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SYNTHESES, PROPERTIES, INFRARED AND RAMAN SPECTRA OF METHYL–VINYL–TIN(IV) SALTS

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SUMMARY

The syntheses of the following compounds are reported: $(CH_3)(CH_2{=}CH)_2SnI$, $(CH_3)(CH_2{=}CH)_2SnNCS$, $(CH_3)(CH_2{=}CH)_2SnOCOCH_3$, and $(CH_2{=}CH)_3SnNCS$. All of these organotin compounds were found to be monomeric in chloroform. A comparative examination of their infrared and Raman spectra, taken together with spectra of the related compounds $(CH_3)_3SnNCS$, $(CH_3)_3SnOCOCH_3$, $(CH_2{=}CH)_3SnOCOCH_3$, and $(CH_2{=}CH)_3SnI$, has enabled assignments of bands to be made to Sn–C vibrational modes. On the basis of comparisons between spectra obtained from solids, liquids and solutions it is concluded that non-planar SnC_3 moieties are present in these compounds. Analysis of the characteristic vibrations of the NCS group suggests that this is bonded to tin through the nitrogen end in each of the compounds examined. The ν(Sn–I) frequency from $(CH_2{=}CH)_3SnI$ has been found at 182 cm^{-1}.

INTRODUCTION

Previous work[1] with trialkyl- and triaryltin carboxylates and their simple derivatives has established that these compounds, of general formula $R_3SnOCOR'$, are commonly polymeric in the solid state but that depolymerisation occurs upon dissolving in an organic solvent. An important diagnostic tool in this work has been found in the vibrational bands associated with the SnC_3 moiety, this assuming a planar configuration in the solid polymers but a pyramidal arrangement in the solution monomers. In contrast to this, evidence from infrared[2,3] and Raman[3] spectroscopy points to a non-planar but also non-pyramidal SnC_3 moiety for the solid state as well as for the solution species when the R group above is vinyl, $CH_2{=}CH$–.

The solid compounds $(CH_3)_3SnX$, with X being F, OCOH, NCS, CN, and $N(CN)_2$, all have been shown[4–8] to have polymeric structures containing five-coordinate tin atoms, planar SnC_3 moieties being sited within a trigonal bipyramidal arrangement involving bridging X ligands. It is of interest to examine whether trivinyltin compounds involving monodentate ligands which, unlike carboxylate, are incapable of increasing the tin coordination number beyond four in the monomers, show further structural changes. In addition, mixed methyl–vinyl–tin compounds of the form $(CH_3)_n(CH_2{=}CH)_{3-n}SnX$, with $n=0$, 1, and 3, and X=I, NCS, and $OCOCH_3$, might be expected to show transitional structural characteristics, and features in their spectra which bear on this will be examined here.

EXPERIMENTAL

Tetramethyltin, tetravinyltin and trimethyltin chloride, commercially available, were used without further purification.

All solvents and chemicals used were of reagent grade.

IR spectra were recorded on a Perkin–Elmer Model 457 equipped with KBr optics, using the prepared compounds dispersed in Nujol or hexachlorobutadiene, as pure liquid films, or in chloroform solution. Raman spectra were recorded on an instrument using a Hilger and Watts D330/331 double monochromator and a Coherent Radiation model 52 argon laser.

Melting points (uncorrected) were determined with a Gallenkamp apparatus using open capillaries. Molecular weights were obtained in chloroform with a Mechrolab Model 302B vapour phase osmometer.

Preparations of the compounds $(CH_3)_n(CH_2{=}CH)_{3-n}SnX$ *($n=0, 1, 3$; $X=I$, NCS, $OCOCH_3$)*

Methyldivinyltin iodide, $CH_3)(CH_2{=}CH)_2SnI$. A starting material for this preparation was methyltrivinyltin, $(CH_3)(CH_2{=}CH)_3Sn$. This was prepared by reacting methyltin trichloride, CH_3SnCl_3, with vinylmagnesium bromide, $(CH_2{=}CH)$-MgBr, in THF. B.p. 117°/760 mmHg. (Found: C, 39.25; H, 5.44; Sn, 55.85. $C_7H_{12}Sn$ calcd.: C, 39.13; H, 5.63; Sn, 55.24%).

Methyltrivinyltin (6.2 g, 29 mmol) was reacted with a stoichiometric amount of iodine in diethyl ether under reflux during a period of 24 h. The ether was distilled off at reduced pressure, leaving a product boiling at 50–52°/7 mmHg. (Found: C, 18.98; H, 2.92; I, 40.02; Sn, 38.02; mol. wt. in $CHCl_3$, 348. C_5H_9ISn calcd.: C, 19.08; H, 2.88; I, 40.33; Sn, 37.71%; mol. wt., 314.71.)

Methyldivinyltin isothiocyanate, $(CH_3)(CH_2{=}CH)_2SnNCS$. To 14.3 g (86.4 mmol) of freshly prepared dry silver thiocyanate suspended in 50 ml of boiling benzene was added 4.5 g (14.4 mmol) of methyldivinyltin iodide dissolved in 50 ml of benzene. After refluxing for about 4 h, the insoluble silver salt was filtered off and the liquid residue obtained after evaporation of the benzene was dried under vacuum. The product was a yellowish oily liquid; it decomposed on distilling under vacuum. (Found: C, 29.24; H, 3.70; N, 5.40; S, 12.84; Sn, 48.56. mol. wt. in $CHCl_3$, 255. C_6H_9NSSn calcd.: C, 29.30; H, 3.67; N, 5.69; S, 13.04; Sn, 48.27%; mol. wt., 245.89.)

Methyldivinyltin acetate, $(CH_3)(CH_2{=}CH)_2SnOCOCH_3$. To a weighed amount of mercury(I) acetate (1.5 g, 2.9 mmol) suspended in methanol (50 ml) was added trivinylmethyltin (1.24 g, 5.8 mmol) as in the procedure previously followed for trimethyltin acetate[9]. The crystalline product melted at 123–125°. (Found: C, 33.85; H, 4.78; Sn, 49.27; mol. wt. in $CHCl_3$, 267. $C_7H_{12}O_2Sn$ calcd.: C, 34.06; H, 4.90; Sn, 48.08%; mol. wt. 246.85.)

Trivinyltin isothiocyanate, $(CH_2{=}CH)_3SnNCS$. To 11 g (66 mmol) of freshly prepared dry silver thiocyanate suspended in 50 ml of boiling benzene was added 3.26 g (10 mmol) of trivinyltin iodide dissolved in 50 ml of benzene. After refluxing for about 5 h the insoluble silver salt was filtered off and the liquid residue obtained as an oil. After evaporation of the benzene this was dried under vacuum over P_2O_5. The product was a pale yellow oil. (Found: C, 32.31; H, 3.53; N, 5.41; S, 12.30; Sn,

TABLE 1

MOLECULAR WEIGHTS OF $(CH_3)_n(CH_2{=}CH)_{3-n}SnX$ (n=0, 1, 3; X=I, NCS, $OCOCH_3$) IN $CHCl_3$ SOLUTION

Compounds	*Concn. (mg/ml)*	*Mol. wt. found*	*Mol. wt. formal*	*i*
$(CH_3)_3SnNCS$	22.25	237	221.87	1.06
(solid)	11.12	227		1.02
	5.56	218		0.98
	2.78	227		1.02
		220		0.99
$(CH_2{=}CH)_2(CH_3)SnNCS$			245.89	
(liquid)	6.17	266		1.08
	3.08	266		1.08
	1.54	256		1.04
		255		1.03
$(CH_2{=}CH)_3SnNCS$	9.05	281	257.90	1.09
(liquid)	4.52	287		1.11
	2.25	276		1.07
	1.12	270		1.04
		274		1.06
$(CH_2{=}CH)_2(CH_3)SnI$	18.60	376	314.71	1.19
(liquid)	9.30	387		1.23
	4.65	383		1.21
	2.32	325		1.03
		348		1.10
$(CH_2{=}CH)_3SnI$	14.50	373	326.72	1.14
(liquid)	7.25	368		1.12
	3.62	374		1.14
	1.81	356		1.09
		362		1.10
$(CH_3)_3SnOCOCH_3$	17.76	280	222.83	1.26
(solid)	8.88	270		1.21
	4.44	262		1.17
	2.22	257		1.15
		253		1.13
$(CH_2{=}CH)_2(CH_3)SnOCOCH_3$	20.77	296	246.85	1.20
(solid)	10.38	282		1.14
	5.19	273		1.10
		267		1.07
$(CH_2{=}CH)_3SnOCOCH_3$	10.50	299	258.86	1.15
(solid)	5.25	289		1.11
	2.62	278		1.07
	1.31	272		1.05
		271		1.04

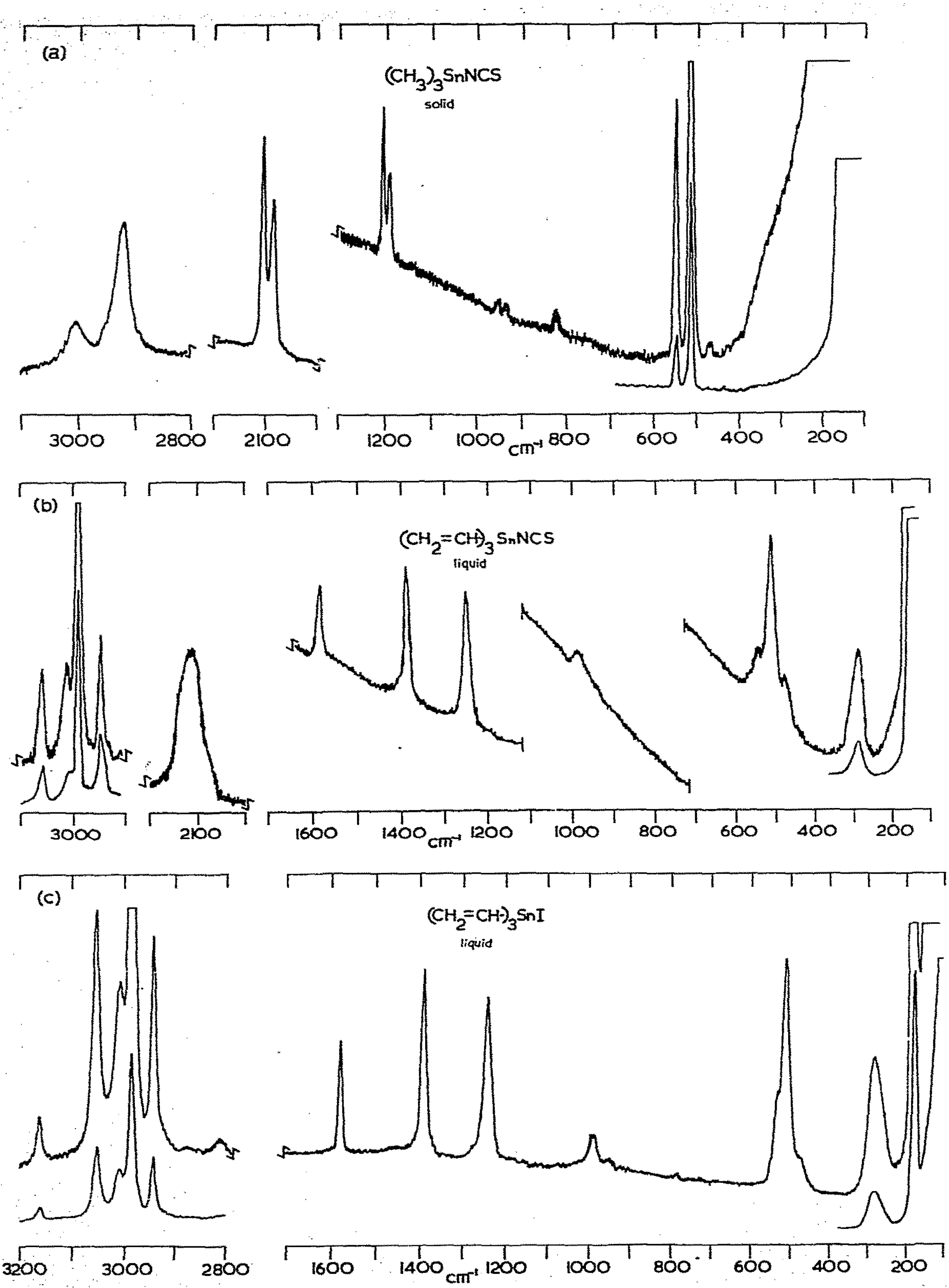

Fig. 1. Raman spectra of the compounds $(CH_3)_3SnNCS$, $(CH_2{=}CH)_3SnNCS$ and $(CH_2{=}CH)_3SnI$.

46.90; mol. wt. in $CHCl_3$, 274. C_7H_9NSSn calcd.: C, 32.60; H, 3.51; N, 5.43; S, 12.43; Sn, 46.02%; mol. wt., 257.90.)

Trimethyltin isothiocyanate, acetate, and trivinyltin iodide and acetate were prepared as in the procedures described in the literature[2,9-11].

RESULTS AND DISCUSSION

The molecular weight determinations reported in the previous sections show all the compounds examined to be monomeric in chloroform solution. The trivinyltin compound was earlier reported[2] (erroneously) to exist as a trimer in chloroform. Detailed results from the osmometry are given in Table 1.

Raman spectra obtained from the compounds $(CH_3)_3SnNCS$, $(CH_2{=}CH)_3SnNCS$ and $(CH_2{=}CH)_3SnI$ are reproduced in Fig. 1, and in Fig. 2 are shown infrared spectra from the Sn–C stretching region[1,2] for the full range of compounds examined in this work, *i.e.* $(CH_3)_n(CH_2{=}CH)_{3-n}SnX$, with $n=0, 1, 3$, and $X=I$, NCS, and $OCOCH_3$. In Table 2 are summarised the band frequencies obtained from the infrared spectra in regions associated with Sn–C and N–C (of the NCS group) stretching modes.

TABLE 2

IR DATA FROM MULLS, PURE LIQUID FILMS, AND CHLOROFORM SOLUTIONS
Optics KBr, 1 mm path length.
All frequencies in cm^{-1}; s, strong; m, medium; w, weak; v, very; (sh), shoulder; (br), broad.

Compounds	*Nujol mull*		*Liquid film*		*Chloroform solution*	
	ν(Sn–C)	*ν(N–C)*	*ν(Sn–C)*	*ν(N–C)*	*ν(Sn–C)*	*ν(N–C)*
$(CH_3)_3SnNCS$	552 s	2090 (sh)			552 s	2050 vs
(solid)		2075 s			518 w	
		2050 s				
$(CH_2{=}CH)_2(CH_3)SnNCS$			548 s	2060 vs(br)	550 s	2060 vs
(liquid)			510 (sh)		515 w	
			478 s		475 m	
$(CH_2{=}CH)_3SnNCS$			542 s	2070 (sh)	545 s	2050 vs
(liquid)			515 (sh)	2050 vs	520 w	
			495 s (br)		480 s	
$(CH_2{=}CH)_2(CH_3)SnI$			540 s		540 s	
(liquid)			510 m		515 m	
			470 m		470 m	
$(CH_2{=}CH)_3SnI$			538 s		538 s	
(liquid)			510 s		510 (sh)	
			475 s (br)		475 s(br)	
$(CH_3)_3SnOOCCH_3$	552 s				545 s	
					515 m	
$(CH_2{=}CH)_2(CH_3)SnOOCCH_3$	550 s				545 s	
	545 (sh)				515 w	
	515 w				475 s	
	485 m					
$(CH_2{=}CH)_3SnOOCCH_3$	540 m				540 m	
	510 (sh)				515 (sh)	
	485 m				485 m	

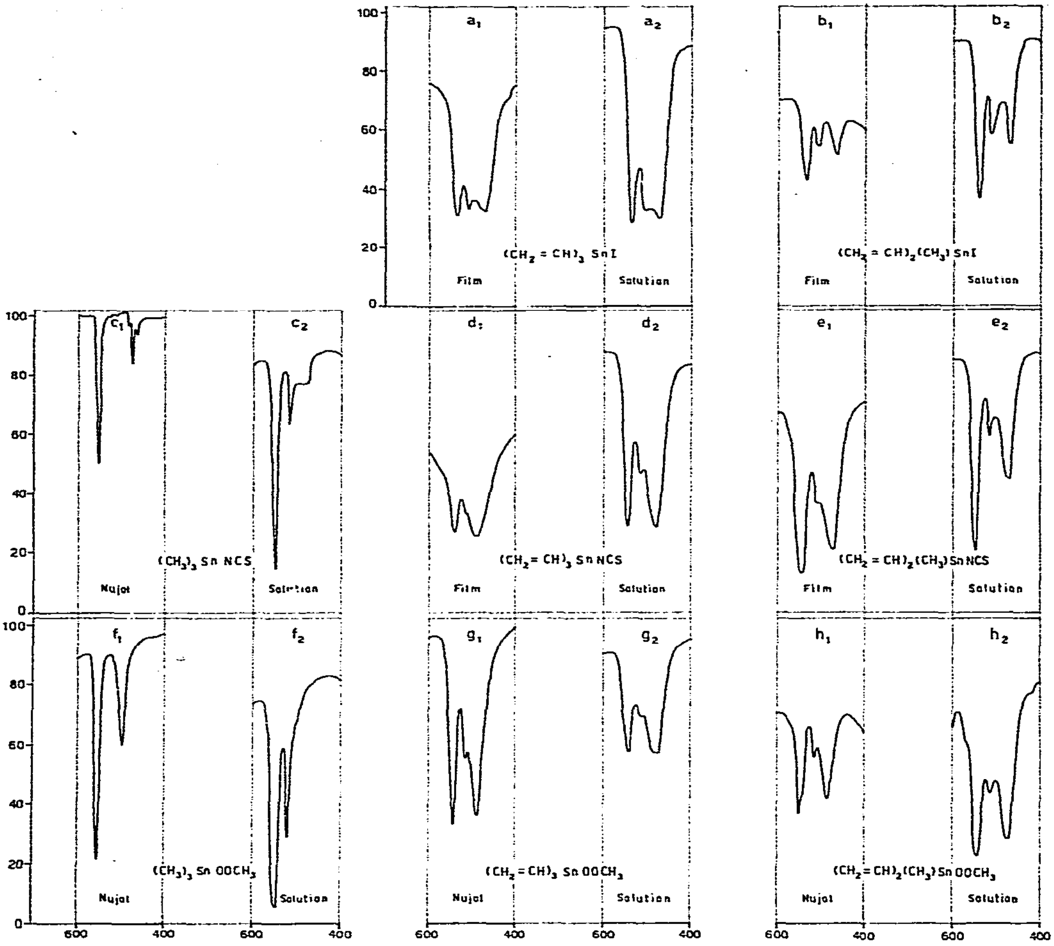

Fig. 2. IR spectra in the Sn–C stretching region of the compounds $(CH_3)_n(CH_2{=}CH)_{3-n}SnX$ (n=0, 1, 3; X=I, NCS, OCOCH$_3$) in CHCl$_3$ solution (optics KBr).

a_1 : film	a_2 : concn. 14.5 mg/ml.
b_1 : film	b_2 : concn. 18.6 mg/ml.
c_1 : Nujol mull	c_2 : concn. 8.9 mg/ml.
d_1 : film	d_2 : concn. 9.0 mg/ml.
e_1 : film	e_2 : concn. 12.7 mg/ml.
f_1 : Nujol mull	f_2 : concn. 19.3 mg/ml.
g_1 : Nujol mull	g_2 : concn. 9.0 mg/ml.
h_1 : Nujol mull	h_2 : concn. 14.5 mg/ml.

For the compounds containing the NCS group the spectra provide the means of establishing the manner of binding to the tin atom. From a comparison of the spectra for the compounds involved (see Fig. 1 and Table 2) it is apparent that the manner of the NCS group bonding is the same for all the R_3SnNCS compounds, regardless of whether R is CH_3 or $CH_2{=}CH$. The work of Turco and Pecile[12] established frequency ranges for the ν_1 and ν_2 modes of NCS according to whether the group is *N*- or *S*-bonded, and the ν_3 mode also has been shown to be useful in this context[13]. Unfortunately, the ν_2 band (at 690–720 cm^{-1} for M–SCN, and 780–860 cm^{-1} for M–NCS) is intrinsically very weak in both the infrared and Raman spectra and so is not useful here for diagnostic purposes, but the frequency of the ν_1 band (strong in both IR and Raman), being shifted up by less than 40 cm^{-1} from the free ion value[13] of 2070 cm^{-1}, does suggest *N*-bonding. Furthermore, the NCS ν_3 mode frequencies, observed in the Raman spectra of $(CH_3)_3SnNCS$ and $(CH_2{=}CH)_3SnNCS$ at 476 and 474 cm^{-1}, respectively, conform with that predicted for *N*-bonding[13], and the ν_1 infrared intensity criterion proposed by Pecile[14] also supports *N*-bonding of NCS to Sn. Thus the observed products of ν_1 band half-widths ($\Delta\nu_{\frac{1}{2}}$, cm^{-1}) and extinction coefficients (ε_{max}, $M^{-1}\cdot cm^{-1}$) for the compounds $(CH_3)(CH_2{=}CH)_2SnNCS$, $(CH_2{=}CH)_3SnNCS$, and $(CH_3)_3SnNCS$ are found to be 4.0, 3.8 and $4.2 \times 10^{-4}\ M^{-1}\cdot cm^{-2}$, respectively, clearly establishing all three as isothiocyanates by Pecile's criterion. It is known from X-ray work that the trimethyltin compound has the isothiocyanate form in the solid state[6].

Previous work with both methyl- and vinyl-tin compounds[1-3,5,9] has shown the Sn–C stretching region of the vibrational spectra to be particularly informative with regard to the structural arrangement of ligands about the metal centre. The spectra shown in Fig. 2 and data summarised in Table 2 show clearly that while the $(CH_3)_3Sn$ group appears to generate but a single band in solid compounds, and two bands in solution, the $(CH_3)_n(CH_2{=}CH)_{3-n}Sn$ groups (n=0, 1, 3) generate three characteristic bands in this 400–600 cm^{-1} region. For the trivinyltin carboxylates, $(CH_2{=}CH)_3SnOCOX$, with X = CH_3, CH_2Cl, $CHCl_2$ and CF_3 it has previously been suggested[3] that the band structure in the Sn–C stretching region is indicative of C_{2v} symmetry for the SnC_3 moiety, this arising from the vinyl groups occupying both axial and equatorial positions in the coordination trigonal bipyramid about the tin atom. As is apparent from the spectra presented in Fig. 2, substitution of NCS or I for the carboxylate group leaves the band pattern in the Sn–C stretching region effectively unchanged. This appears to eliminate the possibility that the monodentate ligands result in a pyramidal four-coordinate structure about the central tin atom, for this would lead to local C_{3v} symmetry for the SnC_3 moiety and only two infrared bands in the Sn–C stretching region of the spectrum. The experimental result suggests the conservation of trigonal bipyramidal five-coordinate structures, with the fifth coordination site being occupied by a solvent molecule in solution, and by a nearest-neighbour interaction in the solid state, probably through unsymmetrical ligand bridges such as have been established[6] for solid $(CH_3)_3SnNCS$. It is less surprising to find band structures indicative of low symmetry SnC_3 groups in the spectra of the mixed methyl–vinyl–tin compounds, but the marked similarity between these spectra in the Sn–C stretching region and those given by the trivinyltin compounds is suggestive of closely similar structural and bonding characteristics. An alternative possibility which must be considered is that one of the three bands under discussion in the 400–600 cm^{-1} region finds its origin in a totally different mode of vibration. By analogy with assignments made for some vinylsilicon compounds[15], an Sn–C=C deformation mode might be expected to make a contribution in this region. Although there is no direct evidence for this alternative assignment, the conclusions based on a triplet of Sn–C stretching mode bands must remain only tentative at this stage.

More certainty can be attached to the assignment of the Sn–I stretching mode, at least for the compound $(CH_2{=}CH)_3SnI$, the Raman spectrum of which is given in

Fig. 1. From the comparison of spectra in Fig. 1 and from previous work with alkyltin iodides[16,17] it is clear that the intense and polarised Raman band at 182 cm^{-1} is due to the Sn–I stretching fundamental.

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