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# Crystal structure of bis(2-aminopyridinium)dimethyltetrachlorostannate(IV) and its formation by hydrolysis of dimethyltin dichloride

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## Abstract

The structure of $(C_5H_7N_2)_2[Sn(CH_3)_2Cl_4]$ has been determined by X-ray diffraction. The compound crystallizes in the orthorhombic system, space group *Pbca* (No. 61), with unit cell dimensions $a$ 15.585(2), $b$ 17.561(2), $c$ 7.088(1) Å, and $Z = 4$. The structure consists of hydrogen-bonded chains of alternating $[Sn(CH_3)_2Cl_4]^{2-}$ anions and pairs of $C_5H_7N_2{}^+$ cations. Each *trans*-dimethyltetrachlorostannate(IV) octahedral unit is surrounded by four 2-aminopyridinium ions and is involved in ten hydrogen-bonding interactions with $d(N-H \cdots Cl)$ ranging from 3.242(12) to 3.463(12) Å. $^1H$ NMR data show that $(C_5H_7N_2)_2[Sn(CH_3)_2Cl_4]$ is formed along with 1,3-dichloro-1,1,3,3-tetramethyldistannoxane in the reaction of $Sn(CH_3)_2Cl_2$ and $C_5H_6N_2$ in moist $CDCl_3$; the fact that hydrolysis of the dimethyltin dichloride takes place is related to the relatively high basicity and low coordinating tendency of 2-aminopyridine.

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## Introduction

Reactions of alkyltin(IV) halides with bases in the presence of even low concentrations of water frequently produce alkyltin(IV) hydrates or hydrolyzates [1–3]. These reactions are of interest because of their relevance to organotin interactions with biological systems. This paper reports the crystal structure of $(C_5H_7N_2)_2[Sn(CH_3)_2Cl_4]$ and $^1H$ NMR data on the formation of the compound from mixtures of dimethyltin dichloride and 2-aminopyridine in moist $CDCl_3$.

## Experimental

Reagents and solvents were obtained commercially and used as such. Preparations were performed in systems open to the air. Crystals of the compound were prepared from $CDCl_3$ or $CH_2Cl_2/C_6H_{12}$ solutions of dimethyltin dichloride and 2-aminopyridine in a range of molar ratios. A well formed crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm mounted on a Philips PW 1100 diffractometer was used for determination of the cell dimensions and to measure intensity data.

*Crystal data.* $C_{12}H_{20}Cl_4N_4Sn$, $M = 480.822$, orthorhombic, space group *Pbca* (No. 61), $a$ 15.585(2), $b$ 17.561(2), $c$ 7.088(1) Å, $U$ 1939.9 Å$^3$, $Z = 4$, $D_c$ 1.646 g cm$^{-3}$, $F(000) = 952$, $\mu$(Mo-$K_\alpha$) 17.3 cm$^{-1}$.

*Data collection.* 1712 independent reflections in the range $2 < 2\theta < 50°$ were collected by the $\theta$–$2\theta$ step-scan method using Mo-$K_\alpha$ monochromated radiation ($\lambda$ 0.7107 Å). Reflections with $I > 3\sigma(I)$ were considered as observed (1292). The intensities were corrected for Lorentz and polarization effects, but not for absorption.

*Determination and refinement of the structure.* The positions of the chlorine atoms were obtained from a three-dimensional Patterson-Fourier synthesis. The remaining non-hydrogen atoms were located in a subsequent electron-density map. The hydrogen atoms were located from a Fourier difference map but not refined. Final refinements were carried out with anisotropic thermal parameters for all

Table 1

Fractional coordinates

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Sn | 0.0 | 0.0 | 0.0 |
| Cl(1) | 0.0047(1) | −0.1348(1) | −0.1608(2) |
| Cl(2) | 0.1610(1) | 0.0226(1) | −0.0946(2) |
| C(1) | −0.0378(4) | 0.0490(4) | −0.2596(9) |
| N(1) | 0.1879(3) | 0.1990(3) | 0.0267(6) |
| N(2) | 0.3077(3) | 0.1317(3) | 0.1090(8) |
| C(2) | 0.2705(3) | 0.1985(3) | 0.0816(7) |
| C(3) | 0.3122(3) | 0.2681(3) | 0.1098(7) |
| C(4) | 0.2683(4) | 0.3344(3) | 0.0763(8) |
| C(5) | 0.1827(4) | 0.3331(4) | 0.0170(8) |
| C(6) | 0.1446(3) | 0.2652(3) | −0.0097(7) |

non-hydrogen atoms. The final conventional $R$ factor was 0.0565 *. Scattering factors for all atoms were those incorporated in the program SHELX [4]. Positional parameters for the non-hydrogen atoms are listed in Table 1.

*$^1H$ NMR spectra.* Measurements were performed on a JEOL FX-90Q spectrometer. Chemical shifts were measured relative to the $CHCl_3$ resonance and referred to TMS.

## Results and discussion

The structure of the compound is shown in Fig. 1 with the atom-numbering scheme. Bond distances and angles are listed in Table 2. The structure is centrosymmetric at the tin atom. Each *trans*-dimethyltetrachlorostannate(IV) octahedral unit is surrounded by four 2-aminopyridinium cations and is involved in ten hydrogen bonds with $d(N-H \cdots Cl)$ ranging from 3.242(12) to 3.463(12) Å. The Cl(1) and Cl(2) atoms are respectively two- and three-coordinated to N atoms. Each $[Sn(CH_3)_2Cl_4]^{2-}$ anion is bonded in different ways to two pairs of $C_5H_7N_2^+$ cations, but all the 2-aminopyridinium units are equivalent. Each $C_5H_7N_2^+$ cation uses its imino hydrogen atom for hydrogen bonding to two chlorine atoms of a $[Sn(CH_3)_2Cl_4]^{2-}$ anion and its amino hydrogen atoms for hydrogen bonding to one chlorine in the same anion and two chlorine atoms in a neighboring anion. Thus the structure consists of hydrogen-bonded chains of alternating $[Sn(CH_3)_2Cl_4]^{2-}$ anions and pairs of $C_5H_7N_2^+$ cations. The structure differs from that of the analogous pyridinium compound, for which pairs of pyridinium cations and *trans*-dimethyl-

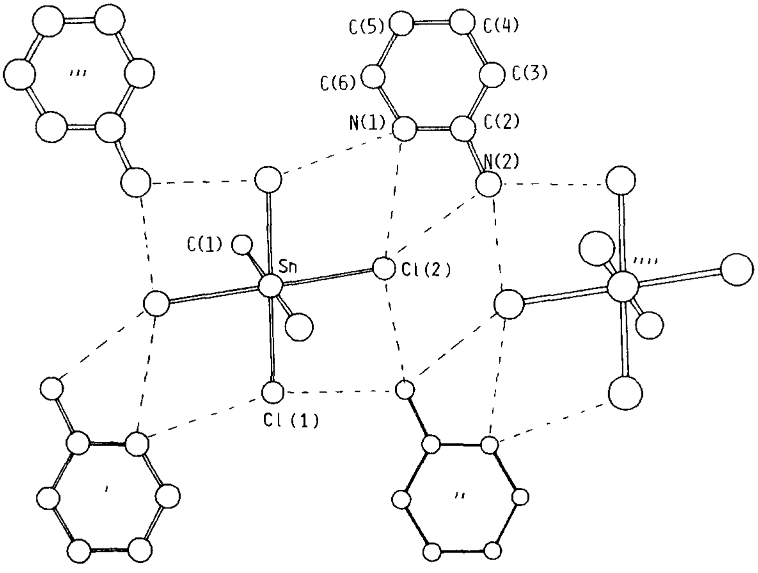

Fig. 1. Perspective drawing of the structure of $(C_5H_7N_2)_2[Sn(CH_3)_2Cl_4]$. (′) $-x, -y, -z$; (″) $1/2-x, -y, -1/2+z$; (‴) $1/2+x, y, 1/2-z$; (⁗) $1/2-x, -y, 1/2+z$.

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* $w = 1/(\sigma^2(F)+0.002F^2)$.

Table 2

Bond distances (Å) and angles (°)

| | | | |
|---|---|---|---|
| *Cation* | | | |
| N(1)–C(2) | 1.346(6) | C(6)–N(1)–C(2) | 122.1(5) |
| C(2)–C(3) | 1.399(7) | N(1)–C(2)–C(3) | 118.7(5) |
| C(3)–C(4) | 1.371(8) | C(2)–C(3)–C(4) | 119.1(5) |
| C(4)–C(5) | 1.399(8) | C(3)–C(4)–C(5) | 120.9(5) |
| C(5)–C(6) | 1.345(8) | C(4)–C(5)–C(6) | 118.5(5) |
| C(6)–N(1) | 1.368(8) | C(5)–C(6)–N(1) | 120.6(5) |
| C(2)–N(2) | 1.323(7) | N(1)–C(2)–N(2) | 117.9(5) |
| | | N(2)–C(2)–C(3) | 123.4(4) |
| *Anion* | | | |
| Sn–C(1) | 2.115(6) | C(1)–Sn–Cl(1) | 89.8(2) |
| Sn–Cl(1) | 2.628(1) | C(1)–Sn–Cl(2) | 89.0(2) |
| Sn–Cl(2) | 2.627(1) | Cl(1)–Sn–Cl(2) | 89.9(0) |
| *Hydrogen bonds* | | | |
| N(1) ··· Cl(1) | 3.344(12) | | |
| N(1) ··· Cl(2) | 3.242(12) | | |
| N(2) ··· Cl(2) | 3.313(12) | | |
| N(2) ··· Cl(1'''') | 3.349(12) | | |
| N(2) ··· Cl(2'''') | 3.463(12) | | |

tetrachlorotin(IV) anions are hydrogen bonded to form discrete $(C_5H_6N)_2[Sn(CH_3)_2Cl_4]$ units [5].

The Sn–C bond length in the 2-aminopyridinium compound is close to values reported for other dimethyltetrachlorotin(IV) compounds [3,5], but appreciable differences are found in Sn–Cl bond lengths. In the 2-aminopyridinium compound there are two practically identical Sn–Cl bond lengths, but two different Sn–Cl bond lengths are found in the pyridinium compound (2.625(9) and 2.603(2) Å [5]), and in the compound bis[2-(aminocarbonyl)anilinium]dimethyltetrachlorostannate (IV) dihydrate (2.6047(5) and 2.6189(5) Å [3]), where *trans*-dimethyltetrachlorotin (IV) anions are held by a network of hydrogen bonds into a three-dimensional lattice. The amount of lengthening of the Sn–Cl bonds in these complexes can be related to the extent of hydrogen bond formation and indicates that the net effect of hydrogen-bonded interactions is greatest in the 2-aminopyridinium compound. The fact that the same bond length is found for Sn–Cl(1) and Sn–Cl(2) in this compound can be ascribed to a balance of factors, namely the number of hydrogen bonds formed by each chlorine or nitrogen atom, the type of nitrogen atom (NH or $NH_2$), and possibly the presence of Cl–Sn–Cl *trans* effects.

Analysis of $^1H$ NMR spectra of the system $Sn(CH_3)_2Cl_2/C_5H_6N_2$ in moist $CDCl_3$ shows that crystals of $(C_5H_7N_2)_2[Sn(CH_3)_2Cl_4]$ are formed through reactions (1,2).

$$4Sn(CH_3)_2Cl_2 + 2H_2O + 4C_5H_6N_2 \rightleftharpoons [Cl(CH_3)_2Sn{-}O{-}Sn(CH_3)_2Cl]_2 + 4C_5H_7N_2^+ + 4Cl^- \qquad (1)$$

$$Sn(CH_3)_2Cl_2 + 2C_5H_7N_2^+ + 2Cl^- \rightleftharpoons (C_5H_7N_2)_2[Sn(CH_3)_2Cl_4] \qquad (2)$$

Formation of 1,3-dichloro-1,1,3,3-tetramethyldistannoxane is shown by the appearence of two 1 : 1 signals at $\delta$ 1.17, $J(^{119}Sn{-}^1H)$ 80.3, $J(^{117}Sn{-}^1H)$ 77.0 Hz, and

$\delta$ 1.23, $J(^{119}Sn-^{1}H)$ 84.3, $J(^{117}Sn-^{1}H)$ 80.6 Hz, in agreement with reported values for this compound [2]. The NH resonance displayed by the initial spectra of the mixtures at lower field with respect to the free base is consistent with the presence of protonated 2-aminopyridine in solution. The spectra in the methyl region also show a concentration dependent resonance with intensity falling to zero as $(C_5H_7N_2)_2[Sn(CH_3)_2Cl_4]$ separate (e.g., $\delta$ 1.36, $J(^{119}Sn-^{1}H)$ 83.2, $J(^{117}Sn-^{1}H)$ 79.5 Hz for a solution of 0.09 $M$ $Sn(CH_3)_2Cl_2$ and 0.14 $M$ $C_5H_6N_2$, and $\delta$ 1.21, $J(^{119}Sn-^{1}H)$ 72.9, $J(^{117}Sn-^{1}H)$ 69.3 Hz for a solution of 0.15 $M$ $Sn(CH_3)_2Cl_2$ and 0.1 $M$ $C_5H_6N_2$). These results can be accounted for in terms of rapid reversible coordination of $Sn(CH_3)_2Cl_2$ with chloride ion formed by hydrolysis and/or with 2-aminopyridine. The spectrum of a saturated solution of $(C_5H_7N_2)_2[Sn(CH_3)_2Cl_4]$ ($< 5 \times 10^{-3}$ $M$) shows in the methyl region a resonance at $\delta$ 1.25, $J(^{119}Sn-^{1}H)$ 72.2, $J(^{117}Sn-^{1}H)$ 69.3, shifted to $\delta$ 1.30, $J(^{119}Sn-^{1}H)$ 89.1, $J(^{117}Sn-^{1}H)$ 85.0 Hz, by addition of 0.01 $M$ $[(C_6H_5)_4As]Cl \cdot H_2O$.

Hydrolysis of $Sn(CH_3)_2Cl_2$ in moist organic solvents in the presence of bases has been described previously [2,3]. The reaction of dimethyltin dichloride and anthranilamide in chloroform has been found to give the anthranilinium salt of the anion $[Sn(CH_3)_2Cl_4]^{2-}$, in a process analogous to the reaction involving 2-aminopyridine, but the suggested hydrolysis product is $(CH_3)_2SnO$ [3]. The strength of the base involved is, of course, an important factor in the ease of these hydrolysis reactions. It is significant, however, that in the reaction of $Sn(CH_3)_2Cl_2$ with 1-methylimidazole, carried out under conditions similar to those used for the reaction of 2-aminopyridine, coordination of the ligand is observed [6] instead of hydrolysis, although the two bases have similar $pK_a$ values (7.1 [1-methylimidazole] and 6.7 [2-aminopyridine]) It can be inferred that formation of aquo or hydroxo complexes of $Sn(CH_3)_2Cl_2$ is the first step in the hydrolysis, and this is prevented by predominant formation of adducts with the base in the case of 1-methylimidazole. The fact that 2-aminopyridine is not as effective a ligand as 1-methylimidazole, probably because of steric effects, is supported by comparison of spectra of mixtures of the bases and $Sn(CH_3)_3Cl$ in $CDCl_3$, in which no hydrolysis occurs. The methyl resonances of free 0.37 $M$ $Sn(CH_3)_3Cl$ at $\delta$ 0.65, $J(^{119}Sn-^{1}H)$ 57.8, $J(^{117}Sn-^{1}H)$ 55.2 Hz, is shifted to $\delta$ 0.68, $J(^{119}Sn-^{1}H)$ 69.1, $J(^{117}Sn-^{1}H)$ 66.0 Hz, by addition of 0.37 $M$ 1-methylimidazole, consistent with adduct formation, whereas no appreciable changes occur in a solution of the tin chloride and an equimolar amount of 2-aminopyridine.

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