

Studies of the reaction of dimethyltin dichloride with mercaptoacetic acid in the presence of amines and crystal structure of $[(n\text{-Pr})_3\text{NH}][\text{Me}_2\text{Sn}(\mu^2\text{-SCH}_2\text{COO})\text{Cl}]$

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Abstract

A series of new five-coordinated ionic organotin(IV) complexes with general formula $[\text{Q}][\text{Me}_2\text{Sn}(\mu^2\text{-SCH}_2\text{COO})\text{Cl}]$ (Q = diethylammonium, triethylammonium, di-*i*-propylammonium, tripropylammonium, tri-*n*-butylammonium, pyrimidium, 3-picolinium, methylphenylammonium, dimethylphenylammonium) were synthesized by the reaction of mercaptoacetic acid with dimethyltin dichloride in the presence of an organic base. These complexes have been characterized by elemental analyses, IR and ¹H NMR spectroscopies. The crystal structure of $[(n\text{-Pr})_3\text{NH}][\text{Me}_2\text{Sn}(\mu^2\text{-SCH}_2\text{COO})\text{Cl}]$ was determined by X-ray crystallography. The structure consists of an anion part, and a tri-*n*-propylammonium cation part as a counterion. The tin atom has a distorted *cis*-tbp geometry with two carbon and one sulfur atoms occupying the equatorial positions and the O atom and Cl atom occupying the axial positions. The organotin anion and its counterion are connected through a hydrogen bond between the N atom in the ammonium and the O atom of the carbonyl group with a N–O length of 2.766 Å.

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Keywords: Five-coordinated Tin(IV) complex; Ionic organotin; Crystal structure

1. Introduction

While most of the studies on organotin compounds have been focused on the organotin carboxylates owing to their diversified molecular structures [1,2] and wide range of applications, such as biological activities [3–5], organotin sulfides are another group of organotin compounds that have drawn much current attention because of their good thermal stability and their applications as stabilizers for PVC and related plastic materials. Although compounds of general formulae $\text{R}_3\text{Sn}(\text{SR}')$, $\text{R}_2\text{Sn}(\text{SR}')_2$ and $\text{Sn}(\text{SR}')_4$ were all claimed

to have stabilization properties, diorganotin sulfur compounds, with the general formula $\text{R}_2\text{Sn}(\text{SR}')_2$ are still the mostly studied as the stabilizers [6].

Recently, much interest of organotin sulfide compounds has been concentrated on the syntheses and structure determinations of a series of organotin 1,2 dithiolate complexes, the ligand used include aliphatic derivative, e.g., $\text{SCH}_2\text{CH}_2\text{S}(\text{edt})$ [7], SCH_2CHMeS [7], alkenyl derivatives [8], e.g., $\text{SCH}=\text{CHS}$ [9], $\text{SC}(\text{CN})=\text{C}(\text{CN})\text{S}(\text{mnt})$ [9], aryl derivatives, $\text{SC}_6\text{H}_4\text{S}(\text{bdt})$ [10]. The key feature of this type of organotin compounds lies in that they are made up of two parts, an anionic unit which consists of a *cis*-tbp C_2SnXS_2 , and a cation which is an organoammonium. In the reaction of the mnt ($\text{mnt} = (\text{CN})_2\text{C}_2\text{S}_2$) ligand with MeSnCl_3 and PhSnCl_3 in the presence of

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2.2.6. $[Me_2SnCl(SCH_2COO)][pyridinium]$ **6**

Yield: 56%, m.p. >220 °C. 1H NMR ($CDCl_3$): δ 0.87(6H, t, $SnCH_3 \cdot 2$, $J_{Sn-H} = 74.0$), 3.71(2H, t, SCH_2 , $^3J_{Sn-H} = 42.8$ Hz), 7.82(2H, m, *o*-H), 8.15(1H, m, *p*-H), 8.28(2H, m, *m*-H) ppm. IR (KBr, cm^{-1}): 3089 $\nu(HN^+)$, 1582 $\nu(OCO)_{asym}$, 1395 $\nu(OCO)_{sym}$, 555 $\nu(Sn-C)$, 432 $\nu(Sn-O)$. Anal. Calc. for $C_9H_{14}ClNO_2SSn$: C, 30.50; H, 3.99; N, 3.95. Found: C, 30.78; H, 4.39; N, 4.17%.

2.2.7. $[Me_2SnCl(SCH_2COO)][picolinium]$ **7**

Yield: 65%, m.p. >220 °C. 1H NMR ($CDCl_3$): δ 0.87(6H, t, $SnCH_3 \cdot 2$, $J_{Sn-H} = 73.8$), 2.57(3H, s, CH_3), 3.71(2H, t, SCH_2 , $^3J_{Sn-H} = 2.8$ Hz), 7.75–8.22(4H, m, C_5H_4) ppm. IR (KBr, cm^{-1}): 3093 $\nu(HN^+)$, 1554 $\nu(OCO)_{asym}$, 1400 $\nu(OCO)_{sym}$, 552 $\nu(Sn-C)$, 436 $\nu(Sn-O)$. Anal. Calc. for $C_{10}H_{16}ClNO_2SSn$: C, 32.60; H, 4.39; N, 3.80. Found: C, 32.78; H, 3.89; N, 3.67%.

2.2.8. $[Me_2SnCl(SCH_2COO)][H_2NPhMe]$ **8**

Yield: 60%, m.p. >220 °C. 1H NMR ($CDCl_3$): δ 0.79(6H, t, $SnCH_3 \cdot 2$, $J_{Sn-H} = 74.3$), 2.97(6H, s, NCH_3), 3.47(2H, t, SCH_2 , $^3J_{Sn-H} = 46.8$ Hz), 7.35–8.42(5H, m, C_6H_5) ppm. IR (KBr, cm^{-1}): 3051 $\nu(HN^+)$, 1571 $\nu(OCO)_{asym}$, 1390 $\nu(OCO)_{sym}$, 558 $\nu(Sn-C)$, 434 $\nu(Sn-O)$. Anal. Calc. for $C_{11}H_{18}ClNO_2SSn$: C, 34.54; H, 4.75; N, 3.66. Found: C, 34.24; H, 4.74; N, 3.56%.

2.2.9. $[Me_2SnCl(SCH_2COO)][HNPhMe_2]$ **9**

Yield: 71%, m.p. 101–103 °C. 1H NMR ($CDCl_3$): δ 0.80(6H, t, $SnCH_3 \cdot 2$, $J_{Sn-H} = 74.4$), 2.97(6H, s, $NCH_3 \cdot 2$), 3.47(2H, t, SCH_2 , $^3J_{Sn-H} = 46.8$ Hz), 7.35–8.42(5H, m, C_6H_5) ppm. IR (KBr, cm^{-1}): 3027 $\nu(HN^+)$, 1569 $\nu(OCO)_{asym}$, 1380 $\nu(OCO)_{sym}$, 560 $\nu(Sn-C)$, 436 $\nu(Sn-O)$. Anal. Calc. for $C_{12}H_{20}ClNO_2SSn$: C, 36.35; H, 5.09; N, 3.53. Found: C, 36.30; H, 4.79; N, 3.67%.

2.3. Crystal structure determination

The colorless crystals of $[(n-Pr)_3NH][Me_2Sn(\mu^2-SCH_2COO)Cl]$ suitable for X-ray crystallography study were obtained from a dilute ethanol solution. A crystal with approximate dimensions of $0.40 \times 0.25 \times 0.20$ mm was selected for data collection on a BRUKER SMART 1000 diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structure was solved by direct methods and refined on F^2 with anisotropic parameters for all non-hydrogen atoms. All calculations were performed using SHELXL program on PC computer.

Of the 5705 reflections measured (max = 26.52°), 3985 were independent, of which 3185 had $I > 2\sigma(I)$. The positions of the non-hydrogen atoms were found from the three-dimensional Patterson and Fourier synthesis. Block-diagonal least squares refinement with

Table 1
Crystal and structure refinement data for compound **4**

Empirical formula	$C_{13}H_{30}ClNO_2SSn$
Formula weight	418.58
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	10.497(5)
<i>b</i> (Å)	10.515(4)
<i>c</i> (Å)	10.844(5)
α (°)	74.734(7)
β (°)	68.943(7)
γ (°)	62.203(6)
Volume (Å ³)	981.4(8)
<i>Z</i>	2
Absorption coefficient (mm ⁻¹)	1.543
<i>F</i> (000)	428
Crystal size (mm)	$0.40 \times 0.25 \times 0.20$
θ Range for data collection	$2.82\text{--}24.45^\circ$
Reflections collected /	5705
Independent reflections [R_{int}]	3985 [0.0232]
Data/restraints/parameters	3985/0/175
Goodness-of fit on F^2	0.990
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0327$, $wR_2 = 0.0730$
<i>R</i> indices (all data)	$R_1 = 0.0474$, $wR_2 = 0.0786$
Goodness-of-fit on F^2	0.991
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0327$, $wR_2 = 0.0730$
<i>R</i> indices (all data)	$R_1 = 0.0474$, $wR_2 = 0.0786$
Largest diff. peak and hole ($e \text{ \AA}^{-3}$)	0.478 and -0.383

isotropic temperature factors for hydrogen atoms, and non isotropic for other atoms, gave the final $R = 0.0704$ ($R_w = 0.0786$, $S = 0.990$). Final atomic coordinates are listed in Table 1, selected bond lengths and bond angles in Table 2. The structure of **1**, together with atomic numbering scheme, is depicted in Fig. 1.

Table 2
Bond lengths (Å) and angles (°) for $[(n-Pr)_3NH][Me_2Sn(\mu^2-SCH_2COO)Cl]$

Sn(1)–C(4)	2.115(4)	O(1)–Sn(1)–S(1)	81.28(7)
Sn(1)–C(3)	2.116(4)	C(4)–Sn(1)–Cl(1)	95.71(14)
Sn(1)–O(1)	2.213(2)	C(3)–Sn(1)–Cl(1)	93.81(13)
Sn(1)–S(1)	2.4026(12)	O(1)–Sn(1)–Cl(1)	170.72(7)
Sn(1)–Cl(1)	2.5138(13)	S(1)–Sn(1)–Cl(1)	89.61(4)
O(1)–C(1)	1.265(4)	C(11)–N(1)–C(8)	114.1(3)
O(2)–C(1)	1.236(4)	C(11)–N(1)–C(5)	112.8(2)
S(1)–C(2)	1.802(4)	C(8)–N(1)–C(5)	110.6(2)
C(1)–C(2)	1.517(5)	C(1)–O(1)–Sn(1)	21.3(2)
C(5)–C(6)	1.475(5)	C(2)–S(1)–Sn(1)	98.45(13)
C(6)–C(7)	1.511(5)	O(2)–C(1)–O(1)	123.2(3)
C(8)–C(9)	1.502(5)	O(2)–C(1)–C(2)	117.5(3)
C(9)–C(10)	1.510(5)	O(1)–C(1)–C(2)	119.3(3)
C(11)–C(12)	1.498(5)	C(1)–C(2)–S(1)	117.1(3)
C(12)–C(13)	1.522(5)	C(6)–C(5)–N(1)	114.0(3)
C(4)–Sn(1)–C(3)	121.89(19)	C(5)–C(6)–C(7)	111.7(3)
C(4)–Sn(1)–O(1)	90.10(15)	C(9)–C(8)–N(1)	114.5(3)
C(3)–Sn(1)–O(1)	89.22(15)	C(8)–C(9)–C(10)	110.4(3)
C(4)–Sn(1)–S(1)	117.60(13)	N(1)–C(11)–C(12)	114.1(3)
C(3)–Sn(1)–S(1)	119.65(14)	C(11)–C(12)–C(13)	111.1(3)

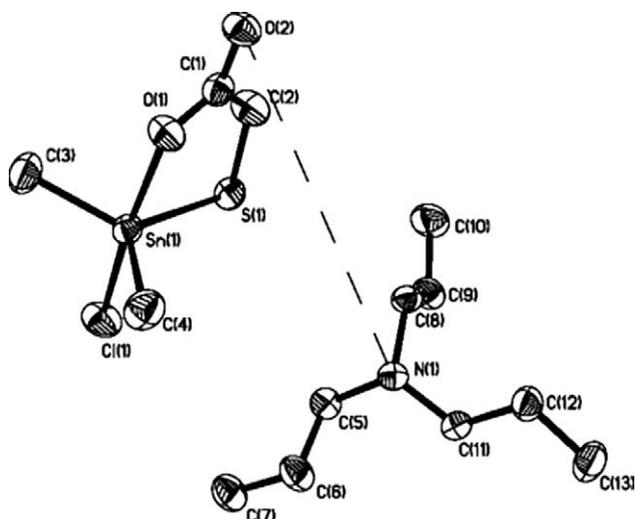


Fig. 1. Molecular structure of $[(n\text{-Pr})_3\text{NH}][\text{Me}_2\text{Sn}(\mu^2\text{-SCH}_2\text{COO})\text{Cl}]$, H-atoms omitted for clarity.

3. Results and discussion

3.1. IR

In the spectrum of the ligand, the strong, well-developed band at 1600 cm^{-1} is assigned to $\nu(\text{S-H})$. However, the absence of the characteristic absorption of $\nu(\text{S-H})$ indicates the S involving in the coordination to tin atom. Medium to weak bands in the region $430\text{--}453\text{ cm}^{-1}$ are assigned to Sn–O, those in the region $548\text{--}560\text{ cm}^{-1}$ indicate the presence of Sn–C bands [15]. The absorption frequencies of asymmetry ($\nu\text{CO}_2^{\text{as}}$) and symmetry (νCOO^{s}) of carbonyl groups are in the region $1554\text{--}1620$ and $1347\text{--}1403\text{ cm}^{-1}$, respectively. The difference between the two frequencies ($\Delta\nu\text{CO}_2$) is $154\text{--}171\text{ cm}^{-1}$. This is much lower than the $\Delta\nu\text{COO}$ value for a monodentate carboxylate. This can be ascribed to the fact that there exists a strong hydrogen bonding between N atom in the ammonium ion and the O atom in the carbonyl group. The carbonyl oxygen donates part of its electrons to the hydrogen bonding, which makes the difference between the absorption frequencies of asymmetry ($\nu\text{COO}^{\text{as}}$) and symmetry (νCOO^{s}) of carbonyl groups decrease.

3.2. ^1H NMR

^1H NMR spectra of the compounds are mainly composed of three parts: methyl protons (SnCH_3), methylene protons in SCH_2 moiety and amine protons. The existence of the hydrogen bonding between protons in R_3HN^+ and carbonyl ($\text{C}=\text{O}$) oxygens cause the ammonium protons to appear in a much lower field range from 10 to 11 ppm as a weak signal than those in the original amines. In some cases, the rapid exchange of ammonium protons with deuterated solvent would

cause the weak signals to disappear. Methyl protons are in the region of $0.77\text{--}0.87$ ppm. The chemical shifts of the protons in SCH_2 exhibit signals at $3.41\text{--}3.71$ ppm as a triplet which is caused by the long distance ($^{119}\text{Sn}\text{--}^1\text{H}$) coupling. The spin–spin coupling constant $^3J(^{119}\text{Sn}\text{--}^1\text{H})$ is in the range $37.4\text{--}46.8$ Hz. Protons on the carbon atoms of the ammonium ions have observed in their normal positions.

3.3. Crystal structure

The molecular structure and molecular packing of **4**, $[(n\text{-Pr})_3\text{NH}][\text{Me}_2\text{Sn}(\mu^2\text{-SCH}_2\text{COO})\text{Cl}]$, are shown in Figs. 1 and 2, respectively. The crystal data are listed in Table 1. Selected bond lengths and bond angles are in Table 2.

The Fig. 1 shows that the tin atom in anion is coordinated by five atoms with O(1) and Cl(1) at axial positions and C(3), C(4), S(1) forming the equatorial plane. The anion has a slightly-distorted *cis*-trigonal bipyramidal geometry around tin atom with the Sn–S–C–O metallocycle having envelope conformation. Few examples of *cis*-tbp geometries are found in the structural literature of triorganotin carboxylate compounds. The structure of the $[\text{Me}_2\text{SnCl}(\text{mercaptoacetato})]$ anion in the present stannate is similar to that in literature in that both compounds possess a five-membered chelate ring. The axial skeleton is a little bent, (Cl–Sn–O angle of 170.72°). In such a structure, the sum of the angles between the tin atom and the equatorial ligating atoms (i.e. two C atoms and one S atom) is the $359.1(2)^\circ$ compared to the ideal octahedral value of 360° . The distribution of these 360° , which should normally be 120° for each angle, is almost equal with C(4)–Sn(1)–C(3), C(4)–Sn(1)–S(1) and C(3)–Sn(1)–S(1) being $121.89(19)^\circ$, $117.60(13)^\circ$ and $119.65(14)^\circ$, respectively. This indicates that the Sn atom is almost exactly on the equatorial plane. It is displaced only 0.0443 \AA out of the plane defined by C(3), C(4), S(1), which well agrees with the ideal

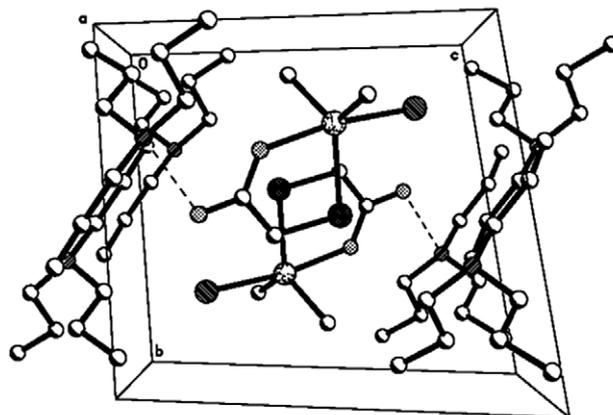


Fig. 2. Cell packing of $[(n\text{-Pr})_3\text{NH}][\text{Me}_2\text{Sn}(\mu^2\text{-SCH}_2\text{COO})\text{Cl}]$.

TBP. The Fig. 2 shows that there is existence of mutual interaction through the hydrogen-bonding between the cation and the anion moieties; the distance of N–O is 2.766 Å, which is much shorter than the sum of Van der Waals radii for N and O of 3.2 Å. The hydrogen bonding greatly affects the distribution of the electrons on the carbonyl group, this is observed by the two identical C–O bond distances at 1.237(4) Å (O(1)–C(23)) and 1.261(4) Å (O(2)–C(23)). This is in agreement with the lowering value of the difference between the absorption frequencies of asymmetry ($\nu_{\text{CO}_2^{\text{as}}}$) and symmetry ($\nu_{\text{CO}_2^{\text{s}}}$) of carbonyl groups.

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Appendix A. Supplementary data

Crystallographic data for the structures reported in this paper have been deposited with Cambridge Crystallographic Data Center and allocated the deposition number CCDC 264151 for 4. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK

(fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.04.022.

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