Structural Studies of Diorganotin(IV) Carboxylates. X-ray and NMR Structures of Me$_2$Sn(OAc)$_2$ and a 7-Coordinate Tin Anion, Me$_2$Sn(OAc)$_3$⁻NMe$_4$⁺·2CHCl$_3$[†]

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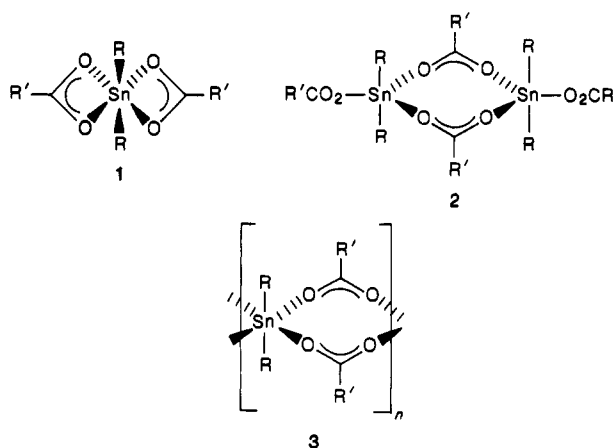
The X-ray crystal and molecular structure of Me$_2$Sn(OAc)$_2$ is reported and compared with previous predictions based on other structural methods. The molecule is found to be monomeric and 6-coordinate at tin in the solid state. The Me–Sn–Me angle of 135.9 (2)° is in close agreement with the value predicted from solid-state and solution NMR studies. ^{119}Sn NMR data are also reported for this compound. Me$_2$Sn(OAc)$_2$ crystallizes in the monoclinic space group C2/c (No. 15) with *a* = 12.712 (2) Å, *b* = 5.220 (1) Å, *c* = 14.365 (3) Å, *β* = 92.80 (1)°, and Z and 4; R refined to 0.022 and R$_w$ to 0.029 for 1041 reflections. Me$_2$Sn(OAc)$_2$ reacts with Me$_4$N⁺OAc⁻ in CHCl$_3$ solution to give a quantitative yield of Me$_2$Sn(OAc)$_3$⁻NMe$_4$⁺. Me$_2$Sn(OAc)$_3$⁻NMe$_4$⁺ crystallizes with two molecules of CHCl$_3$ in orthorhombic space group Pbca (No. 61) with *a* = 16.717 (2) Å, *b* = 17.475 (2) Å, *c* = 18.242 (3) Å, and Z = 8; R refined to 0.059 and R$_w$ to 0.047 for 1723 reflections. Me$_2$Sn(OAc)$_3$⁻NMe$_4$⁺ is 7-coordinate at tin and has a Me–Sn–Me angle of 165.8°. CHCl$_3$ in the crystal lattice is weakly hydrogen bonded to several oxygens of the tin complex. Solution ^{1}H, ^{13}C, and ^{119}Sn and solid-state ^{13}C NMR studies provide evidence for retention of the high coordination number in solution and for rapid, reversible acetate exchange in solution.

Diorganotin dicarboxylates are widely used in industry as homogenous catalysts for polyurethane and RTV silicone polymerizations and for transesterification reactions.[1] Notwithstanding these important applications, the structure[2-4] and mechanisms of action of even simple diorganotin dicarboxylates remain a matter of speculation. Recently, a new structural interpretation,[5] based on solid-state and solution ^{13}C NMR data for Me$_2$Sn(OAc)$_2$, was put forth for diorganotin dicarboxylates. In this paper we report the first X-ray crystal structure of a diorganotin dicarboxylate. In addition, the first X-ray structural study of a 7-coordinate organotin anion, a diorganotin tricarboxylate, is reported.

Results and Discussion

Molecular Structure of Me$_2$Sn(OAc)$_2$. A wide variation in carboxylate bonding modes is known from X-ray studies for organotin carboxylates. These range from nonbridging mono- and bidentate carboxylates (as in tricyclohexyltin 3-indoylacetate[6] and several triphenyltin aminobenzoates,[7] respectively) to bridging with two or three bonding interactions to tin (as in the polymeric compounds Me$_3$SnOAc[8] and {[Me$_2$Sn(OAc)]$_2$O}$_2$,[5] respectively). Three distinct structures, 1, 2, and 3, have been proposed for simple diorganotin dicarboxylates. Interpretations of NMR and IR data for various diorganotin dicarboxylates have led to the conflicting proposed solution structures 1[2] and 2,[3] though cryoscopic molecular weight measurements for Me$_2$Sn(OAc)$_2$ in benzene clearly favor a monomeric species.[2b] On the original basis of differences between the solution and solid-state carboxylate stretching region of the IR spectrum of Me$_2$Sn(OAc)$_2$ (one band at 1600 cm⁻¹ was observed for Me$_2$Sn(OAc)$_2$ in solution, but an additional band at 1560 cm⁻¹, attributed to a bridging carboxylate, was observed for a crystalline film), polymeric structure 3[2b] has been the accepted solid-state structure for diorganotin dicarboxylates. Our recent report[5] that the tin–carbon coupling constant, |^{1}J(^{119}Sn,^{13}C)|, of Me$_2$Sn-

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(OAc)$_2$ is the same in the solid-state and in solution led us to propose that the solution and solid-state structures are essentially the same. Analysis of |^{1}J(^{119}Sn,^{13}C)| and the solution tin–hydrogen coupling constant, |^{2}J(^{119}Sn,^{1}H)|, indicated[9] an Me–Sn–Me angle of about 135°; the sum of

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(3) Mitchell, T. N. *J. Organomet. Chem.* 1973, *59*, 189.

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(5) Lockhart, T. P.; Manders, W. F.; Holt, E. M. *J. Am. Chem. Soc.* 1986, *108*, 6611.

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(7) Swisher, R. G.; Vollano, J. F.; Chandrasekhar, V.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* 1984, *23*, 3147.

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(9) The following empirical correlations relating the Me–Sn–Me angle and the magnitude of the tin–carbon[10] and tin–hydrogen[11] coupling constants have been described: |^{1}J(^{119}Sn,^{13}C)| = 10.7 × (Me–Sn–Me angle) − 778; Me–Sn–Me angle = (0.0161)(|^{2}J(^{119}Sn,^{1}H)|)^2 − (1.32 × |^{2}J-(^{119}Sn,^{1}H)|) + 133.4.

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Table I. NMR Data for Me₂Sn(OAc)₂ and Me₂Sn(OAc)₃⁻NMe₄⁺

	^{119}Sn NMR		^{1}H NMR		^{13}C NMR	
compd, solv	chem shift, ppm	line width at half-height, Hz	Sn–Me chem shift, ppm	$\|^1J(^{119}Sn, {}^1H)\|$, Hz	Sn–Me chem shift, ppm	$\|^1J(^{119}Sn, {}^{13}C)\|$ Hz
Me₂Sn(OAc)₂						
CD₂Cl₂	−120	≤7	0.94	83.3	3.7[a]	665[a]
solid-state					3.8[a]	665[a]
Me₂Sn(OAc)₃⁻NMe₄⁺						
CDCl₃ (<0.1 M)	b		0.94	96	10.4	913
CD₂Cl₂ (0.3 M)	−295	20	0.72	99.6	10.9	937
acetone-d_6						
0.125 M	−286	20	0.65	103.9	10.1	911
0.30 M	−289	15	0.66	104.2	10.3	920
solid-state					12.6, 9.9	840 (av)

[a] C₆D₆ solution.[5] [b] Insufficient solubility for ^{119}Sn NMR analysis.

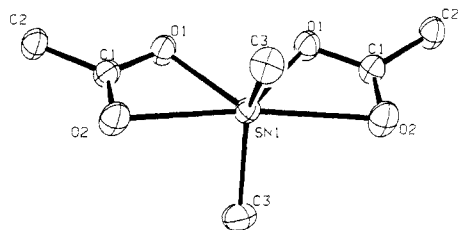**Figure 1.** ORTEP plot of Me₂Sn(OAc)₂ showing atom numbering scheme.

all the available data were taken as strongly favoring structure 1 for Me₂Sn(OAc)₂ and other diorganotin dicarboxylates.

The extreme moisture sensitivity of Me₂Sn(OAc)₂ blocked our previous efforts to test rigorously the NMR structure prediction by X-ray diffraction. Using inert atmosphere techniques, we have now succeeded in obtaining the X-ray crystal and molecular structure of Me₂Sn(OAc)₂. Positional parameters are given in Table II and selected bond angles and distances in Table III. It is clear from the ORTEP plot (Figure 1) of Me₂Sn(OAc)₂ that the general features predicted from the NMR analysis are correct. Tin has a coordination number of 6 and adopts a highly distorted octahedral conformation (it may alternately be described as a bicapped tetrahedron with oxygens O(2) and O(2a) capping the faces). Tin and the atoms of the acetate groups are nearly coplanar; the maximum deviation out of the SnO₄ plane is 0.07 Å for O(2). The acetates are anisobidentate, with Sn–O distances of 2.106 (2) and 2.539 (2) Å, both of which are significantly shorter than the sum of the van der Waals radii[12] (3.68 Å). The Me–Sn–Me angle, 135.9 (2)°, is remarkably close to that predicted[5] from solid-state NMR data (135°). The angle between the Me₂Sn and SnO₄ planes is 89.1°. The molecules are separated by normal van der Waals contacts in the crystal.

Some new and published NMR data for Me₂Sn(OAc)₂ are collected in Table I. The relatively small, negative ^{119}Sn chemical shift of Me₂Sn(OAc)₂ in CD₂Cl₂ solution, −120 ppm, provides additional evidence[13] of the large range of chemical shifts that may be observed for 6-coordinate dimethyltin(IV) compounds and points to the vulnerability of estimates of coordination number based only on this one parameter.[14] The available solution or solid-state $\|^1J$-(^{119}Sn,^{13}C)$\|$ values and ^{119}Sn chemical shift data for Bu₂Sn(OAc)₂,[3,15] Me₂Sn(benzoate)₂,[13a] and Me₂Sn(lau-

Table II. Fractional Coordinates (×10⁴) and Isotropic Thermal Parameters for Me₂Sn(OAc)₂

atom	x	y	z	B(iso), Å²
Sn(1)	0.0	1542.9 (4)	2500.0	1.8 (1)′
O(1)	−513 (1)	4644 (4)	1657 (1)	2.3 (1)′
O(2)	−1034 (2)	1131 (4)	949 (2)	3.1 (1)′
C(1)	−981 (2)	3496 (5)	955 (2)	2.1 (1)′
C(2)	−1424 (2)	5119 (6)	172 (2)	2.5 (1)′
C(3)	1318 (2)	34 (7)	1867 (2)	3.1 (1)′
H(2)	−1297 (38)	6730 (78)	291 (32)	3.5 (9)
H(2′)	−2104 (33)	4852 (89)	19 (29)	4.1 (9)
H(2″)	−1198 (36)	4534 (109)	−358 (35)	4.9 (10)
H(3)	1093 (37)	−42 (103)	1255 (36)	5.6 (10)
H(3′)	1496 (47)	−1190 (100)	2149 (41)	4.8 (12)
H(3″)	1869 (40)	766 (103)	2023 (34)	4.3 (10)

Table III. Interatomic Distances (Å) and Bond Angles (deg) for Me₂Sn(OAc)₂

Interatomic Distances			
Sn(1)–O(1)	2.106 (2)	C(2)–H(2)	0.872 (41)
Sn(1)–O(2)	2.539 (2)	C(2)–H(2′)	0.893 (42)
Sn(1)–C(3)	2.098 (3)	C(2)–H(2′)	0.880 (50)
O(1)–C(1)	1.293 (3)	C(3)–H(3)	0.912 (52)
O(2)–C(1)	1.237 (3)	C(3)–H(3′)	0.783 (57)
C(1)–C(2)	1.496 (4)	C(3)–H(3′)	0.820 (55)

Intramolecular Angles			
O(1)–Sn(1)–O(1)[a]	79.5 (1)	O(2)–Sn(1)–C(3)	88.7 (1)
O(1)–Sn(1)–O(2)[a]	134.57 (7)	C(3)–Sn(1)–C(3)[a]	135.9 (2)
O(1)–Sn(1)–O(2)	55.14 (7)	Sn(1)–O(1)–C(1)	102.1 (2)
O(2)–Sn(1)–O(2)[a]	170.3 (1)	Sn(1)–O(2)–C(1)	83.3 (2)
O(1)–Sn(1)–C(3)	105.7 (1)	O(1)–C(1)–O(2)	119.4 (3)
O(1)–Sn(1)–C(3)[a]	107.8 (1)	O(1)–C(1)–C(2)	117.8 (2)
O(2)–Sn(1)–C(3)[a]	87.6 (1)	O(2)–C(1)–C(2)	122.8 (3)

[a] Symmetry operation codes: $-x, y, {}^1/_2 - z$.

rate)₂[11] indicated similar structures and strongly suggest that it is, by inference, the common diorganotin dicarboxylate structure.

As mentioned above, the original proposal[2b] for a polymeric structure of Me₂Sn(OAc)₂ is based on the presence of a band at 1560 cm⁻¹ in the IR spectrum of its crystalline films. We previously suggested that the sensitivity of Me₂Sn(OAc)₂ to hydrolysis, and the fact that the hydrolyzate, dimeric [Me₂Sn(OAc)]₂O, has a band at the same frequency, implicates the agency of atmospheric moisture. Although we have not succeeded in eliminating entirely the band at 1560 cm⁻¹ in Nujol mulls and crystalline films of Me₂Sn(OAc)₂ prepared in inert atmosphere, the intensity is widely variable in a way consistent with adventitious hydrolysis.

Preparation and Molecular Structure of Me₂Sn-(OAc)₃⁻NMe₄⁺·2CHCl₃. Interest in the mechanisms of
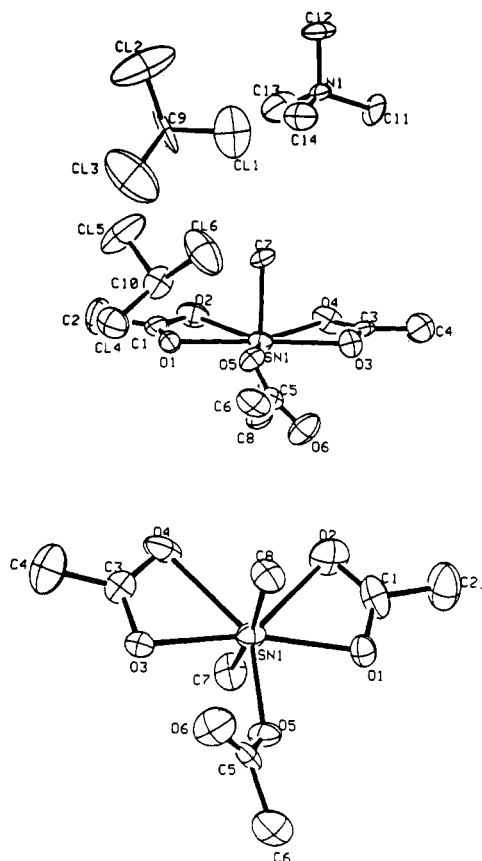
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(14) See discussion in ref 11, footnote 23.

(15) Burke, J. J.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1961**, *83*, 326.

Figure 2. ORTEP plots of $Me_2Sn(OAc)_3^-NMe_4^+$ showing atom numbering scheme. The top view shows the entire structural unit, including $CHCl_3$ molecules of crystallization. The bottom view shows the bonding of the 7-coordinate tin anion.

group 14 nucleophilic substitution reactions has inspired efforts to isolate and characterize higher coordinate anionic complexes of these elements. Direct evidence for the existence of stable, 5-coordinate organosilicon and organotin anions bearing simple organic and electronegative substituents has been accumulated recently.[16-20] Most striking have been recent studies from Reich's laboratory[21], which have shown that simple pentaorganostannylate anions can exist in solution at low temperatures.

We have found that the addition of $NMe_4^+OAc^-$ to $Me_2Sn(OAc)_2$ in nonpolar solvent gives a quantitative yield of crystalline $Me_2Sn(OAc)_3^-NMe_4^+$, mp 176-179 °C. Integration of solution ^1H NMR spectra and elemental analysis of the isolated crystalline solid established the 1:1 composition of the product. Substantial changes in ^2J-($^{119}Sn,^1H$), $^1J(^{119}Sn,^{13}C)$, and the ^{119}Sn chemical shift (Table I) in solution relative to $Me_2Sn(OAc)_2$ indicated that the reaction product persists in solution and strongly suggested an increase in the coordination number of tin.

Crystals of $Me_2Sn(OAc)_3^-NMe_4^+$ grown from $CHCl_3$ solution were suitable for X-ray diffraction study (positional parameters for $Me_2Sn(OAc)_3^-NMe_4^+\cdot2CHCl_3$ are given in Table IV and bond lengths and bond angles in Table V). As shown in the ORTEP plots, Figure 2, $Me_2Sn(OAc)_3^-NMe_4^+$ crystallizes as a monomeric, ionic

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(19) Hobbs, C. A.; Smith, P. J. *J. Organomet. Chem.* **1981**, *206*, 59 and references cited therein.

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Table IV. Fractional Coordinates ($\times10^4$) and Isotropic Parameters for $Me_2Sn(OAc)_3^-NMe_4^+\cdot2CHCl_3$

atom	x	y	z	B(iso), $Å^2$
Sn(1)	936.4 (6)	1545.0 (5)	1353.0 (5)	2.4 (1)'
Cl(1)	2376 (4)	3298 (3)	3556 (3)	8.8 (2)'
Cl(2)	3180 (4)	2873 (5)	4820 (3)	12.7 (3)'
Cl(3)	2280 (5)	1796 (3)	4047 (4)	13.1 (3)'
Cl(4)	3035 (3)	−819 (2)	1613 (2)	5.0 (1)'
Cl(5)	3201 (4)	396 (3)	2650 (3)	9.0 (2)'
Cl(6)	3735 (3)	608 (3)	1180 (4)	8.4 (2)'
O(1)	1168 (5)	526 (5)	2115 (5)	2.7 (3)'
O(2)	578 (6)	1464 (6)	2695 (5)	4.1 (3)'
O(3)	884 (6)	2410 (5)	425 (5)	3.1 (3)'
O(4)	308 (6)	2854 (5)	1418 (6)	3.7 (3)'
O(5)	1625 (5)	818 (6)	676 (5)	2.8 (3)'
O(6)	897 (8)	790 (6)	−325 (5)	4.8 (4)'
N(1)	4567 (6)	3432 (8)	1608 (5)	2.9 (3)'
C(1)	865 (11)	799 (9)	2695 (8)	3.6 (5)'
C(2)	927 (13)	340 (9)	3385 (8)	5.7 (5)'
C(3)	511 (9)	2954 (8)	779 (8)	2.5 (4)'
C(4)	299 (11)	3642 (9)	348 (10)	5.7 (6)'
C(5)	1448 (9)	580 (8)	42 (8)	2.5 (4)'
C(6)	2048 (11)	−3 (9)	−261 (8)	4.5 (5)'
C(7)	1965 (9)	2119 (9)	1767 (7)	3.3 (4)'
C(8)	−234 (8)	1157 (9)	1123 (7)	3.5 (4)'
C(9)	2339 (10)	2709 (8)	4309 (9)	4.8 (6)'
C(10)	3014 (10)	181 (10)	1742 (8)	4.4 (5)'
C(11)	4153 (10)	3947 (8)	1103 (8)	4.3 (5)'
C(12)	5252 (9)	3841 (10)	1979 (8)	4.5 (5)'
C(13)	4019 (11)	3153 (10)	2209 (8)	6.3 (6)'
C(14)	4884 (9)	2736 (8)	1238 (10)	4.8 (5)'

Table V. Interatomic Distances (Å) and Bond Angles (deg) for $Me_2Sn(OAc)_3^-NMe_4^+\cdot2CHCl_3$

Interatomic Distances			
Sn(1)–O(1)	2.291 (9)	O(1)–C(1)	1.267 (17)
Sn(1)–O(2)	2.525 (9)	O(2)–C(1)	1.257 (17)
Sn(1)–O(3)	2.271 (8)	O(3)–C(3)	1.308 (15)
Sn(1)–O(4)	2.520 (9)	O(4)–C(3)	1.228 (16)
Sn(1)–O(5)	2.113 (9)	O(5)–C(5)	1.263 (15)
Sn(1)–C(7)	2.129 (14)	O(6)–C(5)	1.197 (16)
Sn(1)–C(8)	2.113 (13)	N(1)–C(11)	1.463 (15)
Cl(1)–C(9)	1.717 (16)	N(1)–C(12)	1.511 (16)
Cl(2)–C(9)	1.712 (20)	N(1)–C(13)	1.509 (17)
Cl(3)–C(9)	1.669 (15)	N(1)–C(14)	1.489 (18)
Cl(4)–C(10)	1.764 (17)	C(1)–C(2)	1.496 (18)
Cl(5)–C(10)	1.726 (16)	C(3)–C(4)	1.479 (20)
Cl(6)–C(10)	1.749 (16)	C(5)–C(6)	1.533 (20)
Intramolecular Angles			
O(1)–Sn(1)–O(2)	53.7 (3)	Sn(1)–O(4)–C(3)	88.2 (9)
O(1)–Sn(1)–O(3)	167.3 (3)	Sn(1)–O(5)–C(5)	127 (1)
O(1)–Sn(1)–O(4)	138.3 (3)	C(11)–N(1)–C(12)	110 (1)
O(1)–Sn(1)–O(5)	78.2 (3)	C(11)–N(1)–C(13)	112 (1)
O(2)–Sn(1)–O(3)	138.7 (3)	C(11)–N(1)–C(14)	113 (1)
O(2)–Sn(1)–O(4)	84.6 (3)	C(12)–N(1)–C(13)	107 (1)
O(2)–Sn(1)–O(5)	131.5 (4)	C(12)–N(1)–C(14)	109 (1)
O(3)–Sn(1)–O(4)	54.2 (3)	C(13)–N(1)–C(14)	106 (1)
O(3)–Sn(1)–O(5)	89.1 (3)	Cl(1)–C(9)–Cl(2)	108 (1)
O(4)–Sn(1)–O(5)	143.2 (3)	Cl(1)–C(9)–Cl(3)	110 (1)
O(1)–Sn(1)–C(7)	90.8 (4)	Cl(2)–C(9)–Cl(3)	111 (1)
O(1)–Sn(1)–C(8)	91.6 (4)	Cl(4)–C(10)–Cl(5)	110 (1)
O(2)–Sn(1)–C(7)	82.8 (4)	Cl(4)–C(10)–Cl(6)	109.3 (9)
O(2)–Sn(1)–C(8)	87.4 (4)	Cl(5)–C(10)–Cl(6)	110 (1)
O(3)–Sn(1)–C(7)	89.0 (5)	O(1)–C(1)–O(2)	120 (1)
O(3)–Sn(1)–C(8)	91.7 (4)	O(3)–C(3)–O(4)	120 (1)
O(4)–Sn(1)–C(7)	83.8 (5)	O(5)–C(5)–O(6)	126 (1)
O(4)–Sn(1)–C(8)	85.1 (5)	O(1)–C(1)–C(2)	118 (2)
O(5)–Sn(1)–C(7)	92.9 (5)	O(2)–C(1)–C(2)	121 (2)
O(5)–Sn(1)–C(8)	101.3 (5)	O(3)–C(3)–C(4)	116 (1)
C(7)–Sn(1)–C(8)	165.8 (6)	O(4)–C(3)–C(4)	124 (2)
Sn(1)–O(1)–C(1)	98.5 (9)	O(5)–C(5)–C(6)	113 (1)
Sn(1)–O(2)–C(1)	87.7 (9)	O(6)–C(5)–C(6)	120 (1)
Sn(1)–O(3)–C(3)	97.7 (8)		

solid bearing two molecules of $CHCl_3$ crystallization solvent. The tin coordination number can be assigned unambiguously as 7, and the overall structure is pentagonal-bipyramidal: the two methyl groups occupy the apical

O(1)···C(10)	3.217 (18)
O(1)···C(11)(i)	3.363 (16)
O(2)···C(14)(ii)	3.173 (18)
O(3)···C(9)(iii)	3.178 (17)
O(4)···C(12)(ii)	3.397 (18)
O(4)···C(13)(ii)	3.345 (19)
O(5)···C(10)	3.227 (18)
O(6)···C(11)(iv)	3.274 (21)
O(6)···C(12)(iv)	3.268 (18)

[a] Symmetry operation codes: i, $1/2 - x, -1/2 + y, z$; ii, $-1/2 + x, y, 1/2 - z$; iii, $x, 1/2 - y, -1/2 + z$; iv, $-1/2 + x, 1/2 - y, -z$.
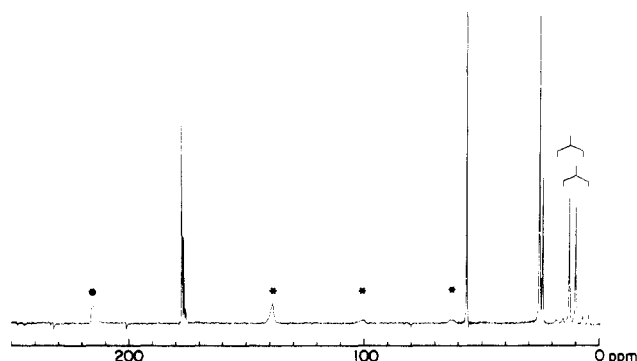
Figure 3. High-resolution solid-state ¹³C NMR spectrum of Me₂Sn(OAc)₃⁻NMe₄⁺ at 75 MHz. Assignments: doublet at 177.0, 176.1 ppm, Me¹³CO; singlet at 56.2 ppm, Me₄N⁺; doublet at 25.3, 23.8 ppm, ¹³CH₃CO; doublet at 12.6, 9.9 ppm, Me₂Sn. The fused ¹¹⁷Sn, ¹¹⁹Sn satellites coupled to the tin methyls are indicated. Spinning sidebands are labeled with an asterisk.

positions ($\angle$Me–Sn–Me = 165.8°), and five acetate oxygens lie in the pentagonal plane (the maximum deviation of an atom out of the SnO₅ plane is 0.06 Å). Two acetate groups are anisobidentate [average Sn–O distances of 2.285 (short bond) and 2.523 Å (long bond)], and a third acetate is unidentate (bonding Sn–O distance = 2.113 (9) Å, nonbonded Sn–O distance = 3.34 Å). The longer Sn–O distance of the bidentate acetates is essentially unchanged from that in Me₂Sn(OAc)₂, but the shorter distance is 0.1 Å greater in Me₂Sn(OAc)₃⁻. This might reflect either steric crowding around tin in the anionic complex or electronic repulsion associated with bringing a fifth negatively charged group into bonding with tin. The CHCl₃ of recrystallization appears to be weakly hydrogen bonded to acetate oxygens O(1), O(3), and O(5) (Table VI) and was chemically labile, being lost readily under vacuum or on standing. Although several other 7-coordinate organotin compounds are known,[22] we believe this to be the first report of a 7-coordinate anionic organotin complex.

The solid-state ¹³C NMR spectrum of a fully dried sample of Me₂Sn(OAc)₃⁻NMe₄⁺ is shown in Figure 3. While the relationship of the molecular structure of Me₂Sn(OAc)₃⁻NMe₄⁺ in the absence of CHCl₃ to that found by X-ray is uncertain, the multiplicity of the ¹³C resonances of the solvent-free solid is just that expected from the crystal structure: a 2:1 ratio is observed for the acetate methyl and carboxylate carbons, consistent with a 2:1 ratio of bidentate to monodentate acetates, and a 1:1 doublet for the methyls bonded to tin, as expected for two symmetry-unrelated methyls. Tin–carbon coupling constants, $^1J(^{119}\text{Sn},^{13}\text{C})$, of about 866 and 820 Hz were measured for the two methyls bonded to tin; from the averaged

value of 840 ± 20 Hz, an Me–Sn–Me angle of about 151° is estimated. The difference between the estimated solid-state angle and that observed by X-ray can be attributed either to a change in molecular structure occurring upon the loss of CHCl₃ or to inaccuracy of the coupling constant–bond angle correlation, which was developed by using data for neutral 4-, 5-, and 6-coordinate methyltin compounds.[10] With good confidence, however, the sizeable difference between the solid-state and solution values of $^1J(^{119}\text{Sn},^{13}\text{C})$ (70–100 Hz) can be attributed to a real difference in the structure of Me₂Sn(OAc)₃⁻NMe₄⁺.

A comparison of the X-ray and solid-state and solution NMR results provides some insight into the behavior of Me₂Sn(OAc)₃⁻NMe₄⁺ in solution. Both the ¹H and ¹³C NMR spectra at 26 °C show complete equilibration of the acetate groups, indicating rapid interconversion of the bidentate and monodentate acetates on the NMR time scale. There is also a considerable effect of solvent on the coupling constants and ¹¹⁹Sn chemical shift of Me₂Sn(OAc)₃⁻NMe₄⁺ (Table I), which could arise either from the influence of solvent on the position of the equilibrium shown or on molecular structure.

$$\text{Me}_2\text{Sn(OAc)}_2 + \text{NMe}_4^+\text{OAc}^- \rightleftharpoons \text{Me}_2\text{Sn(OAc)}_3^-\text{NMe}_4^+$$

The modest concentration effect on NMR data for Me₂Sn(OAc)₃⁻NMe₄⁺ in acetone solution (Table I) provides some evidence of partial dissociation. The occurrence of relatively broad lines (15–20 Hz at half-height) in the ¹¹⁹Sn NMR spectra is also consistent with partial dissociation of Me₂Sn(OAc)₃⁻NMe₄⁺ (line broadening, however, could also reflect conformational changes at tin arising from acetate group scrambling).[23] The low solubility of NMe₄⁺OAc⁻ in nonprotic solvents prevented our probing the effect of excess NMe₄⁺OAc⁻ on the ¹¹⁹Sn chemical shift and line width. However, solutions containing varying ratios of Me₂Sn(OAc)₂ and Me₂Sn(OAc)₃⁻NMe₄⁺ (total tin concentration 0.25 M) gave rise to ¹¹⁹Sn resonances at averaged chemical shifts and averaged values of $^1J(^{119}\text{Sn},^{13}\text{C})$ and $^2J(^{119}\text{Sn},^1\text{H})$, indicating that intermolecular acetate group exchange is rapid on the NMR time scale. This result establishes that partial dissociation of Me₂Sn(OAc)₃⁻NMe₄⁺ in solution would result in a single, averaged ¹¹⁹Sn chemical shift.

That the predominant methyltin species in solution is Me₂Sn(OAc)₃⁻NMe₄⁺ seems clear from the similarity of the Me–Sn–Me angles estimated from $^1J(^{119}\text{Sn},^{13}\text{C})$ (158–160°) and $^2J(^{119}\text{Sn},^1\text{H})$ (155–171°) to the angle found by X-ray (165.8°). The very large shift of the ¹¹⁹Sn resonance for solutions of Me₂Sn(OAc)₃⁻NMe₄⁺ relative to Me₂Sn(OAc)₂ also argues for nearly complete association in solution. A minimum value of the equilibrium constant for the equation as written above can be estimated from the data for the 0.125 M acetone solution in Table I. Assuming a "safe" lower limit for the ratio Me₂Sn(OAc)₃⁻/Me₂Sn(OAc)₂ = 4, an equilibrium constant >1.6 × 10² M⁻¹ is obtained, which corresponds to $\Delta G < -3.0$ kcal mol⁻¹ at 26 °C.

It appears that even modest changes in the counterion can have a dramatic affect on the stability of the tin anion. Thus, the ¹H NMR spectrum of Me₂Sn(OAc)₃⁻NEt₄⁺, which was isolated as a crystalline solid in low yield from the reaction of Me₂Sn(OAc)₂ with NEt₄⁺OAc⁻, showed only free, unassociated Me₂Sn(OAc)₂ in CDCl₃ solution. A crystal structure of the solid was not pursued. Our attempt to prepare the sodium salt of Me₂Sn(OAc)₃⁻ was unsuccessful.

(22) For a bibliography of organotin X-ray structures see: Smith, P. J. *J. Organomet. Chem. Libr.* **1981**, *12*, 97; Britton, D.; Dunitz, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2971.

(23) Evidence for rapid intramolecular equilibration of the acetate oxygens in di- and triorganotin(IV) acetates has been obtained from ¹⁷O NMR studies: Lycka, A.; Holecek, J. *J. Organomet. Chem.* **1985**, *294*, 179.

Conclusions

The excellent agreement of the NMR prediction and X-ray structure determination for $Me_2Sn(OAc)_2$ reinforces the power of the NMR-structure correlations developed previously[10,11] for the structural analysis of methyltin(IV) compounds in solution and in the solid state. While the correlations lead to plausible estimates of the Me–Sn–Me angle for 7-coordinate $Me_2Sn(OAc)_3^-NMe_4^+$ in the solid state and in solution, their accuracy could not be evaluated directly because of the instability of the X-ray characterized crystalline modification. Nevertheless, the coupling constant data for $Me_2Sn(OAc)_3^-NMe_4$ provide evidence of a significant change in structure in the two phases.

The most striking result of this study is the discovery that 6-coordinate $Me_2Sn(OAc)_2$ is capable of adding a third acetate group, giving rise to a diorganotin(IV) anion with a coordination number of 7. Solution and solid-state NMR data for $Me_2Sn(OAc)_3^-NMe_4^+$ provide evidence that the complex is thermodynamically stable in solution relative to dissociation and indicate that, in addition to the well-characterized pentasubstituted di- and triorganotin(IV) halide anions, organotin(IV) compounds bearing other, less strongly electron-withdrawing ligands can give rise to stable, isolable anionic complexes. A clear implication of the results obtained for the reaction of $Me_2Sn(OAc)_2$ with $NMe_4^+OAc^-$ is that nucleophilic substitution reactions of even 5- and 6-coordinate tin compounds can, and may frequently, proceed by associative mechanisms involving anionic tin intermediates of high coordination number. Such mechanisms may in fact be the rule for the many industrially important reactions catalyzed by diorganotin dicarboxylates.

Experimental Section

$Me_2Sn(OAc)_2$ was prepared by the method of Okawara.[2b] X-ray diffraction quality crystals, elongated blocks, were obtained upon cooling of a dilute hexane solution.

$Me_2Sn(OAc)_2^-NMe_4^+$ was isolated in 94% yield from a $CHCl_3$ solution (5 mL) of 0.80 g of $Me_2Sn(OAc)_2$ and 0.40 g of $Me_4N^+OAc^-$ (both 0.003 mol); mp 176–179 °C (sample after drying). Crystals suitable for X-ray diffraction were obtained by slow cooling of a dilute $CHCl_3$ solution. The crystals were unstable to loss of $CHCl_3$ of crystallization on standing at room temperature, turning opaque and becoming powdery on the surface. The X-ray structural analysis was carried out in the presence of excess $CHCl_3$. $Me_2Sn(OAc)_3^-NMe_4^+$ appeared to be somewhat less moisture sensitive than $Me_2Sn(OAc)_2$, although exposure of a $CDCl_3$ solution to air in an open NMR tube for 16 h resulted in ca. 50% degradation. IR (Nujol mull): 1635 (sh), 1615 (m), 1488 (m), 1322 (s), 1011 (m), 949 (m), 924 (m), 795 (m), 722 (m), 661 cm^{-1} (s). Anal. (of crystals from $CHCl_3$ solution after drying briefly under vaccum) Calcd for $C_{12}H_{27}O_6SnN$: C, 36.03; H, 6.80. Found: C, 36.05; H, 7.13.

A solution of $Me_2Sn(OAc)_2$ containing 1 equiv of $Et_3NH^+OAc^-$ in $CHCl_3$ to which some hexane had been added gave a low yield (11%) of large blocklike crystals on standing for several days at room temperature. The composition of the isolated crystals was determined by ^1H NMR, which integrated correctly for $Me_2Sn(OAc)_3^-NMe_4^+$.

NMR Spectroscopy. Solution spectra were obtained on a General Electric NT-300 spectrometer at 300.75 MHz for ^1H, 75 MHz for ^{13}C, and 112.1 MHz for ^{119}Sn. The external reference (0 ppm) used was Me_4Si for ^1H and ^{13}C spectra. ^{119}Sn spectra were referenced to Me_4Sn (0 ppm) and obtained by using a DEPT

pulse sequence[24] where the final proton pulse (θ pulse) was set between 35° and 40°. MLEV16 decoupling was used during the acquisition.

The solid-state ^{13}C NMR (MAS) spectrum of $Me_2Sn(OAc)_3^-NMe_4^+$ was obtained on a Bruker CXP-300 spectrometer at 75.5 MHz. Dry nitrogen gas was used to drive MAS rates of 2–3 kHz. Hartmann–Hann matching condition for cross-polarization (CP) was calibrated by using adamantane, and both CP (5 ms) and decoupling (40 ms) were performed at the same proton-decoupling amplitude (71 kHz). A 4-s recycle delay was used, and the spectrum was obtained after 1800 scans. Chemical shifts are reported relative to Me_4Si with an external sample of adamantane as reference.

Crystal Structure Determinations and Refinements. Both crystal structures were determined with ω-scan data obtained on a Syntex R3 diffractometer equipped with a low-temperature apparatus operaing at –100 °C, graphite monochromator, and Mo $K\alpha$ radiation source ($\lambda = 0.71073$ Å). The structures were solved via the heavy-atom method by using a local program system (J.C.C.). Refinement was by full-matrix least squares on F, minimizing $\sum w(|F_o| - |F_c|)^2$ with weights $\propto [\sigma^2 (I) + 0.0009 I^2]^{-1/2}$, and included anomalous terms for Sn and C(1). The atomic scattering factors were taken from the tabulations of Cromer and Waber[25a]; anomalous dispersion corrections were by Cromer.[25b]

Crystal data for $Me_2Sn(OAc)_2$: colorless, block, ca. 0.34 × 0.22 × 0.46 mm, monoclinic b, $C2/c$ (No. 15); $a = 12.712$ (2), $b = 5.220$ (1), $c = 14.365$ (3) Å; $\beta = 92.80$ (1)°; $V = 952.1$ Å^3; $Z = 4$; fw = 266.85; $D_{calcd} = 1.861$ g/cm^3; μ(Mo) = 26.63 cm^{-1}; 1290 data collected; $5.7° \leq 2\theta \leq 55.0°$; maximum h,k,l = 16,6,18; data octants = + + –, – + –; scan width = 2.20° ω; scan speed = 2.90–9.80°/min; typical half-height peak width = 0.44 ω; 3 standards collected 8 times, adjusted for a 3% decrease in intensity, no absorption correction; 1041 unique reflections with $I \geq 3.0\sigma(I)$; 75 parameters; refined anisotropic, all non-hydrogen atoms; isotropic, H; final $R = 0.022$, $R_w = 0.029$, error of fit = 1.68, max Δ/σ = 0.66, largest residual density = 0.55 e/Å^3, near the tin.

Crystal data for $Me_2Sn(OAc)_3^-NMe_4^+\cdot 2CHCl_3$: colorless, rectangular block, ca. 0.34 × 0.30 × 0.45 mm, from $CHCl_3$; orthorhombic, $Pbca$ (No. 61); $a = 16.717$ (2), $b = 17.475$ (2), $c = 18.242$ (3) Å; $V = 5329.0$ Å^3, $Z = 8$; fw = 638.79; $D_{calcd} = 1.592$ g/cm^3; μ(Mo) = 15.95 cm^{-1}; 6117 total data collected; $4.0 \leq 2\theta \leq 53.0$; maximum h,k,l = 20,21,22; data octants = + + +; scan width 1.00° ω; scan speed = 2.00–9.00°/min, typical half-height peak width = 0.23° ω, 3 standards collected 32 times, adjusted for a 7% decrease in intensity, no absorption correction; 1723 unique reflections with $I \geq 3.0\sigma(I)$; 253 parameters; refined anisotropic, all non-hydrogen atoms; fixed atoms, H; final $R = 0.059$, $R_w = 0.047$; error of fit = 1.27, max $\Delta/\sigma = 0.13$, largest residual density = 1.00 e/Å^3, 1.86 Å from C9 in a position suggesting an alternate orientation for this chloroform molecule.

Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, interatomic distances, intramolecular angles, and intermolecular angles (4 pages); listings of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

(24) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323.
(25) (a) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2b. (b) *Ibid.*, Table 2.3.1.