Synthesis, Infrared, and Tin-119 Mössbauer Spectroscopic Characterization of Seven-co-ordinate Diorganotin(IV) Adducts with 2,6-Diacetylpyridine Acylhydrazones, including the *X*-Ray Crystal Structure of $SnEt_2$(dapt) [H_2dapt = 2,6-diacetylpyridine bis(2-thenoylhydrazone)] *

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The synthesis and the i.r. and ^{119}Sn Mössbauer spectroscopic characterization of $SnEt_2$(dapt), SnBuCl(dapt) [H_2dapt = 2,6-diacetylpyridine bis(2-thenoylhydrazone)], and $SnBu_2$(daps) [H_2daps = 2,6-diacetylpyridine bis(salicyloylhydrazone)] are reported together with the *X*-ray crystal structure of the first compound. The structure consists of monomeric units in which the tin atom exhibits a nearly pentagonal-bipyramidal co-ordination geometry with the equatorial plane defined by the N_3O_2 donor set of the hydrazone ligand and the two ethyl groups in the apical positions. Some disorder occurs in both the thienyl moieties.

As an extension of research programmes in our laboratories related to the study of the chelating properties of acylhydrazones in transition metal complexes [1,2] as well as to the chemistry and structure of seven-co-ordinate tin,[3,4] we have been interested in examining tin and organotin complexes with acylhydrazones.[5,6] In order to obtain a fuller understanding of the flexibility and versatility of bis-acylhydrazones as ligands towards main group elements and examine the influence exerted by the organic substituent R (R = Et, Pr, Bu, or Ph) σ-bonded to tin and by the geometry of the acylhydrazones on the occurrence of pentagonal-bipyramidal stereochemistries, we have investigated the chelating properties of 2,6-diacetylpyridine bis(2-thenoylhydrazone) (H_2dapt) and the related bis(salicyloylhydrazone) (H_2daps) in three new organotin complexes of formulae $SnEt_2$(dapt), SnBuCl(dapt), and $SnBu_2$(daps).

This paper deals with the preparation and the i.r. and ^{119}Sn Mössbauer spectroscopic characterization of these three complexes, and with the crystal and molecular structure of one of them, namely $SnEt_2$(dapt). In addition, the i.r., ^{119}Sn Mössbauer, and ^{119}Sn n.m.r. of other seven-co-ordinate tin adducts, whose synthesis and *X*-ray structures have been previously reported, are also included for comparison.

Experimental

All reagents were of the highest grade commercially available. Dibutyldichlorotin and dichlorodiethyltin were purchased from Strem Chemical Co. and used without further purification.

Elemental C, H, and N analyses were carried out on Perkin-Elmer model 240 automatic equipment. Determination of tin was by atomic absorption spectroscopy on a Perkin-Elmer model 303-H6A 70 instrument. Infrared spectra (4 000—200 cm^{-1}) for KBr discs were recorded on a Perkin-Elmer model 283 B spectrophotometer. ^{119}Sn N.m.r. spectra were recorded on a JEOL FX60Q spectrometer under nuclear Overhauser effect (n.O.e.)-suppressed conditions and are accurate to ±0.5 p.p.m. Details of our Mössbauer spectrometer and related procedures have been published elsewhere.[7]

Syntheses.—2,6-Diacetylpyridine bis(2-thenoylhydrazone) (H_2dapt) and 2,6-diacetylpyridine bis(salicyloylhydrazone) (H_2daps) were prepared according to published procedures.[1,8]

The syntheses of all the complexes were carried out according to the following general procedure. Under a nitrogen atmosphere, the hydrazone was suspended in dry, boiling methanol and a solution of the diorganotin dichloride in anhydrous acetone, added. The mixture was allowed to reflux for several minutes. After some days, by slow evaporation of the solvents, a gold-yellow crystalline product separated out in high yields. Experimental chemical analyses are in agreement with the formulae (calculated values in parentheses): $SnEt_2$(dapt), $C_{23}H_{25}N_5O_2S_2Sn$ [Found: C, 47.70 (47.10); H, 4.40 (4.30); N, 11.85 (11.95); Sn, 20.85 (20.25)%]; SnBuCl(dapt), $C_{23}H_{24}ClN_5O_2S_2Sn$ [Found: C, 44.90 (44.50); H, 4.20 (3.90); N, 10.85 (11.30); Sn, 19.50 (19.15)%]; $SnBu_2$(daps), $C_{31}H_{37}N_5O_4Sn$ [Found: C, 55.90 (56.20); H, 5.70 (5.65); N, 10.70 (10.55); Sn, 18.30 (17.90)%].

X-Ray Data Collection, and Solution and Refinement of the Crystal Structure of $SnEt_2$(dapt).—*Crystal data.* $C_{23}H_{25}N_5O_2S_2Sn$, $M = 586.29$, $a = 11.007(5)$, $b = 12.293(5)$, $c = 18.223(10)$ Å, $\beta = 95.15(5)°$, $U = 2\,456(2)$ Å^3, $Z = 4$, $D_c = 1.586$ g cm^{-3}, $F(000) = 1\,184$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 12.3 cm^{-1}.

Single crystals of the title compound were difficult to obtain, due to their tendency to occur as twins. The sample used for the analysis, even though essentially single, yielded reflections of widely varying widths. The crystal, of size 0.13 × 0.15 × 0.33 mm, was mounted on a computer-controlled Siemens AED automated diffractometer, which was employed to determine cell dimensions and to collect intensity data using Nb-filtered Mo-K_α radiation. Accurate unit-cell and orientation parameters were determined by a least-squares fit to the angular settings of 21 intense diffractometer-centred reflections chosen in diverse regions of reciprocal space. The automatic peak searching, centring, and indexing programs in conjunction with a cell reduction program showed the crystal to be monoclinic and the systematic extinctions observed in the data unambiguously indicated the space group $P2_1/c$.

In measuring the intensities, a θ–2θ scan technique was

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Final fractional atomic co-ordinates for $SnEt_2(dapt)$ (× 10^4) with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Sn	2 530(1)	2 861(1)	5 480(1)	C(14)	3 624(19)	5 123(18)	3 606(12)
O(1)	1 793(12)	2 066(13)	6 483(7)	C(15)	3 187(17)	5 211(16)	5 801(11)
O(2)	2 836(13)	4 405(10)	6 135(7)	S(1)	592(8)	−745(8)	7 005(5)
N(1)	1 509(13)	462(14)	5 809(9)	C(1)	888(16)	543(16)	7 004(10)
N(2)	2 002(13)	1 074(13)	5 254(9)	C(2)	434(9)	1 233(10)	7 654(6)
N(3)	2 866(15)	2 308(15)	4 306(9)	C(3)	−91(19)	246(19)	8 096(12)
N(4)	3 291(13)	4 273(13)	4 777(9)	C(4)	3(20)	−745(20)	7 794(13)
N(5)	3 354(16)	5 285(13)	5 079(9)	S(2)	3 614(8)	7 437(7)	5 804(5)
C(5)	1 453(18)	1 121(20)	6 388(11)	C(16)	3 343(17)	6 268(18)	6 190(11)
C(6)	2 112(17)	557(19)	4 643(11)	C(17)	3 223(11)	6 361(12)	7 035(7)
C(7)	1 814(20)	−602(16)	4 526(11)	C(18)	3 363(23)	7 631(22)	7 097(15)
C(8)	2 620(17)	1 348(19)	4 099(12)	C(19)	3 606(25)	8 172(23)	6 503(16)
C(9)	2 763(21)	913(20)	3 370(12)	C(20)	4 358(14)	2 370(13)	5 918(9)
C(10)	3 194(22)	1 700(21)	2 875(12)	C(21)	4 664(26)	1 281(27)	5 934(16)
C(11)	3 346(19)	2 777(23)	3 082(11)	C(22)	773(21)	3 505(22)	5 160(13)
C(12)	3 200(18)	3 053(17)	3 808(11)	C(23)	−19(35)	2 899(34)	4 672(21)
C(13)	3 366(18)	4 175(17)	4 079(10)				

Table 2. Selected bond distances (Å) and angles (°) for $SnEt_2(dapt)$ with e.s.d.s in parentheses

Sn–O(1)	2.285(14)	Sn–O(2)	2.251(13)	O(1)–C(5)	1.23(3)	C(6)–C(8)	1.53(3)	N(5)–N(4)	1.36(2)
Sn–N(2)	2.300(16)	Sn–C(20)	2.182(15)	C(5)–N(1)	1.34(3)	C(5)–C(1)	1.51(3)	N(4)–C(13)	1.29(2)
Sn–N(3)	2.306(17)	Sn–C(22)	2.122(23)	N(1)–N(2)	1.41(2)	C(20)–C(21)	1.38(4)	C(13)–C(12)	1.47(3)
Sn–N(4)	2.356(16)			N(2)–C(6)	1.30(3)	O(2)–C(15)	1.24(2)	C(15)–C(16)	1.48(3)
						C(15)–N(5)	1.35(3)	C(22)–C(23)	1.40(4)

O(1)–Sn–N(2)	68.4(6)	Sn–C(20)–C(21)	119(2)	N(1)–N(2)–Sn	119(1)	C(15)–N(5)–N(4)	109(2)
N(2)–Sn–N(3)	67.1(6)	Sn–C(22)–C(23)	118(2)	C(6)–N(2)–Sn	125(1)	N(5)–N(4)–C(13)	119(2)
N(3)–Sn–N(4)	67.6(6)	Sn–O(1)–C(5)	115(1)	N(2)–C(6)–C(8)	108(2)	N(5)–N(4)–Sn	118(1)
N(4)–Sn–O(2)	67.9(5)	O(1)–C(5)–N(1)	130(2)	Sn–O(2)–C(15)	117(1)	C(13)–N(4)–Sn	122(1)
O(2)–Sn–O(1)	89.0(5)	C(5)–N(1)–N(2)	107(2)	O(2)–C(15)–N(5)	127(2)	N(4)–C(13)–C(12)	114(2)
C(20)–Sn–C(22)	172.4(8)	N(1)–N(2)–C(6)	115(2)				

employed with a maximum 2θ value of 45.0°, which was successively lowered to 42.0° in view of the rapid fall off of high-angle reflection intensities. From the 3 072 reflections, 2 795 were unique and 1 249 had $I > 2\sigma(I)$. A reference reflection, monitored after each set of 75 reflections, showed only small statistical fluctuations in intensity over the period of the experiment. One quadrant of data ($\pm h$, $+k$, $+l$) was collected at room temperature and the reflection profiles were analysed according to a modified version of the procedure of Lehmann and Larsen.[9] The intensity data were corrected for Lorentz and polarization effects, but not for absorption as the linear absorption coefficient is sufficiently small and the crystal used was of roughly cylindrical shape.

The position of the tin atom was found by using a three-dimensional Patterson map, which was calculated from the entire set of data, and all remaining non-hydrogen atoms were located through a combination of structure factor calculations and difference-Fourier syntheses. The structure was refined by using a full-matrix least-squares procedure minimizing the function $\Sigma w(|F_o - F_c|)^2$. Unit weights were used initially, while in the last stages of refinement a weighting scheme of form $w = [\sigma^2(F_o) + 0.006\,340\ F_o^2]^{-1}$ was applied, which did not reduce the R index, but yielded appreciably lower estimated standard deviations. Both of the thienyl moieties were found to exhibit disorder at S(1), C(2), S(2), and C(17) positions, the evidence for this being reflected in abnormal isotropic thermal parameters for these atoms and in a smeared electron density distribution in the corresponding region. The best resolution of the disorder was achieved by considering two images for each ring related to each other by a pseudo-two-fold axis passing through the C(hydrazidic)–C(thienyl) bond and such that S and C are statistically interchanged between the two sites. All the four peaks were refined as sulphur atoms, the population parameters being based on an iterative procedure which minimized the difference between the thermal parameters. The final values correspond to occupancies of 0.57 [S(1),S(2)] and 0.43 [C(2),C(17)]. Anisotropic thermal parameters were used for all non-hydrogen atoms, excepting those of the thienyl and ethyl moieties which were restricted to isotropic thermal motion. No attempt was made to include hydrogen atoms. Convergence was reached with R and R' equal to 0.0573 and 0.0738, respectively. The final difference map had no electron density greater than 0.60 e Å^{-3} and the largest residual was near one of the ethyl groups, possibly indicating a slight positional disorder of this moiety. A strong low-order reflection, 1 1 1, was removed as it had $F_o \ll F_c$. Throughout the analysis atomic scattering factors for neutral atoms were used. Real and imaginary dispersion corrections for Sn and S were applied to the calculated structure factors.

Calculations were performed on a Cray X-MP/12 computer of CINECA (Casalecchio di Reno, Bologna) with the financial support of the University of Parma. The SHELX 76 suite of programs[10] was used together with other crystallographic computed programs which have been cited elsewhere.[6] Final positional parameters are listed in Table 1, and selected bond distances and angles are given in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

X-*Ray Crystallography of* SnBuCl(dapt).—*Crystal data.* $C_{23}H_{24}ClN_5O_2S_2Sn$, $M = 620.6$, triclinic, space group $P\bar{1}$,

Table 3. Comparison of the main i.r. bands (cm^{-1})

H_2dapt	$SnEt_2$(dapt)	SnBuCl(dapt)	H_2daps	$SnBu_2$(daps)	Assignment
3 160ms			3 260m		ν(NH)
1 695ms					
1 655 (sh)	1 600w		1 690m		
1 640vs, br	1 575m	1 575m	1 650vs	1 620m	ν(CO)
				1 590s	
			1 605s		
1 570ms	1 552m	1 555w	1 570 (sh)	1 545m	Ring
			1 560 (sh)		
1 515ms	1 525s	1 525s	1 545vs	1 520s	δ(NH) + ν(CN)
1 445m	1 490vs, br	1 490 (sh)	1 490m	1 485s	$\delta(CH)_{aryl}$
	1 445 (sh)	1 435ms	1 455vs	1 450ms	
1 410s	1 420s	1 420s		1 400w	$\delta(CH)_{alkyl}$
	1 408s	1 405s			
1 315ms	1 315vs	1 320s	1 305s	1 250ms	ν(CN) + δ(NH)
	530mw, 500mw	555w, 520w		535mw	ν(Sn–C)
	480mw, 430m	480w, 445m		410ms	ν(Sn–O)

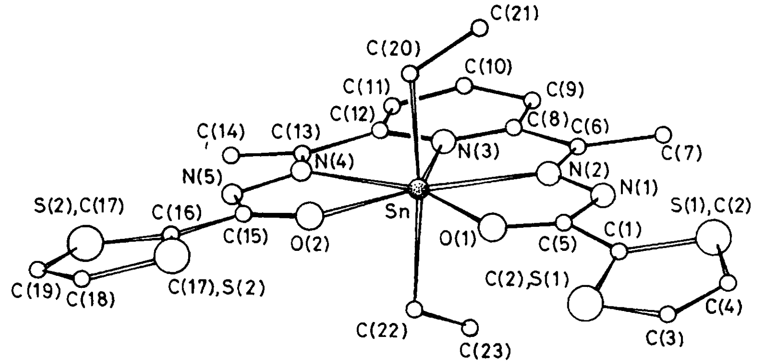

Figure. The asymmetric unit of $SnEt_2$(dapt) showing the atomic labelling scheme

a = 30.864(9), b = 14.966(5), c = 8.572(3) Å, α = 85.41(4), β = 83.88(4), γ = 94.72(3)°, Z = 6.

Although reduced cell calculations did not reveal any symmetry higher than triclinic, the occurrence of three crystallographically independent molecules in the asymmetric unit has to be considered as highly suspect. In addition, a satisfactory refinement of the structure proved impossible, presumably due to twinning and/or disorder effects. Nevertheless, there is no doubt that the compound is correctly identified and that the basic structure is correct. In all the three molecules, which seem to show only trivial structural differences, the tin atom exhibits a slightly distorted seven-co-ordinate pentagonal-bipyramidal co-ordination, in which the butyl group and a chlorine atom reside in the apical positions.

X-Ray Structure of $SnEt_2$(dapt).—A perspective view of the asymmetric unit with the atom labelling scheme is shown in the Figure. The molecule resides on a general position thus giving four formula units per unit cell. The tin atom is seven-co-ordinate, lying in an approximate pentagonal-bipyramidal environment, where two oxygen and three nitrogen atoms from the hydrazone molecule form the equatorial ligand set and the two ethyl groups are the apical ligands. Due to the geometric requirements of the hydrazone structure the pentagon is not regular, as one of the five sides, namely that involving O(1) and O(2), is remarkably longer (*ca.* 0.6 Å) than the other four. Consistent with this, the angle subtended at tin by the two oxygens is significantly enlarged to 89.0(5)° from that in an idealized pentagonal bipyramid (72°), while the other equatorial angles range from 67.1(6) to 68.4(6)°. The largest deviation from the plane of best fit through the five equatorial atoms is 0.04 Å for N(4), with the tin atom lying exactly on it.

The Sn–O and Sn–N bond distances, which average 2.268 and 2.321 Å, respectively, are in good agreement with the range (Sn–O, 2.187—2.273; Sn–N, 2.266—2.337 Å) found in two other seven-co-ordinated pentagonal bipyramidal diorganotin(IV) derivatives containing a quinquedentate hydrazone ligand in the pentagonal 'girdle,' namely $SnPr^n{}_2$(daps)[8] and $SnPh_2$(dapa)[5] [H_2dapa = 2,6-diacetylpyridine bis(2-aminobenzoylhydrazone)]. The Sn–C distances in the three compounds are quite similar and evidently insensitive to the differing nature of the σ-bonded organic group.

There is only one metal complex of H_2dapt which can be compared with the present one, namely $Zn_2(dapt)_2$,[1] in which the hydrazone is also deprotonated and involves two oxygens and three nitrogens in co-ordination to the metal. Apart from these similarities, the two compounds exhibit significant differences that warrant a brief mention. The hydrazone moiety in the tin compound confirms the propensity of this class of ligands to function as an approximately planar, quinquedentate donor so producing seven-co-ordinate stereochemistries, while in the zinc derivative the organic molecule is not planar, its side-chains being twisted by considerably large amounts out from the plane of the central pyridine ring. A second noteworthy feature which is distinctive for the two compounds is that in the zinc derivative the hydrazone unusually bridges through the pyridine nitrogen two six-co-ordinated metal atoms to give a dimeric structure.

The intermolecular contacts are of the normal van der Waals type, the closest approach between atoms of neighbouring

Table 4. ^{119}Sn Mössbauer data (mm s^{-1}) for seven-co-ordinated organotin compounds

Compound[a]	I.s.[b] (mm s^{-1})	Q.s.[c] (mm s^{-1})	Γ[d]	C–Sn–C (calc.)[e]	C–Sn–C (obs.)
(**1**) SnEt$_2$(dapt)[f]	1.31	3.72	0.88, 0.89	166 (150)	172.4[f]
(**2**) SnBuCl(dapt)[f]	0.75	1.80	0.94, 1.04		
(**3**) SnBu$_2$(daps)[f]	1.27	3.73	0.94, 0.94	167 (151)	
(**4**) SnPr$_2$(daps)[f]	1.31	3.82	0.88, 0.86	180 (155)	170.4[g]
(**5**) SnPh$_2$(dapa)[f]	0.89	3.12		175 (131)	176.4[h]
(**6**) SnBuCl(dapa)[f]	0.72	1.61	0.90, 0.86		
(**7**) SnBu$_2$Cl$_2$·aip[f]	1.69	4.19	0.97, 1.14	162[i] (180)	158.3[j]
(**8**) SnPh$_2$(NO$_3$)$_2$·Ph$_3$PO[f]	1.36	4.28	0.94, 0.87	180[k] (180)	178.0[l]
(**9**) SnPh$_2$(NO$_3$)$_2$·Ph$_3$AsO[f]	1.32	4.03	0.97, 0.94	157[k] (180)	156[m]
(**10**) SnEt$_2$Cl$_2$·oxphen		3.94[n]		150[i] (180)	150.4[o]
(**11**) SnMe$_2$(NCS)$_2$·terpy		4.29[p]		168[i] (180)	173.7[q]

[a] Abbreviations: H$_2$dapt = 2,6-diacetylpyridine bis(2-thenoylhydrazone), H$_2$daps = 2,6-diacetylpyridine bis(salicyloylhydrazone), H$_2$dapa = 2,6-diacetylpyridine bis(2-aminobenzoylhydrazone), aip = 2-phenyl-3-(*N*-2′-pyridylmethylimino)-4-oxo-1,2,3,4-tetrahydroquinazoline, oxphen = 2-(5-methyl-1,2,4-oxadiazol-3-yl)-1,10-phenanthroline, terpy = 2,2′:6′,2″-terpyridyl. [b] ±0.01 mm s^{-1}. [c] ±0.02 mm s^{-1}. [d] Full-width at half-height. [e] Calculated using equation (1), with {alkyl} = −0.97, {aryl} = −0.78 mm s^{-1}. Values in parentheses correspond to the predicted angles using the respective partial q.s. values for five- or six-co-ordinate systems. See text for discussion. [f] This work. [g] Ref. 8. [h] Ref. 5. [i] Calculated using {alkyl} = −1.09 mm s^{-1}. [j] C. Pelizzi, G. Pelizzi, and P. Tarasconi, *Polyhedron*, 1983, **2**, 145. [k] Calculated using {aryl} = −1.07 mm s^{-1}. [l] M. Nardelli, C. Pelizzi, and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1978, 131. [m] M. Nardelli, C. Pelizzi, G. Pelizzi, and P. Tarasconi, *Inorg. Chim. Acta*, 1978, **30**, 179. [n] F. E. Smith, personal communication. [o] L. Prasad, T. Le Page, and F. E. Smith, *Acta Crystallogr., Sect. B*, 1982, **38**, 2890. [p] J. C. May and C. Curran, *J. Organomet. Chem.*, 1972, **39**, 289. [q] D. V. Naik and W. Scheidt, *Inorg. Chem.*, 1973, **12**, 272.

Table 5. ^{119}Sn N.m.r. data for seven-co-ordinated organotin compounds and related compounds

Compound[a]	δ(^{119}Sn)/p.p.m.[b]	Co-ordination number
SnBu$_2$(daps)[c]	−452	7
SnBu(ox)$_3$[d]	−561	7
SnMe$_2$(NCS)$_2$(terpy)[d]	−409	7
SnMe$_2$(ox)$_2$[e]	−237	6
SnBu$_2$(ox)$_2$[e]	−262	6
SnBu$_2$(OMe)$_2$[e]	−159	5
SnBu$_2$(OBu^t)$_2$[e]	−34	4
SnPh$_2$(NO$_3$)$_2$·Ph$_3$PO[c]	−630	7
SnPh$_2$(NO$_3$)$_2$·Ph$_3$AsO[c]	−561	7
SnPh$_2$(ox)$_2$[e]	−397	6
SnPh$_2$(acac)$_2$[e]	−514	6
SnPh$_2$(sab)[e]	−329	5
SnPh$_2$(OSiPh$_3$)$_2$[e]	−188	4

[a] See Table 4 for abbreviations; H$_2$sab = *N*-(2-hydroxyphenyl)salicylaldimine, ox = oxamate, acac = acetylacetonate. [b] SnMe$_4$ as reference. [c] This work. [d] J. Otera, T. Hinoishi, and R. Okawara, *J. Organomet. Chem.*, 1980, **202**, C93. [e] B. Wrackmeyer, *Ann. Rep. NMR Spectrosc.*, 1985, **16**, 73.

molecules being 3.23(3) Å between O(1) of the asymmetric unit and C(10) at x, $\frac{1}{2} - y$, $\frac{1}{2} + z$.

Spectroscopy.—The main vibrational bands of H$_2$dapt, H$_2$daps, and the three tin complexes are listed in Table 3 together with the relative assignments. The disappearance of the ν(NH) bands as a consequence of deprotonation of the ligand is evident owing to the anhydrous nature of all the chelates. In all the complexes amide I [ν(CO)] and amide II [δ(NH) + ν(CN)] bands undergo negative and positive shifts, respectively. This spectroscopic pattern is similar to that of transition metal complexes which we have previously examined.[1,2] The vibrational bands involving the tin atom mainly refer to Sn–O and Sn–C bonds, while for the ν(Sn–N) band assignment is rather difficult.

While i.r. data give valuable information regarding the composition of the adducts, they give no indication as to their structures. To address this latter question, we have recorded ^{119}Sn Mössbauer and, solubility permitting, ^{119}Sn n.m.r. spectra, of a range of seven-co-ordinated organotin complexes (Tables 4 and 5), including the three novel compounds described herein.

For those complexes containing an SnR$_2$ moiety, quadrupole splitting (q.s.) values fall in the range 3.12—4.29 mm s^{-1}. These values can arise from organotin compounds of co-ordination five, six, or seven at the metal,[11] and as such are not diagnostic of this structural parameter. However, the q.s. in such compounds has been used to estimate the C–Sn–C angle, and as far as five- and six-co-ordinated tin is concerned, this has met with some success.[12–14] Certainly, in a series of related compounds the trends in C–Sn–C can be predicted, even if the accuracy of the predicted angle is of the order of ±13°. It is thus of interest to evaluate this model for seven-co-ordinated diorganotin compounds in the light of the crystallographic data now available for derivatives of quinquedentate ligands.

The model assumes the q.s. arises from point charge hydrocarbon groups separated by an C–Sn–C angle of $(180 - 2\theta)°$, with contributions from other ligands being ignored. This assumption leads to estimated q.s. data which may be in ±0.4 mm s^{-1} error in comparison with the observed value, although in the case of six-co-ordinated SnR$_2$ compounds the agreement is often well within this range. The model uses equation (1),

$$|\text{q.s.}| = 4\{\text{R}\}(1 - 3\cos^2\theta\sin^2\theta)^{\frac{1}{2}} \qquad (1)$$

where {R} denotes the partial quadrupole splitting (of the group R) arising from either the alkyl or aryl groups. For five- and six-co-ordinated tin, the working values for {alkyl} and {aryl} are −1.03 and −0.95 mm s^{-1} respectively,[12] but these values yield C–Sn–C angles which are in poor agreement with crystallographic observation for seven-co-ordinate systems (see values in parentheses, Table 4). However, the model does appear to retain some validity for seven-co-ordinate compounds on the basis of the observed 2:1 ratio of q.s. values for (**1**) and (**2**) which is expected since {Cl} = 0.0 mm s^{-1} by definition.[15] The q.s. value for (**6**) is also reasonable in this light, allowing for the variation in ligands.

Compounds (**1**) and (**4**) allow us to evaluate a working value for {alkyl} in seven-co-ordinate systems embodying quinquedentate ligands using the crystallographic data and observed q.s. values. Equation (1) yields {alkyl} = −0.94 and −1.00 mm s^{-1} respectively, which show reasonable internal consistency, and using an average value (-0.97 mm s^{-1}) we predict a C–Sn–C angle in (**3**), for which no structural data are available, of 167°. From the q.s. value for (**5**), we obtain an estimate for {aryl} in similar seven-co-ordinate systems of -0.78 mm s^{-1}.

However, both these partial quadrupole splittings give poor correlations between observed and calculated C–Sn–C angles when applied to seven-co-ordinate diorganotin compounds which involve bonding between the metal and a series of ligands of low denticity. Compounds (**7**), (**10**), and (**11**) form a group which allows a consistent value of {alkyl} in seven co-ordinate tin compounds of this second type to be estimated as -1.09 mm s^{-1} (average of -1.11, -1.09, and -1.07 mm s^{-1} respectively). Similarly, (**8**) and (**9**) yield an alternative value for {aryl} of -1.07 mm s^{-1} (average of -1.07 and -1.07 mm s^{-1} respectively).

The value of {R}, of course, need not be a constant from compound to compound even when the co-ordination number is invariant. Sham and Bancroft[12] have pointed out that the *effective* constance of {R} for a particular co-ordination number merely implies that the model contains two or more compensating variables. For the two types of seven-co-ordinate diorganotins studied herein, the two pairs of {R} values probably arise from the need to compensate for neglecting different equatorial ligand sets, one of which involves an ordered, relatively planar moiety, the other a collective of potentially dissimilar donors which are geometrically freer to adopt a distorted co-ordination sphere.

Of the four partial quadrupole splitting values derived for seven-co-ordinate systems, the two {aryl} values are the more tenuous. For compounds embracing quinquedentate ligands, the value of -0.78 mm s^{-1} is based upon only one available crystallographic study and will clearly be re-evaluated as more data become available. The two $SnPh_2(NO_3)_2$ adducts (**8**) and (**9**) do give a consistent value of {aryl} which suggests that it may be a good initial estimate for low-denticity systems of this type. Our reservation here arises from the fact that $SnMe_2(NO_3)_2$ gives poor agreement for the six-co-ordinate model using the accepted value of {alkyl} = -1.03 mm s^{-1} for this co-ordination number, which suggests that $\{NO_3^-\}$ may be too significant to be ignored.* Thus, the value of {aryl} = -1.07 mm s^{-1} might work well for diphenyltin nitrate systems, but this is not necessarily so for other similar seven-co-ordinated diphenyltin compounds.

Mössbauer q.s. values for two seven-co-ordinated compounds containing the SnRCl moiety [(**2**) and (**6**)] appear to be the first available data for such arrangements. Unfortunately, such data also cannot be used as diagnostic of seven-co-ordinated tin, since six-co-ordinated complexes of similar composition, *e.g.* $SnRCl_3L_2$ (L_2 = bidentate or two unidentate donors) give rise to similar q.s. values.[16,17]

As a diagnostic of tin co-ordination number, ^{119}Sn n.m.r. chemical shifts are potentially more useful than Mössbauer q.s. values due to the greater range and sensitivity of the former parameter. Our attempts to evaluate this supposition with respect to seven-co-ordinated organotin complexes have been somewhat thwarted by the exceedingly low solubility of most of the materials. Data for three compounds are shown in Table 5, along with data for related systems of lower co-ordination for comparison. For two of the three seven-co-ordinated compounds studied [(**3**) and (**8**)], solutions were made up in co-ordinating solvents ([$^2H_6$]acetone and [$^2H_4$]methanol, respectively), which gives rise to the question of structural integrity in solution. For the derivative of the quinquedentate ligand [(**3**)], it is unlikely that acetone would replace part of the ligand in co-ordinating to tin, on 'chelate effect' grounds. This is a more likely possibility for (**8**), but presumably the resulting complex will retain a co-ordination about tin of seven. It is clear from Table 5 that seven-co-ordinate complexes give rise to higher field shifts than corresponding six-co-ordinated systems of similar composition, thus providing a more reliable guide to co-ordination number than the Mössbauer experiment. Moreover, Table 5 indicates a continuous upfield shift in resonances for compounds of similar composition but with co-ordination numbers increasing from four to seven.

Conclusions

119-Tin n.m.r. chemical shifts provide a clearer diagnostic discrimination between six- and seven-co-ordinate tin compounds than does Mössbauer spectroscopy. The C–Sn–C angle in seven-co-ordinate diorganotin compounds can be estimated using established point-charge procedures and using values of {R} of -0.97 and -0.78 mm s^{-1} for dialkyl- or diaryl-tin derivatives of a single quinquedentate ligand respectively. For seven-co-ordinate derivatives involving ligands of low denticity, {R} = -1.09 or -1.07 mm s^{-1} respectively are more appropriate. These values are based on a limited crystallographic data set, and no doubt will be subject to refinement as more structural data become available.

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* Reasonable agreement between the observed and calculated C–Sn–C angles occurs if $SnMe_2(NO_3)_2$ is assumed to be tetrahedral and {Me} = -1.37 mm s^{-1} is used. However, this analysis is not consistent with the observed crystal structure.[12]