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Synthesis and Molecular Structures of Six-Coordinate Stannabicyclooctanes, $ROOCCH_2CH_2Sn(S_2CNMe_2)(XCH_2CH_2)_2Y$ (X = O, S; Y = O, S, NMe)

Ok-Sang Jung, Jong Hwa Jeong, and Youn Soo Sohn*

Division of Chemistry, Korea Institute of Science and Technology, Seoul 136-791, Korea

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New hexacoordinate stannabicyclooctanes $ROOCCH_2CH_2Sn(L)(XCH_2CH_2)_2Y$ (**1** R = Me, L = Me_2NCS_2, X = S, Y = O; **2** R = Me, L = Cl, X = S, Y = O; **3** R = Me, L = Me_2NCS_2, X = S, Y = S; **4** R = Me, L = Me_2NCS_2, X = O, Y = NMe; **5** R = Et, L = Me_2NCS_2, X = O, Y = NMe) have been prepared and characterized. The molecular structures of the representative compounds **1** and **5** were determined by X-ray analysis. **1** crystallizes in the triclinic space group $P\bar{1}$ ($Z = 2$) with $a = 10.514$ (2) Å, $b = 11.617$ (2) Å, $c = 8.071$ (2) Å, $\alpha = 107.23$ (2)°, $\beta = 108.12$ (2)°, $\gamma = 91.51$ (2)°, and $V = 887.2$ (5) Å^3. The structure was refined to $R = 0.026$. **5** crystallizes in the monoclinic space group *Pnma* ($Z = 4$) with $a = 15.080$ (2) Å, $b = 9.765$ (1) Å, $c = 13.120$ (2) Å, and $V = 1932.0$ (6) Å^3. The structure was refined to $R = 0.045$. Hexacoordination around the tin atom is achieved by a Sn–Y transannular dative bond (Sn–O, 2.615 (2) Å for **1**; Sn–N, 2.322 (7) Å for **5**) and a chelating dithiocarbamate in both structures. For **1**, however, unusually unsymmetrical chelation of the dithiocarbamate ligand (Sn–S(1), 3.094 (1) Å; Sn–S(2), 2.492 (1) Å) resulted in a highly distorted octahedral arrangement in contrast to the isobidentate chelation of the dithiocarbamate ligand in **5**. The IR and ^1H and ^{119}Sn NMR data have shown that **3** and **4** have the structures similar to those of **1** and **5**, respectively, both in the solid state and in solution and that their coordinate structures are retained in solution.

Introduction

Stannabicyclooctanes[1-8] of the type $R_2Sn(XCH_2CH_2)_2Y$ (X = O, S, CH_2; Y = O, S, NMe; R = Cl, alkyl, aryl) have received remarkable attention in recent years because of their structural interests due to transannular Sn–Y interaction and because of their mechanistic aspect of intramolecular ligand exchange. X-ray studies[5,8] on some selected stannabicyclooctanes have shown that their structure is basically trigonal bipyramidal. However, since the bond order of Sn–Y interaction depends strongly on the electronegativity of the ligating atoms (X) and groups (R) and the nature of the donating atom Y itself, coordinate structures intermediate between tetrahedral and trigonal bipyramidal are observed.[5,8]

In order to expand the coordination sphere of the bicyclic stannatranes we have prepared new hexacoordinate stannabicyclooctanes $ROOCCH_2CH_2Sn(S_2CNMe_2)(XCH_2CH_2)_2Y$ (R = Me, Et; X = O, S; Y = O, S, NMe) by employing potentially bidentate ester and dithiocarbamate groups instead of simple alkyl or aryl group. In this paper important structural features of the isolated compounds both in the solid state and in solution will be discussed by means of spectral data along with a pair of crystal structures of representative compounds **1** and **5**.

Experimental Section

All manipulations were performed under dinitrogen atmosphere with the use of standard Schlenkware techniques. Chemicals were reagent grade from commercial sources and used without further purification. Solvents were dried prior to use when necessary. Chemical analyses were carried out by the Chemical Analysis Laboratory at KIST. The molecular weights were determined cryoscopically in benzene by using a Cryette A automatic cryoscope. The infrared spectra in the 4000–400-cm^{-1} region were measured on KBr pellets with an Analect Instrument fx 6160 FT-IR spectrometer. All NMR spectra were measured in chloroform solution. ^1H NMR spectra were recorded on a JEOL JNM DMX 60 or a Bruker AM-200 spectrometer, and ^{119}Sn NMR spectra on a Bruker AM-200 operating at 74.63 MHz (^{119}Sn) in pulse mode with Fourier transform at ambient temperature (23 ± 2 °C). The chemical shifts are relative to internal Me_4Si (^1H) and external Me_4Sn (^{119}Sn) for the indicated nuclei.

$CH_3OOCCH_2CH_2SnCl_3$ and $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)Cl_2$ were prepared by the literature[9,10] and author's[11] procedures, respectively.

Synthesis of $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)(SCH_2CH_2)_2O$ (1). $O(CH_2CH_2SH)_2$ (1.38 g, 10 mmol) and sodium (0.51 g, 22 mmol) in 100 mL of methanol were stirred for 1 h at 50 °C. The solution was added dropwise to a solution of $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)Cl_2$ (3.97 g, 10 mmol) in 100 mL of benzene, and the resulting solution was stirred for 2 h at room temperature. The reaction mixture was cooled to about 0 °C, and the NaCl formed was removed by filtration. The solvent from the filtrate was removed under reduced pressure at 25 °C. The resultant solid was recrystallizd from benzene. The colorless crystalline solid (mp 146–147 °C) was obtained in 80% yield. MW measured: 448.1 (theory: 462.2). Anal. Calcd for $C_{11}H_{21}NO_3S_4Sn$: C, 28.50; H, 4.58; N, 3.03. Found: C, 28.41; H, 4.53; N, 2.96.

Synthesis of $CH_3OOCCH_2CH_2SnCl(SCH_2CH_2)_2O$ (2). $O(CH_2CH_2SH)_2$ (1.38 g, 10 mmol) and sodium (0.51 g, 22 mmol) in 100 mL of methanol were stirred for 1 h at 50 °C. The solution was added dropwise to a solution of $CH_3OOCCH_2CH_2SnCl_3$ (3.12 g, 10 mmol) in 100 mL of benzene. Then the reaction mixture was treated in the same manner as used for the preparation of **1**. The crude product was recrystallized from a benzene–ethanol pair (1:10). The colorless crystalline solid (mp 54–55 °C) was obtained in 72% yield. MW measured: 389.2 (theory: 377.5).

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Anal. Calcd for $C_8H_{15}ClO_3S_2Sn$: C, 25.46; H, 4.01. Found: C, 25.40; H, 4.02.

Synthesis of $CH_3OOCCH_2CH_2Sn(S_2CNMe_3)(SCH_2CH_2)_2S$ (3). A solution of $S(CH_2CH_2SH)_2$ (1.54 g, 10 mmol) and sodium (0.51 g, 22 mmol) in 100 mL of methanol was reacted with $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)Cl_2$ (3.97 g, 10 mmol) in 100 mL of benzene according to the same procedure for 1. The resultant solid was recrystallized from a benzene–*n*-hexane solvent pair (1:1). The pale yellow crystalline solid (mp 109 °C) was obtained in 74% yield. MW measured: 453.7 (theory: 478.3). Anal. Calcd for $C_{11}H_{21}NO_2S_5Sn$: C, 27.62; H, 4.45; N, 2.93. Found: C, 27.90; H, 4.45; N, 2.91.

Synthesis of $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)(OCH_2CH_2)_2NMe$ (4). $MeN(CH_2CH_2OH)_2$ (1.19 g, 10 mmol) and sodium (0.51 g, 22 mmol) in 100 mL of methanol were refluxed for 2 h. The solution was added dropwise to a solution of $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)Cl_2$ (3.97 g, 10 mmol) in 100 mL of benzene, and the resulting solution was stirred for 4 h at 50 °C. The NaCl was removed by filtration. The filtrate was condensed to approximately 20 mL, and then *n*-hexane was added slowly to the filtrate to precipitate the product. The white solid (mp 88–90 °C) was obtained in 80% yield. MW measured: 427.1 (theory: 443.1). Anal. Calcd for $C_{12}H_{24}N_2O_4S_2Sn$: C, 32.52; H, 5.46; N, 6.32. Found: C, 31.90; H, 5.51; N, 6.17.

Synthesis of $CH_3CH_2OOCCH_2CH_2Sn(S_2CNMe_2)(OCH_2CH_2)_2NMe$ (5). $MeN(CH_2CH_2OH)_2$ (1.19 g, 10 mmol) and sodium (0.51 g, 22 mmol) in 100 mL of ethanol were refluxed for 2 h. The solution was added dropwise to a solution of $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)Cl_2$ (3.97 g, 10 mmol) in 100 mL of benzene, and then the solution was stirred for 4 h at 50 °C. The NaCl formed was removed by filtration. The solvent from the filtrate was evaporated, resulting in a white solid. The solid product was recrystallized from a benzene–ethyl ether pair (1:4) to yield a colorless crystalline solid (mp 129–131 °C) in 76% yield. Anal. Calcd for $C_{13}H_{26}N_2O_4S_2Sn$: C, 34.15; H, 5.73; N, 6.13. Found: C, 34.10; H, 5.77; N, 6.12.

Crystallographic Analysis of 1 and 5. All the crystallographic data were obtained on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.709\,30$ Å, $\lambda(K\alpha_2) = 0.713\,59$ Å) at an ambient temperature of 23 ± 2 °C. The three intensity standards were monitored during intensity data collections. The data were corrected for Lorentz-polarization effects, decay, and absorption with ψ-scan data. The structure were solved by the heavy-atom method or direct method and Fourier difference techniques[12] and were refined by means of full-matrix least-squares procedures. The non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated by using a C–H distance of 1.08 Å. All calculations were performed on an IBM 3083 computer using SHELX-76, a system of computer programs for X-ray structure determination by G. M. Sheldrick.[12] Crystal parameters and procedural information corresponding to data collection and structure refinement for compounds 1 and 5 are given in Table I.

A single crystal of 1 was mounted inside of a sealed, thin-walled glass capillary. Preliminary diffractometric investigations indicated triclinic $P\bar{1}$ (C_i^1, No. 2).[13] The cell constants were determined by the least-squares refinement of the diffraction geometry for 25 intense reflections having $11 < \theta < 17$.

A single crystal of 5 was glued to the interior of a thin-walled glass capillary, which was then sealed. The unit cell parameters were calculated with 25 intense reflections having $8 < \theta < 14$. From systematic absences ($0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$) 5 belongs to *Pnma* (D_{2h}^{16}, No. 62).[13]

Table I. Crystal Parameters and Experimental Details for 1 and 5

	1	5
formula	$C_{11}H_{21}NO_3S_4Sn$	$C_{13}H_{26}N_2O_4S_2Sn$
fw	462.22	457.17
space group	$P\bar{1}$	*Pnma*
a, Å	10.514 (2)	15.080 (2)
b, Å	11.617 (2)	9.765 (1)
c, Å	8.071 (2)	13.120 (2)
α, deg	107.23 (2)	
β, deg	108.12 (2)	
γ, deg	91.51 (2)	
υ, Å^3	887 (2)	1932.0 (6)
Z	2	4
d_{calcd}, g cm^{-3}	1.73	1.57
cryst dimens, mm	0.34 × 0.42 × 0.50	0.40 × 0.50 × 0.58
μ, cm^{-1}	17.65	14.22
λ(Mo Kα radiation), Å	0.710 73	0.710 73
scan method	$\omega/2\theta$	$\omega/2\theta$
no. of data collcd	$h,\pm k,\pm l$, $2 < \theta < 26$	hkl, $1 < \theta < 26$
no. of total observations	3312	1968
no. of unique data $I > 3\sigma(I)$	3093	1080
no. of params refined	185	141
range of transm coeff	0.902–0.908	0.866–0.998
largest shift/esd	0.002	0.36
largest peak, e Å^{-3}	1.52 (0.90 Å from Sn)	0.38
$R = (\sum\lvert F_o - F_c\rvert)/\sum\lvert F_o\rvert$	0.026	0.045
$R_2 = (\sum\lvert F_o - F_c\rvert w^{1/2})/\sum\lvert F_o\rvert w^{1/2}$	0.030[a]	0.056[b]
GOF[c]	0.72	1.27

[a] $w = 1/[\sigma^2(F) + 0.003025F^2]$. [b] $w = 0.540[\sigma^2(F) + 0.000951F^2]$. [c] $GOF = [(\sum w\lvert F_o - F_c\rvert)^2/(N_{data} - N_{params})]^{1/2}$.

Results and Discussion

Preparative Aspects. The difunctional sodium salts $Y(CH_2CH_2XNa)_2$ (Y = O, S, NMe; X = O, S) in alcohol prepared by the method of Dräger[3] were reacted with the (ester)tin(IV) complexes $CH_3OOCCH_2CH_2Sn(L)Cl_2$ (L = Me_2NCS_2, Cl) in benzene to obtain bicyclic stanna complexes 1–5 according to eq 1.

$$CH_3OOCCH_2CH_2Sn(L)Cl_2 + Y(CH_2CH_2XNa)_2 \xrightarrow[50\ ^\circ C]{ROH,\ C_6H_6} ROOCCH_2CH_2Sn(L)(XCH_2CH_2)_2Y + 2NaCl \quad (1)$$

The chemical composition and monomeric nature of the complexes were established by chemical analysis and cryoscopic measurements. In order to prevent possible formation of polymeric species, synthesis was originally carried out in dilute (10^{-3} M) solution, but although more concentrated reactants were used, the same products were resultant. Compound 5 was obtained simply by transesterification of the ester group of 4 employing ethanol solvent instead of methanol. Better crystals suitable for X-ray analysis were obtained from 5 than from 4. For the synthesis of 1 another route starting with the reaction of $CH_3OOCCH_2CH_2SnCl_3$ and $O(CH_2CH_2SNa)_2$ followed by reaction with sodium dithiocarbamate resulted in the same product.

All the complexes were obtained in crystalline solids with relatively high yield (>70%) and are soluble in benzene and in most polar solvents, such as chloroform, acetone, DMF, and DMSO, but insoluble in water and saturated aliphatic hydrocarbons.

Molecular Structure of 1 and 5. The molecular structures and atomic labeling schemes for compounds 1 and 5 are shown in the ORTEP plots of Figures 1 and 2, respectively. Atomic coordinates are listed in Table II for 1 and Table III for 5. Selected bond distances and angles for 1 and 5 are presented in Table IV. The least-squares

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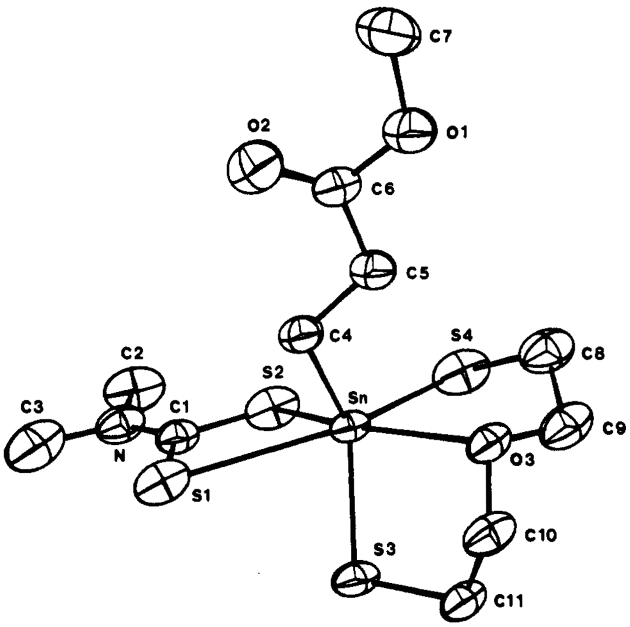

Figure 1. ORTEP drawing of 1 with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 1

atom	x/a	y/b	z/c	U_{eq}, Å^{2a}
Sn	0.2130 (<1)	0.7038 (<1)	1.2111 (<1)	0.033 (<1)
S(1)	0.2403 (1)	0.8564 (1)	0.9652 (1)	0.054 (1)
S(2)	0.0018 (1)	0.7665 (1)	1.0353 (1)	0.055 (1)
S(3)	0.3522 (1)	0.8892 (1)	1.4234 (1)	0.045 (<1)
S(4)	0.0705 (1)	0.6093 (1)	1.3349 (1)	0.061 (1)
C(1)	0.0706 (3)	0.8334 (3)	0.9092 (4)	0.046 (2)
N	0.0146 (3)	0.8653 (3)	0.7752 (4)	0.053 (2)
C(2)	0.1626 (4)	0.8444 (4)	0.7255 (6)	0.074 (3)
C(3)	0.0349 (5)	0.9208 (4)	0.6628 (5)	0.079 (3)
C(4)	0.2841 (3)	0.5744 (2)	1.0195 (4)	0.042 (2)
C(5)	0.2979 (4)	0.4542 (3)	1.0548 (4)	0.050 (2)
C(6)	0.3297 (3)	0.3564 (3)	0.9079 (4)	0.040 (2)
O(1)	0.3506 (3)	0.2565 (2)	0.9597 (3)	0.058 (2)
O(2)	0.3347 (3)	0.3615 (2)	0.7651 (4)	0.079 (3)
C(7)	0.3763 (4)	0.1525 (3)	0.8333 (6)	0.066 (3)
C(8)	0.1822 (4)	0.5202 (3)	1.4531 (5)	0.061 (3)
C(9)	0.3174 (4)	0.5879 (3)	1.5712 (5)	0.057 (2)
O(3)	0.3805 (2)	0.6290 (2)	1.4611 (3)	0.044 (1)
C(10)	0.4932 (3)	0.7224 (3)	1.5684 (4)	0.048 (2)
C(11)	0.4446 (4)	0.8458 (3)	1.6222 (4)	0.049 (2)

[a] Equivalent isotropic U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 5

atom	x/a	y/b	z/c	U_{eq}, Å^{2a}
Sn^b	0.1548 (<1)	0.2500	0.7451 (<1)	0.086 (1)
S	0.2598 (1)	0.4003 (2)	0.8592 (2)	0.084 (2)
C(1)^b	0.3075 (5)	0.2500	0.8972 (7)	0.053 (6)
N(1)^b	0.3780 (5)	0.2500	0.9545 (6)	0.063 (6)
C(2)	0.4220 (5)	0.1237 (9)	0.9887 (7)	0.089 (7)
O(1)	0.0807 (4)	0.0868 (10)	0.7045 (6)	0.124 (9)
C(3)	0.0154 (7)	0.0447 (14)	0.7715 (9)	0.121 (11)
C(4)	−0.0019 (10)	0.1292 (18)	0.8500 (13)	0.226 (18)
N(2)^b	0.0465 (5)	0.2500	0.8710 (5)	0.074 (8)
C(5)^b	0.0752 (9)	0.2500	0.9759 (10)	0.168 (32)
C(6)^b	0.2406 (9)	0.2500	0.6193 (9)	0.209 (47)
C(7)^b	0.2044 (9)	0.2500	0.5167 (8)	0.118 (16)
C(8)^b	0.2746 (8)	0.2500	0.4364 (8)	0.086 (10)
O(2)^b	0.3529 (6)	0.2500	0.4416 (6)	0.132 (13)
O(3)^b	0.2321 (5)	0.2500	0.3522 (5)	0.080 (5)
C(9)^b	0.2841 (10)	0.2500	0.2595 (8)	0.090 (11)
C(10)^b	0.2184 (13)	0.2500	0.1774 (13)	0.158 (30)

[a] Equivalent isotropic U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Half-occupancy.

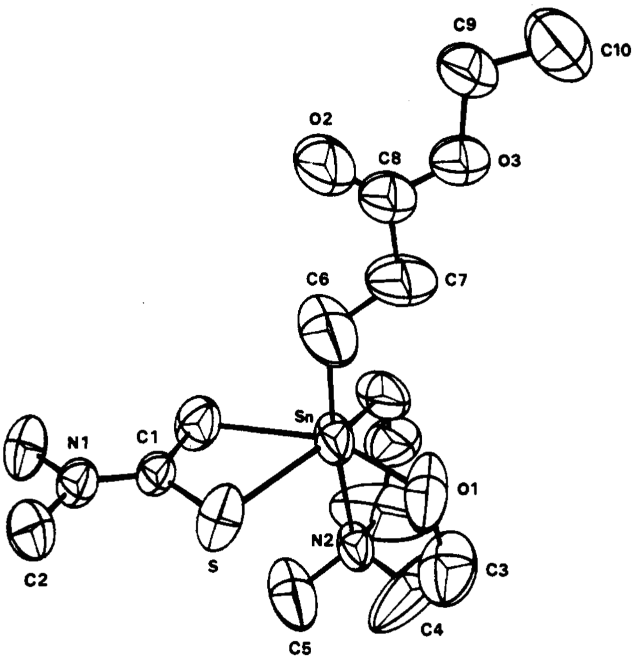

Figure 2. ORTEP drawing of 5 with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table IV. Selected Bond Distances (Å) and Angles (deg) for 1 and 5

1		5	
Sn–S(1)	3.094 (1)	Sn–S	2.627 (2)
Sn–S(2)	2.492 (1)	Sn–O(1)	2.018 (7)
Sn–S(3)	2.409 (1)	Sn–N(2)	2.322 (7)
Sn–S(4)	2.438 (1)	Sn–C(6)	2.098 (12)
Sn–O(3)	2.615 (2)	C(1)–S	1.709 (5)
Sn–C(4)	2.147 (3)	C(1)–N(1)	1.302 (11)
N–C(1)	1.327 (5)		
S(1)–C(1)	1.692 (4)		
S(2)–C(1)	1.750 (3)		
S(2)–Sn–S(1)	63.1 (<1)	S–Sn–S′	67.9 (1)
S(3)–Sn–S(1)	75.5 (<1)	O(1)–Sn–S	92.5 (2)
S(3)–Sn–S(2)	105.9 (<1)	O(1)′–Sn–S	157.7 (2)
S(4)–Sn–S(1)	149.0 (<1)	O(1)–Sn–)(1)′	104.3 (3)
S(4)–Sn–S(2)	86.0 (<1)	N(2)–Sn–S	91.1 (1)
S(4)–Sn–S(3)	114.7 (<1)	N(2)–Sn–O(1)	78.4 (2)
O(3)–Sn–S(1)	135.6 (1)	C(6)–Sn–S	94.4 (1)
O(3)–Sn–S(2)	159.9 (1)	C(6)–Sn–O(1)	97.7 (2)
O(3)–Sn–S(3)	77.2 (<1)	C(6)–Sn–N(2)	173.5 (4)
O(3)–Sn–S(4)	74.9 (1)	C(1)–S–Sn	86.6 (1)
C(4)–Sn–S(1)	80.3 (1)	C(3)–O(1)–Sn	117.5 (7)
C(4)–Sn–S(2)	108.5 (1)	C(4)–N(2)–Sn	102.9 (7)
C(4)–Sn–S(3)	121.8 (1)	C(5)–N(2)–Sn	117.9 (7)
C(4)–Sn–S(4)	113.2 (1)	C(7)–C(6)–Sn	119.8 (9)
C(4)–Sn–O(3)	85.2 (1)		
C(1)–S(1)–Sn	79.2 (1)		
C(1)–S(2)–Sn	97.9 (1)		
C(11)–S(3)–Sn	103.6 (2)		
C(8)–S(4)–Sn	103.1 (1)		
C(9)–O(3)–Sn	113.4 (3)		
C(10)–O(3)–Sn	109.0 (2)		
C(5)–C(4)–Sn	113.5 (2)		
C(10)–O(3)–C(9)	113.2 (2)		

planes are depicted in Table S-VII (supplementary material).

The geometry around the tin atom in compound 1 exhibits a highly distorted octahedral arrangement with S(1), S(2), S(4), and O(3) in equatorial positions and S(3) and C(4) in apical positions. The central tin atom is nearly on the equatorial plane. The axial C(4)–Sn–S(3) angle of 121.8 (1)° is considerably smaller than the lowest reported values of the corresponding Me–Sn–Me angle, 136° and 137.3° in $Me_2Sn(S_2CNMe_2)_2$[14] and $Me_2Sn[S_2CN(CH_2)_4]_2$,[15] respectively. Such a small axial bond angle is not clearly explained but may be explicable by presuming that hexacoordination of **1** is considered to be achieved by addition of a weak dative Sn–S(1) bond to the basically trigonal-bipyramidal structure with C(4), S(3), and (4) in the trigonal plane, which will be mentioned later in more detail.

Another interesting feature of the structure of **1** is the bonding mode of the dithiocarbamate ligand. The Sn–S(2) distance, 2.492 (1) Å, is a normal value of Sn–S bond distances found in typical anisobidentate bonding complexes such as $Me_2Sn(S_2CNMe_2)_2$ (2.497 (8) Å),[14] $Me_2SnCl(S_2CNMe_2)$ (2.48 (1) Å),[16] and $(t\text{-}Bu)_2Sn(S_2CNMe_2)_2$ (2.489 (1) Å).[17] However, the Sn–S(1) distance of 3.094 (1) Å is considerably longer than the normal values (2.7–2.9 Å) of the corresponding Sn–S distance observed in the anisobidentate mode,[16,17] although it is proximate to the known longest Sn–S bond distance 3.061 (8) Å in $Me_2Sn(S_2CNMe_2)_2$,[14] and thus it lies on the borderline between a coordinated and uncoordinated sulfur–tin interaction.[18] Even if the Sn–S(1) interaction in **1** is not regarded as a coordinative bond, the local geometry of the tin atom can still be reasonably described as a distorted trigonal bipyramid with C(4), S(3), and S(4) in equatorial positions and S(2) and O(3) in apical positions. The central tin atom is nearly on the equatorial plane, and the axial S(2)–Sn–O(3) angle is 159.9 (1)°. Thus the geometry around the tin atom can hardly be determined with certainty solely on the basis of the X-ray data. However, the ^{119}Sn NMR data, as will be shown later, strongly suggest that compound **1** is hexacoordinate, even in solution, and as such Sn–S(1) should be regarded as a weak coordinative bond, as shown in Figure 1. Therefore, the molecular structure of **1** may be considered to be formed by addition of a weak dative Sn–S(1) bond to the basically trigonal-bipyramidal geometry. The dative Sn–O(3) bond distance, 2.615 (2) Å, is longer than that of $PhClSn(SCH_2CH_2)_2O$ (2.41 (1) Å),[2] probably owing to the introduction of the electron-donating dithiocarbamate ligand, but is shorter than that of $Ph_2Sn(SCH_2CH_2)_2O$ (2.66 (1) Å).[4,19] The ester group of **1** does not chelate to the tin atom in contrast to that of the starting compound $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)Cl_2$,[11] presumably due to decrease of Lewis acidity of the tin atom by the additional bondings.

Sn, O(2), O(3), N(1), N(2), C(1), C(6), C(7), C(8), C(9), and C(10) in compound **5** are in the special positions for a mirror plane having half occupancies. Compared with the structure of **1**, the molecular structure of **5** exhibits more clearly an octahedral geometry around the tin atom with S, S′, O(1), and O(1)′ in equatorial positions and C(6) and N(2) in apical positions, but important structural differences are noted. The dithiocarbamate ligand in **5** is bonded to the tin atom in isobidentate fashion with Sn–S and Sn–S′ distances of 2.627 (2) Å, and the transannular dative Sn–N(2) bond is axially positioned along with the tin–carbon bond, resulting in a reasonable axial C(6)–Sn–N(2) angle of 173.5 (4)°, while the dative Sn–O(3) bond in **1** is equatorially positioned. The equatorial atoms S, S′, O(1), and O(1)′ form almost a perfect plane, but the tin atom is not in the equatorial plane but is instead displaced 0.2455 (<1) Å out of this plane toward the carbon atom. The dative Sn–N(2) bond distance of 2.322 (7) Å is almost the same as the value of 2.32 (2) Å in $(t\text{-}Bu)_2Sn(OCH_2CH_2)_2NMe$,[5] which is the shortest so far reported, and considerably shorter than that of $Me_2Sn(SCH_2CH_2)_2NMe$ (2.58 (1) Å).[5] Such strong dative Sn–N interaction and isobidentate bonding of the dithiocarbamate ligand is probably attributed to the electronegative oxygen ligating atoms increasing the Lewis acidity of the tin atom.

Table V. Relevant IR Bands for $ROOCCH_2CH_2Sn(L)(XCH_2CH_2)_2Y$[a]

compd	$\nu(C{=}O)$, cm^{-1}	$\nu(C{-}N)$, cm^{-1}	$\nu(C{-}S)$, cm^{-1}
1	1731 (vs)	1510 (vs)	976 (s)
2	1731 (vs)		
3	1734 (vs)	1512 (vs)	977 (s)
4	1725 (vs)	1533 (vs)	974 (s)
5	1717 (vs)	1527 (vs)	975 (s)

[a] Abbreviations: vs, very strong; s, strong.

Table VI. ^1H and ^{119}Sn NMR Data for $ROOCCH_2CH_2Sn(L)(XCH_2CH_2)_2Y$

compd	$\delta(^1H)$, ppm	$\delta(^{119}Sn)$,[a] ppm
1	3.8 (m, OCH_2–), 3.7 (s, CH_3O–), 3.4 (s, NMe_2), 2.9 (t, –CH_2–), 2.9 (t, –CH_2–), 2.1 (t, –CH_2Sn)	−178.8
2	3.8 (m, OCH_2–), 3.7 (s, –CH_3O), 3.0 (t, SCH_2–), 2.8 (t, –CH_2–), 2.0 (t, –CH_2Sn)	−18.4
3	3.7 (s, CH_3O–), 3.5 (s, NMe_2), 3.0 (t, SCH_2–); 3.0 (t, CH_2S), 2.2 (t, –CH_2Sn)	−196.0
4	4.0 (m, OCH_2–), 3.7 (s, CH_3O–), 3.5 (s, NMe_2), 3.0 (s, NMe), 2.8 (m, –CH_2N), 2.8 (t, –CH_2–), 1.7 (t, –CH_2Sn)	−418.3
5	4.1 (q, CCH_2–), 3.9 (m, OCH_2–), 3.4 (s, NMe_2), 2.9 (s, NMe), 2.8 (m, –CH_2N), 2.7 (t, –CH_2–), 1.7 (t, –CH_2Sn), 1.2 (t, CH_3–)	

[a] Pulse width, 10.0 μs; pulse repetition, 3.0 s.

Comparison of the Sn–N distance in the present hexacoordinate compound **5** with those in pentacoordinate $Me_2Sn(SCH_2CH_2)_2NMe$ and $(t\text{-}Bu)_2Sn(OCH_2CH_2)_2NMe$ exposes an aspect of the coordination nature of organotin compounds. The fact that the dative Sn–N interaction in the more crowded hexacoordinate compound **5** is comparabe to that in pentacoordinate $(t\text{-}Bu)_2Sn(OCH_2CH_2)_2NMe$, involving the same endocyclic ring, and is stronger than that in simple pentacoordinate $Me_2Sn(SCH_2CH_2)_2NMe$ indicates that the electronic rather than the steric effect is dominant in determination of the coordination structure of organotin compounds, as was pointed out earlier.[20]

Spectroscopic Properties. The IR data of the present compounds **1**–**5** are listed for selected stretching modes in Table V. The carbonyl stretching bands $\nu(C{=}O)$ of all the complexes appear in the range 1717–1734 cm^{-1}, much higher than the corresponding frequency (1652 cm^{-1}) of the starting material $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)Cl_2$, which indicates the nonchelating nature of the ester group in the present compounds is consistent with the above-mentioned X-ray data. The close similarities of other stretching modes $\nu(C{-}N)$ and $\nu(C{-}S)$ among the compounds **1**–**3** suggest that the molecular structures of **2** and

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3 are basically the same as that of 1 and so the structure of 4 as that of 5.

The ^{1}H and ^{119}Sn NMR data are summarized in Table VI. The ^{1}H resonance for the CH_3O– groups (3.7 ppm) in 1–4 shows upfield shift by about 0.3 ppm compared to that of the chelated ester group in $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)Cl_2$,[11] implying that the ester group of the present compounds is not coordinated also in solution. On the other hand, the ^{1}H resonance for $-CH_2Y$ exhibits downfield shift by 0.2–0.5 ppm relative to each free ligand $(HXCH_2CH_2)_2Y$.[21] Further downfield shift by 0.7 ppm is observed for the resonance of the $-NCH_3$ groups (2.9 ppm) of 4 and 5 compared to that of $(HOCH_2CH_2)_2NCH_3$ ($\delta(^{1}H)$ = 2.2 ppm).[22] Such deshieldings of ^{1}H resonances for the present compounds support the retention of their Sn–Y transannular dative bonds in solution.

The ^{119}Sn NMR spectrum of the present compounds in noncoordinating solvent ($CDCl_3$) exhibits a unique signal. ^{119}Sn NMR spectroscopy has been used as a powerful tool for discerning the coordination number of the tin atom in organotin compounds.[20,23–29] According to Otera et al.,[24–28] for instance, the $\delta(^{119}Sn)$ value moves upfield by 60–150 ppm for the change of the coordination number of tin from 4 to 5, by 130–200 ppm from 5 to 6, and by 150–300 ppm from 6 to 7. Now comparison of the $\delta(^{119}Sn)$ value of 1 (–178.8 ppm) with that of the chlorine analogue 2 (–18.4 ppm) results in important information on the coordination number of the tin atom. The chlorine atom bonded to tin is found to affect the $\delta(^{119}Sn)$ value to approximately the same degree as a monodentate dithiocarbamate ligand. For example, the $\delta(^{119}Sn)$ value (–224 ppm) of pentacoordinate $(t\text{-Bu})_2SnCl(S_2CNMe_2)$[20] is approximately the same as that (–255 ppm) of $(t\text{-Bu})_2Sn(S_2CNMe_2)_2$[17,20,28] in which one dithiocarbamate group acts as a monodentate ligand, thus yielding the same pentacoordinate structure. On the other hand, the $\delta(^{119}Sn)$ value (–204 ppm) of pentacoordinate $Me_2SnCl(S_2CNMe_2)$[20,30] moves remarkably upfield to –338 ppm in hexacoordinate $Me_2Sn(S_2CNMe_2)_2$,[20,30] formed by replacing the chlorine atom in the pentacoordinate complex with a bidentate dithiocarbamate. Similarly, a remarkable upfield shift was observed from $\delta(^{119}Sn)$ = –239 ppm in pentacoordinate $Cy_2SnBr(S_2CNMe_2)$[20] to –374 ppm in hexacoordinate $Cy_2Sn(S_2CNMe_2)_2$.[20] Now assuming the present compound 2 to be pentacoordinate by retaining the transannular dative bond in solution, as was mentioned earlier in its ^{1}H NMR data, the remarkable upfield shift of the $\delta(^{119}Sn)$ value for 1 from that of 2 by 160.4 ppm clearly indicates that 1 is hexacoordinate even in solution. The $\delta(^{119}Sn)$ value of –196 ppm for 3 is also indicative of hexacoordination. The drastic change to high field of the $\delta(^{119}Sn)$ value in 4 seems to be ascribed to the drastic change in the chemical environment around the tin atom due to change both of the ligating atoms of the cyclic ligand and of the strong transannular dative Sn–N bond. In conclusion, all the stannabicylooctanes involving dithiocarbamate ligand have hexacoordinate structures both in the solid state and in solution, but the unusual distortion of the octahedral arrangement for 1 toward a trigonal bipyramid with a weak coordinative S–Sn bond is presumably due to reduction of the acceptor properties of tin atom by the electron-donating atoms or groups.

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Supplementary Material Available: Tables of positional and thermal parameters of hydrogen atoms (Tables S-I and S-V), anisotropic thermal parameters (Tables S-II and S-VI), bond distances and angles (Tables S-III and S-VII), and least-squares planes for 1 and 5 (Table S-IX) (7 pages); listings of structure factors (Tables S-IV and S-VIII) for 1 and 5 (21 pages). Ordering information is given on any current masthead page.

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(21) ^{1}H NMR of $-CH_2Y$ in $(HXCH_2CH_2)_2Y$ ($CDCl_3$, TMS), ppm: 3.6 (t, X = S, Y = O); 2.8 (s, X = S, Y = S); 3.4 (t, X = O, Y = NMe).

(22) ^{1}H NMR of NMe in $(HOCH_2CH_2)_2NMe$ ($CDCl_3$, TMS), ppm: 2.2 (s).

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