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MÖSSBAUER AND INFRARED SPECTROSCOPIC STUDIES OF SOME ORGANOTIN(IV) SCHIFF BASE COMPLEXES

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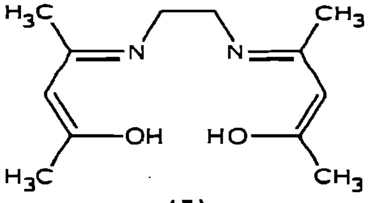
SUMMARY

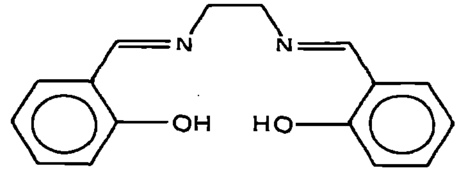
Several organotin(IV) complexes with quadri- and terdentate anionic Schiff base ligands have been investigated in the solid state using ^{119}Sn Mössbauer and IR spectroscopies. Mössbauer parameters derived from both zero-field and magnetically perturbed spectra suggest that the R_2Sn(Salen)(R = Me, Et, Ph) and Me_2Sn(Saldap-2-OH) complexes have similarly distorted *trans*-octahedral structures. However, in Ph_2Sn(HSaldap-2-O) the ligand appears to be only terdentate, leading to a pentacoordinate structure similar to those of the R_2Sn(Sal-*N*-2-OC_6H_4) derivatives (R = Me, Ph). For Ph_3Sn(Sal-*N*-2-OC_6H_4) the asymmetry parameter of the electric field gradient is close to unity, confirming a *mer*-octahedral configuration for this complex.

INTRODUCTION

Considerable attention has been directed recently towards organotin complexes with Schiff bases[1-8], although interpretations of the results are often at variance. For example, Mössbauer spectra[4,5] for some adducts of the type R_2SnCl_2-(H_2Acacen) [H_2Acacen = *N,N'*-ethylenebis(acetylacetone imine) (I)] suggest octahedral structures with *trans* tin–carbon bonds in the solid state, but there is uncertainty about the dispositions of the remaining groups attached to tin. Smith and Dodd[4] assume a *cis*-dichloro arrangement with the neutral ligand acting as a bidentate chelating group, whilst Barbieri *et al.*[5] favour a *trans*-dichloro arrangement in which (I) acts as a bridging group, leading to a polymeric structure.


(I)

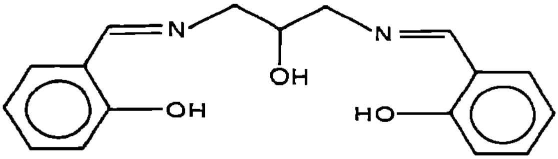
Relatively fewer studies have been reported[3,7,8] on diorganotin(IV) complexes of dianionic quadridentate Schiff bases, such as R_2Sn(Salen) [H_2Salen = *N,N'*-ethylenebis(salicylaldimine) (II)]. The PMR spectrum of Me_2Sn(Salen) is complex[3,7], with two singlets observed for the $SnMe_2$ resonance while the Salen C(H)=N and



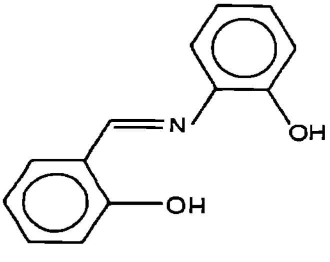
(II)

$(CH_2)_2$ protons are also each observed as two sharp lines. Murray and co-workers[7] interpret these results in terms of a *cis*-dimethyl arrangement and a non-planar quadridentate Salen ligand, although Kawakami *et al.*[3] suggest a mixture of *cis* and *trans* isomers in solution. Mössbauer measurements on the solid complex have been interpreted[8] in terms of a distorted *trans*-dimethyl structure, and this has been confirmed[9] very recently by X-ray crystallography. The X-ray structure shows a nearly planar Sn(ONNO) group and C–Sn–C angle of 160°. It seems likely that the complicated NMR spectrum of this complex in solution is due either to facile decomposition, reaction with the solvent ($CDCl_3$), fluxional behaviour, or some combination of these effects.

The present work was undertaken with a view to studying the solid state structures of several related diorganotin(IV)–Schiff base derivatives via infrared and Mössbauer spectroscopies. In particular it was hoped that magnetically perturbed Mössbauer spectra, from which one can deduce both the sign of the ^{119}Sn quadrupole coupling constant ($e^2 \cdot q \cdot Q$) and magnitude of the asymmetry parameter (η), would provide a sensitive tool for structure elucidation in such complexes. In addition to (II), the Schiff bases employed were *N,N'*-(2-hydroxytrimethylene)bis-(salicylaldimine) [H_2Saldap-2-OH, (III)] and *N*-(2-hydroxyphenyl)salicylaldimine [HSal-*N*-(2-HOC_6H_4), (IV)]. (III) differs from (II) only in that the ethylene bridge between the



(III)



(IV)

two salicylaldimine moieties is replaced by a 2-hydroxytrimethylene bridge, whereas (IV) is potentially terdentate rather than quadridentate.

EXPERIMENTAL

The R_2Sn derivatives of (II) (R = Me, Et, Ph) and the Me_2Sn derivatives of (III) and (IV) were prepared by published procedures[7,10]. Analytical data for these and the other complexes reported here are given in Table 1.

TABLE 1

ANALYTICAL DATA FOR ORGANOTIN(IV) SCHIFF BASE COMPLEXES

Compound	*Found (calcd.) (%)*			
	C	*H*	*N*	*Sn*
Me_2Sn(Salen)	51.75	5.07	6.77	28.8
	(52.10)	(4.82)	(6.75)	(28.63)
Et_2Sn(Salen)	54.27	5.69	6.51	
	(54.20)	(5.42)	(6.32)	
Ph_2Sn(Salen)	62.18	4.64	4.88	24.8
	(62.36)	(4.45)	(5.19)	(24.56)
Me_2Sn(Saldap-2-OH)	51.24	5.19	6.51	26.8
	(51.26)	(4.95)	(6.29)	(26.71)
Ph_2Sn(HSaldap-2-O)	61.66	5.04	4.59	20.5
	(61.18)	(4.57)	(4.92)	(20.89)
Me_2Sn(Sal-*N*-2-OC_6H_4)	49.71	4.22	3.73	33.1
	(50.01)	(4.17)	(3.89)	(33.01)
Ph_2Sn(Sal-*N*-2-OC_6H_4)	62.32	4.26	2.64	24.7
	(62.01)	(3.93)	(2.89)	(24.56)
Ph_3Sn(Sal-*N*-2-OC_6H_4)	66.24	4.81	2.27	21.4
	(66.22)	(4.45)	(2.49)	(21.15)

Reaction of triphenyltin hydroxide with H_2Salen

1.83 g (5.0 mmol) of triphenyltin hydroxide and 0.67 g (4.0 mmol) of H_2Salen were azeotropically distilled in benzene for 4 h. Upon cooling a yellow solid was precipitated, whose analytical data, melting point, IR and Mössbauer spectra were identical to an authentic sample of Ph_2Sn(Salen).

Preparation of Ph_2Sn[Sal-N-(2-OC_6H_4)]

0.72 g (4.0 mmol) of freshly prepared diphenyltin oxide and 0.53 g (4.0 mmol) of H_2Sal-*N*-(2-HOC_6H_4) were refluxed azeotropically in benzene for 1.5 h. The solution was concentrated under vacuum, and orange-brown crystals formed upon standing. Ph_2Sn(HSaldap-2-O) was prepared in a similar manner from diphenyltin oxide and H_2Saldap-2-OH.

Preparation of Ph_3Sn[Sal-N-(2-HOC_6H_4)]

0.73 g (2.0 mmol) of triphenyltin hydroxide and 0.43 g (2.0 mmol) of the Schiff base were refluxed in benzene for 3 h, during which the water formed by the reaction was removed. Upon cooling an orange precipitate appeared which was collected by filtration and recrystallised from benzene.

Spectroscopic measurements

Infrared spectra in the range 4000–250 cm^{-1} were recorded on a Perkin–Elmer 457 instrument, with the samples usually as nujol mulls.

Mössbauer measurements in zero magnetic field were made using a spectrometer which has been described[11], the finely powdered samples being maintained at liquid nitrogen temperature. The room-temperature source was 10 mC $BaSnO_3$, and isomer shifts are reported relative to this source. The data were least-squares

(*continued on* p. 240)

TABLE 2

INFRARED SPECTRA IN THE REGION 1700–250 cm^{-1}[a]

H_2Salen	Me_2SnSalen	Et_2SnSalen	Ph_2SnSalen	H_2Saldap-2-OH	Me_2Sn(Saldap-2-OH)
1637(sh)	1640 m (sh)	1640 (sh)	1640 (sh)	1635 (sh)	1640 (sh)
1633 vs	1630 (sh)	1630 vs		1630 vs	1630 vs
	1621 vs	1628 (sh)	1620 s		1620 vs
1612 s	1600 s	1599 s	1600 s	1610 s	1600 s
1580 vs	1578 w	1579 m		1575 s (br)	1575 m
1565 m			1560 (sh)		1561 w
	1535 s	1542 s	1532 s		
	1528 m	1535 (sh)	1525 (sh)		1526 m
	15 al (sh)				1520 m
1498 vs	1514 w	1495 m	1510 w	1495 (sh)	
1485 s			1480 m	1490 s	1490 m
1470 s*	1460 s		1460 s		
1450 s	1450 m	1440 m	1442 s		1450 s
1440 s					
1420 s			1425 m	1415 m	1420 (sh)
	1405 s	1408 s	1405 s		1390 s
1370 m		1398 m			
				1350 m	
1343 w (sh)	1344 s	1345 s	1340 s (br)	1340 m	1345 s
			1338 (sh)		
1318 m	1315 s (br)	1318 s		1310 w	1324 s
		1298 s	1300 m (br)		
1294 m	1288 w	1288 s			
1284 s				1275 s	1280 s
	1262 vw	1265 vw	1263 w		
1248 m	1245 m	1245 w	1245 w	1245 m	1235 w
1220 m	1200 vw	1220 w		1215 (sh)	
1200 s	1190 s	1190 s	1185 m	1202 s	1190 s
1150 vs	1152 s	1150 s	1147 s	1154 m	1148 s
	1130 m	1130 m	1131 m	1145 m	1130 w
	1125 (sh)			1125 w	
1115 m				1112 m	1118 m
1105 m (sh)	1092 w	1095 w	1085 w	1100 m	1100 w
			1070 w	1080 m	1090 m
			1076 w		
		1055 vw			
1043 s	1043 m	1043 m	1040 w	1045 s	1040 s
	1031 m	1035 m (sh)	1030 w	1033 s	
1020 vs		1020 m	1025 w (sh)	1024 s	1022 s
	988 w	980 m	985 w		
987 m	978 vw	970 m	973 w	968 m	968 m (br)

$Ph_2Sn[HSaldap$-2-$O]$	$HSal$-N-(2-HOC_6H_4)	$Me_2Sn(Sal$-N-2-$OC_6H_4)$	$Ph_2Sn(Sal$-N-2-$OC_6H_4)$	$Ph_3Sn(Sal$-N-2-$HOC_6H_4)$	*Suggested assignments*
1638 (sh)	1640 (sh)				
1630 vs	1632 s		1628 m	1620 (sh)	ν(C=C)
1617 vs	1620 s	1610 vs	1605 s	1608 s	ν(C=N)
1600 s	1590 s	1590 s	1592 s	1592 s	ν(C=C)
1580 m		1585 m	1580 m		
		1565 m	1567 (sh)		
1540 m			1538 s (br)	1545 m	ν(C=N)
1535 s	1530 s	1530 m	1530 m	1538 m (sh)	
		1512 m			
1497 m					Phenyl ring
	1485 s	1480 s	1487 s	1490 m	
				1480 s	
	1470 m				
1440 s	1445 s	1450 s	1442 m		ν(C–N)
1430 m			1432 m	1435 m	
1430 m	1420 m			1425 m	
1400 s		1390 s	1386 s	1393 m	ν(C–N)
	1380 s		1367 m		
1354 m					
1344 s			1348 w		ν(C–O)
1337 s		1336 m	1342 w		
1317 s (br)	1310 m	1327 m	1317 s	1307 m	ν(C–O)
		1300 m	1300 s		
			1285 m	1284 m	
1280 s	1275 s				δ(O–H)
		1268 s	1269 m	1268 s	
1247 m	1247 m	1244 m			
1220 m	1225 s	1215 m	1217 m	1218 s	
1205 m	1205 (sh)				
1200 m					
1195 w	1180 w	1190 w		1190 w	
		1175 w	1172 m	1175 m	
1150 s	1165 m	1150 s	1147 s	1150 s	*o*-Disubst. phenyl
1130 s	1143 s	1132 m	1137 s	1130 m	
1120 m	1120 m	1110 w	1109 w	1118 m	
1100 w	1100 w				
1075 m			1073 m	1072 m	
1070 m			1064 w		
1057 m					
1042 s		1040 w		1040 m	
	1030 m		1030 m		
1023 s	1018 m	1025 w	1025 m	1025 (sh)	*o*-Disubst. phenyl
985 w					
975 m	970 w	966 m	972 w		*o*-Disubst. phenyl

(*continued*)

TABLE 2 (*continued*)

H_2Salen	$Me_2SnSalen$	$Et_2SnSalen$	$Ph_2SnSalen$	$H_2Saldap$-2-OH	Me_2Sn (Saldap-2-OH)
970 m	950 m	945 w	950 w		
936 m				936 m	940 w
900 m	904 m	905 s	903 m		903 m
	890 w	885 w		890 m	885 m
				881 m	
855 s (br)	858 (sh)	855 s	858 w	865 m	865 w
	852 m	845 m	848 w	850 m	850 m
809 w				835 m	810 m
770 s	780 m	775 m (br)	783 w	784 m	775 s
				765 s	765 s
755 vs	760 s	755 s	760 m	755 s	755 s
750 vs	750 (sh)	748 vs	753 s	746 vs	
740 vs	740 m	740 (sh)	731 s	731 s	732 s
720 s	722 w	720 m	723 (sh)	718 m	
			698 m		
			655 w	656 m	655 m
645 m	640 w	645 w	635 w	650 m	635 w
				640 w	
			620 vw		
	600 m	605 m	600 m	595 w	600 s
	575 (sh)	585 s	575 w	585 w	580 s
	568 s	568 w			572 s
560 m				560 w	
556 m	554 (sh)			548 w	550 (sh)
			533 w		
	521 m	525 (br)			520 w
485 m	485 w	486 w	475 w		495 s
470 m	460 m	460 w			479 m
	448 w	443 w		458 m	460 w
			463 s		
430 w			459 s		
				410 w	418 m
	400 m	390 m	397 m	400 w	388 s
375 m	370 m	370 m	368 m	370 w	370 m (sh)
360 m	345 m	355 m	340 m	355 w	
					330 m
315 s	320 w			320 w	321 m
			300 m (br)		300 vw
280 w	280 m		280 vw		
					260 m
					250 m

$Ph_2Sn[HSaldap$- -2-$O]$	$HSal$-N- -(2-HOC_6H_4)	$Me_2Sn(Sal$- -N-2-OC_6H_4)	$Ph_2Sn(Sal$- -N-2-OC_6H_4)	$Ph_3Sn(Sal$- -N-2-HOC_6H_4)	*Suggested assignments*
950 m					
935 w			925 m	932 w	
925 m	914 m	920 m	919 m	920 w	
917 m					
900 m	903 m			908 w	
890 m					
		871 w	875 m	878 s	
	894 w	852 w	855 m	858 w	
850 m			842 m	845 w	
846 m		831 m	833		
788 m		770 m	780 m	774 m	
762 vs	765 s				
751 s				756 m	
740 m	741 s	750 s	748 s	748 m	*o*-Disubst. phenyl
730 s	727 s	730 vs	730 s	730 (sh)	*o*-Disubst. phenyl
724 vs			725 vs	725 s	
693 s			693 s	698 s	
652 w			657 w		
643 w			657 w		
615 vw		610 m	625 vw	618 vw	6b (B_2) phenyl ring
598 m		600 m	605 m		ν(Sn–O)
				582 m	
	570 w	568 m	570 w	568 (sh)	ν_{as}(Sn–C)
550 m	548 m				
535 (sh)	523 m	527 m	536 s		
		520 m			ν_s(Sn–C)
		485 m		490 w	
465 w	475 s	470 m	475 s		
455 w	450 w				
445 s			448 m	453	16b (B_1) phenyl ring
435 s	435 w	435 w	436 m	445 s	
415 w	420 w				
400 w				402 m	ν(Sn–N)
355 w		352 m	357 m	344 m	ν(Sn–N)
345 m	340 w				
320 m	325 w	318 m	318 m	312 m	
	295 m (br)				
280 m				280 m	
270 m			270 m	270 m	ν_{as}(Sn–phenyl)

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[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; (br), broad; (sh), shoulder.

fitted to Lorentzian line shapes using a programme which imposes no constraints on the fitting parameters. The estimated precision of these measurements is ±0.05 mm $\cdot s^{-1}$.

Magnetically perturbed Mössbauer spectra were recorded with both source and absorber at 4.2 K. The absorber was stationed at the centre of a Westinghouse superconducting solenoid, and magnetic fields up to 50 kG were applied parallel to the direction of the γ-ray beam. The source was driven vertically by an Austin Science Associates model S3 drive unit mounted in the vacuum space of the cryostat. Care was taken to ensure that the source was outside the fringing field of the magnet. Data were fitted to theoretically computed spectra using a programme written by J. C. Scott[12]. The input parameters were the magnitude of the applied field (H_{app}), zero-field quadrupole splitting (ΔE_Q) and linewidth (Γ), and the sign of $e^2 \cdot q \cdot Q$ (which in every case was obvious from a visual inspection of the data). The asymmetry parameter was then varied to obtain the best fit between observed and calculated spectra.

RESULTS AND DISCUSSION

Infrared data in the 1700–250 cm^{-1} region for the Schiff base ligands (II)–(IV) and the organotin complexes derived from them are given in Table 2. The spectra are very complicated and in many cases band assignments cannot be made with certainty. Tentative assignments for a number of the bands, arrived at largely by comparison with previously published suggestions for closely related ligands and complexes[1,2,7-9,13-25], are given in the last column of Table 2.

Our discussion will centre primarily on the ^{119}Sn Mössbauer data given in Table 3, with supporting evidence from the IR spectra. The ΔE_Q values for the R_2Sn-(Salen) complexes lie at the low end of the range normally observed for *trans*-R_2SnX_4 compounds[26,27]. This is not unexpected in view of the reported[9] C–Sn–C angle of 160° in the methyl derivative. Since it is the organic groups which largely determine the magnitude of ΔE_Q, the rather large departure of the Me_2Sn fragment from linearity is reflected in a reduced quadrupole splitting. The very smimilar δ and ΔE_Q values

TABLE 3

MÖSSBAUER PARAMETERS FOR THE COMPLEXES AT 90 K

Compound	δ^a (*mm*$\cdot$*s*$^{-1}$)	ΔE_Q (*mm*$\cdot$*s*$^{-1}$)	Γ_1 (*mm*$\cdot$*s*$^{-1}$)	Γ_2 (*mm*$\cdot$*s*$^{-1}$)
Me_2Sn(Salen)	1.13	+3.42	1.01	1.02
Et_2Sn(Salen)	1.25	3.31	1.13	1.13
Ph_2Sn(Salen)	0.88	+2.88	1.05	1.02
Ph_2Sn(Salen)[b]	0.88	2.86	1.13	1.14
Me_2Sn(Saldap-2-OH)	1.16	3.31	1.09	1.14
Ph_2Sn(HSaldap-2-O)	0.95	+2.05	0.92	1.00
Me_2Sn(Sal-*N*-2-OC_6H_4)	1.14	+3.04	1.23	1.25
Ph_2Sn(Sal-*N*-2-OC_6H_4)	0.99	2.19	0.99	0.86
Ph_3Sn(Sal-*N*-2-OC_6H_4)	1.20	−2.88	1.11	1.10
Me_2SnCl(Ox)[c]	1.26	3.12		
Ph_2SnCl(Ox)[c]	1.12	2.40		

[a] With respect to $BaSnO_3$ at room temperature. [b] Sample prepared from Ph_3SnOH and H_2Salen. [c] Ref. 2.

found for dimethyl and diethyltin(Salen), together with the IR data, leave little doubt that these derivatives have similarly distorted *trans*-octahedral structures in the solid state.

Ph_2Sn(Salen) exhibits significantly lower values of δ and ΔE_Q than do the alkyltin compounds. Some lowering of both parameters is expected from electronegativity considerations and the differences observed here are not inconsistent with trends observed in similar series of presumably isostructural compounds[21,26,27]. For example, a recent study of a large number of Lewis base adducts of R_2SnCl_2(R = Me, Ph)[21] shows differences in δ values between corresponding methyl and phenyl derivatives ranging from 0.10 to 0.26 $mm \cdot s^{-1}$, compared to 0.25 $mm \cdot s^{-1}$ for the Salen complexes. Table 4 gives quadrupole splitting data for eight pairs of dimethyl and diphenyltin compounds, all of which are either believed or known to have *trans*-octahedral structures. In every case the methyl derivative shows the larger splitting, the differences ranging from 0.32 to 0.61 $mm \cdot s^{-1}$. Thus, there is nothing unusual about the difference of 0.54 $mm \cdot s^{-1}$ observed for the R_2Sn(Salen) complexes, and no apparent reason to doubt that Ph_2Sn(Salen) also has a distorted *trans*-octahedral structure, very similar to that of the methyl derivative.

TABLE 4

^{119}Sn MÖSSBAUER QUADRUPOLE SPLITTINGS FOR SOME PAIRS OF *trans*-OCTAHEDRAL DIMETHYL- AND DIPHENYLTIN DERIVATIVES

Compound	$\Delta E_Q(Me)$ $(mm \cdot s^{-1})$	$\Delta E_Q(Ph)$ $(mm \cdot s^{-1})$	$\Delta[\Delta E_Q(Me-Ph)]$ $(mm \cdot s^{-1})$	*Ref.*
$R_2SnCl_4^{-2}$	4.32	3.80	0.52	35
$R_2SnCl_2(Bipy)$[a]	4.08	3.51	0.57	36, 37
$R_2SnCl_2(Py)_2$[b]	4.00	3.39	0.61	38, 37
$R_2SnCl_2(Me_2SO)_2$	4.18	3.86	0.32	21
$R_2SnCl_2(Ph_2SO)_2$	4.19	3.73	0.46	21
$R_2SnCl_2(PyO)_2$[c]	4.02	3.47	0.55	21
$[R_2SnCl(Terpy)]ClO_4$[d]	3.50	3.01	0.49	39
$[R_2SnCl(Terpy)]BPh_4$[d]	3.58	3.24	0.34	39
			Ag. 0.48	

[a] Bipy 2,2'-bipyridine. [b] Py pyridine. [c] PyO pyridine-*N*-oxide. [d] Terpy 2,2',2''-terpyridine.

Barbieri and Herber[8] have recently arrived at somewhat different conclusions concerning the structure of Ph_2Sn(Salen), primarily on the basis of some very crude point-charge calculations. These authors employ the Parish and Platt[28] empirical scale of partial quadrupole splitting (*p.q.s.*) values for methyl and phenyl groups together with the assumption that the contribution of the Salen oxygen and nitrogen atoms to the electric field gradient at tin is the same as that due to four chlorides. Then using C–Sn–C angles of 160° for both molecules Barbieri and Herber[8] compute $|\Delta E_Q|$ values of 3.68 $mm \cdot s^{-1}$ for Me_2Sn(Salen) and 3.27 $mm \cdot s^{-1}$ for Ph_2Sn(Salen). Agreement with the measured values is considered[8] to be satisfactory in the former case but not in the latter, and it is inferred that "the introduction of two phenyl groups into the quasi axial (*trans*) positions with respect to the metal atom would involve considerable steric interaction between the organic ligand and the tetradentate Salen^{2-} moiety^{-8}. Thus they suggest considerably more distortion for the phenyl complex, in order to account for the lower ΔE_Q.

We have measured the Mössbauer spectra of both Me_2Sn(Salen) and Ph_2Sn-(Salen) in applied longitudinal magnetic fields of 50 kG. Comparison of theoretical and observed spectra (see Fig. 1) reveals that in both cases $e^2 \cdot q \cdot Q$ is positive and $\eta = 0.5 \pm 0.1$. (Barbieri and Herber[8] erroneously assume $\eta = 0$ for the methyl derivative.) The sign of the coupling constant is that expected for a *trans*-octahedral species, and the η values show that the departure of the *e.f.g.* tensor from axial symmetry is essentially the same in the two molecules. While these results do not constitute a structure proof for the phenyl complex, they do suggest that its structure is not likely to be very different from the methyl derivative.

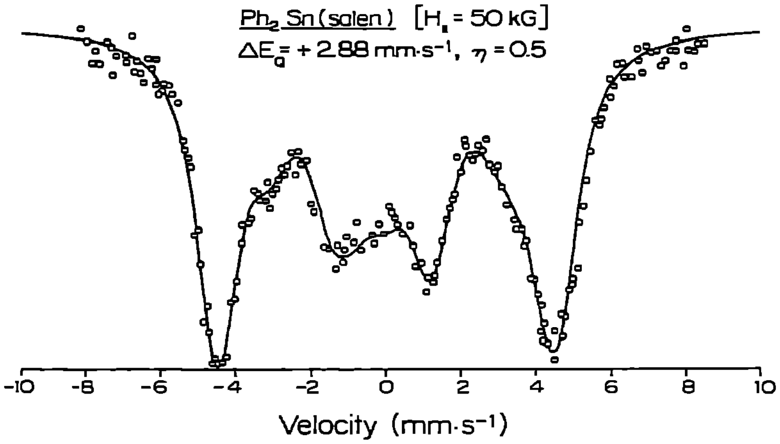


Fig. 1. Mössbauer spectrum of Ph_2Sn(Salen) at 4.2 K in an applied longitudinal magnetic field of 50 kG. The velocity scale is relative to the centroid of the zero-field spectrum (add 0.88 mm·s^{-1} to convert to $BaSnO_3$). The solid line is the theoretically computed spectrum assuming $e^2 \cdot q \cdot Q$ +2.88 mm·s^{-1} and η 0.50.

From the strong similarity in Mössbauer parameters for Me_2Sn(Salen) and Me_2Sn(Saldap-2-OH), we conclude that these two compounds also have similar structures, with the Saldap-2-OH anion acting as a quadridentate group. Further support for this conclusion derives from IR spectra in the ν(O–H) region. Neither of the ligands (II) nor (IV) shows a band in the anticipated region 3600–3200 cm^{-1}, presumably because of intramolecular hydrogen bonding between the phenolic oxygens and the nitrogen atoms. Such hydrogen bonding is not expected for the hydroxyl group on the bridging aliphatic chain in (III), where ν(O–H) is seen at 3450 cm^{-1}. This band is also present in Me_2Sn(Saldap-2-OH) shifted to 3400 cm^{-1}, indicating that the propan-2-ol functional group is not involved in bonding to tin.

On the other hand this band is absent in the spectrum of the diphenyltin derivative of (III), where only a weak, broad absorption at 3200–3160 cm^{-1} is observed. This suggests that at least one phenolic oxygen is not used in bonding and that the tin–oxygen bonding probably involves the other phenolic oxygen and the oxygen atom in the propane chain. Thus, the anion of (III) appears to be acting here as a bidentate, or more likely terdentate ligand, leading to tetra-or pentacoordination

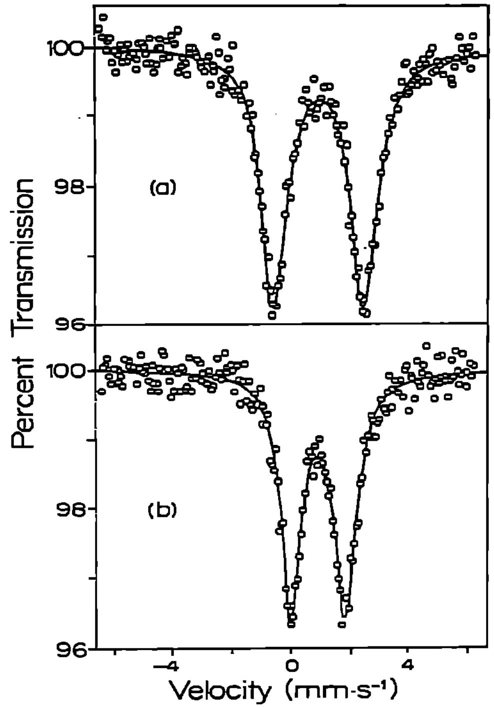


Fig. 2. Mössbauer spectra of (a) Me_2Sn(Saldap-2-OH) and (b) Ph_2Sn(HSaldap-2-O) at liquid nitrogen temperature. The velocity scale is relative to $BaSnO_3$.

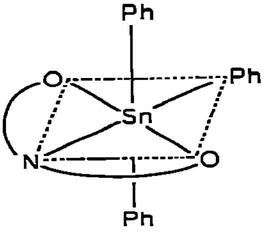
for the tin atom. For this reason we have formulated the complex as Ph_2Sn(HSaldap-2-O). The ^{119}Sn quadrupole splitting is also consistent with this compound having a different structure from the R_2Sn(Salen) complexes and the dimethyltin derivative of (III). ΔE_Q is 0.83 mm·s^{-1} smaller than the value for Ph_2Sn(Salen) and 1.26 mm·s^{-1} smaller than the splitting in Me_2Sn(Saldap-2-OH). For a trigonal bipyramidal R_2SnX_2Y structure with equatorial R groups, one expects a positive quadrupole coupling constant and an asymmetry parameter which is fairly large. In an applied magnetic field of 50 kG we find $e^2 \cdot q \cdot Q > 0$ and $\eta = 0.7 \pm 0.1$ for Ph_2Sn(HSaldap-2-O), in agreement with these expectations. (We should point out that if the R groups were both in apical positions $e^2 \cdot q \cdot Q$ would also be positive but η should be small, while for one apical and one equatorial R group $e^2 \cdot q \cdot Q$ would be negative. These two possibilities can therefore be ruled out.)

The fact that Me_2Sn(Salen) and Ph_2Sn(Salen) appear to be structurally similar whereas the corresponding complexes formed from (III) show such pronounced differences is quite interesting. This suggests that with a bulky diorganotin moiety the latter ligand is able to reduce ring strain in the complex by utilizing the propan-2-ol functional group for coordination to the tin atom.

Both the dimethyl- and diphenyltin derivatives of (IV) show ΔE_Q values consistent with equatorial R groups and trigonal bipyramidal coordination at tin. Indeed, the values are quite similar to those observed[2] in the closely related R_2SnCl-(Ox) (HOx = 8-hydroxyquinoline) compounds (Table 3). For Me_2Sn(Sal-*N*-2-OC_6-

H_4) application of a 50 kG magnetic field reveals that $e^2 \cdot q \cdot Q$ is positive and $\eta = 0.7 \pm 0.1$, essentially identical to the results for Ph_2Sn(HSaldap-2-O). While the difference in ΔE_Q values of 0.85 $mm \cdot s^{-1}$ between the two complexes of (IV) may at first appear to suggest the possibility of different structures, we doubt that such is actually the case. It should be noted that the difference in the corresponding chloro-oxinates is nearly as large (0.73 $mm \cdot s^{-1}$), and for the pentacoordinate derivatives R_2SnCl_2-(R'_2SO) (R' = Me, Et, Pr, Bu) Liengme, *et al.*[21] report an average difference in ΔE_Q of 0.78 $mm \cdot s^{-1}$ between corresponding methyl- and phenyltin complexes.

The triphenyltin derivative of (IV) exhibits an appreciably greater splitting than does the diphenyltin complex, and poses an interesting question concerning its structure. The ΔE_Q value of 2.88 $mm \cdot s^{-1}$ would certainly be consistent with a trigonal bipyramidal structure with the three phenyl groups in the equatorial plane (*cf.* Ph_3SnCl·4-phenylpyridine, ΔE_Q 2.90 $mm \cdot s^{-1}$)[29]. This would imply that the Schiff base anion is acting as a bidentate bridging group leading to a polymeric structure. Another possibility which suggests itself, however, is a *mer*-octahedral structure (V) in which the ligand is terdentate, and which would also be expected[30] to produce a quadrupole splitting of about 3 $mm \cdot s^{-1}$ (A *fac*-octahedral configuration can be eliminated since all three phenyls would be *trans* to an electronegative group and ΔE_Q should be approximately zero[30].) The use of magnetic perturbation Mössbauer spectroscopy is particularly attractive in this case since the two likely structures should yield very different results. For the pentacoordinate structure one expects $e^2 \cdot q \cdot Q$ to be negative and $\eta \approx 0$, whereas the *mer*-octahedral case should show $\eta \approx 1$ with the sign of the *e.f.g.* depending on fine details of the electronic distributions in Sn–O and Sn–N bonds and the values of the bond angles at the tin atom. In fact, for a *mer*-R_3SnX_3 system $V_{xx} = 0$, $V_{yy} = -V_{zz}$ and $\eta = 1$ (the V_{ii} are the diagonal elements of the *e.f.g.* tensor). In an applied field of 50 kG, the Mössbauer spectrum of Ph_3Sn-(Sal-*N*-2-OC_6H_4) is nearly symmetrical in appearance, and we estimate that $\eta \approx 0.9$ with $e^2 \cdot q \cdot Q$ negative. A detailed fit to theoretically computed spectra was not attempted since the large asymmetry parameter so clearly rules out a bridged pentacoordinate structure with equatorial phenyl groups.



(V)

It is interesting to compare the reactions of (II) and (IV) with Ph_3SnOH in refluxing benzene. In the former case cleavage of one of the tin–phenyl bonds results and the sole product isolated is Ph_2Sn(Salen), shown by melting point, analytical data, IR and Mössbauer data (Table 3) to be identical to a sample of Ph_2Sn(Salen) prepared in the usual way from Ph_2SnCl_2. In the latter case, where the ligand is potentially only terdentate, the Ph_3Sn moiety remains intact. Thus, in their organotin complexes both anionic ligands appear to have strong tendencies to act as chelating groups using their maximum ligating abilities, rather than as bidentate groups bridging two organotin fragments. Similar behaviour is observed in tin(IV) halide complexes with (II) of the type SnX_2(Salen) (X = Cl, Br, I), in which the $Salen^{2-}$ ion is quadridentate and the halogens occupy *trans* positions[31]. On the other hand the neutral Schiff bases (I) and (II) appear to be only bidentate in adducts of the types $R_2SnCl_2(H_2L)$[4,5] and $SnX_4(H_2L)$ (X = Cl, Br, I)[31].

The rather low isomer shift values for the Schiff base complexes, compared with other five- and six-coordinate di-organotin derivatives, indicates a reduction in the effective "s" electron density at the tin nucleus. Since no large variation in tin–nitrogen bonding is anticipated this reduction may be attributed to highly polar tin–oxygen bonds, resulting in an increased removal of "*s*" electron density from tin. This interpretation is supported by the rather long Sn–O bond lengths observed[9] in Me_2Sn(Salen) (2.19–2.25 Å), as compared to some other Sn–O bonds [$Me_2Sn(Ox)_2$[32], 2.11 Å; $(C_6H_{11})_3SnOCOMe$[33], 2.12 Å]. In addition, the variation in the two Sn–C bond lengths (2.06 and 2.19 Å) in Me_2Sn(Salen) reported by Calligaris *et al.*[9] is interesting. The former is very short, even shorter than that found for Me_2SnF_2[34] and much shorter than that observed for $Me_2Sn(Ox)_2$[32] (2.16 Å). The distortion of the Me_2Sn(Salen) molecule, presumably arising largely from the ligand geometry, may cause an increase in the "*p*" orbital mixing in the tin–carbon bonds with a concomitant screening of the "*s*" electron density and a lower isomer shift.

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