

# Solution and Solid-State Molecular Structures of $\text{Me}_2\text{Sn}(\text{OAc})_2$ (I) and Its Hydrolyzate, $([\text{Me}_2\text{Sn}(\text{OAc})]_2\text{O})_2$ (II), by Solution and Solid-State $^{13}\text{C}$ NMR. X-ray Diffraction Study of II

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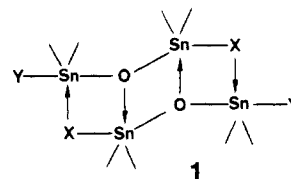
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**Abstract:** On the basis of solution and solid-state  $^{13}\text{C}$  NMR and other published data,  $\text{Me}_2\text{Sn}(\text{OAc})_2$  is believed to be monomeric and to adopt a highly distorted *trans*-dimethyl octahedral conformation in both phases. The Me–Sn–Me angle is estimated from  $^{13}\text{C}$  and  $^1\text{H}$  NMR data [solid-state and solution  $|^1J(^{119}\text{Sn}, ^{13}\text{C})| = 665 \text{ Hz}$ ; solution  $|^2J(^{119}\text{Sn}, ^1\text{H})| = 82.5 \text{ Hz}$ ] to be ca.  $135^\circ$ . Evidence from solid-state  $^{13}\text{C}$  NMR for the existence of a second crystalline modification of a second crystalline modification of  $\text{Me}_2\text{Sn}(\text{OAc})_2$  is presented. Analyses of solid-state or solution  $^{13}\text{C}$  NMR data for  $\text{Bu}_2\text{Sn}(\text{OAc})_2$ ,  $\text{Me}_2\text{Sn}(\text{benzoate})_2$ , and  $\text{Me}_2\text{Sn}(\text{laurate})_2$  indicate closely related structures.  $([\text{Me}_2\text{Sn}(\text{OAc})]_2\text{O})_2$ ,  $\text{Sn}_4\text{O}_{10}\text{C}_{16}\text{H}_{36}$ , crystallizes in space group *Pa* with  $a = 16.386(5) \text{ \AA}$ ,  $b = 7.780(2) \text{ \AA}$ ,  $c = 11.183(5) \text{ \AA}$ ,  $\alpha = \gamma = 90.0^\circ$ ,  $\beta = 103.61(3)^\circ$ , and  $Z = 2$  (data measured at  $27^\circ\text{C}$ );  $R$  refined to 4.7% ( $R_w = 5.4\%$ ). The distannoxane forms tightly bonded dimeric units with a central  $\text{Sn}_2\text{O}_2$  ring; an overall polymeric structure arises from an additional bonding interaction ( $D_{\text{Sn-O}} = 2.56(1) \text{ \AA}$ ) between an exocyclic tin and a carboxylate oxygen of adjacent dimers. Unlike other characterized dicarboxylato tetraorganodistannoxanes, no center of symmetry was found for  $([\text{Me}_2\text{Sn}(\text{OAc})]_2\text{O})_2$ . Solution  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra indicate the presence of two types of tin (endocyclic and exocyclic to the  $\text{Sn}_2\text{O}_2$  ring) in the dimer in solution, both of which are hexacoordinated and adopt distorted *trans*-dimethyl octahedral conformations (Me–Sn–Me angles of ca.  $145^\circ$  and  $141^\circ$ , respectively).

In spite of the wide application of diorganotin dicarboxylates as catalysts and stabilizers,<sup>2</sup> little is known about their molecular structures. Previous IR,<sup>3</sup> NMR,<sup>3–5</sup> and Mössbauer<sup>6</sup> spectroscopic investigations have led to conflicting structural proposals. Unresolved issues include the molecularity of diorganotin dicarboxylates, the relative importance of carboxylate bridging between tin atoms of adjacent molecules in solution and the solid state, and the tin coordination number (CN). The hydrolytic instability of the parent diorganotin dicarboxylate, dimethyltin diacetate  $[\text{Me}_2\text{Sn}(\text{OAc})_2]$ ,<sup>3a</sup> and other simple diorganotin dicarboxylates has hindered structural investigations.

X-ray structures have been determined<sup>7–10</sup> for several dicarboxylato tetraorganodistannoxanes,  $[\text{R}_2(\text{OAc})\text{Sn}]_2\text{O}$ , the first isolable products of the hydrolysis of diorganotin dicarboxylates. In common with other difunctional tetraorganodistannoxanes,<sup>11</sup>  $\text{R}_2(\text{X})\text{SnOSn}(\text{Y})\text{R}_2$  (1: X, Y = halide, hydroxide,  $\text{Me}_3\text{SiO}$ , NCS), they associate as dimers in the solid state, forming four-membered  $\text{Sn}_2\text{O}_2$  rings through interaction of the tin of one distannoxane with the oxide linkage of a second. Bridging of the

electronegative substituents (X,Y), as shown for 1, leads to an increase in the CN of the exocyclic diorganotin(IV) moieties to 5 (or more), and the resulting structures have been referred to as "ladders" or "staircases" depending on their planarity. For



some dicarboxylato tetraorganodistannoxanes, additional bonding interactions between adjacent dimers in the crystalline state have been found<sup>7,8</sup> and produce an overall linear polymeric structure. While the dimeric nature of dicarboxylato tetraorganodistannoxanes is preserved in solution, there are substantial, but poorly characterized,<sup>3b</sup> structural changes relative to the solid state.

The unusual structural features identified for some dicarboxylato tetraorganodistannoxanes and the lack of a clear structural picture for diorganotin dicarboxylates have led us to examine the structures of the parent diorganotin dicarboxylate,  $\text{Me}_2\text{Sn}(\text{OAc})_2$ , and its hydrolysis product,  $([\text{Me}_2\text{Sn}(\text{OAc})]_2\text{O})_2$ . In this study we report new  $^{13}\text{C}$  NMR data that provide considerable insight into their molecular structures in solution and the solid state. The X-ray structure of  $([\text{Me}_2\text{Sn}(\text{OAc})]_2\text{O})_2$  is also described.

## Results and Discussion

Our structural analyses of  $\text{Me}_2\text{Sn}(\text{OAc})_2$  and  $([\text{Me}_2\text{Sn}(\text{OAc})]_2\text{O})_2$  make use of two new NMR/structure relationships: (1) Solid-state  $^{13}\text{C}$  NMR studies of structurally characterized, crystalline methyltin(IV) compounds have revealed<sup>12</sup> that the magnitude of tin–carbon  $J$  coupling,  $|^1J(^{119}\text{Sn}, ^{13}\text{C})|$  ( $|^1J|$ ), is linearly related to the Me–Sn–Me angle (eq 1; where  $\theta$  is the Me–Sn–Me angle, in deg, and  $|^1J|$  is in Hz) for a variety of methyltin(IV) compounds.

$$|^1J| = 11.4(\theta) - 875 \quad (1)$$

(2) A second study has shown<sup>13</sup> that the magnitude of tin–hy-

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**Table I.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Data for  $\text{Me}_2\text{Sn}(\text{OAc})_2$ ,  $\text{Me}_2\text{Sn}(\text{laurate})_2$ , and  $[\text{Me}_2\text{Sn}(\text{OAc})]_2\text{O}$ 

compound	medium	$\text{Me}_2\text{Sn}$ chemical shift, <sup>a</sup> ppm		$ ^1J $ , <sup>b</sup> Hz	$ ^2J $ , <sup>c</sup> Hz	estimated <sup>d</sup> $\angle\text{Me-Sn-Me}$ (deg) from	
		$^{13}\text{C}$	$^1\text{H}$ <sup>b</sup>			$ ^1J $	$ ^2J $
$\text{Me}_2\text{Sn}(\text{OAc})_2$	solution	3.7 ( $\text{C}_6\text{D}_6$ )	0.91 ( $\text{CCl}_4$ )	665	82.5	135	134
	solid state	3.8		665		135	
$\text{Me}_2\text{Sn}(\text{laurate})_2$	solid state	5.2		720		140	
	solution	5.9	0.80	748	86.8	142	140
$[\text{Me}_2\text{Sn}(\text{OAc})]_2\text{O}$	( $\text{CDCl}_3$ )	8.7	0.82	800	89.0	147	143
	solid state	7.7–15.9		<sup>e</sup>			

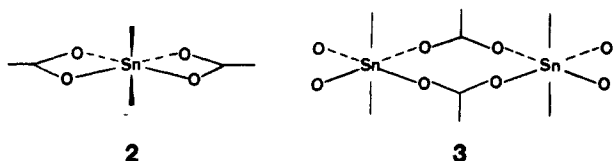
<sup>a</sup> Relative to  $\text{Me}_4\text{Si}$  (0 ppm) in solution, Delrin (89.1 ppm) in solid state. <sup>b</sup> Uncertainty in solid-state  $|^1J|$  values is ca. 10 Hz, 3 Hz in solution. <sup>c</sup> Data from ref 3. <sup>d</sup> Calculated by using eq 1 or 2. Believed accurate to within 5° [see ref 12 and 13]. <sup>e</sup> Not resolved.

drogen  $J$  coupling,  $|^2J(^{119}\text{Sn}, ^1\text{H})|$  ( $|^2J|$ ), is also related to the Me–Sn–Me angle according to the quadratic expression in eq 2.

$$\theta = (0.0161)(|^2J|)^2 - (1.32)(|^2J|) + 133.4 \quad (2)$$

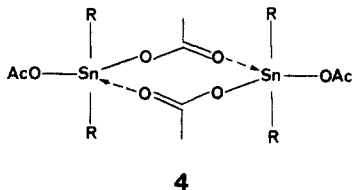
These relationships provide a simple method for estimating, with reasonable accuracy (within about 5°), Me–Sn–Me angles of crystalline<sup>14</sup> or amorphous<sup>15</sup> methyltin(IV) solids. They also allow estimates to be made of the solution structures of methyltin(IV) compounds from  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements and provide an important tool for comparing molecular structures in the solid state and solution.

**Solid-State and Solution Structure of  $\text{Me}_2\text{Sn}(\text{OAc})_2$ .** From cryoscopic molecular weight measurements, Okawara and co-workers<sup>3b</sup> determined that  $\text{Me}_2\text{Sn}(\text{OAc})_2$  is monomeric in benzene solution. In the solution IR spectrum both symmetric and antisymmetric  $\text{SnC}_2$  stretching bands were identified and  $\text{Me}_2\text{Sn}(\text{OAc})_2$  was suggested to have a nonlinear Me–Sn–Me moiety. The  $\text{CO}_2$  antisymmetric stretching frequency at  $1600\text{ cm}^{-1}$  was taken to indicate bidentate acetate ligands and distorted octahedral coordination at tin (2). The appearance of an additional  $\text{CO}_2$  antisymmetric stretching band ( $1560\text{ cm}^{-1}$ ) in the crystalline film was interpreted<sup>3</sup> as reflecting a change to a polymeric structure (3) in which the tin atoms are linked via bridging acetate groups.

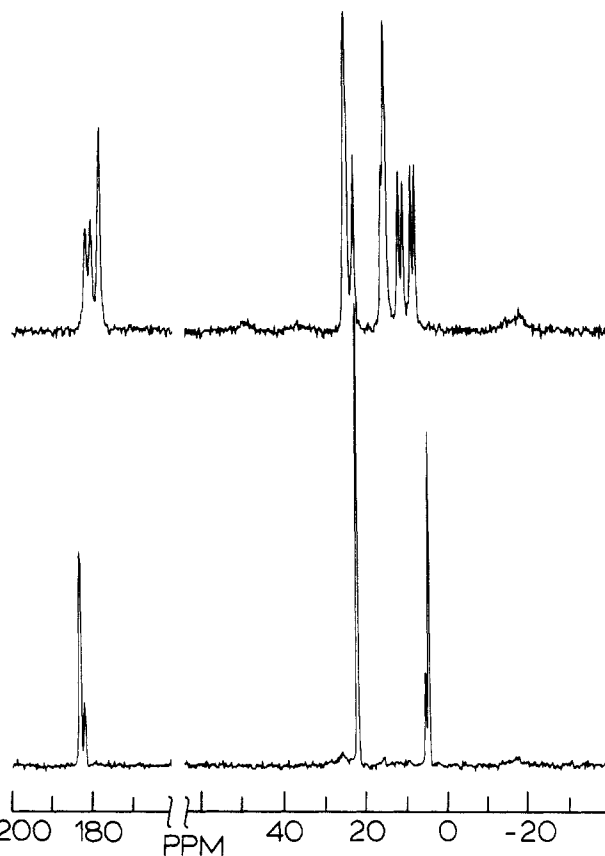


Given the extreme moisture sensitivity of  $\text{Me}_2\text{Sn}(\text{OAc})_2$ , however, it is conceivable that the new  $\text{CO}_2$  band in the crystalline film is due to formation of the hydrolysis product,  $[\text{Me}_2\text{Sn}(\text{OAc})]_2\text{O}$  [ $\nu(\text{CO}) = 1560\text{ cm}^{-1}$ ], a possibility the authors do not address.

A different structural interpretation was given to the solution  $^{13}\text{C}$  NMR data for  $n\text{-Bu}_2\text{Sn}(\text{OAc})_2$  (4).<sup>4</sup> The small  $|^1J|$  value of neat  $n\text{-Bu}_2\text{Sn}(\text{OAc})_2$  (630 Hz) compared to that of  $n\text{-Bu}_2\text{Sn}(\text{acetylacetonate})_2$  (914 Hz), which adopts a *trans*-dibutyl octahedral configuration, was taken to indicate a tin CN of 5 rather than 6. This interpretation conflicts with the observation of



Okawara<sup>3a</sup> that  $|^2J|$  of  $\text{Me}_2\text{Sn}(\text{OAc})_2$  is essentially the same in 20%  $\text{CCl}_4$  solution (82.5 Hz), where it is monomeric, and in the neat liquid at  $85^\circ\text{C}$  (81.7 Hz). The recent observations<sup>12,13</sup> that  $|^1J|$  and  $|^2J|$  depend strongly on the Me–Sn–Me angle provide an



**Figure 1.** Solid-state  $^{13}\text{C}$  NMR spectra of polycrystalline  $\text{Me}_2\text{Sn}(\text{OAc})_2$  (bottom) and  $[\text{Me}_2\text{Sn}(\text{OAc})]_2\text{O}$  (top) at 15.08 MHz.

alternate explanation for the relatively small  $|^1J|$  value observed for  $n\text{-Bu}_2\text{Sn}(\text{OAc})_2$ : the difference  $|^1J|$  between  $n\text{-Bu}_2\text{Sn}(\text{OAc})_2$  and  $n\text{-Bu}_2\text{Sn}(\text{acetylacetonate})_2$  may simply reflect a smaller C–Sn–C angle in the diacetate.

We have obtained solid-state and solution  $^{13}\text{C}$  NMR data for  $\text{Me}_2\text{Sn}(\text{OAc})_2$  and solid-state NMR data for  $\text{Me}_2\text{Sn}(\text{laurate})_2$  (Table I, Figure 1). By eq 1,  $|^1J|$  for  $\text{Me}_2\text{Sn}(\text{OAc})_2$  in solution (665 Hz) corresponds to an Me–Sn–Me angle of  $135^\circ$ . Essentially the same angle ( $134^\circ$ ) is obtained with eq 2 and the  $|^2J|$  reported by Okawara.<sup>3</sup> Taken with the determination by cryoscopic measurements<sup>3b</sup> that  $\text{Me}_2\text{Sn}(\text{OAc})_2$  is monomeric in solution and the IR data which indicate bidentate acetate ligands, the NMR data strongly support monomeric structure 2 in both media. Me–Sn–Me angles of hexacoordinated dimethyltin(IV) compounds have been related to the “bite” angle of the chelating ligand and steric interactions in the coordination sphere of tin.<sup>16,17</sup> These parameters for 2 would differ significantly from those of the eight-membered chelate ring in the alternative structures 3 and

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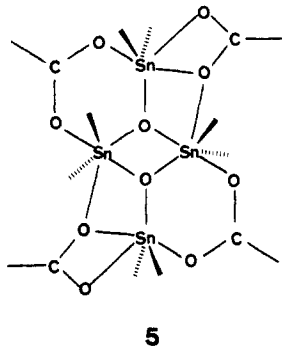
4 and would have given rise to a large difference in the solid-state and solution  $^1\text{J}$  values. The Me–Sn–Me angle and structural features estimated for  $\text{Me}_2\text{Sn}(\text{OAc})_2$  resemble those reported in X-ray studies of dimethyltin bis(*O*-ethylxanthate)<sup>18</sup> and several dimethyltin bis(dithiocarbamate)s<sup>14,19</sup> (these all have chelating  $\text{CS}_2$  ligands and Me–Sn–Me angles between  $130^\circ$  and  $143^\circ$ ). Owing to its extreme hydrolytic sensitivity, we have been unable to successfully mount crystals of  $\text{Me}_2\text{Sn}(\text{OAc})_2$  for X-ray diffraction.

The solid-state  $^{13}\text{C}$  NMR data (Table I) of microcrystalline  $\text{Me}_2\text{Sn}(\text{laurate})_2$  (estimated Me–Sn–Me angle  $140^\circ$ ) strongly suggest a structure similar to that of  $\text{Me}_2\text{Sn}(\text{OAc})_2$ ; solution data<sup>5</sup> indicate similar bonding for  $\text{Me}_2\text{Sn}(\text{benzoate})_2$  ( $^1\text{J} = 664$  Hz). The structure of *n*-Bu<sub>2</sub>Sn(OAc)<sub>2</sub> probably also resembles 2 rather than 4.<sup>4</sup> The slightly smaller  $^1\text{J}$  value of the dibutyltin compound is typical of the difference commonly observed<sup>20</sup> between methyltin(IV) and *n*-butyltin(IV) compounds.

An interesting detail in the solid-state  $^{13}\text{C}$  NMR spectrum of  $\text{Me}_2\text{Sn}(\text{OAc})_2$  (Figure 1) is the presence of small resonances beside those of the tin–methyl and carboxylate carbons. The chemical shifts are inconsistent with the presence of the hydrolysis product or other likely impurities, and the solution  $^{13}\text{C}$  NMR of the sample showed only the three-line spectrum expected for  $\text{Me}_2\text{Sn}(\text{OAc})_2$ . The ratio of the heights of each of the minor resonances to the nearest  $\text{Me}_2\text{Sn}(\text{OAc})_2$  resonance is the same for both ( $3.5 \pm 0.1$ :1), suggesting that they arise from a second crystalline form of  $\text{Me}_2\text{Sn}(\text{OAc})_2$  present in the recrystallized product. Such polymorphism is not uncommon<sup>21</sup> in organotin chemistry, and we have shown<sup>19c</sup> elsewhere that resonances of different crystalline modifications of a methyltin(IV) compound can be resolved by solid-state  $^{13}\text{C}$  NMR.

**Solid-State and Solution Structures of  $[\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O}$ .** Cryoscopic molecular weight measurements<sup>3b</sup> on  $[\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O}$  indicated that it exists predominantly as a dimer in benzene solution at concentrations above 0.03 M. The IR spectrum of  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$  in  $\text{CHCl}_3$  solution showed three  $\text{CO}_2$  antisymmetric stretching bands ( $1630$ ,  $1605$ , and  $1562$   $\text{cm}^{-1}$ ), one of which was attributed<sup>3b</sup> to the monomer; the solid shows a single band at  $1560$   $\text{cm}^{-1}$ . Our solid-state and solution (0.3 M)  $^{13}\text{C}$  NMR data for  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$  confirm that different structures are present in these media (Table I).

X-ray studies of several dicarboxylato tetraorganodistannoxanes<sup>7–10</sup> have indicated that they adopt structure 5. As a consequence of the  $C_2$  symmetry axis of 5, a relatively simple solid-state  $^{13}\text{C}$  NMR spectrum was expected for  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$  (there can be a maximum of only four unique pairs of methyls). Instead, six distinct tin–methyl  $^{13}\text{C}$  resonances are



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resolved for polycrystalline  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$  (Figure 1). Similarly, in place of the two carboxylate carbon resonances

Table II. Positional Parameters for  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$ 

atom	$x^a$	$y^a$	$z^a$
Sn1	0.3677	0.3112 (2)	0.4655
Sn2	0.5610 (1)	0.1971 (2)	0.4704 (1)
Sn3	0.4220 (1)	0.2277 (2)	0.1638 (2)
Sn4	0.5146 (1)	0.2473 (2)	0.7750 (2)
O1	0.4843 (11)	0.2418 (17)	0.5901 (16)
O2	0.4427 (9)	0.2428 (18)	0.3475 (14)
O11	0.2597 (13)	0.3689 (32)	0.2924 (20)
O12	0.2835 (12)	0.2056 (35)	0.1448 (22)
C11	0.2354 (16)	0.2862 (32)	0.2034 (24)
C12	0.1453 (13)	0.2854 (38)	0.1346 (27)
O21	0.6674 (11)	0.1316 (25)	0.6361 (18)
O22	0.6518 (11)	0.2985 (26)	0.7905 (19)
C21	0.6966 (15)	0.2172 (35)	0.7376 (27)
C22	0.7996 (21)	0.2262 (41)	0.7819 (32)
O31	0.5436 (9)	0.2437 (19)	0.0104 (12)
O32	0.5637 (8)	0.2213 (20)	0.2132 (12)
C31	0.5896 (12)	0.2315 (22)	0.1128 (18)
C32	0.6856 (12)	0.2215 (33)	0.1412 (28)
O41	0.3834 (8)	0.2036 (19)	0.7954 (13)
O42	0.3163 (9)	0.3708 (19)	0.6437 (12)
C41	0.3166 (12)	0.2865 (23)	0.7361 (18)
C42	0.2323 (22)	0.2634 (33)	0.7909 (27)
C1A	0.3099 (19)	0.0682 (35)	0.4720 (31)
C1B	0.3799 (19)	0.5840 (29)	0.4667 (28)
C2A	0.6257 (23)	0.4333 (44)	0.4550 (34)
C2B	0.5628 (18)	−0.0713 (26)	0.4372 (28)
C3A	0.4122 (20)	−0.0332 (35)	0.0965 (29)
C3B	0.4036 (19)	0.4883 (35)	0.0925 (27)
C4A	0.5100 (15)	0.5156 (28)	0.8138 (23)
C4B	0.5367 (17)	−0.0151 (29)	0.8117 (21)

<sup>a</sup> Estimated standard deviations are in parentheses.

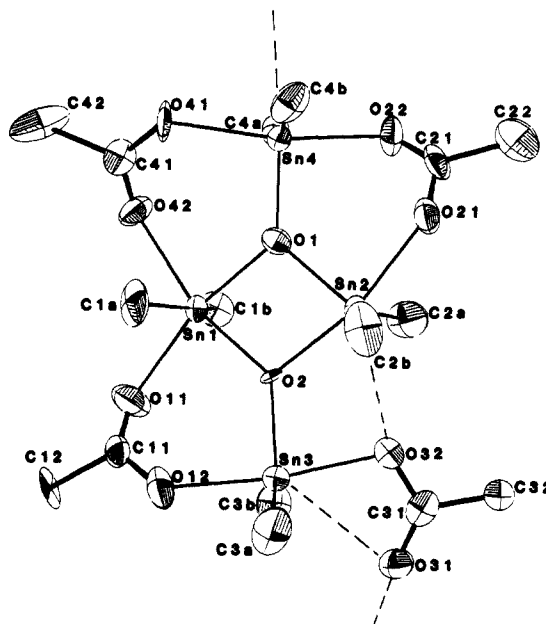


Figure 2. ORTEP drawing of  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$  showing the atom numbering scheme. The dashed line indicates bonds to the adjacent dimer. (The drawing is a projection down the  $b$  axis with the origin in the lower left corner,  $a$  horizontal, and  $c$  vertical.)

expected, three are found. The complexity of the spectrum and the loss of  $J$  coupling information owing to overlap of the satellite resonances ruled out the possibility of making a satisfactory structural assignment from the NMR data alone. Because of the apparent uniqueness of  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$  relative to other structurally characterized dicarboxylato tetraorganodistannoxanes, an X-ray diffraction study was undertaken.<sup>22</sup>

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**Table III.** Bond Angles (deg) and Distances (Å) for  $([\text{Me}_2\text{Sn}(\text{OAc})_2\text{O}]_2)^a$ 

O1-Sn1	2.15 (2)	Sn3-O12	2.24 (2)
O1-Sn2	2.07 (2)	Sn4-C4a	2.14 (2)
O1-Sn4	2.01 (2)	Sn4-C4b	2.10 (2)
O2-Sn1	2.07 (2)	Sn4-O22	2.25 (2)
O2-Sn2	2.12 (1)	Sn4-O41	2.24 (1)
O2-Sn3	2.00 (2)	Sn4-O31	2.56 (1)
Sn1-C1a	2.12 (3)	O11-C11	1.17 (3)
Sn1-C1b	2.13 (2)	O12-C11	1.30 (4)
Sn1-O42	2.38 (2)	C11-C12	1.50 (3)
Sn1-O11	2.34 (2)	O21-C21	1.30 (3)
Sn2-C2a	2.15 (4)	O22-C21	1.22 (4)
Sn2-C2b	2.12 (2)	C21-C22	1.64 (4)
Sn2-O32	2.89 (1)	O31-C31	1.22 (2)
Sn2-O21	2.28 (2)	O32-C31	1.29 (2)
Sn3-C3a	2.16 (3)	C31-C32	1.53 (3)
Sn3-C3b	2.17 (3)	O41-C41	1.31 (2)
Sn3-O31	2.92 (2)	O42-C41	1.22 (2)
Sn3-O32	2.26 (1)	C41-C42	1.65 (4)
Sn1-O1-Sn2	101.8 (7)	O12-Sn3-O31	139.9 (7)
Sn1-O1-Sn4	128.9 (9)	O12-Sn3-C3a	84.5 (11)
Sn2-O1-Sn4	128.9 (8)	O12-Sn3-C3b	89.2 (11)
Sn1-O2-Sn2	102.6 (6)	O32-Sn3-O31	48.7 (4)
Sn1-O2-Sn3	133.2 (7)	O32-Sn3-C3a	93.0 (9)
Sn2-O2-Sn3	124.1 (8)	O32-Sn3-C3b	99.0 (9)
C1a-Sn1-C1b	158.1 (12)	O31-Sn3-C3a	80.8 (10)
C2a-Sn2-C2b	143.2 (14)	O31-Sn3-C3b	78.4 (9)
C3a-Sn3-C3b	139.2 (11)	O1-Sn4-O41	95.2 (6)
C4a-Sn4-C4b	157.5 (9)	O1-Sn4-O22	94.8 (7)
O1-Sn1-C1a	95.1 (8)	O1-Sn4-O31'	176.0 (5)
O1-Sn1-C1b	100.3 (8)	O1-Sn4-C4a	102.6 (8)
O1-Sn1-O42	86.6 (6)	O1-Sn4-C4b	99.8 (7)
O1-Sn1-O11	165.5 (8)	O41-Sn4-O22	170.0 (6)
O1-Sn1-O2	77.3 (6)	O41-Sn4-O31'	81.0 (5)
O2-Sn1-C1a	97.4 (10)	O41-Sn4-C4a	92.7 (8)
O2-Sn1-C1b	101.0 (10)	O41-Sn4-C4b	87.6 (9)
O2-Sn1-O4a	163.9 (4)	O22-Sn4-O31'	89.0 (6)
O2-Sn1-O11	88.2 (7)	O22-Sn4-C4a	83.9 (8)
O42-Sn1-C1a	84.0 (10)	O22-Sn4-C4b	91.9 (9)
O42-Sn1-C1b	81.5 (10)	O31'-Sn4-C4a	84.3 (7)
O42-Sn1-C11	107.9 (7)	O31'-Sn4-C4b	74.3 (7)
O11-Sn1-C1a	86.7 (10)	Sn1-O42-C41	132 (1)
O11-Sn1-C1b	82.3 (9)	Sn4-O41-C41	126 (1)
O1-Sn2-C2a	107.1 (11)	Sn1-O11-C11	130 (2)
O1-Sn2-C2b	108.3 (10)	Sn3-O12-C11	130 (2)
O1-Sn2-O21	88.6 (7)	Sn4-O22-C21	124 (2)
O1-Sn2-O32	141.8 (5)	Sn2-O21-C21	130 (2)
O1-Sn2-O2	77.9 (6)	Sn2-O32-C31	162 (1)
O2-Sn2-C2a	101.4 (4)	Sn3-O32-C31	108 (1)
O2-Sn2-C2b	95.7 (8)	Sn3-O31-C31	78 (1)
O2-Sn2-O21	165.5 (7)	Sn4'-O31-C31	153 (1)
O2-Sn2-O32	64.6 (5)	O11-C11-O12	125 (2)
O21-Sn2-C2a	87.7 (10)	O11-C11-C12	112 (2)
O21-Sn2-C2b	83.3 (9)	O12-C11-C12	122 (3)
O21-Sn2-O32	129.4 (6)	O21-C21-O22	123 (2)
O32-Sn2-C2a	75.0 (10)	O21-C21-C22	115 (2)
O32-Sn2-C2b	83.5 (9)	O22-C21-C22	121 (2)
O2-Sn3-O12	91.4 (8)	O31-C31-O32	124 (2)
O2-Sn3-O32	80.5 (6)	O31-C31-C32	125 (2)
O2-Sn3-O31	128.7 (5)	O32-C31-C32	110 (2)
O2-Sn3-C3a	113.1 (9)	O41-C41-O42	122 (2)
O2-Sn3-C3b	107.3 (9)	O41-C41-C42	116 (2)
O12-Sn3-O3a	169.8 (8)	O42-C41-C42	122 (2)

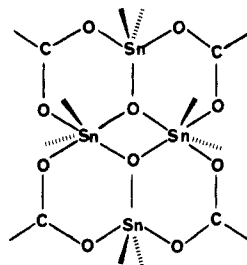
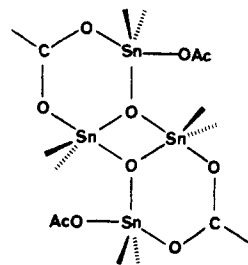
<sup>a</sup> Primes (') indicate interaction between adjacent dimers.

Positional parameters of  $([\text{Me}_2\text{Sn}(\text{OAc})_2\text{O}]_2)$  are given in Table II, bond angles and distances in Table III, and an ORTEP<sup>23</sup> view in Figure 2. For comparison, relevant structural parameters of all structurally characterized (dicarboxylato)tetraorgano-distannoxanes are collected in Table IV. The X-ray analysis confirms the low symmetry of  $([\text{Me}_2\text{Sn}(\text{OAc})_2\text{O}]_2)$  indicated by the solid-state NMR data. In the solid state  $[\text{Me}_2\text{Sn}(\text{OAc})_2\text{O}]$  exists as a dimer made up of planar  $\text{Sn}_2\text{O}_2$  rings [standard de-

viation = 0.05 Å from plane; Sn-O av. = 2.10 Å, O-Sn-O = 77.6 (6)°, Sn-O-Sn = 102.2 (7)°] which are edge-bridged by acetate ligands. There are two distinct types of acetate groups in the molecule; three are bidentate, bridging two tin atoms and lying on planes which form angles 33.79° (av) with the  $\text{Sn}_2\text{O}_2$  plane, and one acetate is bidentate to a single tin atom but has interactions with two additional tin atoms (the plane of this acetate forms an angle of 14.85° with the  $\text{Sn}_2\text{O}_2$  plane). Unlike  $([\text{Me}_2\text{Sn}(\text{OAc})_2\text{O}]_2)$ , other characterized dicarboxylato tetraorganodistannoxanes have centrosymmetric arrangements of acetates about the  $\text{Sn}_2\text{O}_2$  ring; in these molecules one pair of acetates are each bidentate, bridging pairs of tin atoms, and the other two acetate groups are each bidentate to a single tin atom but have additional close distances either to one other tin atom (as in **5**)<sup>9,10</sup> or to two tin atoms (one interdimer Sn-O interaction).<sup>7,8</sup>

In the  $([\text{Me}_2\text{Sn}(\text{OAc})_2\text{O}]_2)$  crystal there is an additional short bonding interaction [2.56 (1) Å] between exocyclic Sn4 and carboxylate oxygen O31' of the adjacent dimer, giving rise to a polymer structure (no other interatomic distances <3.54 Å were found). The geometry at Sn4 supports the bonding nature of the Sn4-O31' interaction: Sn4 has a distorted octahedral (rather than trigonal-bipyramidal) configuration, with a Me-Sn-Me angle of 157.5 (9)° and an approximately square planar geometry of the four bound oxygens. Substantially longer interdimer Sn-O' distances were found (Table IV) for each of the exocyclic tin atoms in  $([\text{Me}_2\text{Sn}(\text{O}_2\text{CCF}_3)_2\text{O}]_2)$ ,<sup>8</sup> 3.0 Å, and  $([\text{Me}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{Cl})_2\text{O}]_2)$ ,<sup>7</sup> 3.2 Å; a CN of 7 was assigned to the exocyclic tin atoms of the latter distannoxane. The three remaining Sn atoms in the  $([\text{Me}_2\text{Sn}(\text{OAc})_2\text{O}]_2)$  dimer also have CN = 6 and adopt rather common<sup>21</sup> distorted octahedral configurations. As expected from discussions<sup>16</sup> of the relationship of the Me-Sn-Me angle to bonding in the  $\text{SnX}_4$  square plane in hexacoordinated diorganotin(IV) compounds, the largest angles are associated with the tin centers (Sn1, Sn4) having the least distorted  $\text{SnO}_4$  square plane and shortest Sn-O contacts (compare particularly Sn1 to Sn2, Sn4 to Sn3).

The solution <sup>13</sup>C and <sup>1</sup>H NMR data (Table I) for  $(\text{Me}_2\text{Sn}(\text{OAc})_2\text{O})_2$  are more amenable to analysis than the solid-state NMR data. Under the conditions of the measurement (0.3 M),  $[\text{Me}_2\text{Sn}(\text{OAc})_2\text{O}]$  was present in solution as the dimer<sup>3b</sup> and the two equal-sized  $\text{Me}_2\text{Sn}$  resonances may be assigned to the endo and exocyclic tin atoms. Me-Sn-Me angles, estimated from the *J* coupling data by using eq 1 and 2, are 141° for the upfield and 145° for the downfield methyl resonances (averages from the <sup>1</sup>*J* and <sup>2</sup>*J* values). Three reasonable dimer structures can be enumerated: **6**, in which the acetates are bidentate and symmetrically bridge two tin atoms, resulting in CNs of 5 for the exocyclic and 6 for the endocyclic tin atoms; **7**, in which both the endo- and exocyclic tin atoms have CN = 5; **5**, in which both the endo- and exocyclic tin atoms have CN = 6.

**6****7**

Although the presence of oxygen in the trigonal plane of the pentacoordinated, exocyclic tin atoms in **6** and **7** might produce an increase in the Me-Sn-Me angle owing to orbital rehybridization,<sup>24</sup> the large Me-Sn-Me angles indicated by NMR favor hexacoordinated endo- and exocyclic tins as in **5**. The crystal

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(24) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

Table IV. Comparison of Selected Bond Distances and Angles in Dicarboxylato Tetraorganodistannoxanes

compound	$D(\text{Sn-O}), \text{\AA}$		Sn-O (carboxylate) intermolecular	$D(\text{Sn-C}), \text{\AA}$	$\angle \text{Me-Sn-Me}, \text{deg}$	ref
	endocyclic	exocyclic				
$([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$	2.07 (2) $\times$ 2 2.15 (2) 2.12 (1)	2.01 (2) 2.00 (2)	2.56 (1)	2.12 (3), 2.13 (2) 2.15 (4), 2.12 (2) 2.16 (3), 2.17 (3) 2.14 (2), 2.10 (2)	158.1 (12) 143.2 (14) 139.2 (11) 157.5 (9)	this work
$([\text{Me}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{Cl})]_2\text{O})_2$	2.07 (1) 2.10 (1)	2.03 (1)	3.18 (2)	2.11 (3), 2.09 (3) 2.21 (3), 2.09 (3)	145.6 (8) 158.5 (9)	7
$([\text{Me}_2\text{Sn}(\text{O}_2\text{CCF}_3)]_2\text{O})_2$	2.039 (5) 2.137 (4)	2.040 (4)	2.996 (6)	2.104 (10) $\times$ 2 2.107 (9) $\times$ 2	147.5 (3) 148.9 (2)	8
$([(\text{CH}_2=\text{CH})_2\text{Sn}(\text{O}_2\text{CCF}_3)]_2\text{O})_2^a$	2.08 2.11	2.06				9
$([n\text{-Bu}_2\text{Sn}(\text{O}_2\text{CCl}_3)]_2\text{O})_2$	2.03 (2) 2.12 (2)	2.05 (2)	<i>b</i>	2.08 (5), 2.13 (3) 2.11 (3), 2.07 (5)	143 (2) 137 (2)	10

<sup>a</sup> Partial structure determination;  $R = 0.20$ . <sup>b</sup> There are no  $\text{Sn}\cdots\text{O}$  intermolecular distances  $< 4.00 \text{\AA}$ .

structure of  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$  (Figure 2) provides an idea of the Me-Sn-Me angles that are likely for a structure of this type. The endocyclic tins in **5** should resemble Sn2 closely and the exocyclic tins Sn3. The similarity of the estimated Me-Sn-Me angles in solution (145 and  $141^\circ$ ) to the angles observed in the solid state for Sn2 and Sn3 [143.2 (14) and 139.2 (11) $^\circ$ , respectively] supports **5** as the solution structure of  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$ . The upfield  $^1\text{H}$  and  $^{13}\text{C}$  resonances, which have the smaller  $J$  couplings, are further identified with the exocyclic  $\text{Me}_2\text{Sn}$  and the downfield resonance with the endocyclic  $\text{Me}_2\text{Sn}$  moiety on the basis of recent studies<sup>25</sup> of  $[\text{Me}_2\text{SnCl}]_2\text{O}$  and a variety of disubstituted tetraorganodistannoxanes,  $n\text{-Br}_2(\text{X})\text{SnOSn}(\text{Y})\text{-}n\text{-Bu}_2$  (X, Y = combinations of Cl, Br, OH, OPh) by solution  $^1\text{H}$  and  $^{119}\text{Sn}$  NMR.

## Conclusions

An empirical relationship of  $[^1J]$  with the Me-Sn-Me bond angle, developed in solid-state  $^{13}\text{C}$  NMR studies, and another relating  $[^2J]$  and the Me-Sn-Me angle  $[^2J]/\text{angle}$  relationship have been used to investigate the solution and solid-state structures of  $[\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O}$  and its hydrolysis product,  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$ . The similarity of the structural data for  $\text{Me}_2\text{Sn}(\text{OAc})_2$  in the solid state and in solution, along with comparison to appropriate model compounds, strongly indicates  $\text{Me}_2\text{Sn}(\text{OAc})_2$  to be monomeric, have a CN of 6, and adopt a distorted octahedral configuration in the solid state as well as in solution. Analysis of solution NMR data for  $\text{Me}_2\text{Sn}(\text{benzoate})_2$  and  $n\text{-Bu}_2\text{Sn}(\text{OAc})_2$  and solid-state NMR data for  $\text{Me}_2\text{Sn}(\text{laurate})_2$  indicates that these dimethyltin dicarboxylates are similar in configuration to  $\text{Me}_2\text{Sn}(\text{OAc})_2$ .

The ability of solid-state NMR to reveal structurally interesting features of complex molecules has been demonstrated for  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$ , whose complex solid-state  $^{13}\text{C}$  NMR spectrum is inconsistent with the symmetry of related, structurally characterized distannoxanes. An X-ray diffraction study confirmed the low symmetry and unusual structure of this dicarboxylato tetraorganodistannoxane. The solution structure of  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$  has been assigned by analysis of the  $J$  coupling data in the solution  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

## Experimental Section

**Materials.** The solid-state  $^{13}\text{C}$  NMR spectrum of  $\text{Me}_2\text{Sn}(\text{laurate})_2$  indicated it was of high purity as obtained from a commercial source.  $\text{Me}_2\text{Sn}(\text{OAc})_2$  was prepared as described in the literature.<sup>3b</sup> Recrystallization from warm  $n$ -heptane gave clear colorless needles. All manipulations of  $\text{Me}_2\text{Sn}(\text{OAc})_2$  were carried out under a dry, inert atmosphere ( $\text{N}_2$ ) to prevent hydrolysis, which otherwise occurred in a few seconds on exposure to ambient air. The solid-state NMR sample was loaded into a sample rotor within an inert atmosphere drybox; no hydrolysis of solution or solid-state NMR samples handled in this way was

Table V. Crystal Data for  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$ 

formula	$\text{Sn}_4\text{O}_{10}\text{C}_{16}\text{H}_{36}$
mol wt	863.2
<i>a</i> , $\text{\AA}$	16.386 (5)
<i>b</i> , $\text{\AA}$	7.780 (2)
<i>c</i> , $\text{\AA}$	11.183 (5)
$\alpha$ , deg	90.0
$\beta$ , deg	103.61 (3)
$\gamma$ , deg	90.0
<i>V</i> , $\text{\AA}^3$	1385.5 (8)
<i>F</i> (000)	824.0
$\mu(\text{Mo K}\alpha)$ , $\text{cm}^{-1}$	36.19
$\lambda(\text{Mo K}\alpha)$ , $\text{\AA}$	0.71069
<i>D</i> <sub>calcd</sub> , $\text{g cm}^{-3}$	2.069
<i>Z</i>	2
obsd reflns	3113
<i>R</i> / <i>R</i> <sub>w</sub> /GOF	4.7%/5.4%/3.1
space group	<i>Pa</i>
absences obsd	$h0l, h = 2n + 1$
resid. dens, $\text{e \AA}^{-3}$	0.46
crystal dims, mm	$0.2 \times 0.2 \times 0.3$

observed.  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$  was prepared in a slight variation of the literature procedure:<sup>3b</sup>  $\text{H}_2\text{O}$  (0.2 mL) was added to a solution of  $\text{Me}_2\text{Sn}(\text{OAc})_2$  (ca. 0.4 g) in 15 mL of MeOH. The mixture was heated to  $50^\circ\text{C}$  to give a homogeneous solution; slow cooling yielded small colorless crystals in ca. 75% yield [mp  $240^\circ\text{C}$  dec (lit.<sup>3b</sup> mp  $236^\circ\text{C}$ )].

**NMR Spectroscopy.** Solid-state  $^{13}\text{C}$  NMR spectra were obtained on samples of ca. 0.4 g at 15.08 MHz by using a homebuilt instrument with a probe temperature of 304 K. The high-resolution spectra were acquired with 60-MHz high-power proton decoupling, spin-locking cross-polarization with the  $^1\text{H}$  and  $^{13}\text{C}$  fields matched at 57 kHz for 2 ms and magic angle spinning at 2300 Hz. Dwell times of 50  $\mu\text{s}$  and repetition rates of 6 s were used.  $^{13}\text{C}$  chemical shifts are relative to internal secondary standard Delrin ( $89.1 \pm 0.3 \text{ ppm}$ ). Because of the similar gyromagnetic ratios of the spin- $1/2$  isotopes  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  (1:1.046) and their similar natural abundances (7.6 and 8.6%, respectively), the magnitude of  $^1J$ -( $^{119}\text{Sn}, ^{13}\text{C}$ ) for  $\text{Me}_2\text{Sn}(\text{OAc})_2$  was calculated by multiplying the separation of the fused  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  satellites by 1.023.

Solution  $^{13}\text{C}$  NMR spectra were recorded on a Bruker WM-400 spectrometer (100.6 MHz for  $^{13}\text{C}$ ). Solutions were ca. 10% by weight dimethyltin(IV); dry benzene- $d_6$  was employed as solvent for  $\text{Me}_2\text{Sn}(\text{OAc})_2$ .  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  values are reproducible to  $\pm 3 \text{ Hz}$ .

**Crystal Structure Determination and Refinement.** A crystal of  $([\text{Me}_2\text{Sn}(\text{OAc})_2]_2\text{O})_2$  was sealed in a capillary and mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table V) were determined by least-squares refinement of the best angular positions for 15 independent reflections ( $2\theta > 15^\circ$ ) during normal alignment procedures using molybdenum radiation ( $\lambda = 0.71069$ ). Data (3928 reflections) were collected at room temperature ( $27^\circ\text{C}$ ) with use of a variable scan rate, a  $\theta$ - $2\theta$  scan mode, and a scan width of 1.2 below  $K\alpha_1$  and 1.2 above  $K\alpha_2$  to a maximum  $2\theta$  value of  $116^\circ$ . Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections, and as the intensities of these reflections showed less than 6% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects.

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After removal of redundant and space group forbidden data, 3113 reflections were considered observed [ $I > 3.0\sigma(I)$ ]. The structure was solved for heavy-atom positions with MULTAN<sup>80,26</sup>. Initial refinement of heavy-atom positions was completed in centric space group  $P2_1/a$ . While locations for the oxo atoms, one acetate, and the methyl carbon atoms attached to tin were readily apparent from a difference Fourier synthesis and these positions were stable to refinement, the positioning of the remaining acetate group was not possible. Positions located failed to refine or refined to chemically unreasonable positions. When atomic coordinates were refined in the acentric cell  $Pa$  the positions of two acetate groups, unrelated by a center of symmetry, were clearly apparent. Thus refinement was completed in the acentric cell. However, the coordinates of the majority of the atoms of the asymmetric unit remain related by the removed center of symmetry, and thus problems of correlation of parameters complicate refinement. This difficulty appears in the temperature parameters for methyl groups of acetate ions and in bond distances involving these atoms. The positioning of tin and oxygen atoms appears well established. Successive least squares/difference Fourier cycles allowed location of the remainder of the non-hydrogen atoms. Refinement of scale factor, positional, and anisotropic thermal parameters

for all non-hydrogen atoms was carried out to convergence. The use of the acentric space group,  $Pa$ , was justified by the noncentric relationship of carboxylates O31, O32, C31, C32 and O41, O42, C41, C42 (Table II) although the rest of the molecule is nearly centrosymmetric. Hydrogen positions were not apparent from a difference Fourier synthesis calculated after final anisotropic refinement of all non-hydrogen parameters. The final cycle of refinement [function minimized  $\sum(|F_o| - |F_c|)^2$ ] led to a final agreement factor,  $R = 4.7\%$ ,  $R = (\sum||F_o| - |F_c||)/\sum|F_o|100$ . Anomalous dispersion corrections were made for Sn. Scattering factors were taken from Cromer and Mann.<sup>27</sup> Unit weights were used until the final cycles of refinement when a weight =  $1/\sigma F$  was applied;  $R_w = 5.4$ . Tables of anisotropic thermal parameters,  $F_o$ , and  $F_c$  and calculated equations of planes are available as supplementary material.

**Registry No.**  $\text{Me}_2\text{Sn}(\text{OAc})_2$ , 13293-57-7;  $\text{Me}_2\text{Sn}(\text{laurate})_2$ , 5926-79-4;  $[\text{Me}_2\text{Sn}(\text{OAc})]_2\text{O}$ , 2179-99-9.

**Supplementary Material Available:** Tables of anisotropic thermal parameters and calculated equations of planes (3 pages); tables of  $F_o$  and  $F_c$  (23 pages). Ordering information is given on any current masthead page.

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## Metal-Stabilized Rare Tautomers of Nucleobases. 1. Imino-oxo Form of Cytosine: Formation through Metal Migration and Estimation of the Geometry of the Free Tautomer

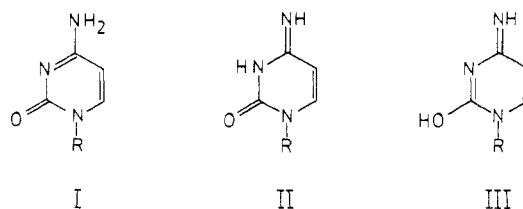
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**Abstract:** A way is presented according to which the geometry of rare nucleobase tautomers is estimated by (i) preparing metal complexes of the rare tautomers, (ii) determining the crystal structure of the metal complex as accurately as possible, and (iii) "subtracting" the effect of the metal on the ligand geometry. The preparation, crystal structures, and spectroscopic (<sup>1</sup>H NMR, Raman) properties of two modifications of a complex of Pt<sup>IV</sup> with the model nucleobase 1-methylcytosine (1-MeC), *trans,trans,trans*-[Pt(NH<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>N<sub>3</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, is reported. In the two compounds, neutral 1-MeC ligands are coordinated to Pt through the deprotonated exocyclic N4' positions with N3 protonated. Thus the 1-MeC ligands are in the rare imino-oxo tautomer form of cytosine. **5a** crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 5.819(2) \text{ \AA}$ ,  $b = 7.178(2) \text{ \AA}$ ,  $c = 13.626(7) \text{ \AA}$ ,  $\alpha = 90.72(4)^\circ$ ,  $\beta = 105.82(3)^\circ$ ,  $\gamma = 94.02(8)^\circ$ ,  $V = 545.9 \text{ \AA}^3$ , and  $Z = 1$ . **5b** crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 8.892(1) \text{ \AA}$ ,  $b = 11.496(1) \text{ \AA}$ ,  $c = 11.010(1) \text{ \AA}$ ,  $\beta = 100.05(2)^\circ$ ,  $V = 1108.2 \text{ \AA}^3$ , and  $Z = 2$ . The structures were refined to  $R = 0.020$ ,  $R_w(F) = 0.020$  in **5a** and  $R = 0.040$ ,  $R_w(F) = 0.045$  in **5b** on the basis of 1911 (**5a**) and 2525 (**5b**) independent reflections. The geometries of the 1-MeC ligands in **5a** and **5b** differ from that of the normal, uncomplexed 1-MeC tautomer with significant differences in C4-N4' and N1-C2 bond lengths (shorter in **5**), in N3-C4 and C2-N3 bond lengths (longer in **5**), as well as in ring angles at positions 2, 3, and 4. The effect of Pt<sup>IV</sup> on the geometry of the cytosine ring is suggested to be minimal and essentially restricted to the exocyclic imino group by slightly lengthening the C4-N4' bond. Formation of **5** occurs in three distinct steps, all of which have been detected in solution, and the respective species have been isolated: (i) Pt coordination via N3, (ii) chelate formation through N3 and N4' with elimination of H<sub>2</sub>O from the complex, and (iii) addition of H<sub>2</sub>O to the complex with reformation of Pt-OH and opening of the Pt-N3 bond. The acidity of the rare 1-MeC tautomer in its Pt<sup>IV</sup> complexed form (deprotonation at N3) has been determined as ca. 5.8 (pK<sub>a1</sub>) and 8.2 (pK<sub>a2</sub>).

The rare tautomers of the naturally occurring nucleobases have been the subject of numerous studies, both with respect to their possible biological role in base-mispairing and mutagenesis,<sup>2</sup> and their physical properties such as relative energy, geometry, acidity, etc.<sup>3</sup> Apart from detection problems of rare tautomers present in proportions lower than  $10^{-4}$ , a major difficulty with quantum-

Chart I



mechanical calculations on relative energies of tautomers represents the geometry approximation used for the respective tautomer.<sup>4</sup>

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(3) For a review see, e.g.: Kwiatkowski, J. S.; Pullman, B. *Adv. Heterocycl. Chem.* **1975**, *18*, 199.