carbonyl were in the range recorded for model 1:1 electrolytes,[15] whereas measurements on the initial solution indicated the starting material was a nonelectrolyte.

Isolation of [RuCl(CO)$_2$TDPME]PF$_6$. A suspension of 111 mg of RuCl$_2$(CO)TDPME and 40 mg (an excess) of NH$_4$PF$_6$ in 8 ml of acetone was stirred under 40 psi of CO for 4 hr. The suspension color changed from yellow to white. Water was added dropwise, yielding initially a colorless solution and then a white precipitate. The solid was collected, washed with water, and dried to yield 105 mg of white powder. The infrared spectrum contained a strong band at 835 cm^{-1} characteristic of PF$_6^-$ as well as the two ν_{CO}.

Anal. Calcd for C$_{43}$H$_{39}$ClO$_2$P$_4$F$_6$Ru: C, 53.68; H, 4.09; Cl, 3.68. Found: C, 54.71; H, 5.12; Cl, 3.23.

Registry No. Ru(CO)$_2$(TDPME), 37843-33-7; Ru(CO$_3$)-(CO)(TDPME), 37843-34-8; RuCl$_2$(CO)(TDPME), 37843-

(15) P. Uguagliati, G. Deganello, L. Busetto, and U. Belluco, *Inorg. Chem.*, 8, 1625 (1969).

35-9; [RuCl(CO)$_2$(TDPME)]Cl, 37843-36-0; [RuCl(CO)$_2$-(TDPME)]PF$_6$, 37843-37-1; [RuBr(CO)$_2$(TDPME)]Br, 37897-34-0; RuBr$_2$(CO)(TDPME), 37843-38-2; TDPME, 22031-12-5; Ru, 7440-18-8; SO$_2$, 7446-09-5.

Crystal and Molecular Structure of Bis(2,4-pentanedionato)dimethyltin(IV)[1]

G. A. MILLER[2] and E. O. SCHLEMPER*[3]

The crystal structure of bis(2,4-pentanedionato)dimethyltin(IV), (CH$_3$)$_2$Sn(C$_5$H$_7$O$_2$)$_2$, has been determined from three-dimensional X-ray diffraction data. Unit cell dimensions are $a = 7.12 \pm 0.01$ Å, $b = 13.87 \pm 0.02$ Å, $c = 7.69 \pm 0.01$ Å, and $\beta = 104.7 \pm 0.2°$. The monoclinic space group is $P2_1/n$. The density by flotation is 1.59 g/cm^3. Two molecules in the unit cell give a calculated density of 1.57 g/cm^3. By visual estimation of film data, the intensities of 1195 independent reflections were obtained. The structure was solved by three-dimensional Patterson and Fourier methods and refined by full-matrix least-squares to a final conventional R factor of 7.9%. The arrangement of the atoms about the tin forms a nearly perfect octahedron. The 2,4-pentanedionate acts as a bidentate ligand bonding to the tin atom through the oxygen atoms. The bond distances in the octahedron are as follows: Sn–C(3), 2.14 (2) Å; Sn–O(1), 2.20 (1) Å; Sn–O(2), 2.18 (1) Å. The space group and the presence of only two molecules in the unit cell require the tin atom to be on a center of symmetry, and therefore the two methyl groups bonded to the tin must be in trans positions.

Introduction

The crystal structure of the bis(2,4-pentanedionato)-dimethyltin(IV) molecule has been determined to resolve some of the controversy that has occurred over the structure of this compound in the literature. A literature survey shows that until 1969, most authors felt that the methyl groups should be in the trans positions. The techniques used in those studies were Raman, infrared, nmr, and Mossbauer.[4-7] In 1969, Moore and Nelson,[8] on the basis of a dipole moment study, assigned the compound the cis structure.

In the work of McGrady and Tobias[6] the infrared and Raman spectra were used to compare the structure of the compound in solution to that in the solid. If the methyl groups were in the trans position, then the skeletal symmet-

(1) An initial report of this work was made at the 5th Midwest Regional Meeting of the American Chemical Society, Kansas City, Mo., Oct 29-31, 1969; see Abstracts, No. 319.
(2) Taken in part from the Ph.D. dissertation of G. A. Miller, University of Missouri, 1973.
(3) Author to whom correspondence should be addressed.
(4) M. M. McGrady and R. S. Tobias, *Inorg. Chem.*, 3, 1157 (1964).
(5) Y. Kawasaki, T. Tanaka, and R. Okawara, *Bull. Chem. Soc. Jap.*, 37, 903 (1964).
(6) M. M. McGrady and R. S. Tobias, *J. Amer. Chem. Soc.*, 87, 1909 (1965).
(7) B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *Chem. Commun.*, 7, 390 (1968).
(8) C. Z. Moore and W. H. Nelson, *Inorg. Chem.*, 8, 138 (1969).

rical stretching vibrations should be only Raman active with the antisymmetrical skeletal vibrations being only infrared active. If the methyl groups were in the cis positions, then all skeletal vibrations would be Raman and infrared active. The observed bands were in keeping with a trans structure in both the solid and solution. However, it was noted that the symmetrical C–O vibration which should have been Raman active was absent.

From the dipole moment values obtained in benzene (2.95 D) and cyclohexane (3.19 D) Moore and Nelson[8] assigned the cis structure to the compound since the trans structure should have a dipole moment of zero. They felt that a cis type structure with some distortion from a true octahedron would equally well fit the accumulated data.

Experimental Section

Crystal Preparation. The crystals were prepared by the use of a slight modification of methods previously published.[6,8] Dimethyltin oxide (2.75 g, 0.02 mol) was added to 10 ml of 2,4-pentanedione and refluxed for 5.5 hr. The clear solution was decanted and kept at 0° overnight. The colorless crystals were then dissolved in hot benzene containing a small amount of 2,4-pentanedione and recrystallized; mp 177-179°. *Anal.* Calcd for C$_{12}$H$_{20}$O$_4$Sn: C, 41.54; H, 5.81. Found: C, 41.63; H, 5.82.

X-Ray Data. Bis(2,4-pentanedionato)dimethyltin(IV) crystallizes in the monoclinic system with $a = 7.12 \pm 0.01$ Å, $b = 13.87 \pm 0.02$ Å, $c = 7.69 \pm 0.01$ Å, and $\beta = 104.7 \pm 0.2°$. A flotation measurement in aqueous KI solution gave a density of 1.59 ± 0.01 g/cm^3. A calculated density of 1.569 ± 0.005 g/cm^3 is obtained assuming two molecules per unit cell. The systematic extinctions require that on

$h0l$, $h + l = 2n$, and on $0k0$, $k = 2n$, which gives the space group as $P2_1/n$.

A crystal approximately 0.3 mm $\times$ 0.5 mm $\times$ 0.6 mm was mounted in a glass capillary to prevent decomposition. The long dimension of the crystal, the c axis, was coincident with the capillary axis. Mo Kα radiation (λ 0.7107 Å) with a Zr filter was used to obtain the relative intensity measurements. Weissenberg photographs were taken of the $hk0$–$hk6$ zones using 1-mil brass sheets between a series of four films. The precession photographs were of the $0kl$–$2kl$ and $h0l$–$h2l$ zones using timed exposures of 0.5, 1.5, 6, and 24 hr. The relative intensities were estimated by visual comparison with a film strip consisting of a series of timed exposures of a selected reflection. The usual Lorentz and polarization corrections were made.[9] The relative intensities of 1195 independent reflections were measured. The linear absorption coefficient was calculated to be 20.0 cm^{-1}; absorption corrections were not made. A rough estimate[10] of the absorption factors indicated a range of less than 15% for a given Weissenberg layer. Reflections with intensities below background were not included in any calculations. From a three-dimensional Patterson synthesis all nonhydrogen atoms were found since the tin atom was located at the origin of the unit cell. This was in agreement with subsequent Fourier and difference Fourier syntheses.

In the least-squares refinement scattering factors for neutral tin[11a], oxygen,[11b] and carbon[11b] were used. Anomalous dispersion effects for tin[11c] were included in F_c.[11d] The weighting scheme, which minimizes the function $\Sigma w(|F_o|^2 - |F_c|^2)^2$, $w = 1/\sigma^2(F_o^2)$, was chosen to make the average value of $(|F_o^2| - |F_c^2|)/F_o^2$ nearly independent of F_o^2; thus, $\sigma = -0.05555(kF_o)^4 + 0.785(kF_o)^2$ for $(kF_o)^2 \leqslant 7.80$; $\sigma = -0.02299(kF_o)^4 + 0.530 (kF_o)^2$ for $7.80 < (kF_o)^2 \leqslant 13.0$; $\sigma = -0.001232 (kF_o)^4 + 0.246(kF_o)^2$ for $13.0 < (kF_o)^2 \leqslant 50.0$; $\sigma = -0.00623(kF_o)^4 + 0.494 (kF_o)^2$ for $50.0 < (kF_o)^2 \leqslant 60.0$; $\sigma = +0.00613(kF_o)^4 - 0.248(kF_o)^2$ for $60.0 < (kF_o)^2 \leqslant 65.0$; $\sigma = -0.00153(kF_o)^4 + 0.252(kF_o)^2$ for $65.0 < (kF_o)^2 \leqslant 96.0$; $\sigma = -0.0012(kF_o)^4 + 0.170(kF_o)^2$ for $96.0 < (kF_o)^2 \leqslant 339.0$; $\sigma = +0.00019(kF_o)^4 + 0.067(kF_o)^2$ for $339.0 < (kF_o)^2 \leqslant 756.0$; and $\sigma = -0.00034(kF_o)^4 + 0.511(kF_o)^2$ for $756.0 < (kF_o)^2 \leqslant 1017.0$ where $k = 0.311$. Three cycles of least-squares refinement with all atoms given anisotropic thermal expressions converged giving values of $R(F^2) = 0.147$, $R(F^2) = \Sigma(|F_o|^2 - |kF_c|^2)/\Sigma |F_o|^2$, and $R(wF^2) = 0.196$, $R(wF^2) = [\Sigma w(|F_o|^2 - |kF_c|^2)^2/(\Sigma w|F_o|^2)^2]^{1/2}$. The maximum change in any positional parameter at this stage was one-fifth of the estimated standard deviation of that parameter. The conventional R, $\Sigma(|F_o| - |kF_c|)/\Sigma|F_o|$, was 0.079.

The largest electron density residual on the difference Fourier was 2.9 e/Å^3 which was associated with the tin atom. All other residual peaks were less than 1.0 e/Å^3. No attempt was made to include the hydrogen atoms.

The observed and calculated structure factors ($\times 10$) appear only in the microfilm edition of this journal.[12] The positional and thermal parameters are given in Table I.

Results

General Nature of the Structure. The complete structure study confirms that the 2,4-pentanedionate ligands are chelating. The oxygen atoms of the 2,4-pentanedionate ligands and the two methyl groups complete the octahedral coordination about the tin atom as shown in Figure 1. The question of whether the methyl groups are cis or trans in the
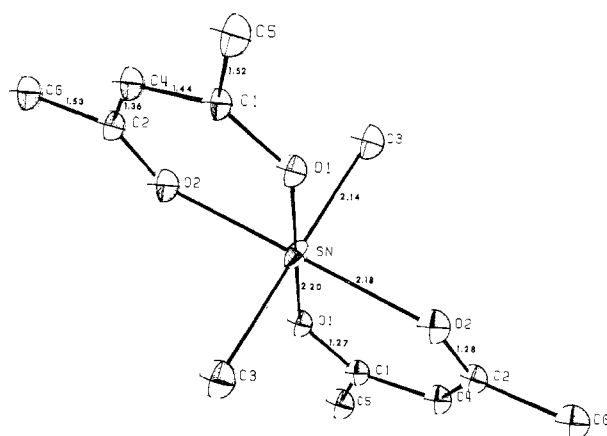
(9) All calculations were performed on the IBM 360/65 computer of the University of Missouri Computer Research Center. The data were placed on a common scale using the interlayer scaling program of Hamilton, Rollett, and Sparks. Other programs used included a version of A. Zalkin's FORDAP program, Brown University's version of the Busing–Levy ORFLS least-squares program by R. Eisenberg, W. R. Busing and H. A. Levy's error function program, and other data handling programs of W. C. Hamilton and J. A. Ibers.

(10) "International Tables for X-Ray Crystallography," Vol. 2, Kynoch Press, Birmingham, England, 1958, pp 291–312.

(11) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962: (a) p 211; (b) p 202; (c) 216; (d) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964).

(12) This listing of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-677.

Figure 1. Bond distances around the tin atom in $(CH_3)_2Sn(C_5H_7O_2)_2$.

solid was actually settled when the space group was determined and two molecules were found per unit cell. This puts the tin atom on a special position, a center of symmetry, and thus the methyl groups must be in trans positions. It is interesting to note that when two chlorine atoms are substituted for the two methyl groups the chlorine atoms are cis as determined by a three-dimensional X-ray analysis by the authors.[13]

Intramolecular and intermolecular distances were calculated out to 4 Å. No unusually short intermolecular distances were observed. The intramolecular bond distances are given in Table II and shown in Figure 1. Intermolecular distances less than 4 Å are given in Table III.

The 2,4-pentanedionate ligand defines a least-squares plane which has the equation $5.98x - 7.46y - 2.19z - 0.00835 = 0$. The maximum deviation of any ligand atom from the plane was 0.03 $\pm$ 0.02 Å indicating no significant deviation from planarity; including the tin atom with the 2,4-pentanedionate ligand introduces no deviation from planarity.

The anisotropic thermal motion can best be observed in Figure 2. The root-mean-square amplitudes of the thermal ellipsoids are given in Table IV. The thermal motion of the tin atom is greatest perpendicular to plane of the ligand and toward the trans methyl groups. The oxygen atoms have their minimum amplitude along the tin-oxygen bonds. The thermal motion of each carbon atom of the ligand is clearly anisotropic with the minimum along the carbon-carbon bonds. The thermal motion of the trans methyl groups is more nearly isotropic than that of the other carbon atoms but still has a minimum along the tin-carbon bond. The errors on the light-atom thermal parameters are 10–20 times those on the tin atom.

A view of the unit cell contents is shown in Figure 3, and a stereoscopic pair of one molecule is shown in Figure 2.

Discussion

Bond Distances and Angles. All bond distances and angles (Table II) seem chemically reasonable. The bond distances and angles between chemically equivalent atoms are equal within 2σ except for the bonds C(2)-C(4), 1.36 (2) Å, and C(1)-C(4), 1.44 (2) Å. The average of these two distances (1.40 Å) does agree with that found in the analogous dichloro compound of tin.[13] There is no obvious chemical reason for the difference in these two bond distances.

A comparison of the Sn-C(CH$_3$) and Sn-O bond distances with those in related compounds is given in Table V. The range for Sn-C(CH$_3$) bond distances is from 2.06 (1) to 2.22

(13) G. A. Miller and E. O. Schlemper, unpublished work.

Table I.

Positional Parameters[a]

Atom	x	y	z
Sn	0	0	0
O(1)	0.152 (1)	0.1341 (7)	−0.036 (1)
O(2)	0.129 (2)	0.0185 (6)	0.286 (1)
C(1)	0.259 (1)	0.1851 (9)	0.085 (2)
C(2)	0.239 (2)	0.089 (1)	0.360 (2)
C(3)	0.246 (3)	−0.082 (1)	−0.022 (3)
C(4)	0.301 (2)	0.164 (1)	0.274 (2)
C(5)	0.352 (3)	0.272 (1)	0.022 (3)
C(6)	0.307 (3)	0.080 (2)	0.523 (2)

Thermal Parameters[a,b]

	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Sn	0.0163 (2)	0.00335 (5)	0.0093 (2)	−0.0025 (1)	0.0002 (1)	0.002 (1)
O(1)	0.024 (2)	0.0045 (5)	0.013 (1)	−0.0039 (9)	0.001 (1)	0.0007 (7)
O(2)	0.034 (3)	0.0042 (7)	0.011 (1)	−0.0024 (8)	0.003 (2)	0.0014 (6)
C(1)	0.017 (2)	0.0041 (6)	0.019 (3)	0.0000 (1)	0.008 (2)	−0.001 (1)
C(2)	0.016 (2)	0.0062 (8)	0.013 (2)	0.003 (1)	0.001 (2)	0.000 (1)
C(3)	0.023 (3)	0.007 (1)	0.028 (4)	0.000 (1)	0.004 (3)	0.000 (2)
C(4)	0.017 (2)	0.0059 (8)	0.014 (2)	−0.001 (1)	0.001 (2)	−0.003 (1)
C(5)	0.027 (4)	0.0050 (8)	0.027 (4)	−0.003 (1)	0.005 (3)	0.001 (1)
C(6)	0.027 (4)	0.013 (2)	0.011 (2)	0.006 (2)	0.002 (2)	−0.004 (2)

[a] Standard deviations given in parentheses. [b] The anisotropic temperature factors are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
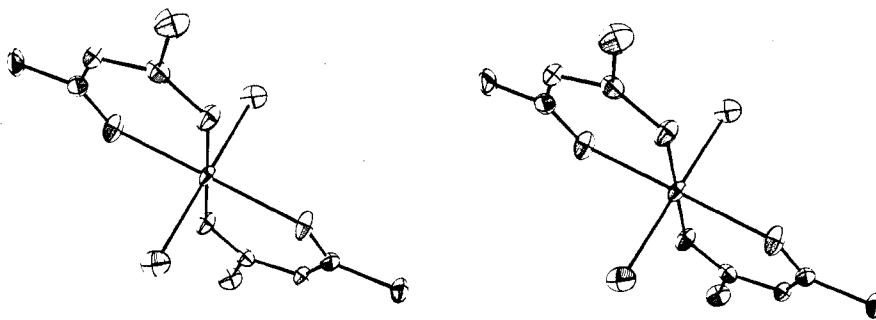

Figure 2. Stereoscopic view of one molecule of $(CH_3)_2Sn(C_5H_7O_2)_2$ showing thermal ellipsoids. The two views constitute a stereoscopic pair and can be viewed with a small hand stereoscope.

Table II. Intramolecular Distances and Angles for $(CH_3)_2Sn(C_5H_7O_2)_2$[a]

Distance, Å		Angle, deg	
Sn–C(3)	2.14 (2)	C(3)–Sn–C(3)	180 (0)[b]
Sn–O(1)	2.20 (1)	C(3)–Sn–O(1)	90 (1)
Sn–O(2)	2.18 (1)	C(3)–Sn–O(2)	90 (1)
O(1)–C(1)	1.27 (2)	O(1)–Sn–O(2)	86 (1)
O(2)–C(2)	1.28 (2)	Sn–O(1)–C(1)	127 (1)
C(2)–C(4)	1.36 (2)	Sn–O(2)–C(2)	126 (1)
C(1)–C(4)	1.44 (2)	O(1)–C(1)–C(4)	124 (1)
C(1)–C(5)	1.52 (2)	C(1)–C(4)–C(2)	130 (1)
C(2)–C(6)	1.53 (2)	C(4)–C(2)–O(2)	127 (1)
		O(1)–C(1)–C(5)	116 (1)
		C(4)–C(1)–C(5)	120 (2)
		C(4)–C(2)–C(6)	120 (2)
		O(2)–C(2)–C(6)	113 (2)

[a] Standard deviations given in parentheses. [b] Symmetry fixed.

Table III. Intermolecular Distances[a] (Å)

O(1)–C(4)	3.79 (4)	C(1)–C(3)	3.94 (4)	C(3)–C(1)	3.94 (4)
O(1)–C(5)	3.76 (4)	C(2)–C(5)	3.82 (4)	C(3)–C(5)	3.89 (4)
O(2)–C(5)	3.71 (4)	C(2)–C(6)	3.92 (4)	C(5)–C(6)	3.78 (4)

[a] Standard deviations given in parentheses.

Table IV. Rms Amplitudes (Å) of the Ellipsoids of Vibration along the Principal Axes

	Axis 1	Axis 2	Axis 3
Sn	0.148 (2)	0.164 (2)	0.231 (2)
O(1)	0.18 (1)	0.18 (1)	0.28 (1)
O(2)	0.16 (1)	0.20 (1)	0.30 (1)
C(1)	0.18 (1)	0.20 (1)	0.24 (2)
C(2)	0.17 (1)	0.20 (2)	0.26 (2)
C(3)	0.24 (2)	0.26 (2)	0.29 (2)
C(4)	0.16 (2)	0.22 (2)	0.26 (2)
C(5)	0.20 (2)	0.26 (2)	0.29 (2)
C(6)	0.16 (2)	0.23 (2)	0.38 (2)

(2) Å and for Sn–O from 2.11 (1) to 2.35 (3) Å. The Sn–C(CH₃) bond distance of 2.14 (2) Å and the Sn–O bond distance of 2.19 (1) Å reported in this work are well within these ranges of previously published values. The sum of the covalent radii for tin and carbon (2.17 Å[14a]) agrees with the Sn–C(CH₃) bond distance (2.14 (2) Å) determined in this work. However, the sum of the covalent radii for tin and oxygen (2.11 Å[14b]) is smaller than the observed Sn–O bond

(14) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960: (a) pp 224, 229; (b) p 224.

distance (2.19 (1) Å). The wide range of bond distances might be due to a variation in ionic bond character and Sn hybridization from compound to compound.

Bonding. Potentially the tin atom has the 5s, 5p, and 5d orbitals available for bonding to give the observed octahedral geometry. It is generally felt that, without highly electronegative groups or atoms bonded to the tin, the 5d orbitals will not be greatly involved in the bonding and that, with groups bonded which differ greatly in electronegativity, the 5s orbital will be maximized toward the trans positions

Table V. Comparison of Average Bond Distances in $(CH_3)_2Sn(C_5H_7O_2)_2$ with Those of Related Compounds

Bond	Compound	Geometry	Distance, Å	Ref
Sn–C(CH₃)	$(CH_3)_2Sn(C_5H_7O_2)_2$	Octahedron	2.14 (2)	a
Sn–C(CH₃)	$(CH_3)_2Sn(C_9H_6NO)_2$	Distorted octahedron	2.16 (2)	b
Sn–C(CH₃)	$[(CH_3)_2(C_5H_5NO)_2SnCl_2$	Octahedron	2.22 (2)	c
Sn–C(CH₃)	$[(CH_3)_2SnCl(terpy)]^+$	Distorted octahedron	2.12 (4)	d
Sn–C(CH₃)	$(CH_3)_2SnCl_2(DMSO)_2$	Octahedron	2.08 (5)	e
Sn–C(CH₃)	$(CH_3)_2SnF_2$	Octahedron	2.06 (1)	f
Sn–C(CH₃)	$CH_3Sn(NO_3)_3$	Pentagonal bipyramid	2.092	g
Sn–C(CH₃)	$(CH_3)_2SnCl[S_2CN(CH_3)_2]$	Distorted trigonal bipyramid	2.18 (5)	h
Sn–C(CH₃)	$(CH_3)_3SnCN$	Trigonal bipyramid	2.16 (3)	i
Sn–C(CH₃)	$(CH_3)_3SnNCS$	Trigonal bipyramid	2.13 (5)	j
Sn–C(CH₃)	$[(CH_3)_3SnCl_3]^-$	Trigonal bipyramid	2.11 (5)	d
Sn–C(CH₃)	$(CH_3)_3SnF$	Distorted trigonal bipyramid	2.11	k
Sn–C(CH₃)	$(CH_3)_3SnS_2CN(CH_3)_2$	Distorted tetrahedron	2.21 (3)	l
Sn–C(CH₃)	CH_3SnH_3	Tetrahedron	2.14	m
Sn–O	$(CH_3)_2Sn(C_5H_7O_2)_2$	Octahedron	2.19 (1)	a
Sn–O	$(CH_3)_2SnCl_2(DMSO)_2$	Octahedron	2.35 (3)	e
Sn–O	$(CH_3)_2(C_5H_5NO)_2SnCl_2$	Octahedron	2.25 (2)	c
Sn–O	$(CH_3)_2Sn(C_9H_6NO)_2$	Distorted octahedron	2.11 (1)	b
Sn–O	$SnCl_4 \cdot 2SeOCl_2$	Distorted octahedron	2.12 (2)	n
Sn–O	$CH_3Sn(NO_3)_3$	Pentagonal bipyramid	2.232 (6) (equatorial) 2.148 (6) (axial)	g
Sn–O	$Sn(NO_3)_4$	Dodecahedron	2.161 (7)	o

a This work. *b* E. O. Schlemper, *Inorg. Chem.*, 6, 2012 (1967). *c* E. A. Blom, B. R. Penfold, and W. T. Robinson, *J. Chem. Soc. A*, 913 (1969). *d* F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc. A*, 3019 (1968). *e* N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc. A*, 1257 (1970). *f* E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, 5, 995 (1966). *g* G. S. Brownlee, A. Walker, S. C. Nyburg, and J. T. Szymanski, *J. Chem. Soc. D*, 18, 1073 (1971). *h* K. Furue, T. Kimura, N. Yasuoka, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Jap.*, 43, 1661 (1970). *i* E. O. Schlemper and D. Britton, *Inorg. Chem.*, 5, 507 (1966). *j* R. A. Forder and G. M. Sheldrick, *J. Organometal. Chem.*, 21, 115 (1970). *k* H. C. Clark, R. J. O'Brien, and J. Trotter, *J. Chem. Soc.*, 2332 (1964). *l* G. M. Sheldrick and W. S. Sheldrick, *J. Chem. Soc. A*, 490 (1970). *m* L. E. Sutton, Ed., "Interatomic Distances," The Chemical Society, London, 1958. *n* Y. Hermodson, *Acta Crystallogr.*, 13, 656 (1960). *o* C. D. Garner, D. Sutton, and S. C. Wallwork, *J. Chem. Soc. A*, 1949 (1967).
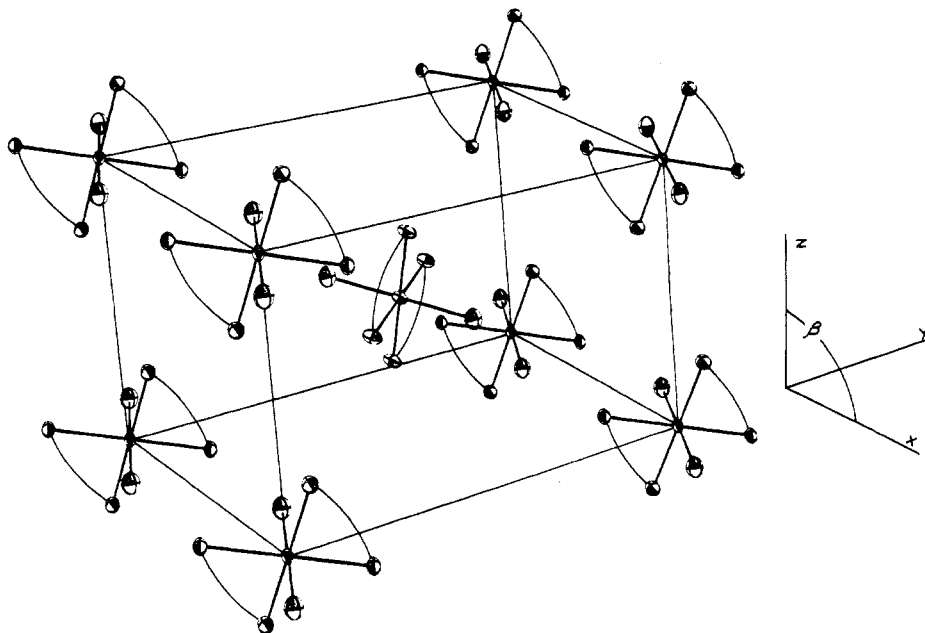
Figure 3. Unit cell contents of $(CH_3)_2Sn(C_5H_7O_2)_2$.

which in this case are the methyl groups. The maximization of the s character to the methyl groups is in line with the predictions of Bent[15] and the nmr data obtained by McGrady and Tobias.[4]

There have been qualitative MO bonding schemes proposed to explain the bonding in tin complexes without the use of d orbitals. McGrady and Tobias[6] proposed for $(CH_3)_2Sn$-$(C_5H_7O_2)_2$ that the bonds to the axial methyl groups were mainly sp hybrids while those to the equatorial oxygens were

mainly composed of the remaining 5p orbitals. Beattie and McQuillan[16] proposed the use of three-center bonds for tin complexes. Schlemper[17] used and extended this three-center multielectron approach to include a qualitative MO scheme for $(CH_3)_2Sn(C_9H_6NO)_2$.

An adaptation of this bonding scheme to $(CH_3)_2Sn$-$(C_5H_7O_2)_2$ would require the axial σ bonds to the methyl groups to be of sp character and the equatorial σ bonds to

(15) H. A. Bent, *J. Inorg. Nucl. Chem.*, 19, 43 (1961).

(16) I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, 1519 (1963).

(17) See ref *b*, Table V.

the ligands to be of the three-center, four-electron type, using the other two 5p orbitals. Molecular orbitals, constructed from the $(CH_3)_2Sn$ group and the ligands, would result in bonding, nonbonding, and antibonding orbitals. The four electrons from the ligand would occupy the bonding and nonbonding orbitals.

A relationship between the tin–proton coupling constants and the hybridization of the atomic orbitals on the tin has been noted[18] and has been used in correlating the amount of s character in a tin–carbon bond. Using the value given by McGrady and Tobias[6] for the ^{119}Sn–H coupling constants of $(CH_3)_2Sn(C_5H_7O_2)_2$ in deuteriochloroform leads to the prediction of approximately 50% s character in the Sn–CH_3 bond. This is in accordance with the proposed sp hybridization given in the molecular orbital scheme.

(18) J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, 83, 3903 (1961).

It should be clearly noted that the bonding of the 2,4-pentanedionate ligands to the $(CH_3)_2Sn$ moiety may involve a high percentage ionic character. Some involvement of the 5d orbitals in the bonding is also likely, but the extent of such involvement is not established.

The structure of $(CH_3)_2Sn(C_5H_7O_2)_2$ in solution and the solid state has been investigated[19] by Ramos and Tobias in a laser Raman study. The correlation between the single-crystal laser Raman data and those obtained in benzene solution suggest that the compound retains the trans arrangement of the methyl groups in solution.[20]

(19) V. R. Ramos and R. S. Tobias, *Spectrochim. Acta*, in press.
(20) The space group, unit cell dimensions, and trans configuration have been established independently by E. G. Miller and R. C. Fay, private communication.

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High Resolution Boron-11 Nuclear Magnetic Resonance. IV. Boron–Boron Coupling Constants in Apically Substituted Pentaborane(9) Derivatives[1,2]

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Substituent effects on ^{11}B–^{11}B coupling constants have been observed for apically substituted pentaborane(9) derivatives, 1-XB_5H_8, where X = H, Cl, Br, I, CH_3, C_2H_5, $CH(CH_3)_2$, and $Si(CH_3)_3$. The value of J_{BB} has been observed to vary from 13.8 to 25.1 Hz. The effect of the substituent on the coalescence temperature of the quartet is discussed. In general, for similar substituents, J_{BB} has been observed to be more sensitive than J_{CC}. Attempts to synthesize other 1-XB_5H_8 systems, where X = CN, C_2H, C_6H_5, $C(CH_3)_3$, and $CH(Br)CH_3$, are also discussed along with the reaction between acetonitrile and B_5H_9.

Introduction

Three important factors affecting nuclear spin–spin coupling constants between quadrupolar nuclei are the type of bonding involved, the substituents attached to one or both of the nuclei, and the temperature. We have previously discussed $J_{^{11}B^{11}B}$ values for three-center two-electron BHB bonds in diborane(6) and tetraborane(10).[1] In addition we have examined the temperature dependence of the value of J_{BB}[3] in pentaborane(9).[4] Numerous investigators have discussed the ^{11}B and ^1H nmr spectra of apically substituted pentaborane(9) derivatives.[5]

In 1959 Williams and coworkers[6] compared the line width of the resonance of the apex boron in B_5H_9 with the line width of the resonances of boron nuclei in analogous environments in several other boron hydrides. The resonance of the apex boron was observed to be broader than the other

(1) Part III: J. D. Odom, P. D. Ellis, D. W. Lowman, and M. H. Gross, *Inorg. Chem.*, 12, 95 (1973).
(2) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971; this paper is based, in part, on the thesis submitted by D. W. L. to the Graduate School of the University of South Carolina in partial fulfillment of the requirements for the M.S. degree.
(3) Henceforth, J_{BB} will be used to represent $J_{^{11}B^{11}B}$.
(4) D. W. Lowman, P. D. Ellis, and J. D. Odom, *J. Magn. Resonance*, 8, 289 (1972).
(5) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969, and references therein.
(6) R. E. Williams, S. G. Gibbins, and I. Shapiro, *J. Amer. Chem. Soc.*, 81, 6164 (1959).

resonances studied. Thus, it became necessary to conclude that the broadening in the apical resonance of B_5H_9 is characteristic of the molecule and not of the ^{11}B nucleus. Therefore, it was concluded that unresolved boron–boron coupling and not nuclear quadrupole broadening was more important in the apex resonance broadening. Based on the apex resonance line width of *ca.* 160 Hz and considering only the apex boron connected to four ^{11}B nuclei in the base, Williams and coworkers[6] predicted that the ^{11}B (apex) to ^{11}B (base) coupling constant was "<13+ Hz."

From ^{11}B nuclear spin–lattice relaxation time, T_1, studies, Allerhand, Odom, and Moll[7] concluded that the expected ^{11}B line widths should be quite narrow at room temperature for B_5H_9—about 5 and 0.5 Hz for the base and apex, respectively. Complex unresolved splittings were postulated as an explanation for the observed broad line widths (over 40 Hz). Leach and Onak[8] proposed that the apex ^{11}B resonance in 1-methylpentaborane(9) should resolve into a 1:3:3:1 quartet from long-range coupling to the methyl hydrogens. This was not observed. A 1:1:1:1 quartet was observed by these authors in the ^1H nmr of 1-methylpentaborane(9) for the methyl hydrogens spin coupled to the apex boron, only upon decoupling the basal borons. The authors proposed that the expected 1:3:3:1 quartet might be obscured by unresolved homonuclear spin–spin coupling

(7) A. Allerhand, J. D. Odom, and R. E. Moll, *J. Chem. Phys.*, 50, 5037 (1969).
(8) J. B. Leach and T. Onak, *J. Magn. Resonance*, 4, 30 (1971).