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SOLID-STATE ASSOCIATION IN ORGANOTIN COMPOUNDS CONTAINING BULKY ORGANIC GROUPS. TRICYCLOHEXYLTIN HYDROXIDE

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Summary

Tricyclohexyltin hydroxide is shown to share the hydroxy-bridged polymeric structure of its methyl analogue on the basis of its ambient temperature ^{119m}Sn Mössbauer spectrum, similar QS value and its ν(O—H) in the infrared. Fragments larger than the parent molecular ion are observed in the mass spectrum, but these may arise from a rapid dehydration/condensation to bis(tricyclohexyltin) oxide.

Triorganotin compounds containing atoms with lone pairs of electrons adopt higher coordination whenever favorable conditions exist [1]. The choice of coordination number and geometry is often governed by the size of the substituent groups at tin [2] and by the degree of branching in the ligand [3]. Nonbonded interactions of the cyclohexyl group in organotin compounds have been reviewed [4]. In the well-studied acetate series, the structure of the tricyclohexyltin analogue consists of discrete units in the solid [5], with the three cyclohexyl groups apparently effectively preventing the close approach of a second acetate group. Both the tribenzyltin [6] and trimethyltin [7] derivatives crystallize in the carboxylate-bridging form. The triorganotin hydroxides, whose structures have been less extensively studied, are complicated by interconversion to the oxides and by possible contamination with the carbonates (eqn. 1). The solid state structure of trimethyltin hydroxide consists of chains of oxygen atoms almost equidistant between planar trimethyltin groups [8]. The results of a recent study of tricyclohexyltin hydroxide by tin-119m Mössbauer spectroscopy suggested a similar five-coordinate structure based upon quadrupole splitting data [9]. Another study of triorganotin hydroxides and of bis(triorganotin) oxides by infrared and Mössbauer spectroscopy neglected the tricyclohexyltin derivatives [10]. We have recently reported the structure of trimethyltin glycinate [11] which is an amino-bridged, five-coordinated polymeric tin compound and from a combination of spectroscopic data, we have shown the

TABLE 1

MÖSSBAUER DATA FOR TRIORGANOTIN HYDROXIDES AND CARBONATES[a]

Compound	δ (±0.06 mm/s)	Δ (±0.12 mm/s)	Γ_1	Γ_2
Me_3SnOH	1.23[b]	2.82[b]	1.14	1.10
$(C_6H_{11})_3SnOH$[c]	1.46[d]	2.98[d]	1.45	1.18
$(Me_3Sn)_2CO_3$	1.34	3.05	1.28	1.24
$(Bu_3Sn)_2CO_3$	1.48[e]	3.24[e]		
$[(C_6H_{11})_3Sn]_2CO_3$	1.62	3.39	0.98	1.33

[a] Recorded at 77 K vs. Ba $^{119m}SnO_3$ (New England Nuclear Corp.) by published techniques [30]. [b] Listed as 1.07 ± 0.03; 2.71 ± 0.03 vs. SnO_2 [13]; as 1.19 ± 0.05; 2.91 ± 0.05 vs. SnO_2 [31]; as 1.14 ± 0.09; 2.97 ± 0.09 vs. Pd(Sn) [32]; as 1.20 and 2.89 vs. SnO_2 [10]. [c] Exhibits ambient temperature spectrum. [d] Listed as 1.40 ± 0.05 and 2.99 ± 0.05 [9]. [e] From Ref. 10.

tricyclohexyltin glycinate to have a similar structure [2]. The comparison between the methyl- and cyclohexyl-tin hydroxides is also of interest in this respect.

$$(R_3Sn)_2CO_3 \xleftarrow[-H_2O]{CO_2} 2R_3SnOH \rightleftharpoons (R_3Sn)_2O + H_2O \qquad (1)$$

The extent of dehydration of tricyclohexyltin hydroxide to form bis(tricyclohexyltin) oxide is uncertain [12], but we have synthesized bis(tricyclohexyltin) carbonate for comparative study. Table 1 lists the ^{119m}Sn Mössbauer data for the compounds studied. The QS values for the two hydroxides are identical within experimental error, and the ratios of QS to IS are greater than ca. 2.1, a situation generally observed for higher than four-coordination at tin [9, 13,14]. Furthermore, tricyclohexyltin hydroxide exhibits a spectrum at ambient temperatures, a behavior always associated with polymeric lattices [14,15]. While several compounds known to form associated solids fail to exhibit ambient temperature spectra (trimethyltin hydroxide is one example), no discretely molecular solids giving rise to this phenomenon are known [14,15].

The infrared ν(O—H) in the solid state is very similar for the two hydroxides (Table 2), with the sharp absorptions confirming the absence of hydrogen bonding, but observation of both ν_{as} and ν_s (SnC_6H_{11}) for the tricyclohexyltin derivative rules out a precisely planar arrangement for the SnC_3 skeleton. In solutions in which trimethyltin hydroxide has been shown to be a dimer [16], ν(O—H) shifts to 3658 cm^{-1} while the ν(O—H) for tricyclohexyltin hydroxide is found at 3638 cm^{-1} in a variety of inert solvents in which the degree of association has not been investigated.

These observations specify that the trimethyl- and tricyclohexyl-tin hydroxides share the five-coordinate, trigonal bipyramidal arrangement in the solid state at ambient temperatures as well as at 77 K, probably of the axially most electronegative type commonly found in organotin chemistry [1], and that the three cyclohexyl groups do not prevent the penetration of the hydroxide of an adjacent molecule to form the associated chain structure. This situation should be contrasted with that in the trineophyltin analogue, where the Mössbauer data suggest four-coordination [9,13,17], but further confirmation is needed since

TABLE 2

INFRARED ABSORPTIONS FOR R_3SnOH (IN cm^{-1})

Me_3SnOH [a,b]	$(C_6H_{11})_3SnOH$ [c]	Assignment
3620m	3615w	ν(O—H)
2985m	2929w	
2915m	2850w	
1406w	1460m	
	1450m	
	1352w	
	1330w	
	1298w	
	1272w	
1195m	1174s	
	1085m	
	1076m(sh)	
	1043m	
	1026w	
	995s	
920s	910s(br)	δ(Sn—OH)
	885m	
	847m	
	808w	
765		ρ_γ(Sn—CH_3)
	725m	
	664m	
	556vw	
540s [d]		ν_{as}(Sn—CH_3)
	491m	ν_{as}(Sn—C_6H_{11}) [e]
	420w	ν_s(Sn—C_6H_{11}) [e]
	352m	
370s	294s	ν(Sn···O)
316w	235m	
	185m	

[a] Taken from ref. 20 with assignments as listed there. [b] Infrared absorptions are also reported in Ref. 33. [c] Run as Nujol and halocarbon oil mulls on Beckman IR-11 and IR-12 spectrometers. [d] A medium band at 504 cm^{-1} is observed in CCl_4 solution and assigned to ν_s(Sn—CH_3) in that phase [20]. [e] We have found tin—carbon bands at 496-490 and 425-415 cm^{-1} in a series of tricyclohexyltin—oxygen compounds studied [2].

ν(O—H) has been reported at 3620 cm^{-1} in the melt (m.p. 145-146° [17]) and hydroxide bridging to form a dimeric Sn_2O_2 ring occurs in $[(h^5\text{-}C_5H_5)Fe(CO)_2\text{-}Sn(C_6H_5)(O_2SC_6H_5)OH]_2$, where the two five-coordinate tin atoms also carry very bulky groups [18]. The high lattice forces in the methyl- and cyclohexyltin solids are sufficient to elevate the melting points (220-222°C for the latter [19]) and to ensure the stability of the two hydroxides against dehydration at ambient temperatures, yet in our hands, even trimethyltin hydroxide sublimes readily at room temperature in vacuo.

Additional evidence from mass spectrometric studies are gathered in Table 3. Trimethyltin hydroxide exhibits an intense peak at *m/e* 329 which can be assigned on the basis of high resolution data as $Me_3SnOSnMe_2^+$. Trimethyltin hydroxide is surprisingly resistant to dehydration, and can be very readily sublimed without decomposition or condensation under high vacuum. Species are found in the mass spectrometer similar to those observed in other polymeric organotin—oxygen compounds [20,21]. Trimethyltin hydroxide decomposes to give

TABLE 3

MASS SPECTROMETRIC DATA FOR TRIMETHYL- AND TRICYCLOHEXYL-TIN HYDROXIDE AND CARBONATE[a]

m/e	Ion	Me_3SnOH	$(Me_3Sn)_2CO_3$	$(C_6H_{11})_3$-$SnOH$	$[(C_6H_{11})_3Sn]_2$-CO_3
44	CO_2^+	1.7[b]	46.2	13.2[b]	0.4
119	Sn^+	25.1[c]	6.7	9.5	9.4
120	SnH^+	11.7[d]	2.0	29.1	18.5
127	$Sn{-}O{-}Sn^{2+}$		4.5		
134	$MeSn^+$	50.2[e]	20.7		
134.5	$MeSn{-}O{-}Sn^{2+}$		1.3		
136	$MeSnH_2^+$	28.1	7.3		
142	$MeSn{-}O{-}SnMe^{2+}$		17.2		
149	Me_2Sn^+	37.2[f]	10.7		
149.5	$Me_2Sn{-}O{-}SnMe^{2+}$		0.8		
150	Me_2SnH^+	22.5	6.3		
157	$Me_2Sn{-}O{-}SnMe_2{}^{2+}$		14.8		
164	Me_3Sn^+	68.0[g]	42.0		
166	Me_2SnOH^+	69.3			
202	$C_6H_{11}Sn^+$			100.0	100.0
254	$Sn{-}O{-}Sn^+$		6.7		
255	$HSn{-}O{-}Sn^+$				6.8
269	$MeSn{-}O{-}Sn^+$	15.6	12.8		
284	$MeSn{-}O{-}SnMe^+$		1.2		
285	$(C_6H_{11})_2Sn^+$			5.8	5.3
299	$Me_2Sn{-}O{-}SnMe^+$	37.7	42.0		
302	$(C_6H_{11})_2SnOH^+$			3.2	
314	$Me_2Sn{-}O{-}SnMe_2^+$		0.6		
329	$Me_3Sn{-}O{-}SnMe_2^+$	100.0[h]	100.0		
339	$C_6H_{11}Sn{-}O{-}SnH_2^+$				4.1
368	$(C_6H_{11})_3Sn^+$			10.1	1.1
420	$(C_6H_{11})_2Sn{-}O{-}Sn^+$			5.4	5.5
464	$(C_6H_{11})_2SnCO_3Sn^+$				1.3
503	$(C_6H_{11})_2Sn{-}O{-}Sn(C_6H_{11})^+$			1.4	
586	$(C_6H_{11})_3Sn{-}O{-}Sn(C_6H_{11})^+$			5.8	
598	$[(C_6H_{11})_2Sn]_2CO^+$				9.1
669	$(C_6H_{11})_3Sn{-}O{-}Sn(C_6H_{11})_2^+$			9.3[i]	
697	$(C_6H_{11})_3Sn[(C_6H_{11})_2Sn]CO_2^+$				20.2

[a] Recorded on an AEI MS-902 mass spectrometer at 70 eV. [b] Background CO_2^+ is listed for comparison purposes. [c] Found: 119.9034; calcd.: 119.9022; Δ = 10 ppm (based on Sn = 120). [d] Found: 120.9111; calcd.: 120.9100; Δ = 9 ppm (based on Sn = 120). [e] Found: 134.9246; calcd.: 134.9256; Δ = 7 ppm (based on Sn = 120). [f] Found: 149.9493; calcd.: 149.9491; Δ = 1 ppm (based on Sn = 120). [g] Found: 164.9725; calcd.: 164.9726; Δ = 1 ppm (based on Sn = 120). [h] Found: 328.9166; calcd.: 328.9189; Δ = 7 ppm (based on Sn_2 = 238). [i] Found: 669.2210; calcd.: 669.2319; Δ = 15 ppm (based on Sn_2 = 238).

dimethyltin oxide and tetramethyltin as the only tin-containing species [19]. Tricyclohexyltin hydroxide likewise gives a fragment at *m/e* 669 in the mass spectrometer which can be formulated as $(C_5H_{11})_3SnOSn(C_5H_{11})_2^+$ from high resolution data. The peak is far less intense, and the data do not serve to distinguish the origin of this fragment as a portion of the associated structure of solid tricyclohexyltin hydroxide that survives transfer to the gas phase, or as a result of rapid dehydration/condensation under the high vacuum conditions of the mass spectrometer to give bis(tricyclohexyltin) oxide.

Both trimethyltin hydroxide and carbonate exhibit the *m/e* 329 ion, $Me_3SnOSnMe_2^+$, as the most abundant. In the cyclohexyl compounds, on the other hand, the ions assigned as $(C_6H_{11})_3SnOSn(C_6H_{11})_2^+$(669), $(C_6H_{11})_2SnOSn(C_6H_{11})_2^+$ (586), $(C_6H_{11})_2SnOSnC_6H_{11}^+$(503) and $(C_6H_{11})_2SnOH^+$(302) in the spectrum of the hydroxide do not appear in the spectrum of the carbonate, but are replaced by ions which can be assigned to $(C_6H_{11})_3Sn[(C_6H_{11})_2Sn]CO_2^+$(697), $[(C_6H_{11})_2Sn]_2CO^+$(598), $(C_6H_{11}Sn)_2CO_3^+$(464), $C_6H_{11}SnOSnH_2^+$(339) and $SnOSnH^+$(255). In both cyclohexyltin compounds, $C_6H_{11}Sn^+$(202) is the most abundant ion.

The comparison between the methyl and cyclohexyl spectra reflects the greater availability of hydrogen from the cyclohexyl groups during fragmentation to give species such as SnH^+(120). The abundances of the methyltin ions are in the order $Me_3Sn^+ > MeSn^+ > Me_2Sn^+$ for both derivatives, but $C_6H_{11}Sn^+$ is the most abundant in both of its dervatives with $(C_6H_{11})_3Sn^+$ and $(C_6H_{11})_2Sn^+$ present in small amounts. Doubly charged ions are common in the spectrum of $(Me_3Sn)_2CO_3$, and the amount of CO_2^+ is significant, while in the cyclohexyl analogue doubly-charged ions are not observed, and the release of $C_6H_{11}O$ is a principal process in the fragmentation. As a further comparison, the high resolution mass spectrum of tricyclohexylsilanol consists of relatively few ions:

TABLE 4

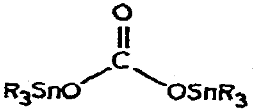
INFRARED ABSORPTIONS FOR $(R_3Sn)_2CO_3$ (IN cm^{-1})

R = Me[a,b]	R = Et[a,c]	R = C_6H_{11}[d]	Assignment
		2930w	
		2855w	
1553	1540	1512s	C=O str.
1534	1520		
		1460w	
		1448m	
1379	1370	1360m	C—O—O antisym. str.
		1330m	
		1271m	
		1260m(sh)	
		1175m	
		1095w	
1072	1073	1063w	C—O—O sym. str.
		1045w	
		996m	
		910vvw	
		885m	
		845m	
839	840	830m	non-planar rock
		810vw	
741	756	730m	C—O—O bending and planar rock
705	723	668m	
		570s	
546	519	492m	Sn—C asym. str.
518	494	420m	Sn—C sym. str.
		371w	
		322m	
381	385	258s	Sn—O str.

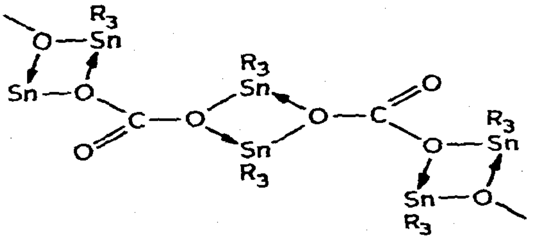
[a] Taken from ref. 24 with assignments as listed there. [b] Infrared absorptions are also reported in ref. 34. [c] Infrared absorptions are also reported in ref. 35. [d] Run as Nujol and halocarbon oil mulls on Beckman IR-11 and IR-12 spectrometers.

$(C_6H_{11})_3SiOH$, 20.7%; $(C_6H_{11})_2SiOH$, 100%; $C_6H_{11}(H)SiOH$, 76.4%; $C_6H_{11}SiOH$, 1.0%; $C_6H_{11}SiO$, 1.9%; $C_6H_{11}Si$, 4.8% [22].

Free carbonate ion has D_{3h} symmetry and is expected to give rise to four vibrations, three of which are infrared active as in barium carbonate which gives absorptions at 1420, 857 and 692 cm^{-1} [23]. For a mono- or bi-dentate carbonate group having C_{2v} symmetry, all six resulting bands should be infrared active [23]. The infrared data in Table 4, following Sato's assignments [24], are consistent with the idea that the C_{2v} carbonate groups interact with non-planar R_3Sn groups, and that neither group is ionic. The Mössbauer data suggest that there is only one kind of tin environment, but the quadrupole splittings cannot be used to distinguish four- or five-coordination, and the absence of mass spectral fragments above the monomer or an ambient temperature Mössbauer spectrum is negative evidence. Monomeric structures in the solid containing four-coordinated tin have been proposed on the basis of infrared evidence for the methyl- [24] and ethyl-tin [25] derivatives:



but the corresponding nitrate takes up a trigonal bipyramidal structure with planar trimethyltin groups in the solid monohydrate [26], and the question of whether the sulfate moiety is chelating in monomeric $(R_3Sn)_2SO_4$ units [27,28] or bridging in an associated lattice [3,29] has been the focus of recent controversy. Further interactions with the tin atom would have to take place preserving the local C_{2v} symmetry of the CO_3 group, and therefore, not involve the unique oxygen. These requirements are met in:



in which at least one oxygen occupies an equatorial position and the SnC_3 skeleton is non-planar.

Experimental

Trimethyltin hydroxide was purified by sublimation. The tricyclohexyltin hydroxide used (Anal. Found: C, 56.24; H, 9.11; Sn, 30.82. Calcd.: C, 56.13; H, 8.90; Sn, 30.82%.) was titrated with Karl-Fischer reagent (Found: OH, 4.57. Calcd.: OH, 4.67%.) and the presence of insoluble bis(tricyclohexyltin) oxide tested by weighing (Found: 0.16. Calcd.: 0%.).

Bis(trimethyltin) carbonate was prepared by bubbling carbon dioxide overnight through a solution of trimethyltin hydroxide (1 g) in 100 ml of benzene.

The solid isolated was infusable above 210°C (lit. m.p. > 200°C) [26].

Bis(tricyclohexyltin) carbonate was prepared by bubbling carbon dioxide through a solution of tricyclohexyltin hydroxide (1 g) in 100 ml of dry benzene overnight. Bis(tricyclohexyltin) carbonate (m.p. 195-197°C) remained after the solvent was evaporated. Anal. Found: C, 54.80; H, 8.38; Sn, 29.69. Calcd.: C, 55.80; H, 8.36; Sn, 29.81%.

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