative to $(\text{p.q.s.})_{\text{O}^{\text{I}}}^{\text{tet}} = (\text{p.q.s.})_{\text{O}^{\text{I}}}^{\text{tba}} = (\text{p.q.s.})_{\text{O}^{\text{I}}}^{\text{oct}} = 0$ as appropriate, and assuming idealized geometries, it has been possible to compare observed quadrupole splittings with calculated values and considerable success has been achieved in assigning Sn-C stereochemistries in several methyl- and phenyl-tin compounds. Seemingly, as pointed out by Clark *et al.*,¹ small distortions in geometry do not affect the magnitude of the quadrupole splitting as much as the asymmetry parameter, η .

Mixed-ligand complexes, that is complexes having both alkyl and phenyl groups on tin, have, however, received scant Mössbauer attention. These compounds, which would allow a detailed appraisal of the stereochemical preferences of these groups in octahedral and trigonal-bipyramidal co-ordination, would also provide a more rigorous test of the additivity approximations.

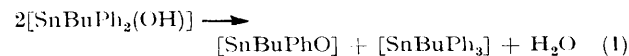
In this study, we report the preparation and Mössbauer parameters of several tin(IV) compounds $[\text{SnBuPh}_2]$, $[\text{SnBu}_2\text{Ph}]$, and $[\text{SnBuPh}]$ co-ordinated to oxygen and nitrogen donors. Some nitrogen-donor complexes of $[\text{SnBuPh}]$ have previously been prepared by Jaura *et al.*,⁵ but the Mössbauer spectra of only five compounds have been recorded.^{6,7} The complexes of $[\text{SnBuPh}]$ reported herein also extends the previously reported study of Bancroft and co-workers⁸ as well as of ours,⁹ on analogous $[\text{Sn}^{\text{IV}}\text{MePh}]$ complexes. No Mössbauer investigations have been reported to date on $[\text{SnBu}_2\text{PhX}]$ and $[\text{SnBu}$

$\text{Ph}_2\text{X}]$ or on their complexes, documented herein for the first time. Our interest in the mixed triorganotin compounds also stems in part from studies currently underway aimed at determining their biocidal properties relative to their biologically important $[\text{SnBu}_3]$ and $[\text{SnPh}_3]$ analogues.^{10,11}

EXPERIMENTAL

Starting Materials.—The compounds $[\text{SnBu}_2\text{PhBr}]$ and $[\text{SnBuPh}_2\text{Br}]$ were prepared by the monobromination of $[\text{SnBu}_2\text{Ph}_2]$ and $[\text{SnBuPh}_3]$ respectively in carbon tetrachloride or methanol at 0 °C and had boiling points in satisfactory agreement with literature¹² values. Their purity, as well as that of $[\text{SnBuPhCl}_2]$, which was prepared according to the method of Jaura *et al.*,⁵ was established by n.m.r. integral analysis. Difficulty was experienced in the distillation of $[\text{SnBu}_2\text{PhBr}]$ *in vacuo*, due to redistribution reactions, which produced $[\text{SnBu}_2\text{Br}_2]$, and, consequently, the yields obtained (ca. 40%) were lower than those reported by Rosenberg *et al.*¹² Higher yields of $[\text{SnBu}_2\text{PhBr}]$ were obtained by alkaline hydrolysis of the undistilled product to bis(dibutylphenyltin) oxide,¹³ a clear liquid [Found: C, 53.8; H, 7.50. Calc. for $\text{C}_{28}\text{H}_{46}\text{OSn}_2$: C, 52.85; H, 7.30%; $\nu_{\text{asym}}(\text{Sn-O-Sn}) = 762 \text{ cm}^{-1}$] and any diorganotin bromides present as impurities were converted to the insoluble oxides, which could be removed by filtration. Subsequent treatment of $[(\text{SnBu}_2\text{Ph})_2\text{O}]$ with $[\text{NH}_4]\text{Br}$ in refluxing toluene¹⁴ afforded $[\text{SnBu}_2\text{PhBr}]$; a similar reaction with $[\text{NH}_4]\text{Cl}$ gave the analogous chloride, which was used without further purification.

In contrast to $[\text{SnBu}_2\text{PhBr}]$, the alkaline hydrolysis of $[\text{SnBuPh}_2\text{Br}]$ in diethyl ether gave $[\text{SnBuPh}_2(\text{OH})]$ (Found: C, 55.05; H, 5.65. Calc. for $\text{C}_{16}\text{H}_{20}\text{OSn}$: C, 55.35; H, 5.75%, m.p. 73–75 °C) which has not been reported previously. An attempt to prepare $[(\text{SnBuPh}_2)_2\text{O}]$ by dehydration of the hydroxide in toluene using a Dean and Stark trap yielded instead $[\text{SnBuPhO}]$ [m.p. > 300 °C; $\nu_{\text{asym}}(\text{Sn-O-Sn}) = 562 \text{ cm}^{-1}$], presumably by disproportionation, according to equation (1). In the literature, a somewhat parallel



observation has also been made for $[\text{SnMe}_2\text{Ph}(\text{OH})]$.¹⁵

† Part 7 is ref. 29.

The compound $[\text{SnBuPh}_2(\text{O}_2\text{CMe})]$ [Found: C, 55.75; H, 5.70. Calc. for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{Sn}$: C, 55.6; H, 5.65%; m.p. 94–95 °C (lit.,¹⁶ 100 °C)] was obtained by treating a methanolic solution of the corresponding hydroxide with a stoichiometric amount of glacial acetic acid. The compound $[\text{SnBu}_2\text{Ph}(\text{O}_2\text{CMe})]$ (Found: C, 52.1; H, 7.15. Calc. for $\text{C}_{16}\text{H}_{26}\text{O}_2\text{Sn}$: C, 52.05; H, 7.10%; m.p. 65–67 °C) was prepared by refluxing equimolar quantities of $[\text{SnBu}_2\text{PhBr}]$ and silver acetate in carbon tetrachloride. A similar reaction in acetone between $[\text{SnBu}_2\text{PhBr}]$ and silver thiocyanate gave $[\text{SnBu}_2\text{Ph}(\text{SCN})]$ (Found: C, 48.35; H, 6.40; N, 3.80; S, 8.55. Calc. for $\text{C}_{15}\text{H}_{23}\text{NSSn}$: C, 48.95; H, 6.30;

thiole (phen) complexes of $[\text{SnBuPhX}_2]$ (X = Cl or SCN), warm benzene was used.

$[\text{SnBuPhCl}_2(\text{H}_2\text{salen})]$ was synthesised by reacting $[\text{SnBuPhCl}_2]$ in benzene solution with *NN'*-ethylenebis(salicylideneimine) (H_2salen).²⁰ The solution was stirred for 3 h and concentrated to obtain the crude product which was recrystallised from the same solvent as yellow plates.

$[\text{SnBuPh}(\text{quin})_2]$ was obtained by azeotropic distillation in toluene of $[\text{SnBuPhO}]$ and quinolin-8-ol (Hquin). It was obtained as yellow crystals (75% yield) and in the u.v. showed bands (CHCl_3 solution) at 377 (log $\epsilon = 3.72$) and 334.8 nm (log $\epsilon = 3.53$) with a shoulder at 319.6 nm.

TABLE I

Analytical data on $[\text{SnBuPh}]$ complexes and element–oxygen stretching frequencies (principal bands in italics)

(a)	Complex	Decomp. p. (θ_c /°C)	Analyses (%) ^a		$\nu(\text{E}-\text{O})/\text{cm}^{-1}$ (E = P, As, N, C, or S)
			C	H	
(a)	Type $[\text{SnBuPhX}_2\text{L}_2]$				
	X = Cl, L = dmsO	68	35.15 (35.0)	5.35 (5.40)	884, 904, 922
	PPh_3O	93–95	62.5 (62.75)	5.05 (5.00)	1 150
	hmpa ^b	70–71	38.85 (38.75)	7.40 (7.35)	1 192, 1 170, 1 132
	AsPh_3O	128–129	57.8 (57.05)	4.45 (4.55)	872, 850
	py	60–62	51.15 (49.85)	5.15 (5.00)	
(b)	Type $[\text{SnBuPhX}_2\text{L}']$				
	X = Cl, L' = bipy	204–206	50.15 (50.05)	4.65 (4.60)	
	X = SCN, L' = bipy	165–166	49.75 (50.3)	4.25 (4.20)	
	X = Cl, L' = phen	246–247	51.95 (52.4)	4.55 (4.35)	
	X = SCN, L' = phen	207–208	52.6 (52.5)	4.15 (4.00)	
	X = Cl, L' = dppoc	223–224	57.55 (57.3)	5.15 (5.05)	1 152, 1 122, 1 088
	X = SCN, L' = dppoc	224–225	56.95 (57.1)	4.85 (4.75)	1 180, 1 156, 1 136, 1 120, 1 084, 1 072
	X = Br, L' = dppoc	208–210	51.35 (51.3)	4.55 (4.50)	
	X = Cl, L' = dppom ^c	261–262	56.35 (56.8)	4.95 (4.90)	
	X = Cl, L' = bipyo ^d	181–182	46.6 (46.9)	4.15 (4.30)	1 270, 1 220, 1 202
	X = Cl, L' = H_2salen	117–118	51.95 (52.75)	5.20 (5.15)	
(c)	Type $[\text{SnBuPhL}'_2]$				
	L' = bzbz	104–105	68.0 (68.5)	5.30 (5.40)	
	quin ^e	184–186	61.7 (62.15)	5.05 (4.80)	
(d)	Other				
	$[\text{SnBuPhCl}_2(\text{dpcp})]$ ^f	84–85	56.0 (56.65)	4.60 (4.55)	1 888, 1 868, 1 826; 1 598, 1 584, 1 566 ^g
	$[\text{SnBuPhCl}(\text{quin})]$ ^h	116–118	52.95 (52.75)	4.50 (4.65)	
	$[\text{SnBuPhCl}(\text{S}_2\text{CNEt}_2)]$ ⁱ	60–61	40.8 (41.25)	5.65 (5.50)	
	$[\text{SnBuPh}(\text{bipyo})_2][\text{BPh}_4]_2$ ^j	130–131	72.8 (73.15)	5.60 (5.50)	1 256, 1 212
	$[\text{PPh}_3\text{CH}_2\text{Ph}][\text{SnBuPhCl}_3]$	134	59.2 (59.0)	5.10 (5.05)	

^a Calculated values are given in parentheses. ^b % N: 12.05 (12.3). ^c % Cl: 9.75 (9.60); % P: 7.85 (8.35). ^d % N: 5.45 (5.45). ^e % N: 5.10 (5.15). ^f % Cl: 13.4 (13.4). ^g Coupled C=O and C=C vibrations (ref. 9). ^h % N: 3.20 (3.25). ⁱ % N: 3.20 (3.20). ^j % N: 4.60 (4.40).

N, 3.80; S, 8.70%; m.p. 48–49 °C). The compound $[\text{SnBuPh}(\text{SCN})_2]$ (Found: C, 39.15; H, 3.65; N, 7.50. Calc. for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{S}_2\text{Sn}$: C, 39.15; H, 3.80; N, 7.60%; m.p. 77 °C) was synthesised from the corresponding chloride by a metathetical reaction with $\text{K}[\text{SCN}]$ in absolute ethanol and recrystallisation was effected from benzene, with the solution eluted through Florisil prior to concentration.

Complexes.—The neutral and cationic complexes of $[\text{SnBu}_2\text{PhBr}]$, $[\text{SnBu}_2\text{PhCl}]$, $[\text{SnBuPh}_2\text{Br}]$, $[\text{SnBuPhCl}_2]$, and $[\text{SnBuPh}(\text{SCN})_2]$ with the oxygen-donor ligands, dimethyl sulphoxide (dmsO), PPh_3O , AsPh_3O , hexamethylphosphoramide (hmpa), diphenylcyclopropanone (dpcp), $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ (dppom), $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ (dppoe), and 2,2'-bipyridine *NN'*-dioxide (bipyo), were prepared by methods^{9,17–19} previously outlined. Dry diethyl ether was used as the solvent medium in the preparation of the complexes $[\text{SnBuPhCl}_2(\text{py})_2]$ (py = pyridine) and $[\text{SnBuPh}(\text{SCN})_2(\text{bipy})]$ (bipy = 2,2'-bipyridyl), while for the phenan-

$[\text{SnBuPhCl}(\text{quin})]$ was obtained from $[\text{SnBuPh}(\text{quin})_2]$ by a stoichiometric reaction with $[\text{SnBuPhCl}_2]$ in warm benzene. The resulting orange-brown solution was concentrated, chilled in ice, and triturated in the presence of an equal amount of light petroleum. The solution was then decanted from a small amount of tarry material and upon further concentration and addition of dry diethyl ether yielded orange crystals (>80% yield). In chloroform solution the following bands were located in the u.v.: 387 nm (log $\epsilon = 4.06$) and shoulders at 338 and 320 nm.

An attempt to prepare $[\text{SnBu}_2\text{Ph}(\text{quin})]$ from $[(\text{SnBu}_2\text{Ph})_2\text{O}]$ and two equivalents of Hquin in refluxing toluene returned only $[\text{SnBu}_2(\text{quin})_2]$.

$[\text{SnBuPh}(\text{dbm})_2]$ was synthesised from $[\text{SnBuPhO}]$ and dibenzoylmethane (Hdbm) in refluxing toluene. After the removal of water (Dean and Stark trap), the toluene was evaporated off to yield a viscous orange oil, which was dissolved in the minimum amount of dichloromethane

TABLE 2
Analytical data on [SnBu₂Ph] and [SnBuPh₂] complexes

Complex	Decomp. p. (θ, °C)	Analyses (%) ^a	
		C	H
[SnBu ₂ PhCl(PPh ₃ O)] ^b	69—71	60.65 (61.6)	6.10 (5.75)
[SnBu ₂ PhBr(PPh ₃ O)] ^c	76—78	58.45 (57.5)	6.00 (5.75)
[SnBu ₂ PhCl(AsPh ₃ O)] ^d	103—105	56.65 (57.55)	5.60 (5.75)
[SnBu ₂ PhBr(AsPh ₃ O)] ^e	108—110	54.3 (53.95)	5.40 (5.40)
[SnBu ₂ Ph(PPh ₃ O) ₂] [BPh ₄] ^f	102—106	74.45 (74.95)	6.50 (6.20)
[SnBu ₂ Ph(AsPh ₃ O) ₂] [BPh ₄] ^g	141—143	69.5 (69.8)	5.90 (5.80)
[SnBu ₂ Ph(dppoe)][BPh ₄] ^h	219—223	72.55 (72.55)	6.35 (6.35)
[SnBuPh ₂ Br(PPh ₃ O)]	116—117	59.4 (59.35)	4.85 (4.95)
[SnBuPh ₂ Br(AsPh ₃ O)]	135—143	54.35 (55.6)	4.50 (4.15)
[SnBuPh ₂ (PPh ₃ O) ₂][BPh ₄]	136—137	75.4 (75.7)	5.75 (5.70)
[SnBuPh ₂ (AsPh ₃ O) ₂] [BPh ₄] ⁱ	172—173	70.0 (70.55)	5.45 (5.35)
[SnBuPh ₂ (bipyo)][BPh ₄]	110	71.6 (71.75)	5.55 (5.60)

^a Calculated values are given in parentheses. ^b % P: 4.95 (4.95); % Cl: 5.10 (5.70). ^c % P: 4.45 (4.65); % Br: 11.35 (11.95). ^d % Cl: 4.95 (5.30). ^e % Br: 10.75 (11.2). ^f % P: 4.95 (5.20). ^g % P: 6.10 (5.85).

followed by dropwise addition of light petroleum to obtain a pale yellow solid. This was recrystallised from CH₂Cl₂ after purification by passage through a Florisil column and decantation from some initial precipitate obtained upon the slow addition of a small amount of hexane.

TABLE 3
Mössbauer parameters (mm s⁻¹) of six-co-ordinate [SnRR'X₂L₂] complexes

Compound	SnMe ₂ ^a		SnBu ₂		SnMePh ^b		SnBuPh ^c		SnPh ₂ ^a	
	c.s.	q.s.	c.s.	q.s.	c.s.	q.s.	c.s.	q.s.	c.s.	q.s.
(1) [SnRR'Cl ₂]	1.56	3.55			1.44	3.11	1.47 ^d	3.25 ^d	1.38	2.82
(2) [SnRR'Cl ₂ (py) ₂]	1.37	3.92			1.30	3.66	1.48	3.57	1.32	3.39
(3) [SnRR'Cl ₂ (bipy)]	1.46	4.09	1.56 ^e	3.83 ^e	(1.25 ^d)	(3.65 ^d)	(1.40 ^d)	(3.75 ^d)	1.26	3.45
(4) [SnRR'(SCN) ₂ (bipy)]			1.43 ^f	4.04 ^f	1.26	3.75	1.39	3.85	1.26	3.45
(5) [SnRR'Cl ₂ (phen)]	1.32	4.03	1.59 ^e	4.07 ^e	(1.22 ^d)	(3.55 ^d)	(1.02 ^d)	(3.70 ^d)	1.32	4.06
(6) [SnRR'(SCN) ₂ (phen)]			1.42 ^f	4.18 ^f	1.34	3.74	1.42	3.90	1.21	3.37
(7) [SnRR'Cl ₂ (PPh ₃ O) ₂]	1.37	4.30	1.62 ^g	4.11 ^g	1.36	3.99	1.48	3.98	0.82 ^f	2.13 ^f
(8) [SnRR'Cl ₂ (AsPh ₃ O) ₂]	1.31	4.14	1.49 ^g	4.04 ^g	1.36	3.99	1.48	3.98	1.21	3.37
(9) [SnRR'Cl ₂ (bipyo)]	1.39	4.08			1.30	3.69	1.42	3.90	1.28	3.49
(10) [SnRR'Cl ₂ (dppom)]	1.44	4.32			1.30	3.67	1.42	4.06	1.27	3.78
(11) [SnRR'Cl ₂ (dppoe)]	1.27	4.19			1.38	4.24	1.44	4.31	1.26	3.65
(12) [SnRR'(SCN) ₂ (dppoe)]							1.38	4.44		
(13) [SnRR'Cl ₂ (H ₂ salen)]	1.37 ^h	4.06 ^h	1.62 ^h	4.49 ^h			1.36	3.73	1.26 ^h	3.89 ^h
(14) [SnRR'(bipyo) ₂][BPh ₄] ₂	1.26	4.00					1.42	3.80		

^a From refs. 1—3 and 36. ^b Ref. 8. ^c This work (± 0.05 mm s⁻¹). ^d Ref. 6. ^e Ref. 27. ^f Ref. 26. ^g F. P. Mullins, *Canad. J. Chem.*, 1971, **49**, 2719. ^h R. Barbieri, G. Alonzo, A. Silvestri, N. Burriesci, N. Bertazzi, G. Stocco, and L. Pellerito, *Gazzetta*, 1974, **104**, 885.

[SnBuPh(acac)₂] was prepared by treating TI[acac] (acac = acetylacetonate)²¹ with [SnBuPhCl₂] in hot benzene. It was obtained as a light brown oil after removal of the solvent, and was placed under vacuum for several weeks. Trituration with some dry light petroleum at the end of this period yielded a white solid (143—145 °C decomp.). A completely satisfactory elemental analysis could not be obtained for this compound on account of some contamination from [SnBuPhO].

[SnBuPhCl(SCSNET₂)]. This was prepared by treating TI[SCSNET₂]²² in stoichiometric amount with [SnBuPhCl₂] in CHCl₃. The precipitated TICl was filtered off using a Kieselguhr filter-cake and the filtrate eluted through a small column of activated alumina. Upon concentration and cooling, white crystals of the product were deposited. {I.r. (cm⁻¹): 994, 988s [ν(C—S)]; 1502vs [ν(C—N) (doublet)]; 382m [ν(S—S)].}

The analytical data and decomposition points of the di- and tri-organotin complexes are listed in Tables 1 and 2 respectively. Table 1 also includes element-oxygen stretching frequencies of the complexed ligands (Nujol mull spectra).

Mössbauer Spectra.—These were obtained using a constant acceleration microprocessor Mössbauer spectrometer (from Cryophysics Ltd., Oxford), with a 512-channel data store. A 15 mCi * Ba¹¹⁹SnO₃ source was used at room temperature and the samples were packed in Perspex discs and cooled to 80 K, using a liquid-nitrogen cryostat. The experimental error in the measured values of centre shift (c.s.) and quadrupole splitting (q.s.) parameters is ± 0.05 mm s⁻¹.

RESULTS AND DISCUSSION

Structure and Bonding in Six-co-ordinate Complexes.—The Mössbauer parameters for the [SnBuPh] compounds are given in Tables 3 and 4, together with earlier data for the corresponding [SnMe₂] (and [SnBu₂]), [SnPh₂], and [SnMcPh] derivatives. It is clear that all the [SnBuPhX₂L₂] complexes (X = Cl, SCN; L = unidentate or $\frac{1}{2}$ bidentate ligand) have quadrupole splittings around 4.00 mm s⁻¹, typical of *trans*-SnR₂ octahedral geometries.^{2,3} The two chlorine atoms or SCN groups may be mutually *cis* or *trans*, depending on the nature of the ligand.^{23,24} In Table 4,† we compare the observed quadrupole splittings with calculated values, assuming

cis disposition of the halogens or SCN groups in the equatorial plane, and, for most compounds, the agreement is well within the error margin of ± 0.4 mm s⁻¹ considered by Clark *et al.*¹ to be satisfactory considering the approximations involved. The quadrupole splitting values all appear to be consistently larger than that of [SnPh₂] complexes, but of the same order as (albeit somewhat less than) [SnMe₂] or [SnBu₂] complexes, *viz.* [SnPh₂] < [SnMePh] \lesssim [SnBuPh] \lesssim [SnBu₂] \sim [SnMe₂]. The trend is consistent with the greater donor strength of alkyl over phenyl, as reflected in their p.q.s. values of -1.03 and -0.95 mm s⁻¹ respectively.^{1,3} The quadrupole splittings for most of the [SnMePh] com-

* Throughout this paper: 1 Ci = 3.7×10^{10} s⁻¹.

† In Tables 4—7, only measured and predicted signs of q.s. are explicitly stated.

TABLE 4

Mössbauer parameters (mm s^{-1}) of $[\text{SnRR}'\text{L}'_2]$ compounds

Compound	c.s.	q.s.	Ref.
<i>trans</i> - $[\text{SnMe}_2(\text{acac})_2]$	1.16	+4.02	<i>a</i>
<i>cis</i> - $[\text{SnMePh}(\text{acac})_2]$	0.62	1.81	<i>b</i>
<i>cis</i> - $[\text{SnBuPh}(\text{acac})_2]$	0.68	1.82	<i>c</i>
<i>cis</i> - $[\text{SnPh}_2(\text{acac})_2]$	0.71	2.07	<i>a</i>
<i>trans</i> - $[\text{SnMe}_2(\text{dbm})_2]$	1.18	+4.08	<i>a</i>
<i>cis</i> - $[\text{SnMePh}(\text{dbm})_2]$	0.63	+1.89	<i>b</i>
<i>cis</i> - $[\text{SnBuPh}(\text{dbm})_2]$	0.84	2.13	<i>c</i>
<i>cis</i> - $[\text{SnPh}_2(\text{dbm})_2]$	0.73	2.15	<i>a</i>
<i>cis</i> - $[\text{SnMe}_2(\text{quin})_2]$	0.88	+2.02	<i>d</i>
<i>cis</i> - $[\text{SnMePh}(\text{quin})_2]$	0.82	1.76	<i>b</i>
<i>cis</i> - $[\text{SnBuPh}(\text{quin})_2]$	0.86	1.93	<i>c</i>
<i>cis</i> - $[\text{SnBu}_2(\text{quin})_2]$	0.86	2.06	<i>d</i>
<i>cis</i> - $[\text{SnBu}_2^1(\text{quin})_2]$	0.85	1.82	<i>d</i>
<i>cis</i> - $[\text{SnPh}_2(\text{quin})_2]$	0.68	+1.69	<i>d</i>

^a Ref. 36. ^b Ref. 8. ^c This work ($\pm 0.05 \text{ mm s}^{-1}$). ^d Ref. 44.

plexes, on the other hand, appear to be midway between $[\text{SnMe}_2]$ and $[\text{SnPh}_2]$ analogues, as reported.⁸ While the limited Mössbauer data on $[\text{SnBu}_2]$ complexes do not allow any firm conclusion, it would appear nevertheless that, in $[\text{SnBuPh}]$ complexes, there is lesser distortion of the C–Sn–C angle than in the $[\text{SnMePh}]$ case and, hence, by implication, greater 5s character in the Sn–C bonds.²⁵ This observation is also in line with the trend in centre shift values.

It is interesting that the *trans*- $[\text{SnR}_2]$ configuration is maintained in the three $[\text{SnBuPh}(\text{SCN})_2]$ complexes studied, although the $[\text{SnPh}_2]$ analogues of these have *cis*- SnPh_2 configurations.²⁶ Complexes of $[\text{SnPh}_2\text{Cl}_2]$ with bipyridine and phenanthroline, however, have *trans*- SnPh_2 stereochemistry²⁷ and, in stability, rank over the corresponding $[\text{SnBu}_2\text{Cl}_2]$ complexes.²⁸ With other nitrogen-donor chelates, such as 2-aminomethylpyridine, $[\text{SnPh}_2\text{Cl}_2]$ yields a *cis* complex²⁹ and this stereochemistry has also been inferred for the bis adducts of diaryl tin dihalides with amides.³⁰ Ho and Zuckerman²³ have suggested that the formation of *trans* or *cis* isomers depends on the size of the donor ligand, but it is probably more accurate to consider the mutual influence of all the ligands on tin.³¹ This includes both steric and electronic factors. The butyl group is no less bulky than a phenyl group, but, being a better σ donor, tends to acquire most of the tin 5s character (Bent's rule³²) so that a linear C–Sn–C structure results, which, for the chelate complexes of $[\text{SnBuPhX}_2]$, in the balance, is still favoured. The three bis-chelate complexes of $[\text{SnBuPh}]$, on the other hand, like the $[\text{SnPh}_2]$ and $[\text{SnMePh}]$ analogues, have *cis*- SnC_2 configurations, with q.s. values around 2 mm s^{-1} . Their lower c.s. values relative to the *trans* structures are also in accord^{2,33} with this interpretation.

The observed q.s. value for $[\text{SnBuPh}(\text{quin})_2]$ is in close agreement with the calculated value (Table 5), and again is seen to be larger than that of $[\text{SnMePh}(\text{quin})_2]$. The value is exactly midway between the values for $[\text{SnBu}_2(\text{quin})_2]$ and $[\text{SnBu}_2^1(\text{quin})_2]$ and also close to the average of the values for $[\text{SnBu}_2(\text{quin})_2]$ and $[\text{SnPh}_2(\text{quin})_2]$. These results may be interpreted as follows. The quin

ligand has a small chelate bite for the relatively large tin atom so that a distorted octahedral structure results,^{25,34} in which C–Sn–C bond angles are larger than required by the regular geometry. This is indeed the case for $[\text{SnMe}_2(\text{quin})_2]$ ³⁵ (C–Sn–C bond angle = 110.7°). Ligand–ligand repulsions may therefore be anticipated to be less important in the oxinates than in structures with regular *cis* geometry. The normal electronic effects are thus manifested in the c.s. and q.s. values. The variations in q.s. values also suggest that the C–Sn–C bond angle increases in the order, $\text{SnPh}_2 < \text{SnMePh} \sim \text{SnBu}_2^1 < \text{SnBuPh} < \text{SnBu}_2$.

Our observation in both *cis* and *trans* structures of larger Mössbauer parameters for $[\text{SnBuPh}]$ over $[\text{SnMePh}]$ is clearly a consequence of the relatively larger Bu–Sn–Ph bond angle, on account of both steric and electronic factors associated with the butyl group.

TABLE 5

Observed and calculated quadrupole splittings (mm s^{-1}) for $[\text{Sn}^{\text{IV}}\text{BuPh}]$ compounds

Compound	Obs. q.s.	Calc. q.s. ^a
(1) $[\text{SnBuPhCl}_2(\text{py})_2]$	3.57	+3.76
(2) $[\text{SnBuPhCl}_2(\text{bipy})]$	3.85	+3.80
(3) $[\text{SnBuPh}(\text{SCN})_2(\text{bipy})]$	4.06	+3.94
(4) $[\text{SnBuPhCl}_2(\text{phen})]$	3.90	+3.88
(5) $[\text{SnBuPh}(\text{SCN})_2(\text{phen})]$	3.93	+4.02
(6) $[\text{SnBuPhCl}_2(\text{PPh}_3\text{O})_2]$	3.98	+4.28
(7) $[\text{SnBuPhCl}_2(\text{AsPh}_3\text{O})_2]$	3.45	+3.92
(8) $[\text{SnBuPhCl}_2(\text{dppom})]$	4.06	+4.16
(9) $[\text{SnBuPhCl}_2(\text{dppoe})]$	4.31	+4.10
(10) $[\text{SnBuPh}(\text{SCN})_2(\text{dppoe})]$	4.44	+4.24
(11) $[\text{SnBuPhCl}_2(\text{bipy})]$	3.90	+3.90
(12) $[\text{SnBuPh}(\text{bipy})_2][\text{BPh}_4]_2$	3.80	+3.84
(13) $[\text{SnBuPhCl}_2(\text{H}_2\text{salen})]$	3.73	+3.85 ^b
(14) $[\text{SnBuPh}(\text{quin})_2]$	1.93	–1.88
(15) $[\text{SnBuPh}(\text{dbm})_2]$	2.13	–1.96
(16) $[\text{SnBuPh}(\text{acac})_2]$	1.82	–1.92

^a Using the p.q.s. values in refs. 2, 3, and 36 and the electric field gradient expressions in ref. 2. For compounds 1–12, the calc. values are for *trans*-Bu–Sn–Ph and *cis*-Cl–Sn–Cl (or *cis*-NCS–Sn–NCS) moieties. For the all-*trans* isomers, the predicted values would be very slightly larger ($\eta \neq 0$). For compounds 14–16, the calc. values are for *cis*-structures. ^b Using a p.q.s. value of -0.055 mm s^{-1} for H_2salen and assuming a polymeric, oxygen-bridged all *trans*-structure for the complex (see ref. h, Table 3).

The bis(β -diketonate) complexes of $[\text{SnRPh}]$ differ from the oxinates in showing lower quadrupole splittings than their $[\text{SnPh}_2]$ analogues (Table 4). Assuming more regular *cis*-octahedral geometries here than in the case of the oxinates, Bancroft and co-workers⁸ have rationalised a similar trend in the $[\text{SnMePh}]$ chelates in terms of lower C–Sn–C bond angles for $[\text{SnMePh}]$ complexes than in the corresponding $[\text{SnPh}_2]$ complexes. On this basis, it would again be expected, but now dominantly on steric grounds, that the C–Sn–C bond angle distortion towards larger values increases in the order, $\text{SnMePh} < \text{SnBuPh} < \text{SnPh}_2$.

There would thus be less 5s character in the R–Sn–Ph bonds than in Ph–Sn–Ph bonds so that the q.s. and c.s. values would be expected to reflect this trend. This is generally seen to be the case, although in the one instance of $[\text{SnBuPh}(\text{dbm})_2]$ the c.s. value is slightly larger than that of $[\text{SnPh}_2(\text{dbm})_2]$. The Mössbauer

parameters for the dbm complexes are larger than for analogous acac complexes, consistent with the greater electronegativity of dbm (greater tin $5p$ electron withdrawal³⁶) over acac. It is instructive that n.m.r. studies^{37,38} on *trans*-[SnMe₂(dbm)₂] reveal a deshielding of the methyl-tin protons relative to *trans*-[SnMe₂(acac)₂],

TABLE 6
Mössbauer data (mm s⁻¹) for five-co-ordinate organotin complexes

Compound	c.s.	q.s.	Ref.
(a) Type [SnRR' ₂ X]			
[SnMe ₃ (SCN)]	1.40	3.77	<i>a</i>
[SnBu ₃ (SCN)]	1.60	3.69	<i>a</i>
[SnBu ₂ Ph(SCN)]	1.47	3.65	<i>b</i>
[SnPh ₃ (SCN)]	1.35	3.50	<i>a</i>
[SnMe ₃ (O ₂ CMe)]	1.35	3.68	<i>c</i>
[SnBu ₃ (O ₂ CMe)]	1.46	3.64	<i>d</i>
[SnBu ₂ Ph(O ₂ CMe)]	1.38	3.47	<i>b</i>
[SnBuPh ₂ (O ₂ CMe)]	1.32	3.45	<i>b</i>
[SnPh ₃ (O ₂ CMe)]	1.28	3.36	<i>e</i>
(b) Type [SnRR' ₂ XL]			
[SnMe ₃ Cl(PPh ₃ O)]	1.45	3.49	<i>f</i>
[SnBu ₂ PhCl(PPh ₃ O)]	1.41	3.52	<i>b</i>
[SnBu ₂ PhBr(PPh ₃ O)]	1.42	3.55	<i>b</i>
[SnBuPh ₂ Br(PPh ₃ O)]	1.34	3.45	<i>b</i>
[SnPh ₃ Cl(PPh ₃ O)]	1.29	3.19	<i>g</i>
[SnPh ₃ Br(PPh ₃ O)]	1.29	3.20	<i>g</i>
[SnBu ₂ PhCl(AsPh ₃ O)]	1.37	3.40	<i>b</i>
[SnBu ₂ PhBr(AsPh ₃ O)]	1.42	3.50	<i>b</i>
[SnBuPh ₂ Br(AsPh ₃ O)]	1.37	3.55	<i>b</i>
[SnPh ₃ Cl(AsPh ₃ O)]	1.29	3.09	<i>h</i>
[SnPh ₃ Cl(dpcp)]	1.29	3.19	<i>b</i>
(c) Type [SnRR' ₂ L ₂][BPh ₄]			
[SnMe ₃ (PPh ₃ O) ₂][BPh ₄]	1.28	3.87	<i>i</i>
[SnBu ₃ (PPh ₃ O) ₂][BPh ₄]	1.52	3.98	<i>j</i>
[SnBu ₂ Ph(PPh ₃ O) ₂][BPh ₄]	1.41	3.93	<i>b</i>
[SnBuPh ₂ (PPh ₃ O) ₂][BPh ₄]	1.28	3.88	<i>b</i>
[SnPh ₃ (hmpa) ₂][BPh ₄]	1.25	3.51	<i>i</i>
[SnMe ₃ (AsPh ₃ O) ₂][BPh ₄]	1.18	3.29	<i>i</i>
[SnBu ₃ (AsPh ₃ O) ₂][BPh ₄]	1.45	3.60	<i>j</i>
[SnBu ₂ Ph(AsPh ₃ O) ₂][BPh ₄]	1.34	3.55	<i>b</i>
[SnBuPh ₂ (AsPh ₃ O) ₂][BPh ₄]	1.25	3.37	<i>b</i>
[SnMe ₃ (dppoe)][BPh ₄]	1.31	3.90	<i>i</i>
[SnBu ₂ Ph(dppoe)][BPh ₄]	1.42	4.15	<i>b</i>
[SnPh ₃ (dppoe)][BPh ₄]	1.23	3.56	<i>i</i>
[SnMe ₃ (bipyo)][BPh ₄]	1.32	3.67	<i>i</i>
[SnBuPh ₂ (bipyo)][BPh ₄]	1.34	3.85	<i>b</i>
(d) Type [SnRR'Cl ₂ L]			
[SnBuPhCl ₂ (dpcp)]	1.52	3.70	<i>b</i>
[SnMe ₂ Cl ₂ (dpcp)]	1.41	3.52	<i>b</i>
[SnBu ₂ Cl(quin)]	1.40	-3.21	<i>b</i>
[SnBuPhCl(quin)]	1.28	2.86	<i>k</i>
[SnPh ₂ Cl(quin)]	1.10	+2.40	<i>k</i>
[SnBu ₂ Cl(S ₂ CNEt ₂)]	1.39	2.76	<i>l</i>
[SnBuPhCl(S ₂ CNEt ₂)]	1.41	2.66	<i>b</i>
[SnPh ₂ Cl(S ₂ CNEt ₂)]	1.14	2.28	<i>l</i>

^a B. Gassenheimer and R. H. Herber, *Inorg. Chem.*, 1969, **8**, 1120. ^b This work (± 0.05 mm s⁻¹). ^c C. Pöder and J. R. Sams, *J. Organometallic Chem.*, 1969, **19**, 67. ^d B. F. E. Ford, B. V. Liengme, and J. R. Sams, *J. Organometallic Chem.*, 1969, **19**, 53. ^e B. F. E. Ford and J. R. Sams, *J. Organometallic Chem.*, 1971, **31**, 47. ^f J. C. Hill, R. S. Drago, and R. H. Herber, *J. Amer. Chem. Soc.*, 1969, **91**, 1644. ^g J. Ensling, P. Gutlich, K. M. Hassellbach, and B. W. Fitzsimmons, *J. Chem. Soc. (A)*, 1971, 1940. ^h Ref. 45. ⁱ Ref. 4. ^j A. J. Crowe, P. J. Smith, and P. G. Harrison, *J. Organometallic Chem.*, submitted for publication. ^k R. C. Poller and J. N. R. Ruddick, *J. Chem. Soc. (A)*, 1969, 2273. ^l B. W. Fitzsimmons and A. C. Sawbridge, *J.C.S. Dalton*, 1972, 1678.

implying some quasi-aromatic character of the chelate rings and tilting of these rings towards the tin-bound methyl groups. This would particularly disfavour *trans* structures when bulky organic groups are attached to tin and, in part, explains the *cis* geometries observed in this study. Our results are also in accord with the ligand-ligand repulsion calculations of Kepert³⁴ which suggest that the *cis* structure is always favoured sterically over *trans* for bis chelates of diorganotin compounds. Evidence for both isomeric forms of the bis chelates in the solid state is still scant, unlike in solution for a number of cases, including [SnMe₂(acac)₂].³⁹ The only report known to us where both *cis* and *trans* isomers have been identified in the solid state is that of Tanaka and co-workers⁴⁰ on the dimethyltin complex of the quadridentate ligand, *NN'*-ethylenebis(salicylideneimine).

Structure and Bonding in Five-co-ordinate Complexes.—Quadrupole splittings and centre shifts for the new five-co-ordinate compounds of [SnBu₂Ph], [SnBuPh₂], and [SnBuPh] are given in Table 6. Table 7 compares

TABLE 7

Observed and calculated quadrupole splittings (mm s⁻¹) for five-co-ordinate [SnRR'₂] and [SnRR'] compounds

Compound	Obs. q.s.	Calc. q.s. ^a
(a) Structure (I)		
[SnBu ₂ Ph(SCN)]	3.65	-3.50
[SnBu ₂ Ph(O ₂ CMe)]	3.47	-3.54
[SnBuPh ₂ (O ₂ CMe)]	3.45	-3.39
[SnBu ₂ PhX(PPh ₃ O)]	3.53 ^b	-3.48
[SnBuPh ₂ Br(PPh ₃ O)]	3.45	-3.33
[SnBu ₂ PhX(AsPh ₃ O)]	3.45 ^b	-3.20
[SnBuPh ₂ Br(AsPh ₃ O)]	3.55	-3.05
[SnBu ₂ Ph(PPh ₃ O) ₂][BPh ₄]	3.93	-3.72
[SnBuPh ₂ (PPh ₃ O) ₂][BPh ₄]	3.88	-3.57
[SnBu ₂ Ph(AsPh ₃ O) ₂][BPh ₄]	3.55	-3.16
[SnBuPh ₂ (AsPh ₃ O) ₂][BPh ₄]	3.37	-3.01
(b) Structure (II)		
[SnBu ₂ Ph(dppoc)][BPh ₄]	4.15	-3.85 ^c
[SnBuPh ₂ (bipyo)][BPh ₄]	3.85	-3.53 ^c
(c) Structure (III)		
[SnMe ₂ Cl ₂ (dpcp)]	3.52	3.25 ^d
[SnBuPhCl(S ₂ CNEt ₂)]	2.66	
[SnBuPhCl(quin)]	2.86	+2.73

^a Using the p.q.s. values in ref. 4 and (p.q.s.)_{dpcp}^{11a} = 0.125 mm s⁻¹. ^b Average of values for X = Cl and Br. ^c Calculated for structure (II) assuming one or both butyl groups apical. ^d Apical dpcp gives slightly better fit than equatorial.

observed and calculated quadrupole splittings, based on our previously reported⁴ additivity expressions for the three representative structures [(I)—(III)] given below, while Table 8 lists i.r. data on ligand-stretching frequencies diagnostic of complexation. In both Tables 6 and 8, we have included literature data on analogous symmetrical triorganotin compounds for comparison purposes.

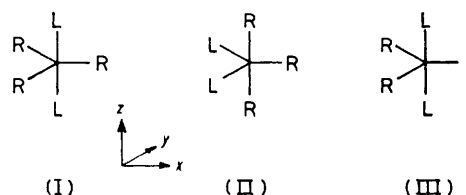


TABLE 8

Element-oxygen stretching frequencies in [SnRR'₂] compounds (principal bands in italics)

Compound	$\nu(\text{E}-\text{O})(\text{cm}^{-1})$ (E = P, As, or C)
[SnMe ₃ (O ₂ CMe)]	1 558 ^a
[SnBu ₃ (O ₂ CMe)]	1 562 ^b
[SnBu ₂ Ph(O ₂ CMe)]	1 552
[SnBuPh ₂ (O ₂ CMe)]	1 543
[SnPh ₃ (O ₂ CMe)]	1 531
[SnMe ₃ Br(PPh ₃ O)]	1 157 ^c
[SnBu ₂ PhCl(PPh ₃ O)]	1 157
[SnBu ₂ PhBr(PPh ₃ O)]	1 156
[SnBuPh ₂ Br(PPh ₃ O)]	1 160
[SnPh ₃ Cl(PPh ₃ O)]	1 149, 1 142 ^c
[SnMe ₃ Br(AsPh ₃ O)]	868 ^c
[SnBu ₂ PhCl(AsPh ₃ O)]	862
[SnBu ₂ PhBr(AsPh ₃ O)]	847, 880
[SnBuPh ₂ Br(AsPh ₃ O)]	848
[SnPh ₃ Cl(AsPh ₃ O)]	860, 870 ^c
[SnMe ₃ (PPh ₃ O) ₂][BPh ₄]	1 144 ^d
[SnBu ₃ (PPh ₃ O) ₂][BPh ₄]	1 142 ^e
[SnBu ₂ Ph(PPh ₃ O) ₂][BPh ₄]	1 139
[SnBuPh ₂ (PPh ₃ O) ₂][BPh ₄]	1 132
[SnMe ₃ (AsPh ₃ O) ₂][BPh ₄]	870 ^d
[SnBu ₃ (AsPh ₃ O) ₂][BPh ₄]	840, 852 ^e
[SnBu ₂ Ph(AsPh ₃ O) ₂][BPh ₄]	840, 851
[SnBuPh ₂ (AsPh ₃ O) ₂][BPh ₄]	836
[SnMe ₃ (dppoe)][BPh ₄]	1 183, 1 150, 1 141, <i>1 094</i> ^f
[SnBu ₂ Ph(dppoe)][BPh ₄]	1 183, 1 156, 1 139, 1 123, <i>1 087</i>
[SnPh ₃ (dppoe)][BPh ₄]	1 181, 1 156, 1 143, <i>1 084</i> ^f
[SnMe ₃ (bipyo)][BPh ₄]	1 254, 1 225, <i>1 208</i> ^f
[SnBuPh ₂ (bipyo)][BPh ₄]	1 256, 1 232, <i>1 211</i>

^a Ref. c, Table 6. ^b Ref. d, Table 6. ^c Ref. 17. ^d V. G. Kumar Das, unpublished work. ^e Ref. j, Table 6. ^f Ref. 19.

It is immediately clear that, for the neutral and cationic triorganotin complexes, as well as for the compounds [SnBu₂PhX] (X = SCN or O₂CMe), the magnitudes of the c.s. and q.s. parameters decrease systematically with increasing phenyl substitution on tin. The isothiocyanate and acetate complexes have quadrupole splittings larger than those estimated for tetrahedral structures. They are therefore considered to be five-coordinate [structure (I)], as a result of apical bridging through S and N in the case of isothiocyanate and oxygens in the case of acetate, such as deduced crystallographically for the corresponding [SnMe₃]^{41,42} and [SnPh₃] compounds.⁴³ The symmetry of the charge distribution about tin in these structures is C_{3v} and this is also the case for [SnRR'₂XL] complexes. We envisage the Sn-C bonds to have maximal s character compared to other tin-ligand bonds. However, on account of the greater electron-withdrawing ability of the phenyl group over alkyl, the c.s. suffers a decrease with progressive phenyl substitution on tin, consistent with the greater sensitivity of c.s. to changes in s-orbital occupancy than p-orbital occupancy. The greater electronegativity of the phenyl group also results in the p-electron imbalance $[-Np_z + \frac{1}{2}(Np_x + Np_y)]$ becoming more negative and, consequently, also the field gradient.⁴⁴ This leads to a more positive value of the quadrupole splitting. It must be noticed at this point that the sign of the q.s. for equatorial [SnR₃L₂] [structure (I)] is

unambiguously negative,² although, in the absence of experimental confirmation, we have not indicated this in Tables 6 and 7. On the other hand, for *mer*-[SnR₃L₂] [structure (II)], as has been pointed out,⁴ predictions of the calculated sign of q.s. and the magnitude of η are unreliable. The non-planar arrangement of the SnC₃ skeleton in this structure imposes somewhat less s character in the two apical Sn-C bonds relative to the equatorial Sn-C bond. The *mer* structure is postulated for the cationic complexes [SnBu₂Ph(dppoe)][BPh₄] and [SnBuPh₂(bipyo)][BPh₄] by analogy with our previous results⁴ on [SnMe₃] and [SnPh₃] analogues. This is supported by the close correspondence between observed and calculated q.s. values. In the [SnBu₂Ph] complex, both the butyl groups are assumed to occupy apical positions, while in the [SnBuPh₂] complex, the axial occupancy is taken up by a butyl and a phenyl. The slightly larger q.s. values based on these arrangements over others yield the best agreement with the observed results. However, the assignment is by no means rigorous, as the differences between the various arrangements fall within the tolerance limit of the additivity model. The calculated q.s. values for [SnRR'₂X] and [SnRR'₂XL] compounds [structure (I)] are also seen to be generally in good agreement with the observed values. This argues for the essential correctness of the additivity treatment and our previous estimates of the p.q.s. values for the ligands. The only exception appears to be [SnBuPh₂Br(AsPh₃O)], for which the difference is slightly beyond 0.4 mm s⁻¹, but the satisfactory result for the corresponding cationic complex [SnBuPh₂(AsPh₃O)₂]-[BPh₄] suggests that an experimental error may be associated with the value for the neutral complex.

We have also examined the relative shifts of the element-oxygen stretching frequencies of the complexed ligands for possible correlation with the quadrupole splittings. As seen in Table 8 for the triorganotin compounds, the negative shift of the P-O or As-O stretching frequency, which gives some guide to the strength of the donor bond,¹⁷ tends to be largest for compounds which have lower q.s. This would suggest that [SnPh₃] and [SnBuPh₂] moieties are somewhat better acceptors than [SnBu₂Ph] and [SnMe₃] (or [SnBu₃]) towards both PPh₃O and AsPh₃O. Our results are in contrast with the observation⁴⁵ that, in complexes of [SnPh₃Cl] with a given donor type, the strongest complexation is associated with the largest q.s. We believe that, since the apical tin-ligand bonds in structure (I) have largely p character, a strong donor-acceptor interaction will result in greater Sn 5p_z orbital population, which would lead to a more positive q.s., as borne out by our studies.

The five-co-ordinate diorganotin complex, [SnBuPhCl(quin)], shows a q.s. value midway between the values observed for the corresponding [SnBu₂] and [SnPh₂] analogues (Table 6). The value is also seen to be in excellent agreement with the calculated⁴ value based on structure (III) (equatorial R groups). The complex retains its five-co-ordinate status in chloroform as

deduced⁴⁶ from its u.v. spectrum, which shows bands displaced to longer wavelengths (see Experimental section) from the free quin value at 313 nm. A similar conclusion was also previously⁹ drawn for [SnMePhCl(quin)], which shows a $J(^{119}\text{Sn-Me})$ value of 82.5 Hz in CDCl_3 relative to 71.3 Hz for the uncomplexed Lewis acid.

The compound [SnBuPhCl(S_2CNEt_2)] shows a quadrupole splitting of 2.66 mm s^{-1} . In the literature,⁴⁷ the observed q.s. of ca. 2.9 mm s^{-1} for R = alkyl in the series of complexes, [SnR₂Cl($\text{S}_2\text{CNR}'_2$)], has been interpreted⁴ in terms of structure (III), and this has been substantiated for [SnMe₂Cl(S_2CNMe_2)] by an X-ray study.⁴⁸ However, it appears that the splitting of ca. 2.3 mm s^{-1} for R = Ph⁴⁷ is equally consistent with the alternative isomeric *cis* structure, with one phenyl group axially disposed and the other situated in the equatorial plane.⁴ The present result for [SnBuPhCl(S_2CNEt_2)], which is close to the average of the splittings observed for [SnBu₂Cl(S_2CNEt_2)] and [SnPh₂Cl(S_2CNEt_2)] (Table 6), seems to favour structure (III) for all three cases.

Structure (III) also appears to yield a better fit of the calculated q.s. with the observed value for the 1 : 1 complex of [SnMe₂Cl₂] with diphenylcyclopropenone, with the ligand occupying an axial position. The value, (p.q.s.)^{tba}_{dpcp}, used for the calculation was derived from the q.s. value of [SnPh₃Cl(dpcp)] for which structure (I) was assumed, and (p.q.s.)^{tbe}_{dpcp} for comparison calculations was then evaluated by means of equation (2).⁴

$$3(\text{p.q.s.})^{\text{tbe}} - 4(\text{p.q.s.})^{\text{tba}} \simeq 0.58 \text{ mm s}^{-1} \quad (2)$$

By way of contrast, the result for [SnBuPhCl₂(dpcp)] is curiously at variance with either structure (III) [q.s. (calc.) = 3.06 mm s^{-1}] or an isomeric *trans* structure [q.s. (calc.) = 4.42 mm s^{-1}]. We do not envisage gross structural deviations from either structure to be the cause here, since for the related complex, [SnMePhCl₂(dpcp)], the n.m.r. spectrum reveals no unusual sensitivity in the $J(^{119}\text{Sn-Me})$ value relative to [SnMePhCl(quin)].⁹ This leads us, tentatively, to speculate an octahedral structure for [SnBuPhCl₂(dpcp)] involving some degree of autocomplexation⁴⁹ *via* the halogens.

We thank the International Tin Research Council, London, for permission to publish this paper. The work described in this paper was initiated while one author (V. G. K. D.) was at the International Tin Research Institute on sabbatical leave.

[0/833 Received, 2nd June, 1980]

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