Inorganica Chimica Acta, 18 (1976) 165–172

Derivatives of Bivalent Germanium, Tin and Lead. Part XVII[1]. Some Oxidative Addition Reactions of Tin(II) Halides

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Received October 3, 1975

Tin(II) halides react readily with benzoyl peroxide to yield tin(IV) dihalide dibenzoates and with lead tetraacetate or mercuric acetate to give analogous tin(IV) dihalide diacetates. With dimethyldisulphide, tin(II) chloride reacts only slowly, but tin(II) bromide reacts during 4 hours in boiling benzene to give $SnBr_2(SMe)_2 \cdot THF$. Molecular oxygen oxidises tin(II) chloride in THF to $SnOCl_2 \cdot 1.5THF$. A donor–acceptor complex is formed between tin(II) bromide and diethylacetylene dicarboxylate, but carbenoid insertion takes place with tin(II) chloride and the same reagent and also with tin(II) chloride, bromide and iodide and dimethylacetylene dicarboxylate. 1:1 THF-solvated adducts of composition $(SnX_2 \cdot EtO_2C\text{–}N{=}N\text{–}CO_2Et)_2 \cdot THF$ (X = Cl, Br) are obtained from the facile reaction of tin(II) chloride or bromide with diethyldiazodicarboxylate. The structures of the products have been investigated using infra-red, Raman, ^1H n.m.r., and tin-119m Mössbauer spectroscopy.

Introduction

The chemistry of divalent tin compounds has attracted much attention because of the formal analogy of such species to the more reactive but less accessible carbenes and silylenes. The chemistry of the carbenoid insertions of silylenes, germylenes, stannylenes, and plumbylenes has been reviewed by Nefedov and Manakov.[2] Examination of the oxidation potentials of Sn^{2+} and Sn^{4+} show that the former is destabilised with respect to the latter, and hence tin(II) derivatives might be expected to undergo facile oxidative addition with suitable reagents. Indeed, we have already encountered systems in which facile oxidation of tin(II) was responsible for the lack of isolation of some types of tin(II) derivatives. Several examples of oxidative addition reactions of organo- and halogenotin(II) compounds have already been characterised, as well as isolated examples for other tin(II) species. Pfeiffer[3] has demonstrated that tin(II) halides are oxidised by elemental halogens slowly at room temperature to give tin(IV) halides, and by molecular oxygen to give the tin(IV) oxide halides. These latter compounds have been synthesised more recently by different methods and investigated in greater depth by Dehnicke[4–6]. Reaction of tin(II) iodide with methyl iodide at 160°C gives only a 25% yield of methyltin(IV) triiodide after 4 hours, whilst the interaction of tin(II) chloride with carbene (generated from CH_2N_2) afforded a polymer with a $–[–SnCl_2–CH_2–SnCl_2–CH_2–]–_n$ backbone. The insertion of tin(II) halides into the metal–metal or metal–halogen bonds of transition metal derivatives may also be regarded as oxidative additions at tin(II). The complexity of this type of reaction and the diversity of products derived therefrom have recently been investigated by Hackett and Manning[7,8]. Bis(cyclopentadienyl)tin is readily oxidised by oxygen to $[(C_5H_5)_2Sn^{IV}O]_n$[9], and by halogens to give $(C_5H_5)_2SnX_2$ (X = Cl, Br, I)[10]. However Noltes and his coworkers[11] have shown that the latter reaction is more complicated, since at room temperature a mixture of $(C_5H_5)_3Sn^{IV}I$, $C_5H_5Sn^{II}I$, and $C_5H_5Sn^{IV}I_3$ are formed upon addition of I_2 to a solution of $(C_5H_5)_2Sn$. Bis(cyclopentadienyl)tin, tin(II) dimethoxide and dithiophenoxide all react smoothly with diphenyl disulphide to afford initially the oxidative addition products $SnX_2(SPh)_2$ (X = C_5H_5, OMe, SPh), which equilibrate to give, in addition, the disproportionation products, SnX_3SPh and $SnX(SPh)_3$. 3,4-Dithiolatotolyltin(II) is immediately oxidised by further 3,4-dithiotoluene to yield bis(3,4-dithiolatotolyl)tin(IV)[12]. Similar processes presumably account for the failure to isolate divalent tin dithiolates from $C_{12}H_{25}SH$ and SnO[13] or hydrated $SnCl_2$[14]. Surprisingly though, tin(II) ethane-1,2-dithiolate did not react with more thiol (6 molar excess) even after 6 hours reflux in benzene[12]. The C–X bonds of organic halides such as methyl iodide, allyl bromide and benzyl bromide react at room temperature with bis(cyclopentadienyl)tin and tin(II) bis(pentane-2,4-dionates) to give the appropriate organobis(cyclopentadienyl)tin(IV) halide and organotin(IV) bis (pentane-2,4-dionate) halide[11].

Although silylenes and germylenes undergo a variety of addition reactions with carbon–carbon double and triple bonds, similar reactions with bivalent tin species are almost totally uncharacterised. However, Noltes *et al.*[11] have reported in a preliminary communication the reactions of bis(cyclopentadienyl)tin, tin(II) dimethoxide and bis(pentane-2,4-dionate) with diethyl acetylenedicarboxylate to give cyclic oligomers of the type $-[-(EtO_2C)C{=}C(CO_2Et){-}SnX_2-]-_n$ ($X = C_5H_5$, OMe, acac; $n = 6, 9$).

In this Paper we report our investigations into the oxidative addition reactions of tin(II) halides with a variety of singly- and multiply-bonded reagents.

Results and Discussion

A change in valence state of tin during a reaction necessarily affects the distribution of 5*s* electrons. Therefore the tin-119*m* Mössbauer isomer shift which provides a measure of the relative tin 5*s* electron density at the nucleus, affords a sensitive and useful guide to the valence state of the tin, and reactions which involve oxidation of tin to the tetravalent state are easily monitored in this way. Some confusion has arisen because of the controversy of the valence state of tin in tin–transition metal derivatives. However, this is of no relevance to the reactions discussed here since no ambiguity arises, all divalent tin materials having isomer shifts in the "tin(II)" region (generally taken to be >2.56 mm s^{-1}) and all tin(IV) products falling unequivocally in the "tin(IV)" region (generally taken to be <2.0 mm s^{-1}) (Table I).

In contrast to the slow reaction of oxygen with tin(II) halides in the solid[3], the passage of dry oxygen through a solution of tin(II) chloride in THF results in the rapid precipitation of $Sn^{IV}OCl_2 \cdot 1.5THF$ as an insoluble, infusible white powder. That the THF is coordinated to tin rather than merely occupying vacant lattice positions is apparent from the lowering of the ν(C–O–C) vibration from 1080 cm^{-1} in free THF to 1040 and 1010 cm^{-1}. In addition, the isomer shift is reduced to 0.03 mm s^{-1} from that of unsolvated $SnOCl_2$ (0.25 mm s^{-1} [15]), indicative of an increase in coordination number at tin[16]. The material also exhibits bands at 498 and 517 cm^{-1} assignable as tin–oxygen stretching frequencies, and two bands at 329 and 279 cm^{-1} indicative of a bent rather than a linear Cl–Sn–Cl arrangement.

TABLE I. Tin-119*m* Mössbauer Data for the Products and Related Compounds (mm s^{-1}).[a]

Compound	δ	Δ
$SnOCl_2 \cdot 1.5THF$	0.03	0
$SnCl_2(OAc)_2$	0.47	0
$SnBr_2(OAc)_2$	0.22	0
$SnCl_2(OOCPh)_2$	0.21	0
$SnBr_2(OOCPh)_2$	0.27	0
$SnBr_2(SMe)_2 \cdot THF$	0.44	0
$SnCl_2$(DMADC)	1.24	2.34
$SnBr_2$(DMADC)	1.33	2.21
SnI_2(DMADC)	1.47	2.07
$SnCl_2$(DEADC)	1.17	2.08
$(SnBr_2)_2$DEADC	3.65	1.44
$SnCl_2$(Azo)·THF	0.32	0
$SnBr_2$(Azo)·THF	0.37	0

[a] DMADC = dimethylacetylene dicarboxylate; DEADC = diethylacetylene dicarboxylate; bipy = 2,2′-bipyridyl; *o*-phen = 1,10-phenanthroline; acac = acetylacetonate; Azo = diethyl diazodicarboxylate.

Dibenzoylperoxide reacts exothermically at room temperature with tin(II) halides to afford tin(IV) dihalide dibenzoates (X = Cl, Br) as highly crystalline solids which appear to be stable in air. Similar tin(IV) dihalide diacetates are obtained by the oxidation of tin(II) halides using lead tetraacetate or mercuric acetate in essentially quantitative yield.

$$\begin{tikzcd}
X_2Sn^{IV}(OAc)_2 & SnX_2 \arrow[l, "Pb(OAc)_4"', "-Pb(OAc)_2"] \arrow[r, "(PhCOO)_2"] \arrow[d, "Hg(OAc)_2", "-Hg"'] & X_2Sn^{IV}(OOCPh)_2 \\
 & X_2Sn^{IV}(OAc)_2 &
\end{tikzcd}$$

All the tin(IV) halide carboxylates exhibit strong bands in the infrared in the region 1550–1610 cm^{-1}, indicating bidentate carboxylate residues as in the trialkyltin derivatives of 2- and 3-pyridylcarboxylic acids, which exhibit bands in the region 1550 and 1620 cm^{-1} [17]. Where carboxylate groups bridge adjacent tin atoms to form coordinate polymers as in Me_3SnO_2CMe[18] and $(PhCH_2)_3SnO_2CMe$[19], the carbonyl stretching frequencies occur at lower energy, at *ca.* 1570 cm^{-1}, whilst $(C_6H_{11})_3SnO_2CMe$, in which the carboxylate group is unidentate, exhibits a carbonyl band at 1655 cm^{-1} [20]. An assignment of the principal ligand bands of the halide carboxylates appears in Table II. Tin–chlorine stretching bands are observed at 340 cm^{-1} for the dibenzoate and *ca.* 320 cm^{-1} for the diacetate, although the latter is uncertain due to the proximity of a broad ligand band at 350 cm^{-1}. The mass spectra (Table III) of both the halide benzoates show no peaks higher than that of monomeric polyisotopic parent ion, confirming that the carboxylate residues function as bidentate rather than bridging bifunctional ligands. The mass spectra of the chloride benzoate recorded at a probe temperature of 100°C (m.p. 97°C) show that under these conditions the ligands are quite mobile, and fragments due to $SnCl_4^+$, $SnCl_3^+$, and $SnCl_3(OOCPh)^+$ ions are observed. The predominant feature of the spectra is the large benzoyloxy peak at m/e = 121. Not unexpectedly, the fragmentation patterns are very similar to those of the tin(II) carboxylates[21], with the two major decomposition routes being successive loss of the carboxylate ligands and decarboxylation to give tin–carbon bonded species.

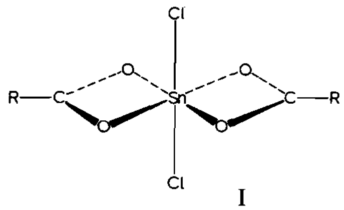
TABLE II. Infra-red Spectra of the Tin(IV) Dihalide Dicarboxylates.

$SnX_2(OOCPh)_2$ (cm^{-1})		$SnX_2(OAc)_2$ (cm^{-1})		Assignment
X = Cl	X = Br	X = Cl	X = Br	
	1600 s	1560 vsbr	1580 vsbr	$\nu(COO)$
1590 s	1580 s			
1420 s	1420 sbr	1420 mssh	1410 ms	$\nu(COO)$
		1029 ms	1020 ms	$\varrho_r(CH_3)$
{680 ms	668 ms	670 ms	660 m	$\delta(OCO)$
\670 ms		630 ms	620 m	$\pi(CH)$

TABLE III. Mass Spectral Data for $X_2Sn(O_2CPh)_2$ (X = Cl, Br) Compounds.

X = Cl		X = Br		Assignment
m/e	Rel. Int.	m/e	Rel. Int.	
432	2.24	521	0.036	$X_2Sn(O_2CPh)_2^+$
397	8.77	441	35.45	$XSn(O_2CPh)_2^+$
361	2.04	361	100	$Sn(O_2CPh)_2^+$
346	2.44			$X_3SnO_2CPh^+$
		316	2.72	$Sn(O_2CPh)Ph^+$
311	11.83			$X_2SnO_2CPh^+$
302	1.63			X_3SnPh^+
276	40.81			$XSnO_2CPh^+$
260	13.46			X_4Sn^+
240	32.65	240	100	SnO_2CPh^+
225	100			X_3Sn^+
196	7.75			$SnPh^+$
190	4.89	279	5.27	X_2Sn^+
155	73.46	199	40.00	XSn^+
119	26.53	119	28.18	Sn^+

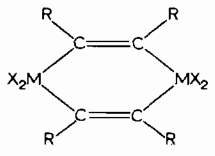
The Mössbauer spectra of the tin(IV) halide carboxylates are listed in Table I. Both tin(IV) halide benzoates exhibit single sharp resonances at 0.21 (X = Cl) and 0.27 mm s^{-1} (X = Br), whereas the spectra of the two acetate derivatives consist of rather broad single lines. These data serve to suggest octahedral coordination about tin, albeit somewhat distorted in the latter case. Further, the presence of only a single Sn–Cl stretching band in the infra-red indicates that the compounds possess the *trans* structure, I.



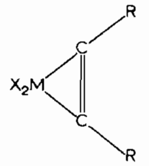
I

Dimethyldisulphide reacts more slowly with tin(II) chloride than any of the other singly-bonded reagents. Examination of the Mössbauer spectrum of a sample of the residue after 18 hours reflux with one equivalent of the disulphide in benzene indicated only *ca.* 25% reaction to give $Sn^{IV}Cl_2(SMe)_2$. Tin(II) bromide reacted more quickly with the same reagent, the THF solvate, $Sn^{IV}Br_2(SMe)_2 \cdot THF$, being isolated in high yield after 4 hours reflux of the reagents in THF followed by extraction with benzene. The reaction was conveniently monitored using Mössbauer spectroscopy at approximately 1 hourly intervals. Bands occurring at 1040 and 918 cm^{-1} confirm the presence of coordinated THF.

Germanium(II) halides react with acetylenes to give 1:1 adducts which have been extensively reviewed by Vol'pin *et al.*[22,23] Electronic aspects of the carbenoid insertion of divalent Group IV derivatives into multiply-bonded species has been well documented by Johnson *et al.*[24] The structure of the 1:1 adducts has been shown to be the six-membered heterocycle, IIa, rather than "monomeric" three-membered ring structure, IIb, in all the cases studied.

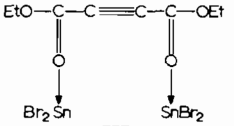


IIa



IIb

Divalent tin compounds do not undergo reaction with simple acetylenes such as diphenyl acetylene under moderate conditions ($SnCl_2$; 2 hr boiling THF). Activated acetylenes such as dialkylacetylene dicarboxylate, however, do react with tin(II) halides in refluxing THF. The interaction of tin(II) bromide with diethylacetylene dicarboxylate results in the formation of a 2 : 1 complex, which exhibits a quadrupole split doublet in the "tin(II)" region (I. S. = 3.65 mm s^{-1}, Q. S. = 1.44 mm s^{-1}) of the Mössbauer spectrum, consistent with the formation of a simple donor–acceptor complex involving coordination of the carbonyl oxygen atoms to tin(III). The infra-red spectrum of this compound shows a band at 1605 cm^{-1}, a lowering of *ca.* 140 cm^{-1} from the parent acetylene, indicative of strong carbonyl oxygen→tin coordination.



III

The reaction of tin(II) chloride with diethylacetylene dicarboxylate and of tin(II) chloride, bromide, and iodide with dimethylacetylene dicarboxylate results in the formation of 1 : 1 adducts, which all exhibit Mössbauer resonances with isomer shifts in the range 1.17 to 1.47 mm s^{-1} indicative of carbenoid interaction of the tin(II) halide with the carbon–carbon triple bond. Possible structures for these adducts include IIa and IIb, although the latter may be reasonably excluded on steric grounds. Noltes *et al.*[11] observed the presence of hexameric, nonameric, and higher-membered cyclic oligomers in benzene solution from the reactions of bis(cyclopentadienyl)tin, tin(II) dimethoxide and bis (pentane-2,4-dionate) with diethylacetylene dicarboxylate. Insolubility preclude colligative measurements in solution for the adducts with the dimethylacetylene ester, but the adduct of tin(II) chloride with the diethylacetylene ester was freely soluble in THF and chloroform, and osmometric data in the latter solvent indicated the presence of oligomers whose average molecular weight corresponded to that of a heptamer. The feature of highest mass observed in the mass spectrum of the $SnCl_2$–$EtO_2CC{\equiv}CCO_2Et$ adduct, however, was the $SnCl_2$-containing polyisotopic fragment at m/e = 359. No fragments containing two tin atoms were observed, indicating that facile cleavage occurs to give "monomeric" fragments of composition $SnCl_2 \cdot$ DEADC in the vapour; other tin-containing fragments together with suggested assignments are listed in Table IV. The derivatives $SnX_2 \cdot MeO_2CC{\equiv}CCO_2Me$ are soluble only in the most strongly coordinating solvents such as DMSO or DMF, suggesting a structure involving fairly low molecular weight species connected by a system of strong intermolecular carbonyl→tin coordinate bonds, which are ruptured only by strong donor molecules. Corroboration of such a strongly intermolecularly-coordinated polymeric lattice is available from X-ray powder photographs, which exhibit broad diffuse lines, and also from the observation of a strong Mössbauer effect at room temperature for the chloride and bromide, both of which indicate polymeric or strongly bound lattices. The vibrational spectra of all four adducts are very similar and are listed in Table V, together with assignments. A broad, intense carbonyl stretching frequency is observed at 1630 to 1640 cm^{-1} for all four derivatives, compared with that in the free acetylenes at 1730 cm^{-1}, consistent with coordination of the carbonyl groups to tin. Weak bands at 1700–1713 cm^{-1} in the spectra of the methyl derivatives indicate that a very small number of the carbonyl bands remain uncoordinated. A similar, but much stronger band in the spectrum of the $SnCl_2 \cdot$ DEADC derivative at 1721 cm^{-1} suggests that, whereas in the methyl derivatives participation of the carbonyl groups in coordination is almost total leading to a strong intermolecularly coordinated lattice, the coordination in the ethyl derivatives is far from complete resulting in a much less strongly bound lattice. Nonlinear Cl–Sn–Cl arrangements are evident for both chloride derivatives from the two Sn–Cl stretching modes observed for each.

Carbonyl oxygen→tin coordination completes octahedral coordination at tin for the methyl derivatives.

TABLE IV. Mass Spectrum of the 1 : 1 Adduct between $SnCl_2$ and Diethylacetylene Dicarboxylate.

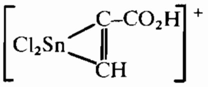
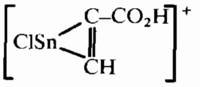
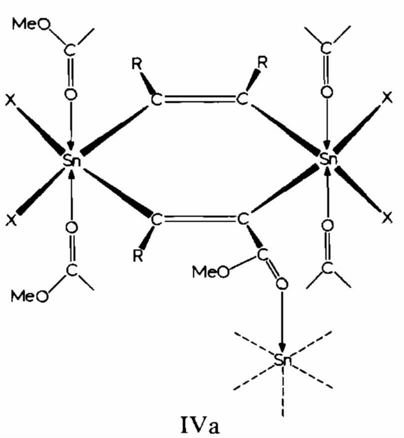
m/e	Relative Intensity	Assignment
361	74.28	P^+
333	22.85	$Cl_2Sn \cdot EtO_2C–C{\equiv}C–CO_2H^+$
305	8.00	$Cl_2Sn \cdot HO_2C–C{\equiv}C–CO_2H^+$
289	17.14	$Cl_2Sn \cdot EtO_2C–C{\equiv}CH^+$
260	48.00	
225	100	
190	77.14	$SnCl_2^+$
155	65.71	$SnCl^+$
119	60.00	Sn^+

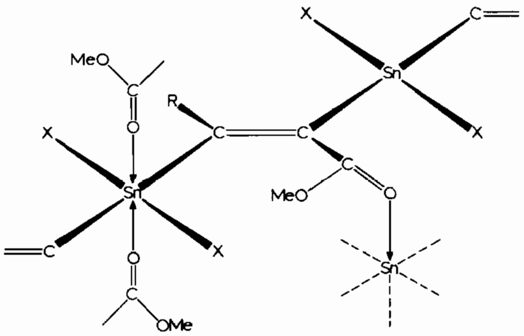
TABLE V. Vibrational Spectra of the Adducts $SnX_2 \cdot (RC{\equiv}CR)$ with Tentative Assignments (cm^{-1}).

X = Cl		X = Br		X = I	X = Cl	Assignment
R = MeO_2C		R = MeO_2C		R = MeO_2C	R = EtO_2C	
Raman	*IR*	*Raman*	*IR*	*IR*	*IR*	
	1713 mwbr		1712 wbr	1700 wbrsh	1721 mw	
1647 w	1641 vsbr		1642 vsbr	1642 vsbr	1630 vsbr	$\nu(C{=}O)$
1573 s		1570 s				
	1550 mshbr		1550 wbrsh	1533wbrsh	1540 wbr	$\nu(C{=}C)$
			1448 vssh			
1445 w	1442 vs	1443 w	1441 vs	1432 vs		$\delta(CH_3)$
			1371 m	1365 m	1400 ms	
1337 w	1347 vs	1334 w	1340 vssh	1335 mssh		$\delta(CH_3)$
	1322 vs		1318 vsbr	1308 vsbr	1310 vsbr	$\nu(C{-}O)$
		1217 w				
1081 s	1080 w	1075 s	1075 vwsh		1098 mw	$\nu_s(C{-}O{-}C)$
1051 w			1050 wsh	1045 wsh		
	1029 m		1030 mw	1025 m	1032 m	$\varrho_r(CH_3)$
939 w	917 ms		914 m	909 m	985 wbr	
807 m	789 m	804 m	788 m	779 m	865 m	
753 w	749 mw	753 w	746 mw	734 w	782 m	$\delta(OCO)$ $\pi(OCO)$
	649 mw		648 mw	640 mw	740 w	
					635 mw	
427 w	415 mw		408 w			
	404 mw		398 w	390 wbr	410 w	$\nu(Sn{-}C)$
					380 w	
		356 w				
336 s	346 ms				335 ms	$\nu_{as}(Sn{-}Cl)$
			359 vw			
315 m	307 msh				310 wsh	$\nu_s(Sn{-}Cl)$
		313 w	310 w	310 wvbr		
		230 s				

Point charge calculations predict Mössbauer quadrupole splitting values of *ca.* 2 mm s^{-1} and *ca.* 4 mm s^{-1} for *cis*-SnC_2X_4 and *trans*-SnC_2X_4 configurations, respectively[25]. The observed values of 2.34, 2.21 and 2.07 mm s^{-1} for the three methyl derivatives therefore serve to rule out a *trans* geometry such as IVb, and moreover are consistent only with the *cis* structure IVa, whose principal feature is a central 1,4-distannahexadienyl ring.



IVa



IVb

Both tin(II) chloride and bromide react exothermically with diethyldiazodicarboxylate in THF to form THF solvated adducts of composition $(SnX_2 \cdot EtO_2CN{=}NCO_2Et)_2 \cdot THF$ (X = Cl, Br). The nature of the solvating THF molecule is not discernable from the infra-red spectra due to masking of the 1100–950 cm^{-1} range by intense ligand bands, but the presence of THF is confirmed by resonances in the ^1H n.m.r. spectra at *ca.* 6.12 and 8.18 in $CDCl_3$ solution. The infra-red spectra of the two derivatives are very similar above 600 cm^{-1} suggesting isostructurality, whilst Sn–Cl stretching bands at 350 and 388 cm^{-1} for the chloride indicate a 'bent' Cl–Sn–Cl arrangement. Strong carbonyl oxygen→tin coordination is again demonstrated by broad, intense bands at *ca.* 1560 and 1500 cm^{-1}, but two additional weak bands at 1750 and 1695 cm^{-1}, slightly lower than the free ligand band at 1780 cm^{-1}, are indicative of a small number of 'free' carbonyl groups. Mass spectroscopic data for the two adducts was confused by facile ligand redistribution which takes place at the temperature of measurement. This was particularly bad for the bromide, where the most predominant features of the spectrum were the polyisotopic peaks corresponding to the $SnBr_n^+$ (n = 1–4) ions. The chloride adduct shows several peaks of higher mass than a simple "monomeric" 1:1 adduct ($SnCl_2 \cdot EtO_2CN{=}NCO_2Et$, m/e = 364) at m/e = 448, 483, and 527, whose polyisotopic distribution showed to contain two tin atoms. Assignment of these peaks is particularly difficult because of the lability of the chlorine atoms. However, the strongest peak in the spectrum occurs at m/e = 293 corresponding to the dehalogenated "monomeric" fragment $Sn(EtO_2CN{=}NCO_2Et)^+$, and a weaker peak at m/e = 364 corresponding to the "monomeric" $Cl_2Sn(EtO_2CN{=}NCO_2Et)^+$ ion. The mass spectral data serve to suggest that the solid may be constructed from two-tin-containing six-membered Sn_2N_4 cyclic units, although facile tin–ligand and ligand redistribution occur. Both derivatives are freely soluble in THF and chloroform, and molecular weight determinations by osmometry in the latter solvent gave the apparently anomalous values of 436 for the bromide and 339 for the chloride, much lower than the expected values of 978 for the bromide and 800 for the chloride for the "dimeric" formulations $[X_2Sn(EtO_2CN{=}NCO_2Et)]_2 \cdot THF$. These low values are most probably due to dissociative processes occurring in solution. The degree of dissociation may be ascertained from the Van't Hoff factor *i*, which has a value of 2.24 for the bromide and 2.36 for the chloride. The extent of dissociation in solution cannot therefore be totally due to a simple loss of the solvating THF molecule:

$$[X_2Sn(EtO_2CN{=}NCO_2Et)]_2 \cdot THF \rightleftharpoons THF + [X_2Sn(EtO_2CN{=}NCO_2Et)]_2$$

and it would seem likely that the extra dissociation arises from halide ionisation in the rather polar solvent used for the measurement ($CHCl_3$):

$$[X_2Sn(EtO_2CN{=}NCO_2Et)]_2 \rightleftharpoons X^- + [X_{1.5}Sn(EtO_2CN{=}NCO_2Et)]_2$$

Tin-119*m* spectra for both compounds exhibit singlet resonances in the range 0.32–0.37 mm s^{-1}, consistent with octahedrally coordinated tin, although no deductions may be inferred concerning the geometrical distribution of the ligands. It would seem highly likely from the spectroscopic data and the solubility of the derivatives, however, that the solid consists of small oligomeric units in which the carbonyl oxygen→tin coordination occurs *intra*molecularly.

Experimental

All manipulations were performed under an atmosphere of dry argon or nitrogen. Infra-red spectra were recorded using Perkin–Elmer 457 or 521 spectrophotometers. Mass spectra were obtained on an AEI MS-902 instrument. Mössbauer spectra were obtained at 77K or at ambient temperature with a Harwell constant acceleration spectrometer against a $Ba^{119m}SnO_3$ source. Data reduction to Lorenztian line shapes was accomplished by standard least-squares methods. Isomer shifts are quoted with respect to $BaSnO_3$. A Mössbauer spectrum is shown in Figure 1.

Tin(II) Chloride and Oxygen

Through a solution of tin(II) chloride (3.79 g; 20 mmol) in dry THF (50 ml) was passed dry oxygen as a fine jet of bubbles. After 10 min the clear solution became turbid and a white solid precipitated whose bulk increased on passage of the gas. The gas was passed for a total of 48 hr, when the solid was filtered off and dried *in vacuo* to yield *tin(IV) oxide dichloride · 1.5THF* as an infusible white powder. Found:

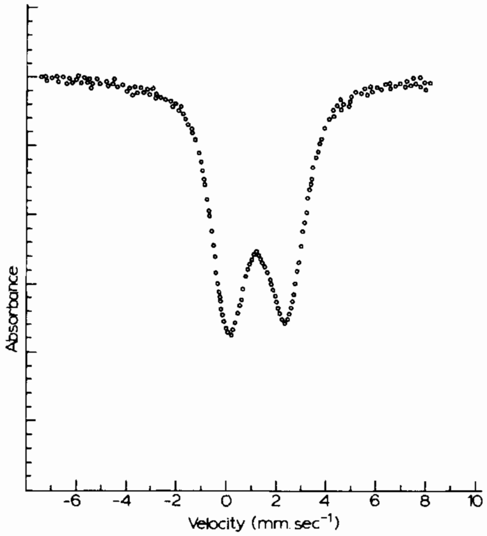


Figure 1. Mössbauer spectrum of the adduct of $SnCl_2$ and dimethylacetylene dicarboxylate at 77 K.

C, 22.63; H, 3.72%. $C_{12}H_{24}O_5Cl_4Sn_2$ requires: C, 22.89; H, 3.80%.

Tin(II) Chloride and Benzoyl Peroxide

Addition of a solution of benzoyl peroxide (2.40 g, 10 mmol) in dry THF (10 ml) to a stirred solution of tin(II) chloride (1.89 g, 10 mmol) in THF (10 ml) resulted in a rapid exothermic reaction. On cooling and partial removal of the solvent *in vacuo, tin(IV) dichloride dibenzoate* crystallised out as long needles which were filtered off and dried *in vacuo*. M.p. (sealed tube) 97°C. Found: C, 39.02; H, 2.89%. $C_{14}H_{10}O_4Cl_2$ Sn requires: C, 38.93; H, 2.33%.

Tin(II) Bromide and Benzoyl Peroxide

The reaction was carried out exactly as in the preceding method using tin(II) bromide. *Tin(IV) dibromide dibenzoate* crystallised out as long translucent needles. M.p. (sealed tube) 79–82°C. Found: C, 33.43; H, 2.48%. $C_{14}H_{10}O_4Br_2Sn$ requires: C, 32.35; H, 1.93%.

Tin(II) Chloride and Lead Tetraacetate

To a stirred solution of tin(II) chloride (1.89 g, 10 mmol) in dry THF (10 ml) was added a solution of lead tetraacetate (4.43 g, 10 mmol) in THF (20 ml). The reaction mixture became warm, and on cooling crystals of *tin(IV) dichloride diacetate* appeared, which were filtered off and dried *in vacuo*. M.p. (sealed tube) 115°C. Found: C, 15.35; H, 1.56; Cl, 21.02%. $C_4H_6O_4Cl_2Sn$ requires: C, 15.56; H, 1.95; Cl, 22.97%.

Tin(II) Bromide and Lead Tetraacetate

The reaction and isolation of *tin(IV) dibromide diacetate* proceeded exactly as in the preceding method. M.p. (sealed tube) ~200°C (with decomp.). Found: C, 11.76; H, 1.31; Br, 39.56%. $C_4H_6O_4Br_2Sn$ requires: C, 12.08; H, 1.52; Br, 40.19%.

Tin(II) Chloride and Mercuric Acetate

To a stirred solution of tin(II) chloride (1.89 g, 10 mmol) in THF (10 ml) was added a solution of mercuric acetate (3.18 g, 10 mmol) in THF (20 ml). The solution was refluxed for 30 min during which time a dark grey precipitate of metallic mercury appeared. The solution was decanted off under argon and on slow evaporation of the solvent *in vacuo* crystals of *tin(IV) dichloride diacetate* appeared. M.p. (sealed tube) 113°C. Found: C, 15.80; H, 1.69; Cl, 21.56%. $C_4H_6O_4Cl_2Sn$ requires: C, 15.56; H, 1.95; Cl, 22.97%.

Tin(II) Bromide and Mercuric Acetate

Using the same procedure as the preceding one, tin(IV) dibromide diacetate was isolated as white crystals. M.p. (sealed tube) ~200°C. Found: C, 11.90; H, 1.29; Br, 39.43%. $C_4H_6O_4Br_2Sn$ requires: C, 12.08; H, 1.52; Br, 40.19%.

Tin(II) Bromide and Dimethyldisulphide

To a refluxing solution of tin(II) bromide (2.79 g, 10 mmol) in THF (30 ml) was added a solution of dimethyl disulphide (0.94 g, 10 mmol) in dry THF (10 ml). The reaction mixture was refluxed for 4 hr in which time the solution became a deep golden yellow colour. The solution was cooled, and the THF removed *in vacuo* to yield a yellow amorphous powder. The product was washed with copious amounts of dry benzene, and the filtrate was then evaporated *in vacuo* to yield *tin(IV) dibromide bis(methylsulphide)·THF* as a pale yellow solid. M.p. (sealed tube) ~180°C (decomp.). Found: C, 16.09%; H, 3.02%. $C_6H_{14}OS_2$ Br_2Sn requires: C, 16.20; H, 3.17%.

Tin(II) Chloride and Dimethylacetylene Dicarboxylate

On mixing a solution of tin(II) chloride (1.89 g, 10 mmol) in THF (5 ml) with a solution of dimethylacetylene dicarboxylate (1.42 g, 10 mmol) in THF (5 ml) there was no apparent reaction. On refluxing a pale yellow tinge appeared, and after 10 min the solution became turbid and a white solid began to precipitate out. The *1:1 adduct* was filtered off and dried. M.p. *ca.* 270°C (with decomp.). Found: C, 20.93; H, 2.08%. $C_6H_6O_4Cl_2Sn$ requires: C, 21.60; H, 2.39%.

Tin(II) Bromide and Tin(II) Iodide with Dimethylacetylene Dicarboxylate

Procedures as in the preceding one. The 1:1 adduct $SnBr_2(MeO_2CC{\equiv}CCO_2Me)$ was isolated as a white powder. M.p. *ca.* 250°C (with decomp.). Found: C, 17.00; H, 1.77; Br, 34.67%. $C_6H_6O_4Br_2Sn$ requires: C, 17.10; H, 1.42; Br, 38.00%. The adduct $SnI_2(MeO_2CC{\equiv}CCO_2Me)$ is a yellow powder. M.p. *ca.* 170°C (with decomp.). Found: C, 12.64; H, 1.68%. $C_6H_6O_4I_2Sn$ requires: C, 13.64; H, 1.08%.

Tin(II) Chloride and Diethylacetylene Dicarboxylate

A mixture of tin(II) chloride (1.89 g, 10 mmol) and diethylacetylene dicarboxylate (1.72 g, 10 mmol) in THF (20 ml) was refluxed for 1 hour. On concentration of the solution the adduct $Cl_2Sn(EtO_2CC{\equiv}CCO_2Et)$ was isolated as a white microcrystalline solid. M.p. 267°C (with decomp.). Found: C, 27.89; H, 3.31%. $C_8H_{10}O_4Cl_2Sn$ requires: C, 26.70; H, 2.80%. Molecular weight (osmometry in $CHCl_3$) = 2525.

Tin(II) Bromide and Diethylacetylene Dicarboxylate

On mixing a solution of tin(II) bromide (2.79 g, 10 mmol) in THF (10 ml) with a solution of diethylacetylene dicarboxylate (1.72 g, 10 mmol) there was an immediate reaction, and the solution became pale golden yellow. $(SnBr_2)_2(EtO_2CC{\equiv}CCO_2Et)$ slowly crystallised out as a pale yellow microcrystalline solid. M.p. (sealed tube) 73°C. Found: 12.88; H, 2.14%. $C_8H_{10}O_4Br_4Sn_2$ requires: C, 13.21; H, 1.38%.

Tin(II) Chloride and Diethyl Diazodicarboxylate

Dropwise addition of a solution of diethyl diazodicarboxylate (1.74 g, 10 mmol) in THF (10 ml) to a stirred solution of tin(II) chloride (1.89 g, 10 mmol) in THF (10 ml) resulted in an exothermic reaction and a decolourising of the pale orange solution to a straw yellow. No product was obtained on cooling, but on concentration of the solution $Cl_2Sn(EtO_2CN{=}NCO_2Et)_2 \cdot THF$ crystallised out as white crystals. M.p. 175°C (with decomp.). Found: C, 22.96; H, 3.40; N, 6.76%. $C_{16}H_{28}N_4O_9Cl_4Sn_2$ requires: C, 24.02; H, 3.53; N, 7.00%. Molecular weight (osmometry in $CHCl_3$) = 339.0.

Tin(II) Bromide and Diethyl Diazodicarboxylate

Using the preceding procedure, $Br_2Sn(EtO_2CN{=}NCO_2Et)_2 \cdot THF$ was isolated as a pale blue microcrystalline solid. M.p. 151°C. Found: C, 18.68; H, 2.75; N, 5.54%. $C_{16}H_{28}N_4O_9Br_4Sn_2$ requires: C, 19.64; H, 2.88; N, 5.73%. Molecular weight (osmometry in $CHCl_3$) = 436.4.

Acknowledgement

We thank the S.R.C. and Albright & Wilson for support in the form of a C.A.S.E. Award (to P.F.R.E.).

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