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SPECTROSCOPIC PROPERTIES OF ORGANOTIN SULPHIDES

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SUMMARY

IR and Raman spectra for $(Me_3Sn)_2S$ and $Me_2Sn(SMe)_2$ are reported and discussed in terms of C_{2v} symmetry. The Raman spectra of nine organotin sulphides all show a characteristic strong band in the range 310–340 cm^{-1}. The mass spectra of $Me_2Sn(SMe)_2$, $(R_3Sn)_2S$ (R = Me or Ph) and $(R_2SnS)_3$ (R = Me, Bu or Ph) have been investigated and confirm that the latter compounds are cyclic trimers; the fragmentation patterns are similar to those of other organotin derivatives and show no unusual features attributable to possible S–Sn π-bonding effects.

INTRODUCTION

Some attention has been given to the possibility of enhancement of the strengths of bonds between tin and sulphur atoms through $(p\text{–}d)\pi$ bonding, and evidence for this type of interaction has been sought from dipole moment measurements[1], vibrational spectroscopy[2–5] and NMR studies[6,7] (^1H, ^{13}C and ^{119}Sn). Recently Schumann has reviewed this evidence[8] in relation to crystallographic[4] and Mössbauer[9] data and has concluded that there is no significant contribution to Sn–S bonding in organotin sulphides from π-donation from sulphur p-orbitals into tin d-orbitals. We report further IR and Raman data which support this conclusion for some simple tin–sulphur systems, and also a study of a number of organotin sulphides including the structurally interesting cyclic compounds $(R_2SnS)_3$ by mass spectroscopy.

EXPERIMENTAL

IR spectra were obtained using a Perkin–Elmer 457 spectrometer (calibration from peaks in the IR spectrum of polystyrene) or with a Grubb Parsons DM4 spectrometer with sampling between polythene plates (400–200 cm^{-1} region). Raman spectra were recorded with a Cary 83 instrument with laser excitation at 488.0 nm (Ar ion). Mass spectra were obtained with an AEI MS902 spectrometer at an ionising voltage of 70 eV.

All compounds were prepared by methods described in the literature, principally those[10] of Abel and Brady: purities were checked by comparison of physical constants with those values reported previously as well as by spectroscopic characterisation.

RESULTS AND DISCUSSION

1. *Vibrational spectra*

IR and Raman spectra for bis(trimethyltin) sulphide and dimethylbis(methylthio)stannane are shown in Table 1, together with the Raman spectrum of trimethyl(methylthio)stannane which is essentially the same as that reported earlier[5]. Comparison of these results confirms that the CH_3 deformation modes of methyl groups attached to tin and sulphur atoms can be separated in the way indicated by Van de Vondel *et al.*, those of the methylthio group occurring at high frequency, and also that the strong IR absorptions with polarised Raman counterparts at ca. 700 cm^{-1} are due to S–C stretching vibrations.

The assignment given in Table 1 for $(Me_3Sn)_2S$ is consistent with a non-linear arrangement for the SnSSn skeleton, possessing C_{2v} symmetry. In particular, the incidence of two bands attributable to Sn–S stretching in both IR and Raman spectra precludes the possibility of high symmetries based on a linear skeleton (belonging to Point Groups D_{3d} or D_{3h}) where the symmetric stretch would be predicted to be

TABLE 1

VIBRATIONAL SPECTRA[a] OF $(Me_3Sn_2)S$ AND $Me_2Sn(SMe)_2$

$(Me_3Sn)_2S$		*Me_3SnSMe*	*$Me_2Sn(SMe)_2$*		*Assignment*
IR	*Raman*	*Raman*	*IR*	*Raman*	
2982 s	2994 w(dP)	2984 w(dP)	2980 m	2980 w(dP)	$\nu_{as}(CH_3)$
2912 s	2920 m(Pol)	2919 m(Pol)	2918 vs	2918 m(Pol)	$\nu_s(CH_3)$
		2845 vw	2835 m		
			1431 s		$\delta_{as}(CH_3)(SMe)$
1385 w(br)					$\delta_{as}(CH_3)$
			1312 vs		$\delta_s(CH_3)(SMe)$
	1198 m(Pol)	1197 m(Pol)		1190 m(Pol)	$\delta_s(CH_3)$
1181 m	1189 w(dP)		1185 w		$\delta(CH_3)$
			958 s		$\rho(CH_3)(SMe)$
762 vs(br)			762 vs(br)		$\rho(CH_3)$
720 s(br, sh)					$\rho(CH_3)$
		699 m(Pol)	694 s	693 m(Pol)	$\nu(S–C)$
530 vs	531 m(dP)	533 m(dP)	541 vs	536 m(dP)	$\nu_{as}(Sn–C)$
509 s	512 vs(Pol)	512 vs(Pol)	518 vs	516 vs(Pol)	$\nu_s(Sn–C)$
366 vs	369 w(dP)				$\nu_{as}(Sn–S)$
319 s	322 s(Pol)	339 s(Pol)	347 vs	340 vs(Pol)	$\nu_s(Sn–S)$
		192 m(Pol)		194 m(Pol)	$\delta(SnSC)$
	147 ms(Pol)	146 ms(dP)		140 m(dP)	$\delta(SnC_3)$
	124 m(Pol)				$\delta(SnC_3)$
	75 w(Pol)				$\delta(SnSSn)$

[a] Frequencies in cm^{-1} throughout; pure liquid samples.

Raman active only with the asymmetric mode appearing only in the IR. A similar conclusion is evident for the triphenyltin analogue; the two Raman bands observed at 327 and 373 cm^{-1} coincide with IR frequencies reported elsewhere[2].

In the case of $Me_2Sn(SMe)_2$, only one fundamental could be observed for both Sn–S and S–C stretching, active in the IR and Raman in each case. The polarisation of the Raman bands indicates that these are the symmetric stretches, the corresponding asymmetric modes not being detected. This is in contrast to predictions based on the expected C_{2v} molecular symmetry.

The low-frequency skeletal bending vibrations are assigned as shown in Table 1 by comparison with related species, although the polarisation properties in the case of $(Me_3Sn)_2S$ do not allow a certain separation of the SnC_3 bending modes. The weak band at 75 cm^{-1} in the latter molecule is attributed to SnSSn bending and is polarised as expected for a vibration of a_1 symmetry for C_{2v}.

Raman data collected for a number of other organotin sulphides are shown in Table 2. In each case there is a very strong band lying within a fairly narrow range (310–340 cm^{-1}) possibly due to the Sn–S stretching vibration of highest symmetry. The position of this Raman band is more characteristic than related IR absorptions, where greater variations in frequency and intensity are observed.

TABLE 2

TIN–SULPHUR STRETCHING FREQUENCIES[a] IN ORGANOTIN SULPHIDES

	$\nu_s(Sn{-}S)^b$	$\nu_{as}(Sn{-}S)^c$
Me_3SnSMe	338 vs	
$Me_2Sn(SMe)_2$	340 vs	
$(Me_3Sn)_2S$	322 s	367 w
$(Ph_3Sn)_2S$	327 vs	373 m
$(Me_2SnS)_3$	319 vs	342 w, 359 w, 363 w
$(Bu_2SnS)_3$	314 vs	360 w, 369 w, 385 w
$(Ph_2SnS)_3$	319 vs	332 w, 351 w, 368 w
$Ph_4Sn_4S_6$	319 vs	333 w, 340 w
$(BuSnS)_2S$	310 vs	335 w(sh)

[a] Observed in Raman spectra, cm^{-1}. [b] Most intense (Sn–S) band. [c] Other (Sn–S) bands.

2. *Mass spectra*

Mass and abundance data for Sn isotopes and for Sn_2 isotope combinations have been published[11]. Calculation of similar data for combinations of three tin atoms gave the results shown in Table 3 and since ^{32}S is 95% abundant, differences between mass distributions for Sn, Sn_2 or Sn_3 fragments allowed unambiguous assignment of multiplets found in the observed spectra. Summing of contributions from individual ions yielded the following metal-containing ion-family relative abundances (normalised to 100) for six organotin sulphides examined:

$Me_2Sn(SMe)_2$: $Me_4SnS_2^+$ (54), $Me_3SnS_2^+$ (83), $Me_2SnS_2^+$ (17), Me_4SnS^+ (13), Me_3SnS^+ (100), Me_2SnS^+ (27), $MeSnS^+$ (70), SnS^+ (15), Me_2Sn^+ (14), $MeSn^+$ (63), Sn^+ (24).

$(Me_3Sn)_2S$: Two-tin fragments: $Me_6Sn_2S^+$ (2), $Me_5Sn_2S^+$ (13). One-tin fragments: Me_3SnS^+ (29), Me_3Sn^+ (100), Me_2Sn^+ (21), SnS^+ (25), $MeSn^+$ (47), Sn^+ (29).

TABLE 3

CALCULATED Sn_3 MASS AND ABUNDANCE COMBINATIONS

Nominal mass	*Peak mass*	*Relative abundance*
344	343.70944	0.52
345	344.71009	0.50
346	345.70878	1.92
347	346.70951	1.77
348	347.70793	6.75
349	348.70822	6.65
350	349.70703	18.82
351	350.70750	19.15
352	351.70669	45.59
353	352.70728	41.27
354	353.70652	77.95
355	354.70735	59.19
356	355.70663	100.00
357	356.70764	57.39
358	357.70690	89.12
359	358.70847	37.75
360	359.70770	65.05
361	360.70993	18.01
362	361.70883	35.56
363	362.71084	8.71
364	363.70976	19.73
365	364.71257	1.64
366	365.71123	5.97
367	366.71387	0.67
368	367.71255	2.85
369	No combination	
370	369.71389	0.37
371	No combination	
372	371.71572	0.15

$(Ph_3Sn)_2S$: Two-tin fragments: $Ph_6Sn_2S^+$ (6), $Ph_5Sn_2S^+$ (63), $Ph_4Sn_2S^+$ (15), $Ph_3Sn_2S^+$ (4). One-tin fragments: Ph_4SnS^+ (4), Ph_4Sn^+ (2), Ph_3SnS^+ (2), Ph_3Sn^+ (100), Ph_2SnS^+ (7), Ph_2Sn^+ (14), $PhSnS^+$ (7), $PhSn^+$ (54), Sn^+ (33).

$(Me_2SnS)_3$: Three-tin fragments: $Me_5Sn_3S_3^+$ (80), $Me_3Sn_3S_3^+$ (12). Two-tin fragments: $Me_4Sn_2S_2^+$ (25), $Me_3Sn_2S_2^+$ (89), $MeSn_2S_2^+$ (28), $Sn_2S_2^+$ (15). One-tin fragments: $Me_4SnS_2{}^+$(19), $Me_3SnS_2^+$ (57), Me_4SnS^+ (27), Me_3SnS^+ (100), Me_2SnS^+ (63), Me_3Sn^+ (98), SnS^+ (18), Me_2Sn^+ (24), $MeSn^+$ (61), Sn^+ (30).

$(Bu_2SnS)_3$: Three-tin fragments*: $Bu_6Sn_3S_2^+$ (1), $Bu_5Sn_3S_3^+$ (7), $Bu_5Sn_3S_2^+$ (1), $Bu_4Sn_3S_3^+$ (1), $Bu_4Sn_3S_2^+$ (1), $Bu_3Sn_3S_3^+$ (1). Two-tin fragments: $Bu_3Sn_2S_2^+$ (100), $Bu_2Sn_2S_2^+$ (34), $BuSn_2S_2^+$ (12), $Sn_2S_2^+$ (27). One-tin fragments: Bu_3Sn^+ (6), Bu_2SnS^+ (25), $BuSnS^+$ (15), $BuSn^+$ (8), SnS^+ (15), Sn^+ (6).

$(Ph_2SnS)_3$: Three-tin fragments*: $Ph_5Sn_3S_3^+$ (1), $Ph_4Sn_3S_2^+$ (1). Two-tin fragments: $Ph_5Sn_2S^+$ (4), $Ph_4Sn_2S_2^+$ (3), $Ph_4Sn_2S^+$ (2), $Ph_3Sn_2S_2^+$ (20), $Ph_3Sn_2S^+$ (16),

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* P^+ ion families also observed, rel. abundance < 1.

Sn_2S^+ (10). One-tin fragments: Ph_4SnS^+ (1), Ph_3SnS^+ (20), Ph_3Sn^+ (77), Ph_2SnS^+ (100), Ph_2Sn^+ (3), $PhSnS^+$ (20), $PhSn^+$ (62), Sn^+ (23).

The observed mass spectra show a number of interesting features. Formulation of the diorganotin sulphides R_2SnS as cyclic trimers in 1942 by Harada[12] has been followed by a number of molecular weight studies[13,14] and the determination of the X-ray crystal structure of $(Ph_2SnS)_3$. Parent ion families $R_6S_3Sn_3^+$ were observed for R = Bu and Ph, and for R = Me a strong family due to ready elimination of one Me group from the trimeric structure was evident. Mass spectroscopy thus confirms that the three compounds are trimeric; no evidence was found for fragments containing more than three tin atoms, although existence of the tetramer of $(Me_3SiCH_2)_2SnS$ has been proposed[15]. The ready fragmentation of the Sn_3S_3 skeleton to give ions containing two or one tin atoms is clear in all three compounds. This is in marked contrast to the situation found for systems where extensive π-bonding is proposed between inorganic nuclei, for example trimeric phosphorazenes where most of the ion-current is carried by fragments retaining the P_3N_3 skeleton[16,17]. The decomposition of $R_6Sn_3S_3$ into smaller fragments is predominant in the order R = Ph > Bu > Me; only in the latter is a significant abundance of a Sn_3 ion observed, that of $Me_5Sn_3S_3^+$. This may be compared with other organometallic molecules for which elimination of an organic radical to give stable ions has been found to be most important for methyl derivatives[11,18]. The only other compound directly related to $(R_2SnS)_3$ to have been examined mass spectroscopically is $(i\text{-}Pr_2GeO)_3$, where much higher abundances for ions containing three metal atoms were observed[19].

The spectra of the remaining compounds, those with two tin–sulphur bonds, appear to possess few common features. Thus while ion families in which both bonds nominally remain intact are abundant for $Me_2Sn(SMe)_2$ and $(Ph_3Sn)_2S$, in $(Me_3Sn)_2S$ one-tin fragments predominate. For $(R_3Sn)_2S$ (R = Me or Ph) the high abundance of R_3Sn^+ is a prominent feature.

The occurrence of a variety of rearrangement ions in the mass spectra of all six compounds is also noteworthy. In particular, those like R_4SnS^+ (R = Me or Ph) clearly indicate transfer of organo groups from tin to sulphur, as has been observed for metal–metal bonded tin compounds[18]. Similarly, in the spectrum of $(Me_2SnS)_3$ the ion family Me_3SnS^+ and not Me_2SnS^+ formed the base-peak multiplet.

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