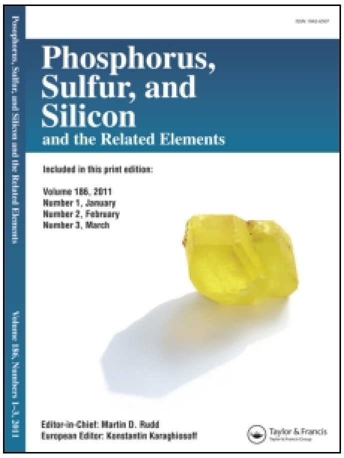

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THE FIRST COMPLETE CRYSTAL STRUCTURE OF A STANNATRANE. TRIMERIC METHYL(2,2',2''-NITRILOTRIETHOXY)STANNANE HEXAHYDRATE

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THE FIRST COMPLETE CRYSTAL STRUCTURE OF A STANNATRANE. TRIMERIC METHYL(2,2′,2″-NITRILOTRIETHOXY)STANNANE HEXAHYDRATE[1,2]

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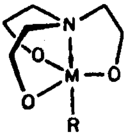
(Received October 21, 1982)

An X-ray analysis of the 1-methylstannatrane hexahydrate $[MeSn(OCH_2CH_2)_3N]_3 \cdot 6H_2O$ (**4**) revealed a trimeric formulation. It crystallizes in the monoclinic space group *C*2/*c* ($Z = 4$) with $a = 9.206$ (3) Å, $b = 13.774$ (5) Å, $c = 26.581$ (4) Å, and $\beta = 93.33$ (2)°. The structure refined to $R = 0.074$ and $R_w = 0.086$. The trimeric unit is disordered about a twofold axis, which passes through the central Sn atom. The geometry around this central atom closely approximates a pentagonal bipyramid. The two crystallographically equivalent end tin atoms have distorted-octahedral geometries. Strong association of the three monomeric methylstannatrane units formally leading to the trimer is suggested by the short Sn—O bond lengths involved. These have values of 2.11 (1) and 2.21 (1) Å, as compared to corresponding values within the monomers of 2.17 (1) and 2.23 (1) Å, respectively. The solid-state structure agrees with solution NMR data suggesting its retention in solution. The trimeric unit is indicated in solution as is the presence of three nonequivalent tin centers. The structure of **4** is compared with other seven-coordinated tin compounds. The six water molecules of **4** appear hydrogen bonded to each other, forming hexagonal rings that contain inversion centers. Additional hydrogen bonding binds the rings to adjacent molecules of **4**.

INTRODUCTION

Although solid-state structures of silatranes[3] and germatranes[4] have been known for some time, similar structural information on stannatranes is lacking.[5] The basic structural entity for the known "atranes" is a trigonal bipyramid (**1**) that contains an apical intramolecular N→M bond formed with triethanolamine acting as a tetradentate ligand.



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Typical of the compounds investigated by crystallography, this structural form has been found for 1-ethylgermatrane,[4] 1-(α-naphthyl)germatrane,[6] 1-phenylsilatrane (α^3, β^7 and γ^8 forms), and 1-(*m*-nitrophenyl)silatrane.[9] These are R-substituted (2,2′,2″-nitrilotriethoxy)germane and -silane derivatives, respectively. X-ray studies show the same structure persists in the related silatranes, methyl(2,2′,3-nitrilodiethoxypropyl)silane (**2**)[10] and phenyl(2,2′,2″-nitrilotriphenoxy)silane (**3**).[11]

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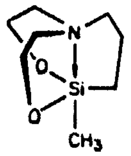

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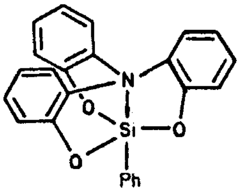
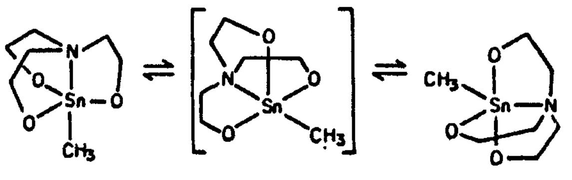


3

NMR studies support the existence of atrane structures in solution for all three elements, Si[12] Ge,[12] and Sn.[13-17] In the case of Si and Ge, the structures indicated are consistent with the results of crystal studies. For the methylstannatrane, temperature dependence of the CH_3 proton splitting pattern was interpreted[13] in terms of intramolecular ligand exchange taking place between four conformations with the exchange being governed by both a ring inversion and a Berry pseudorotational process. The A conformer was indicated to be more stable than the B conformer. Both A and B would have two forms that differ in the relative position of the flap atom in the puckered rings. Ebullioscopic molecular weight measurements supported[14] a monomer formulation.



4-A **4-B**

More recently, the same group of workers[16,17] determined the molecular weight of methylstannatrane in $CHCl_3$ to be trimeric and reinterpreted the previous NMR data[13] in terms of a trimer unit having three nonequivalent hexacoordinated tin atoms. To explain the NMR temperature dependence, a dissociation rotation mechanism is postulated[16] whereby the trimer is converted into its enantiomer, which causes equivalence of two of the three tin atoms (T_c = 6.7°C). The appearance of only one methyl signal at 63°C is suggested[16] to result from dissociation of the trimer to monomeric units.

To establish the solid-state existence of the methylstannatrane system, we undertook a study of its X-ray structure, the results of which are reported here.

EXPERIMENTAL

Methylstannatrane was prepared by the reaction of dimethyltin oxide with triethanolamine in refluxing xylene in the presence of a catalytic amount of KOH according to the preparation of Tzschach and Pönicke.[15] The product was obtained in high yield as a white powder, mp 289–290°C (lit[15] 288–290°C). Recrystallization from a benzene solution by the addition of *n*-hexane to the cloud point, followed by refrigeration for several days, produced only a white powder. Anal. Calcd for $C_7H_{15}NO_3Sn$: C, 30.04; H, 5.40; N, 5.00. Found: C, 29.39; H, 5.73; N, 4.99. Colorless crystals suitable for an X-ray study were obtained by slow air evaporation of a pyridine solution of the compound.

Crystallography of $[CH_3Sn(OCH_2CH_2)_3N]_3 \cdot 6H_2O$ (**4**). All X-ray crystallographic studies were done with an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1)$

= 0.709 30 Å, λ (Kα_2) = 0.713 59 Å) at an ambient temperature of 23 ± 2°C. Details of the experimental and computational procedures have been described previously.[18]

A crystal of **4** having approximate dimensions of 0.20 × 0.18 × 0.15 mm, which was mounted inside of a sealed, thin-walled glass capillary as a precaution against moisture sensitivity, was used for the X-ray studies.

Crystal Data for $[CH_3Sn(OCH_2CH_2)_3N]_3 \cdot 6H_2O$ (**4**): space group *C*2/*c* [C_{2h}^6 – No. 15],[19] $Z = 4$, $a = 9.206$ (3) Å, $b = 13.774$ (5) Å, $c = 26.581$ (4) Å, $\beta = 93.33$ (2)°, $\mu_{\mathrm{MoK}\bar{\alpha}} = 2.291\ \mathrm{mm}^{-1}$; 2946 independent reflections ($+h$, $+k$, $\pm l$) measured by using the θ-2θ scan mode for $2° \leq 2\theta_{\mathrm{MoK}\bar{\alpha}} \leq 50°$; no corrections made for absorption.

The structure was solved by using a combination of Patterson and Fourier difference techniques and refined by using full-matrix least squares.[20] Because of the space group ambiguity, the structure was refined in both *Cc* and *C*2/*c*. Since the refinement in *Cc* led to unsatisfactory correlation between the parameters of atoms that are twofold related in *C*2/*c*, the results of the refinement of *C*2/*c* are reported. In this refinement, the atoms C7, C9, C12, and N2 (involved in the disorder) were refined isotropically,[21] while the remaining independent non-hydrogen atoms were refined anisotropically. No attempt was made to include hydrogen atoms in the refinement. The final agreement factors[22] were $R = 0.074$ and $R_w = 0.086$ for the 1882 reflections having $I \geq 2\sigma_I$. The only peaks of any consequence in a final difference Fourier synthesis were in the immediate vicinity of the Sn atoms.

RESULTS

Solid-State Structure of 4

The atom-labeling scheme for **4** is shown in the ORTEP plot of Figure 1. Atomic coordinates are listed in Table I, and selected bond lengths and angles and O—O

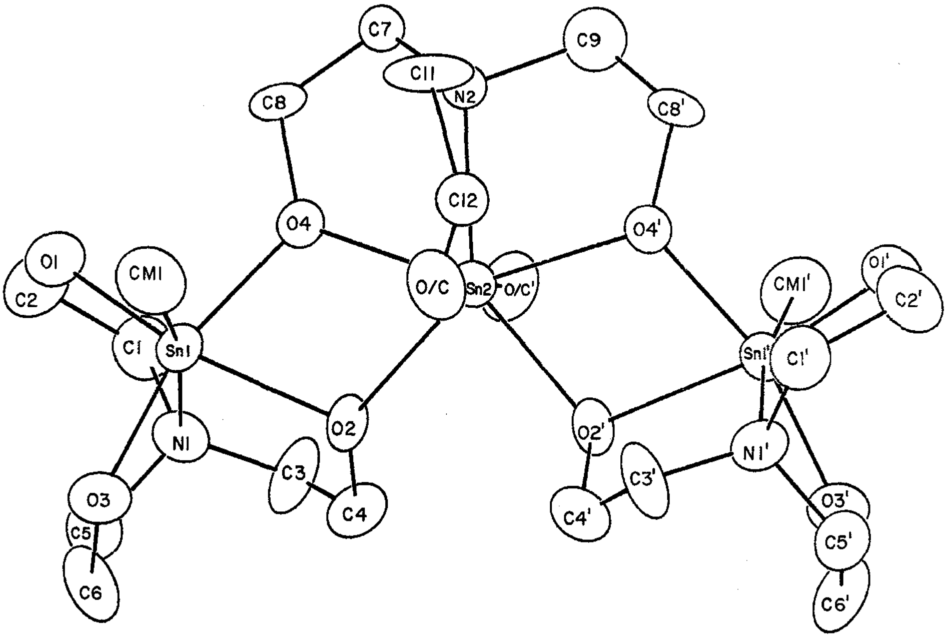


FIGURE 1 ORTEP plot of the $[CH_3Sn(OCH_2CH_2)_3N]_3$ moiety of **4** with thermal ellipsoids at the 50% probability level. Primed atoms are generated from the unprimed ones by the crystallographic twofold axis ($1 - x$, y, $1.5 - z$). Atoms for which primed equivalents are not shown were half-weighted in the refinement. For purposes of clarity, only one set of half-weighted atoms is shown. The hexahydrate arrangement is shown in Figure 3.

TABLE I

Atomic Coordinates ($\times 10^4$) in Crystalline $[CH_3Sn(OCH_2CH_2)_3N]_3 \cdot 6H_2O$ (**4**)[a]

atom type[b]	*x*	*y*	*z*
Sn1	7121 (1)	7993.3 (8)	8609.6 (4)
Sn2[c]	5000[d]	8579 (1)	7500[d]
O1	7132 (12)	8732 (8)	9284 (4)
O2	5840 (13)	7372 (8)	7979 (4)
O3	8084 (12)	6695 (8)	8813 (4)
O4	5747 (13)	9065 (8)	8273 (4)
OW1	2329 (17)	9437 (11)	10367 (6)
OW2	4159 (16)	8040 (11)	10765 (6)
OW3	4461 (17)	6127 (10)	10478 (5)
N1	5287 (14)	7231 (9)	8994 (5)
C1	4692 (19)	7988 (14)	9334 (7)
C2	5982 (21)	8511 (14)	9633 (7)
C3	4138 (21)	6913 (16)	8632 (7)
C4	4878 (24)	6620 (14)	8128 (9)
C5	5942 (20)	6420 (13)	9305 (6)
C6	7224 (19)	5949 (16)	9032 (7)
C8	5870 (21)	10097 (11)	8381 (7)
CM1	9094 (18)	8562 (14)	8342 (8)
O/C	7010 (22)	8565 (14)	7259 (7)
C11[c]	6786 (42)	10358 (24)	7372 (19)
C12[c]	7311 (36)	9294 (25)	7062 (13)
N2[c]	5332 (24)	10254 (14)	7497 (12)
C7[c]	5229 (40)	10732 (25)	7967 (13)
C9[c]	4176 (51)	10670 (34)	7050 (17)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figures 1 and 3. [c] Half-occupancy. [d] Fixed.

distances are presented in Table II. Anisotropic thermal parameters for **4** (Table A), bond parameters for ring atoms (Table B), and least-squares planes (Table C) are provided as supplementary material.

A schematic representation of **4** showing the basic structural features is given in Figure 2. Figure 3 shows the labeling for the hexahydrate unit.

DISCUSSION

The hexahydrate of methylstannatrane, **4**, is trimeric in the solid state, containing a central seven-coordinated tin atom and two end six-coordinated tin atoms. The two terminal stannatrane units are related by a crystallographic twofold axis that passes through the central tin atom, Sn2. Atoms O4 and C8 of the central unit conform to the twofold symmetry, while the remaining ligand atoms of the central unit are disordered about the twofold axis. The atom labeled O/C in Figure 1 is half-occupied by oxygen and half-occupied by carbon. The geometry of the center tin, Sn2, closely approximates a pentagonal bipyramid, while the end tin atoms have distorted-octahedral geometries. The average equatorial angle at Sn2 is 72.5°, nearly the same as that in an idealized pentagonal bipyramid (72°). The average out-of-plane atom distance from the mean equatorial plane is 0.186 Å (plane 1 of Table C).

TABLE II

Selected Bond Lengths (Å), Bond Angles (deg), and O—O Distances (Å) in $[\mathrm{MeSn(OCH_2CH_2)_3N}]_3$ $6\mathrm{H_2O}$ (**4**)[a]

type[b]	bond length	type	bond length	type	dist
Sn1–O1	2.06 (1)	Sn1–O2	2.17 (1)	OW1^{c}–OW2^{c}	2.73 (2)
Sn1–O3	2.05 (1)	Sn2–O4	2.23 (1)	OW1^{c}–OW3^{d}	2.82 (2)
Sn1–O4	2.11 (1)	Sn2–O2	2.21 (1)	OW2^{c}–OW3^{c}	2.76 (2)
Sn1–N1	2.28 (1)	Sn2–N2	2.33 (2)	O1–OW3^{d}	3.17 (2)
Sn1–CM1	2.14 (2)	Sn2–O/C	1.99 (2)	O1–OW1^{g}	2.72 (2)
				O3–OW2^{d}	2.74 (2)

type	bond angle	type	bond angle
O1–Sn1–O2	147.4 (4)	O4–Sn2–O4′	145.0 (5)
O1–Sn1–O3	102.8 (5)	O4–Sn2–N2	70.9 (8)
O1–Sn1–O4	89.8 (4)	O4′–Sn2–N2	74.5 (8)
O1–Sn1–N1	78.7 (4)	O4–Sn2–O2	67.4 (4)
O1–Sn1–CM1	98.5 (6)	O4–Sn2–O2′	146.8 (4)
O2–Sn1–O3	93.8 (4)	O4–Sn2–O/C	93.2 (6)
O2–Sn1–O4	70.3 (4)	O4–Sn2–O/C′	87.1 (6)
O2–Sn1–N1	77.4 (5)	O2–Sn2–O2′	82.2 (6)
O2–Sn1–CM1	108.8 (6)	O2–Sn2–N2	135.0 (8)
O3–Sn1–O4	163.7 (4)	O2′–Sn2–N2	141.8 (8)
O3–Sn1–N1	78.5 (4)	O2–Sn2–O/C	83.0 (6)
O3–Sn1–CM1	92.5 (6)	O2–Sn2–O/C′	96.2 (6)
O4–Sn1–N1	94.1 (5)	N2–Sn2–O/C	88.4 (8)
O4–Sn1–CM1	95.9 (6)	N2–Sn2–O/C′	97.8 (8)
N1–Sn1–CM1	169.6 (6)	OC–Sn2–O/C′	179 (1)
Sn1–O4–Sn2	109.0 (5)	Sn1–O2–Sn2	107.8 (5)
Sn1–N1–C1	105 (1)	Sn2–N2–C7	116 (2)
Sn1–N1–C3	112 (1)	Sn2–N2–C9	106 (2)
Sn1–N1–C5	108 (1)	Sn2–N2–C11	103 (2)
C1–N1–C3	109 (1)	C7–N2–C9	114 (2)
C1–N1–C5	110 (1)	C7–N2–C11	106 (3)
C3–N1–C5	113 (1)	C9–N2–C11	112 (3)

[a] Numbers in parentheses are estimated standard deviations.

[b] Atoms are labeled to agree with Figures 1 and 3. See figure captions for meaning of superscripts on atom labels.

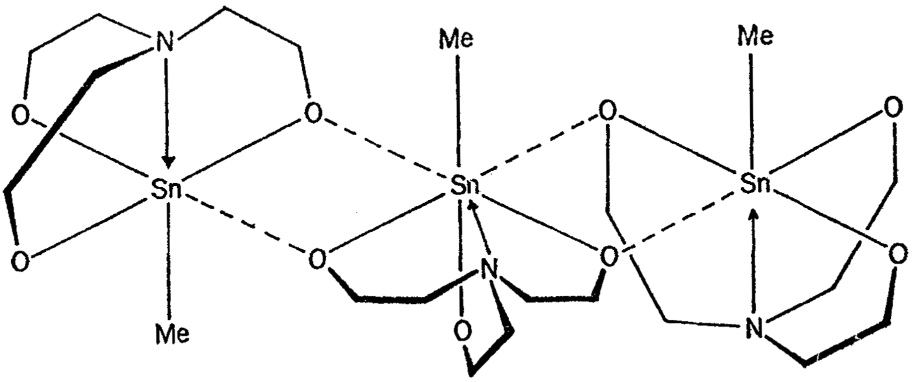


FIGURE 2 Schematic diagram of the $[\mathrm{CH_3Sn(OCH_2CH_2)_3N}]_3$ moiety of **4**. The dashed lines formally indicate the Sn—O bonds arising on forming the trimer from monomer units.

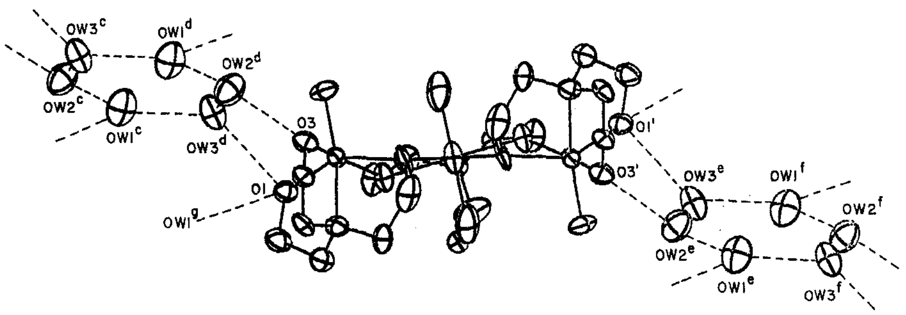


FIGURE 3 ORTEP plot of $[CH_3Sn(OCH_2CH_2)_3N]_3 \cdot 6H_2O$ (**4**) with hydrogen-bonding interactions shown as dashed lines. To illustrate propagation of the hydrogen-bonded network, an additional six water oxygen atoms are shown. The following symmetry operations generate the coordinates of the atoms so marked from those given in the list of coordinates: $' = 1 - x, y, 1.5 - z$; $c = 1 + x, y, z$; $d = 1.5 - x, 1.5 - y, 2 - z$; $e = x - \frac{1}{2}, 1.5 - y, z - \frac{1}{2}$; $f = -x, y, 1.5 - z$; $g = 1 - x, 2 - y, 2 - z$.

The association between the three methylstannatrane units of the trimer appears to be unusually strong. This is indicated by the short Sn1—O4 and Sn2—O2 bond lengths. These bonds, which formally lead to the trimer from the monomeric methylstannatrane molecules, have lengths of 2.11 (1) and 2.21 (1) Å, respectively. These values are shorter than the corresponding intramonomeric values of Sn bonded to trivalent oxygen: 2.17 (1) Å for Sn1—O2 and 2.23 (1) Å for Sn1—O4. The Sn—O bond lengths of the six-coordinated tin atoms are shorter than those of the central tin, as expected from reduced intermolecular repulsions. The same effect is found for the Sn—N bond lengths. The Sn—N bond associated with the six-coordinated tin atoms, 2.28 (1) Å, is shorter than the Sn—N bond connected to the central tin atom, 2.33 (2) Å. As can be seen in Table II, the two independent N atoms, N1 and N2, have nearly tetrahedral geometries. The bond angles about N1 range from 105 (1) to 113 (1)° with an average value of 109.5°, while the bond angles about N2 range from 103 (2) to 116 (2)° also with an average value of 109.5°.

Crowding is suggested between monomeric units of **4**. The CM1—O/C distance is 3.37 (3) Å, which is considerably less than the effective van der Waals diameter of the methyl group,[23] 4.0 Å.

It is interesting to note that the structure of the *tert*-butylstannatrane, *t*-$BuSn(OCH_2CH_2)_3N$,[24] is monomeric with the nitrogen atom and the *tert*-butyl group in the axial positions of a trigonal bipyramid. Presumably, the larger *tert*-butyl group would render the trimer less stable owing to increased steric interactions with groups in neighboring axial positions.

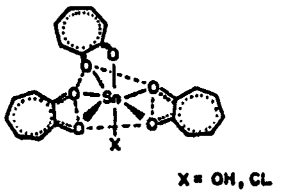
As shown in Figure 3, the oxygen atoms of the water molecules form a six-membered ring centered about an inversion center that has O—O distances (ranging from 2.73 (2) to 2.82 (2) Å, Table II) that suggest hydrogen bonding. In addition, each water oxygen atom is close enough to an oxygen atom of an adjacent stannatrane unit to suggest a hydrogen-bonding interaction. A reasonable model for the observed geometry would be one in which each water molecule donates one H atom to a stannatrane oxygen atom and a second H atom to an adjacent water oxygen atom in the ring. The ring structure is reminiscent of the water arrangement in hexamethylenetetramine hexahydrate,[25] $(CH_2)_6N_4 \cdot 6H_2O$ (plane 2, Table C).

Comparison of 4 with Solution Data

The trimer formulation found for **4** in the solid state agrees with the most recent molecular weight study indicating a trimeric molecule.[16,17] However, the presence of three different kinds of hexacoordinated tin atoms in the trimer inferred from the NMR data[16,17] is not supported by the X-ray structure. Instead, the X-ray structure of **4** shows a central seven-coordinated tin atom and end hexacoordinated tin atoms. Although the terminal Sn atoms are crystallographically equivalent due to the disorder, they are not chemically equivalent. This is consistent with the presence of three types of tin atoms and three types of methyl protons indicated by the NMR spectra. If the X-ray structure of **4** is the one present in solution, one can interpret the fluxional behavior implied by the NMR data[13,16,17] in terms of a ligand-exchange mechanism similar to that cited[6] in the Introduction for the trimer.

Comparison of 4 with Related Compounds

The X-ray crystal structures of some related seven-coordinated tin compounds are in the literature.[26–32] Structures **5–8** all contain chelating ligands with oxygen and nitrogen as donor atoms. Structures **5**,[26] **7**,[28] and **8**[29] resemble pentagonal bipyramids while **6**[27] does not appear to conform to any idealized coordination geometry. The equatorial Sn—O bond lengths of **5** average 2.144 (6) Å for the chloro derivative and 2.164 (6) Å for the hydroxo derivative.[33] The Sn—O bond lengths for **6** average 2.083 (3) Å. In both these cases the Sn—O lengths are significantly shorter than those for the seven-coordinated tin atom in **4**.



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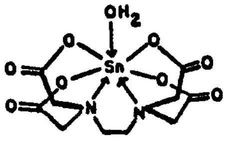

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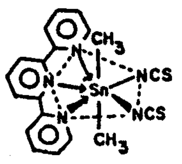

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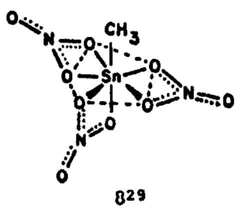
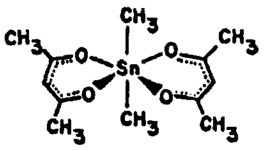


8[29]

Two examples of six-coordinated organotin compounds that contain oxygen donors are bis(2,4-pentanedionato)dimethyltin (**9**)[34] and bis(8-hydroxyquinolinato)dimethyltin (**10**).[35] X-ray crystal structure determination has shown that the average Sn—O bond lengths for **9** and **10** are 2.19 (1) and 2.11 (1) Å, respectively.



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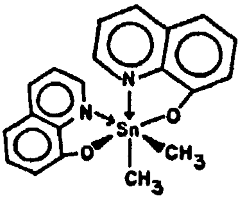
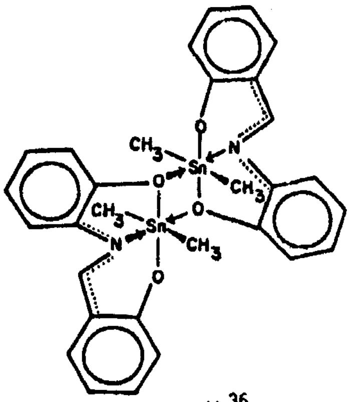


10[35]

Other organotin compounds that have molecules associated through tin-oxygen bridges are $(CH_3)_2Sn(SAB)$ (**11**)[36] and $(n\text{-}C_4H_9)_2Sn(OCH_2CH_2O)$ (**12**).[37]

In both **11** and **12** the Sn—O bonds are divided into strong intramolecular covalent bonds and weaker intermolecular interactions. For compound **11**, the covalent Sn—O bonds average 2.112 (9) Å, while the weak interactions average 2.881 (8) Å.[36] Compound **12**, which has a stronger intermolecular association, has an average Sn—O covalent bond length of 2.07 (1) Å and weak Sn—O interactions averaging 2.50 (1) Å.[37] This division of Sn—O distances into weak interactions and strong covalent bonds is not observed in trimeric methylstannatrane.



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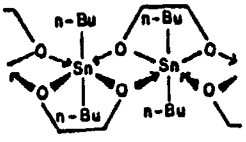

12[37]

ACKNOWLEDGEMENT

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Registry No. **4**, 87453-18-7.

Supplementary Material Available: Thermal parameters (Table A), bond parameters for ring atoms (Table B), least-squares mean planes (Table C), and a listing of observed and calculated structure factor amplitudes for **4** (10 pages). Ordering information is given on any current masthead page.

REFERENCES AND NOTES

1. "Abstracts of Papers," 182nd National Meeting of the American Chemical Society, New York, NY, Aug 1981; American Chemical Society: Washington, D.C., 1981; INOR 144.

2. R. G. Swisher, Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1982.
3. M. G. Voronkov, V. M. Dyakov and J. Kirpichenko, *J. Organomet. Chem.*, **233,** 1 (1982), and references cited therein. J. W. Turley and F. P. Boer, *J. Am. Chem. Soc.*, **90,** 4026 (1968).
4. (a) L. O. Atovmyan, Ya. Ya. Bleidelis, A. A. Kemme and R. P. Shibaeva, *Zh. Strukt. Khim.*, **11,** 318 (1970). (b) Ya. Bleidelis, A. A. Kemme, L. O. Atovmyan and R. P. Shibaeva, *Khim. Geterotsikl. Soedin., Sb.*, **1,** 184 (1968). (c) T. K. Gar, N. Yu. Khromova, S. N. Gurkova, A. I. Gusev and V. F. Mironov, *Zh. Obshch. Khim.*, **50,** 1894 (1980). (d) S. N. Gurkova, A. I. Gusev, I. R. Segel'man, N. V. Alekseev, T. K. Gar and N. V. Khromova, *Zh. Strukt. Khim.*, **22,** 181 (1981).
5. In addition to our preliminary report[1] on the structure of the title compound, the X-ray structure of $MeSn(SCH_2CH_2)_3N$ was reported in part by: A. Tzschach, H. Weichmann and K. Jurkschat, *J. Organomet. Chem. Libr.*, **12,** 293 (1981), referring to unpublished work by M. Dräger.
6. A. A. Kemme, Ya. Ya. Bleidelis, R. P. Shibaeva and L. O. Atovmyan, *Zh. Strukt. Khim.*, **14,** 103 (1973).
7. L. Párkányi, K. Simon and J. Nagy, *Acta Crystallogr., Sect B*, **B30,** 2328 (1974).
8. L. Párkányi, J. Nagy and K. Simon, *J. Organomet. Chem.*, **101,** 11 (1975).
9. J. W. Turley and F. P. Boer, *J. Am. Chem. Soc.*, **91,** 4129 (1969).
10. F. P. Boer and J. W. Turley, *J. Am. Chem. Soc.*, **91,** 4134 (1969).
11. F. P. Boer, J. W. Turley and J. J. Flynn, *J. Am. Chem. Soc.*, **90,** 5102 (1968).
12. MG. G. Voronkov, S. N. Tandura, B. Z. Shterenberg, A. L. Kuznetsov, R. G. Mirskov, G. I. Zel'chan, N. Yu. Khromova, T. K. Gar, V. F. Moronov and V. A. Pestunovich, *Dokl. Akad. Nauk SSSR*, **248,** 134 (1979), and references cited herein.
13. A. Zschunke, A. Tzschach and K. Pönicke, *J. Organomet. Chem.*, **51,** 197 (1973).
14. A. Tzschach, K. Pönicke, L. Korecz and K. Burger, *J. Organomet. Chem.*, **59,** 199 (1973).
15. A. Tzschach and K. Pönicke, *Z. Anorg. Allg. Chem.*, **413,** 136 (1975).
16. See the reference given in footnote 5.
17. K. Jurkschat, C. Mügge, A. Tzschach and A. Zschunke, *Z. Anorg. Allg. Chem.*, **463,** 123 (1980).
18. A. C. Sau, R. O. Day and R. R. Holmes, *Inorg. Chem.*, **20,** 3076 (1981).
19. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 101.
20. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean atomic scattering factors were taken from: Reference 19, Vol. IV, 1974, pp 72–98. For atomic position O/C, which is half-occupied by oxygen and half-occupied by carbon, average scattering factors were used. Real and imaginary dispersion corrections for Sn and O were taken from the same source, pp 149–150.
21. No attempt was made to refine C7, C9, and N2 anisotropically because they were barely resolved from twofold-related disordered atoms. Attempts to refine C12 anisotropically led to nonpositive definite temperature factors.
22. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.
23. L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press: Ithaca, NY, 1960; p 260.
24. M. Dräger, private communication.
25. T. C. Mak, *J. Chem. Phys.*, **43,** 2799 (1965). G. A. Jeffrey, *Acc. Chem. Res.*, **2,** 344 (1969).
26. J. J. Park, D. M. Collins and J. L. Hoard, *J. Am. Chem. Soc.*, **92,** 3636 (1970).
27. F. P. Remoortere, J. J. Flynn and F. P. Boer, *Inorg. Chem.*, **10,** 2313 (1971).
28. D. V. Naik and W. R. Scheidt, *Inorg. Chem.*, **12,** 272 (1973).
29. G. S. Brownlee, A. Walker, S. C. Nyburg and J. T. Szymanski, *J. Chem. Soc. D*, 1073 (1971).
30. L. Coghi, C. Pelizzi and G. Pelizzi, *Gazz. Chim. Ital.*, **104,** 1315 (1974).
31. L. Coghi, C. Pelizzi and G. Pelizzi, *J. Organomet. Chem.*, **114,** 53 (1976).
32. A. Mangia, C. Pelizzi and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 2557 (1973).
33. J. A. Zubieta and J. J. Zuckerman, *Prog. Inorg. Chem.*, **24,** 251 (1978).
34. G. A. Miller and E. O. Schlemper, *Inorg. Chem.*, **12,** 677 (1973).
35. E. O. Schlemper, *Inorg. Chem.*, **6,** 2012 (1967).
36. H. Preut, F. Huber, H. J. Haupt, R. Cefalu and R. Barbieri, *Z. Anorg. Allg. Chem.*, **410,** 88 (1974).
37. R. G. Swisher and R. R. Holmes, unpublished work.