

Figure 2. PLUTO drawing of complex **5** showing the atom-labeling scheme (30% probability ellipsoids). Selected bond distances (Å) and angles (deg): Ni–P2A = 2.175 (3), Ni–O2A = 1.903 (5), Ni–P2B = 2.167 (2), Ni–O2B = 1.881 (7), Fe1–P1A = 2.198 (2), Fe1–C6A = 1.734 (12), Fe1–C7A = 1.979 (9), Fe1–Cp1A = 1.748 (10), O2A–C7A = 1.324 (11), C7A–C8A = 1.346 (11), P2A–C8A = 1.758 (8), P2A–C41A = 1.816 (6), P2A–C51A = 1.821 (6), Fe2–P1B = 2.204 (2), Fe2–C6B = 1.716 (10), Fe2–C7B = 1.989 (12), Fe2–Cp1B = 1.732 (10), O2B–C7B = 1.318 (11), C7B–C8B = 1.363 (13), P2B–C8B = 1.754 (12), P2B–C41B = 1.808 (5), P2B–C51B = 1.814 (7), P2B–Ni–O2B = 84.4 (2), O2A–Ni–O2B = 85.3 (3), P2B–Ni–O2A = 167.9 (2), P2A–Ni–O2B = 169.8 (2), P2A–Ni–P2B = 105.6 (1), P2A–Ni–O2A = 84.5 (2).

in order to generate C–C or C–element bonds with high stereoselectivity.

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Supplementary Material Available: For compounds **3** and **5**, tables of crystal data, data collection, and solution and refinement parameters, bond distances and angles, thermal parameters, and hydrogen atom complete coordinates and Figure S1, showing the structure of **3** with the complete numbering scheme and Newman projection looking from the α -carbon C(7) to the metal, and Figure S2, giving the structure of **5** showing the environment of the metals and the arrangement of the phenyl rings (14 pages); tables of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Influence of Hydrogen Bonding on the Molecular Geometry and Solution-State NMR Properties of $[\text{tmpH}_2][\text{Me}_3\text{SnCl}_2]^1$

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Recently, we have observed some interesting structural distortions from the idealized trigonal-bipyramidal geometry for a pentacoordinate triorganotin(IV) anion possessing a cation capable of extensive hydrogen-bonding interactions, a type of complex not observed for tin until now. Studies of pentacoordinated tin compounds are of special significance in structural tin chemistry³ in view of the implication that five-coordinate tin(IV) intermediates are formed during substitution reactions of organotin compounds. An intimate knowledge of the structural details, therefore, is quite significant in order to understand the nature of the bonding in these compounds and to observe the manner in which the mo-

lecular geometry of the pentacoordinated state is influenced by effects such as hydrogen bonding through direct anion–cation interactions.

Experimental Section

Physical Measurements. NMR spectra were obtained by using Bruker AC 200-MHz, JEOL FX 90-MHz, and JEOL 270-MHz spectrometers. ¹H and ¹³C chemical shifts were referenced to internal CDCl₃. ¹¹⁹Sn chemical shifts were referenced to external Me₄Sn. FT-IR spectra were obtained on a Nicolet spectrometer using Nujol and Hostafon matrices. Elemental analyses were performed at the University of Munich microanalysis laboratory.

Preparation of $[\text{tmpH}_2][\text{Me}_3\text{SnCl}_2]$ (1**).** A mixture of Me₃SnCl (2.51 g, 12.6 mmol) in 20 mL of CH₃CN and an equivalent amount of $[\text{tmpH}_2][\text{Cl}]$ (2.24 g, 12.6 mmol) in 30 mL of CH₃CN were stirred at ambient temperature for 24 h. Concentration of solvent from the reaction mixture in vacuo results in the desired product **1**. A total of 4.72 g (92% yield) of product is obtained, having mp 244–248 °C. The compound is hygroscopic but can be handled indefinitely in the absence of moisture. ¹H(CDCl₃): 0.681 (s, Me₃Sn–, ²J(¹H–¹¹⁹Sn) = 60.0 Hz, ²J(¹H–¹¹⁷Sn) = 56.9 Hz, 9 H); 1.58 (s, CH₃/tmp, 12 H); 1.72 (s, –CH₂–/tmp, 6 H); 8.42 (br s, NH proton/tmp, 2 H). ¹³C(CDCl₃): 0.049 (s, ¹J(¹³C–¹¹⁹Sn) = 400 Hz, ¹J(¹³C–¹¹⁷Sn) = 380 Hz). ¹¹⁹Sn(CDCl₃, 303 K): 153.7 (s). ¹¹⁹Sn(CDCl₃, 213 K): 101.3 (br s). Anal. Calcd for C₁₂H₂₇Cl₂SnN: C, 38.23; H, 7.77; N, 3.71. Found: C, 38.89; H, 8.20; N, 4.05.

X-ray Structural Data for **1.** The compound $[\text{tmpH}_2][\text{Me}_3\text{SnCl}_2]$ crystallizes in the monoclinic space group $P2_1/a$ ^{4b} with $a = 13.884$ (2) Å, $b = 7.694$ (2) Å, $c = 17.109$ (2) Å, $\beta = 90.448$ (2)°, $Z = 4$, and $\mu_{\text{Mo K}\alpha} = 16.807$ cm⁻¹. The crystal used in the X-ray study had maximum dimensions of approximately 0.20 mm × 0.27 mm × 0.20 mm. A total of 2240 independent reflections ($\pm h, \pm k, \pm l$) were measured at 23 ± 1 °C, by using the θ – 2θ scan mode and graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å), for $4^\circ \leq 2\theta \leq 46^\circ$, on an Enraf-Nonius CAD-4 diffractometer. No corrections were made for absorption. The structure was solved by using heavy-atom methods and difference Fourier techniques. Full-matrix least-squares refinement (non-hydrogen atoms anisotropic, methyl and tmp ring hydrogens riding isotropic, function minimized $\sum w(|F_o| - |F_c|)^2$, $w^{1/2} = 2F_o/L_p/\sigma$) led to a conventional unweighted residual $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ of 0.0470 and $R_w = 0.0384$ for the 1800 reflections having $I \geq 2\sigma_I$. Mean atomic scattering factors were taken from ref 4b. Real and imaginary dispersion corrections for Sn, N, and Cl were taken from the same source (pp 149–150). Calculations were performed on a Microvax II computer using the Enraf-Nonius CAD-4 SDP system of programs package.

Results and Discussion

The reaction of equivalent amounts of trimethyltin chloride with 2,2,6,6-tetramethylpiperidinium chloride, $[\text{tmpH}_2][\text{Cl}]$, in acetonitrile solution proceeds according to eq 1 to result in formation of the pentacoordinated tin complex, $[\text{Me}_3\text{SnCl}_2][\text{tmpH}_2]$, in high yield. The anionic tin(IV) complex was first isolated, in good yield, from the novel reaction of a stannyl-functionalized diazaboretidine, $[\text{Me}_3\text{SnN}=\text{B}-\text{Ntmp}]_2$, with methylene chloride or chloroform solvent over time.⁵ Colorless, parallelepipeds of $[\text{tmpH}_2][\text{Me}_3\text{SnCl}_2]$ suitable for an X-ray experiment were grown from CH₂Cl₂ solution.

As shown in Figure 1, the anion can be considered as an axially distorted trigonal-bipyramidal structure of $C_{3v}-3m$ symmetry with three methyl groups located at equatorial sites and two chlorine atoms axially oriented. The three Sn–C bond lengths are all within 0.01 Å of the value of 2.121 (8) Å. The three C–Sn–C bond angles are all within 0.9° of the average value of 118.5 (3)°. The Cl(1)–Sn–Cl(2) fragment is essentially linear at tin, whereas the

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Table I. Selected Structural Parameters for Triorganotin Compounds

compd	Sn-Cl, Å	Sn-C, Å	∠C-Sn-C, deg	∠C-Sn-Cl, deg	∠C-Sn-Cl, deg
Me ₃ SnCl (135 K X-ray) ^a	2.434 (5)	2.14 (3)	117.2 (8)	99.5 (5)	176.8 (2)
(363 K cd) ^b	3.259 (5)				
[Mo ₃ (η ⁵ -C ₅ H ₅) ₃ S ₄][Me ₃ SnCl ₂] ^c	2.351 (7)	2.106 (6)	114.9 (16)	103.2 (6)	
	2.696 (3)	2.12 (1)			
	2.572 (4)				
{Au[S(AuPPh ₃) ₂] ₂ }[Me ₃ SnCl ₂] ^d	2.622 (9)	2.25 (4)	111.8 (20)	92.1 (12)	178.7 (4)
			124.1 (11)	89.4 (13)	
				88.6 (12)	
[tmpH ₂][Me ₃ SnCl ₂] ^e	2.454 (2)	2.117 (8)	118.6 (3)	97.9 (2)	179.2 (2)
	3.034 (3)	2.134 (9)	119.7 (3)	96.1 (2)	
		2.113 (8)	117.1 (3)	97.5 (2)	

^aReference 12. ^bReference 13. ^cReference 10. ^dReference 11. ^eThis study.

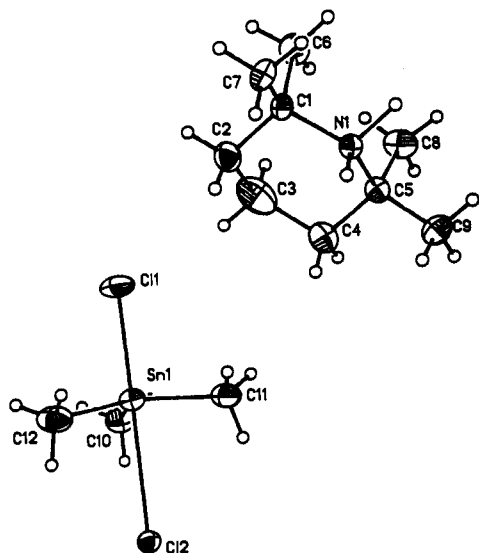


Figure 1. ORTEP plot of [tmpH₂][Me₃SnCl₂] with thermal ellipsoids shown at the 30% probability level. Symmetry operators: $1/2 - x, 1/2 + y, 1/2 - z$. Selected bond lengths (Å): Sn-Cl(1) = 2.454 (2); Sn-Cl(2) = 3.034 (3); Sn-C_{av} = 2.121 (8). Selected bond angles (deg): Cl(1)-Sn-Cl(2) = 179.2 (2); C-Sn-Cl(1)_{av} = 96.8 (2); C-Sn-Cl(2)_{av} = 82.9 (2); C-Sn-C_{av} = 118.5 (3). ESD's are in parentheses.

two Sn-Cl bond lengths are distinctly dissimilar, with the Sn-Cl(2) bond length being the longest reported for a direct Sn-Cl interaction. This difference could be understood by considering the extensive hydrogen-bonding interactions of the [tmpH₂]⁺ cations with one of the axial chlorine atoms of each tin anion, as illustrated in Figure 2. Hydrogen-bonding interactions, as represented by dashed lines, are evidenced by N-Cl(2) contacts involving two independent [tmpH₂]⁺ cations with each [Me₃SnCl₂]⁻ anion that are significantly less (3.248 (8) and 3.168 (7) Å) than the sum of their respective van der Waals radii (3.3 Å).^{6,7} The H-Cl(2) contacts, as well, are significantly shorter (2.339 (8) and 1.957 (8) Å) than the sum of their respective van der Waals radii (3.0 Å).⁷ It should be noted that the two hydrogen peaks are visible in the difference Fourier map and, while having no formal electron density, are required to maintain the electroneutrality of the complex. The IR data for [tmpH₂][Me₃SnCl₂] reflect the hydrogen-bonding effects in the solid state as well, with fundamental N-H stretching vibrations $\nu(\text{NH}_2)_{\text{asym}}$ 2946 cm⁻¹ and $\nu(\text{NH}_2)_{\text{sym}}$ 2772 cm⁻¹ and characteristic N-H deformations (NH₂)_{scissor} 1587 cm⁻¹, (NH₂)_{wag} 1421 cm⁻¹, and (NH₂)_{rock} 883.2 cm⁻¹ observed. The shift in frequency of the antisymmetric stretching mode correlates relatively well with the N-H...Cl(2) bond lengths observed for other complexes exhibiting this type of hydrogen-bonding interaction.^{7,8} The change in the antisymmetric Sn-C

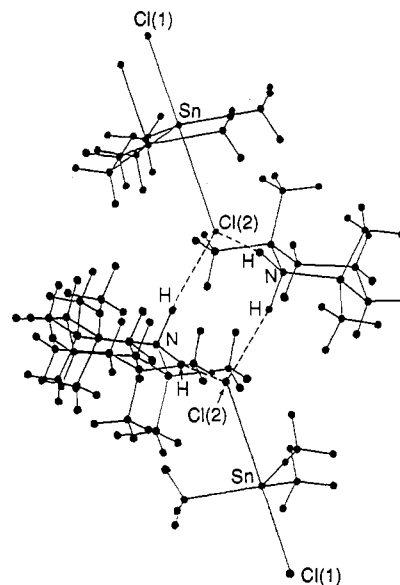


Figure 2. Portion of the molecular packing of [tmpH₂][Me₃SnCl₂] as viewed along the *b* axis. Hydrogen-bonding interactions are represented as dashed lines.

stretch is, as expected, not significant compared to other [cation][Me₃SnCl₂] complexes, while the interesting fundamental stretching mode, $\nu(\text{Sn-Cl})$, is IR inactive.⁹

It is of interest to compare structural parameters of [tmpH₂][Me₃SnCl₂] (1) with X-ray data reported for the same tin anion as a gegenion of two cationic metal clusters^{10,11} along with Me₃SnCl, as summarized in Table I. The Sn-Cl bond distances and the Cl-Sn-Cl bond angles appear to be the most informative bond parameters to compare for these complexes. Me₃SnCl is self-associated in the solid state, consisting of an infinite zigzag chain of Me₃SnCl molecules¹² and is monomeric in the gas phase.¹³ The dissimilar Sn-Cl distances in the solid-state structure of Me₃SnCl have been interpreted in terms of an intramolecular and an intermolecular Sn-Cl bond,¹² although the Sn-Cl contact (3.259 Å) is significantly shorter than the sum of their respective van der Waals radii (3.58 Å).⁷ The same tin anion of the Au(I) complex, although disordered about a crystallographic C₂ axis,¹⁴ exhibits equivalent Sn-Cl bond contacts and an essentially linear Cl-Sn-Cl bond angle. The apparent

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Table II. Selected NMR Parameters for Triorganotin Compounds

compd ^a	² J(¹ H- ¹¹⁹ Sn), Hz	¹ J(¹³ C- ¹¹⁹ Sn), Hz	δ(¹¹⁹ Sn), ppm
Me ₃ SnCl	58.5	379	165.7
[tmpH ₂][Me ₃ SnCl ₂]	60.0	400	120 ^c 56.5 ^d
[Et ₄ N][Me ₃ SnCl ₂]	70.5 ^b		-53 ^e
[Bu ₄ N][Me ₃ SnCl ₂]	70.8	522	-22.13

^aCDCl₃ solution, 33.3 mol %, 303 K, unless otherwise noted.

^bHolmes, R. R.; et al. *J. Organomet. Chem.* **1980**, *197*, 181. ^cCH₂Cl₂ solution, 0.2 M, 303 K. ^dCH₂Cl₂ solution, 0.2 M, 225 K. ^eReference 18a.

nonequivalence of the Sn-Cl bond contacts exhibited by the tin anion of the cationic Mo(IV) complex cannot be interpreted, since only two structural parameters were communicated.¹⁵ The self-association observed for Me₃SnCl in the solid state is apparently disrupted on melting, as demonstrated from reduced IR and Raman ν(Sn-Cl) stretching frequencies.¹⁶ The essentially linear Cl-Sn-Cl bond angle and dissimilar Sn-Cl bond interactions of **1**, then, would appear to reflect the influence of hydrogen bonding in the solid state for this complex. In the solid state, it seems reasonable to conclude that the protons of the tetramethylpiperidinium cation are involved in strong, hydrogen-bonding interactions with an axial chlorine of the tin anion and would be responsible for weakening the Sn-Cl(2) bonding interaction. Comparison of the structural distortions of the C-Sn-C and C-Sn-Cl bond angles of **1** with the complexes in Table I, as well, further reflects distortions from the idealized TBP geometry for the anion.

The solution-state ¹H, ¹³C{¹H}, and ¹¹⁹Sn{¹H} NMR spectra of **1**, along with data for related complexes, were measured, and selected data are summarized in Table II. The important information lies in the magnitudes of the ¹J(¹³C-¹¹⁹Sn), ²J(¹H-¹¹⁹Sn), and δ(¹¹⁹Sn). Since both the one-bond and the two-bond coupling constants are related via the Fermi contact term to the s electron density in the bond, their magnitudes have been used to infer valence electron distribution in tin-carbon bonds.¹⁷ The self-association observed for Me₃SnCl in the solid state is apparently disrupted on dissolution, as demonstrated from comparisons of the magnitude of the one- and two-bond coupling constants in solution-state¹⁸ and solid-state NMR studies.¹⁹ The magnitude of both the one- and two-bond coupling in **1** (60.0 and 400 Hz, respectively) as compared to the Et₄N and n-Bu₄N derivatives of [Me₃SnCl₂]⁻ appear to reflect the influence of hydrogen-bonding effects in solution. The interaction could be interpreted in terms of a redistribution of s electron density in the Sn-C bond, with a concomitant increase in the p character in the Sn-Cl bond in accordance with Bent's principle.²⁰ Comparison of the δ(¹¹⁹Sn) values for **1** with those of the same tin anion of the tetraalkylammonium derivatives appears to reflect the influence of hydrogen-bonding effects as well. A marked downfield shift for **1** compared to the other pentacoordinated tin anions is observed. This decrease in the shielding of the tin nucleus could be interpreted as a reduction of the Sn(5d)-Cl(3p) orbital overlap. Moreover, the tin chemical shifts for **1** are strongly temperature dependent. At the low-temperature limit, the structure of the tin anion could be described as distorted halfway between idealized four- and five-coordinate geometries.

The discussed results imply that reaction 1 represents actually an equilibrium situation which is shifted to the side of [tmpH₂][Me₃SnCl₂] at high concentration or low temperature. Experimental proof comes from further ¹¹⁹Sn NMR studies of this compound in solution. In the concentration range 0.03-1.20 M, δ(¹¹⁹Sn) changes from 170 to 59.7 ppm, the former value corresponding to a highly diluted solution of Me₃SnCl.^{18a} Increased shielding indicates formation of the [Me₃SnCl₂]⁻ anion, but only time-averaged signals are observed at 303 K. The signal at δ(¹¹⁹Sn) = 120 ppm for a 0.2 M solution of **1** at 273 K is shifted to δ = 56.6 ppm at 225 K. This result also indicates that Cl⁻ exchange is rapid on the NMR time scale even at low temperature. In a related study, the same result is obtained from CH₂Cl₂ solutions containing equivalent amounts of Me₃SnCl and pyridinium chloride, with δ(¹¹⁹Sn) changing from 160 to 25.8 ppm for solutions ranging in concentration from 0.02 to 2.2 M. In none of these cases was the ¹¹⁹Sn NMR signal for [Me₃SnCl₂]⁻ observed, which is extrapolated from the concentration dependence of a CH₂Cl₂ solution of [Bu₄N][Me₃SnCl₂] (δ(¹¹⁹Sn) = -17.3 ppm, c = 0.06 M; δ(¹¹⁹Sn) = -50.9 ppm, c = 1.5 M) to be -58 ppm. The increase in shielding with increasing coordination number is a well-known phenomenon in tin chemistry. However, the observed importance of hydrogen bonding on the stability of higher coordination tin complexes is, to our knowledge, a new feature, in the present case the competition of a Lewis acid and a protic acid for chloride as a base. It is conceivable that such an interaction will play an important role in the bioinorganic chemistry of organotin compounds.²¹ A full study of the influence of cation-anion interactions on the pentacoordinated state of triorganotin anions is forthcoming.

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Supplementary Material Available: Details of crystallographic data collection (Table S1), atomic coordinates (Table S2), full bond parameters (Table S3), and anisotropic and isotropic thermal parameters (Tables S4 and S5) (3 pages); observed and calculated structure factors (Table S6) (10 pages). Ordering information is given on any current masthead page.

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Intramolecular Entropy Changes for Transition-Metal Complex Redox Couples: Hexaammineruthenium(III/II) and -cobalt(III/II) Couples

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The entropy change associated with an electron-transfer reaction is equivalent to the difference in the reaction entropies (ΔS_{r,c}^o) for the two redox couples involved. A reaction entropy value can be derived from the temperature dependence of the electrode potential for a redox couple, and values of ΔS_{r,c}^o for a number of transition-metal complex couples have been reported.¹⁻⁵

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