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Structure and Properties of Diestertin(IV) Complexes $(CH_3OOCCH_2CH_2)_2Sn(Ch)Cl$ (Ch = Dimethyldithiocarbamate, Dihydrobis(pyrazolyl)borate)

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

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

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Diestertin(IV) complexes $(CH_3OOCCH_2CH_2)_2Sn(Ch)Cl$ (**1**, Ch = dimethyldithiocarbamate (dtc); **2**, Ch = dihydrobis(pyrazolyl)borate (bpb)) were prepared by reaction of the diestertin(IV) chloride with alkali-metal salts of the corresponding ligands, and their molecular structures were determined by X-ray analysis. The local geometry around the tin atom of **1** ($P2_1/n$; $a = 10.011$ (1), $b = 19.480$ (2), $c = 10.081$ (2) Å; $\beta = 117.39$ (1)°; $Z = 4$; $R = 0.0294$) adopts a distorted trigonal bipyramid with the chelating dtc ligand whereas the geometry of **2** ($Pbcn$; $a = 34.287$ (4), $b = 7.949$ (2), $c = 14.397$ (2) Å; $Z = 8$; $R = 0.0345$) approximates to an octahedral arrangement owing to a weak intramolecular carbonyl oxygen-to-tin coordination of one ester group (Sn–O(1) = 2.745 (6) Å) in addition to the chelating bpb ligand. The reaction of **1** with sodium sulfide ($CHCl_3/H_2O$) in the mole ratio of 2:1 gives two different known diestertin(IV) complexes $(CH_3OOCCH_2CH_2)_2Sn(S_2CNMe_2)_2$ and $[(CH_3OOCCH_2CH_2)_2SnS]_3$. In contrast, the reaction of **2** with sodium sulfide does not give analogous chemical products but instead allows formation of a new zwitterionic species Hbpb, $C_6H_9N_4B$ ($Pbcn$; $a = 15.177$ (2), $b = 7.397$ (1), $c = 14.207$ (1) Å; $Z = 8$; $R = 0.0368$), along with the same trimeric sulfide.

Introduction

Diestertin(IV) compounds have attracted considerable attention because of their applicability as nontoxic PVC stabilizers[1–6] and also because of their structures involving potential intramolecular carbonyl coordination to tin[7–11] ever since the discovery of convenient preparative routes by Hutton and his co-workers.[12,13] It is known that the structure and efficiency of a stabilizer strongly depends on the Lewis acidity of tin atom.[14]

With a view to expanding the chemistry of the organotin family, we have prepared new diestertin complexes $(CH_3OOCCH_2CH_2)_2Sn(Ch)Cl$ (Ch = bpb[15–17] and dtc[18,19]), in which there seem to be remarkable differences in the electronic and steric behavior of the two chelating ligands, which contain nitrogen and sulfur donor atoms, respectively. In this paper the coordination and reactivity of the isolated compounds will be discussed on the basis of their spectra and their crystal structures.

Experimental Section

Manipulations were performed under a nitrogen atmosphere, if necessary, with the use of standard Schlenkware techniques, and all reactions were carried out at room temperature. All chemicals were of reagent grade and used without further purification. Solvents were used directly from freshly opened bottles or dried by standard methods prior to use. Chemical analyses were carried out by the Chemical Analysis Laboratory at KIST. The molecular weight was determined cryoscopically in benzene by using a Cryette A automatic cryoscope. The IR spectra in the 4000–400-cm^{-1} region were measured both on KBr disks and in chloroform solution between KBr windows with a Analect Instrument fx 6160 FT-IR spectrometer. NMR spectra, in $CDCl_3$ or in Me_2SO-d_6 solution, were recorded on a JEOL JNM DMX 60 spectrometer (^{1}H) or a Bruker AM-200 spectrometer operating at 50.32 MHz (^{13}C) and 74.63 MHz (^{119}Sn) in pulse mode with Fourier transform at ambient temperature. The chemical shifts were relative to internal Me_4Si (^{1}H and ^{13}C) and external Me_4Sn (^{119}Sn) for the indicated nuclei.

Diestertin(IV) dichloride,[13] sodium dimethyldithiocarbamate (dtc),[18] and potassium dihydrobis(pyrazolyl)borate (bpb)[15] were prepared according to literature procedures.

Preparation of $(CH_3OOCCH_2CH_2)_2Sn(dtc)Cl$ (1). A solution of Nadtc·$2H_2O$ (1.79 g, 10 mmol) in 50 mL of ethanol was added dropwise to an equimolar solution of $(CH_3OOCCH_2CH_2)_2SnCl_2$ (3.64 g, 10 mmol) in 50 mL of chloroform. The reaction mixture was stirred for 1 h and then filtered. The filtrate was dried under reduced pressure, yielding a white solid. Recrystallization of the white solid from chloroform–petroleum ether (1:1) afforded colorless crystals (mp 68–70 °C) suitable for X-ray study in 74% yield. Anal. Calcd for $C_{11}H_{20}NClO_4S_2Sn$: C, 29.46; H, 4.46; N, 3.12. Found: C, 30.07; H, 4.43; N, 3.09. IR (cm^{-1}): ν(CO), 1725 (KBr); ν(CO), 1723 ($CHCl_3$). ^{1}H NMR ($CDCl_3$, δ): 3.7 (s, 6 H); 3.4 (s, 6 H); 3.0 (t, J = 7 Hz, 4 H); 2.1 (t, J = 7 Hz, 4 H). ^{13}C NMR ($CDCl_3$, δ): 199.0 (CS); 176.2 (CO); 52.1 (CH_3O–); 45.1 (NCH_3); 30.0 (–CH_2–); 26.0 (–CH_2Sn). ^{119}Sn NMR ($CDCl_3$, δ): −258.6.

Preparation of $(CH_3OOCCH_2CH_2)_2Sn(bpb)Cl$ (2). $(CH_3OOCCH_2CH_2)_2SnCl_2$ (3.64 g, 10 mmol) in 40 mL of dichloromethane was added dropwise to a stirred suspension of K(bpb) (1.86 g, 10 mmol) in 40 mL of dichloromethane. After being stirred for 1 h, the reaction mixture was filtered and the filtrate was evaporated to 10 mL. To this solution was carefully added an excess of ethanol (50 mL), and then the solution was left overnight.

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Table I. Crystal and Experimental Details for 1, 2, and Hbpb

	1	2	Hbpb
formula	$C_{11}H_{20}NO_4S_2ClSn$	$C_{14}H_{22}N_4O_4ClBSn$	$C_6H_9N_4B$
fw	448.61	475.31	147.97
space group	$P2_1/n$	*Pbcn*	*Pbcn*
a, Å	10.011 (1)	34.287 (4)	15.177 (2)
b, Å	19.480 (2)	7.949 (2)	7.397 (1)
c, Å	10.081 (2)	14.397 (2)	14.207 (1)
β, deg	117.39 (1)		
V, Å^3	1745.7 (9)	3924 (1)	1601.7 (4)
Z	4	8	8
d_{calcd}, g cm^{-3}	1.71	1.61	1.23
cryst size, mm	0.40 × 0.44 × 0.50	0.42 × 0.44 × 0.58	0.32 × 0.38 × 0.46
μ, cm^{-1}	17.18	13.40	0.48
scan method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
data collcd	$h,k,\pm l$; $1 \le \theta \le 25$	h,k,l; $1 \le \theta \le 25$	h,k,l; $1 \le \theta \le 25$
tot. no. of observns	3358	3498	1653
no. of unique data > $3\sigma(I)$	2549	2118	601
no. of params refined	183	230	136
range of trans coeff	0.932–0.998	0.907–0.997	
largest shift/esd	0.009	0.007	0.07
largest peak, e Å^{-3}	0.42	0.36	0.13
GOF	0.67	2.57	0.79
R	0.0294	0.0345	0.0368
R_w[a]	0.0374	0.0461	0.0378

[a] 1, $w = 1.0/(\sigma^2(F) + 0.006567F_2)$; 2, $w = 3.3074/(\sigma^2(F) + 0.001845F^2)$; Hbpb, $w = 1.0264/(\sigma^2(F) + 0.000358F^2)$.

Colorless crystals (mp 95–97 °C) suitable for X-ray analysis were obtained in 60% yield. Anal. Calcd for $C_{14}H_{22}N_4ClO_4BSn$: C, 35.37; H, 4.63; N, 11.79. Found: C, 35.30; H, 4.55; N, 11.70. IR (cm^{-1}): ν(CO), 1737, 1688 (KBr): ν(CO), 1730, 1689 ($CHCl_3$). ^1H NMR ($CDCl_3$, δ): 8.0 (d, J = 2 Hz, -CH-N-Sn, 2 H); 7.7 (d, J = 2 Hz, -CH-N-B, 2 H); 6.3 (m, J = 1 Hz, -CH-, 2 H); 3.8 (s, CH_3O-, 6 H); 2.9 (t, J = 8 Hz, $-CH_2-$, 4 H); 2.0 (t, J = 8 Hz, $-CH_2Sn$, 4 H). ^{13}C NMR ($CDCl_3$, δ): 177.7 (CO); 140.4, 137.3 (N-CH-); 105.3 (-CH-); 52.5 (CH_3O-); 29.4 ($-CH_2-$); 27.0 ($-CH_2Sn$). ^{119}Sn NMR ($CDCl_3$, δ): -255.4.

Reaction of 1 with Sodium Sulfide. A solution of $Na_2S{\cdot}9H_2O$ (1.20 g, 5 mmol) dissolved in 50 mL of water was added to 1 (4.48 g, 10 mmol) in 50 mL of chloroform, and the reaction mixture was stirred for 1 h. The chloroform layer was separated and evaporated under reduced pressure to obtain a white solid mixture. The crude mixture was recrystallized from a chloroform–petroleum ether (1:1) solvent pair to afford colorless crystals of $(CH_3OOCCH_2CH_2)_2Sn(S_2CNMe_2)_2$ (mp 119–121 °C; lit.[10] mp 116–117 °C), which were separated by filtration. Anal. Calcd for $C_{14}H_{26}N_2O_4S_4Sn$: C, 31.52; H, 4.88; N, 5.25. Found: C, 31.40, H, 4.90; N, 5.21. ^1H NMR ($CDCl_3$, δ): 3.7 (s, 6 H); 3.5 (s, 12. H); 3.0 (t, J = 8 Hz, 4 H); 2.3 (t, J = 8 Hz, 4 H). ^{119}Sn NMR ($CDCl_3$, δ): -438.7. The filtrate was evaporated to dryness and then extracted with ethanol. The extracts were concentrated and cooled to give colorless crystals of $[(CH_3OOCCH_2CH_2)_2SnS]_3$ (mp 72–73 °C; lit.[20] mp 72–73 °C). Molecular weight: measured, 758.4 (calcd, 778.2). Anal. Calcd for $C_{24}H_{42}O_{12}S_3Sn_3$: C, 29.56; H, 4.31. Found: C, 29.60; H, 4.39. ^1H NMR ($CDCl_3$, δ): 3.7 (s, 6 H); 3.0 (t, J = 8 Hz, 4 H); 2.1 (t, J = 8 Hz, 4 H). ^{119}Sn NMR ($CDCl_3$, δ): -232.2.

Reaction of 2 with Sodium Sulfide. A solution of $Na_2S{\cdot}9H_2O$ (1.20 g, 5 mmol) in 20 mL of water was added to a solution of 2 (4.75 g, 10 mmol) in 20 mL of chloroform, and the reaction mixture was stirred for 1 h. A white precipitate formed in the aqueous layer was separated by filtration. The solid product was recrystallized from ethanol to give colorless crystals of Hbpb (mp 132–133 °C) suitable for structure determination. Anal. Calcd for $C_6H_9N_4B$: C, 48.71; H, 6.09; N, 37.89. Found: C, 48.60; H, 6.15; N, 37.30. IR (KBr disk, cm^{-1}): ν(B-H), 2430. ^1H NMR (Me_2SO-d_6, δ): 13.6 (s, 1 H) 7.8 (m, 4 H); 6.3 (m, 2 H). The chloroform layer was evaporated yielding an equimolar mixture of unreacted 2 and $[(CH_3OOCCH_2CH_2)_2SnS]_3$. The reaction of equimolar amounts of sodium sulfide and 2 resulted in the same products without unreacted 2.

Crystal Structure Determinations of 1, 2, and Hbpb. All X-ray crystallographic data were obtained by using an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71067 Å) at ambient temperature (23 (2) °C). All crystals were mounted inside a thin-walled glass capillary, which was sealed as a precaution against moisture and oxygen. Accurate cell dimensions were obtained from the setting angles of 25 well-centered reflections, $9 < \theta < 14$ for 1, $10 < \theta < 13$ for 2, and $10 < \theta < 14$ for Hbpb, by using a least-squares procedure. During the data collection, three standard reflections monitored after every 1 h did not reveal any systematic variation in intensity. All space groups of the crystals were uniquely determined by systematic absences. All calculations were performed on an IBM 3083 computer using SHELX 76,[21] and atomic scattering factors were supplied by the SHELX system. Crystal data and additional details of data collection and refinement are summarized in Table I.

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for 1

atom	*x/a*	*y/b*	*z/c*	U_{eq},[a] Å^2
Sn	0.6504 (<1)	0.1327 (<1)	0.4583 (<1)	0.044 (<1)
Cl	0.8051 (1)	0.1858 (1)	0.7091 (1)	0.059 (1)
S(1)	0.4278 (1)	0.1651 (1)	0.4965 (1)	0.051 (1)
S(2)	0.3903 (1)	0.0965 (1)	0.2222 (1)	0.058 (1)
C(1)	0.3074 (5)	0.1405 (2)	0.3123 (5)	0.048 (3)
N(1)	0.1651 (4)	0.1551 (2)	0.2508 (4)	0.052 (2)
C(2)	0.0665 (7)	0.1383 (3)	0.0945 (7)	0.066 (4)
C(3)	0.0979 (6)	0.1938 (3)	0.3290 (6)	0.071 (4)
C(4)	0.7199 (6)	0.0286 (2)	0.5182 (6)	0.063 (3)
C(5)	0.8711 (6)	0.0202 (3)	0.6571 (6)	0.065 (3)
C(6)	0.9956 (5)	0.0609 (3)	0.6527 (5)	0.055 (3)
O(1)	0.9861 (5)	0.0927 (2)	0.5460 (4)	0.081 (3)
O(2)	1.1184 (4)	0.0571 (2)	0.7808 (4)	0.070 (2)
C(7)	1.2484 (6)	0.0928 (3)	0.7893 (7)	0.080 (4)
C(8)	0.7024 (6)	0.2142 (2)	0.3477 (5)	0.058 (3)
C(9)	0.6412 (6)	0.2088 (3)	0.1815 (6)	0.062 (3)
C(10)	0.6651 (6)	0.1391 (2)	0.1286 (5)	0.054 (3)
O(3)	0.7018 (5)	0.0891 (2)	0.2057 (4)	0.085 (3)
O(4)	0.6354 (6)	0.1395 (2)	–0.0132 (5)	0.084 (4)
C(11)	0.6515 (7)	0.0753 (3)	–0.0766 (7)	0.086 (4)

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

For crystals 1 and 2, the structures were solved by the conventional Paterson method, followed by successive difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters, and the positions of hydrogen atoms were calculated from the refinement. The final values of the refined positional parameters and isotropic thermal parameters

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Table III. Positional Parameters and Equivalent Isotropic Thermal Parameters for 2

atom	*x/a*	*y/b*	*z/c*	U_{eq}, Å^2
Sn	0.1140 (<1)	0.2526 (<1)	0.3347 (<1)	0.040 (<1)
Cl	0.1219 (1)	0.0084 (2)	0.4429 (1)	0.064 (1)
N(11)	0.0526 (2)	0.2458 (6)	0.3746 (4)	0.047 (4)
N(12)	0.0290 (2)	0.3836 (7)	0.3766 (4)	0.051 (5)
C(11)	−0.0071 (2)	0.3331 (10)	0.3923 (5)	0.061 (6)
C(12)	−0.0077 (2)	0.1606 (11)	0.3988 (6)	0.068 (6)
C(13)	0.0306 (3)	0.1108 (9)	0.3878 (5)	0.060 (6)
B	0.0455 (3)	0.5655 (10)	0.3709 (5)	0.050 (6)
N(21)	0.0929 (2)	0.4775 (7)	0.2464 (3)	0.044 (4)
N(22)	0.0646 (2)	0.5847 (6)	0.2739 (4)	0.046 (4)
C(21)	0.1063 (2)	0.5299 (9)	0.1635 (4)	0.047 (4)
C(22)	0.0852 (3)	0.6759 (10)	0.1387 (5)	0.065 (7)
C(23)	0.0591 (2)	0.7043 (8)	0.2094 (5)	0.051 (5)
C(1)	0.1146 (2)	0.1006 (10)	0.2123 (5)	0.053 (5)
C(2)	0.1523 (2)	0.0007 (9)	0.2013 (5)	0.058 (5)
C(3)	0.1875 (2)	0.1100 (9)	0.2169 (4)	0.049 (5)
O(1)	0.1872 (2)	0.2416 (6)	0.2577 (4)	0.065 (4)
O(2)	0.2197 (2)	0.0436 (6)	0.1798 (3)	0.055 (3)
C(4)	0.2550 (2)	0.1384 (13)	0.1901 (6)	0.074 (7)
C(5)	0.1468 (2)	0.4111 (8)	0.4251 (4)	0.050 (5)
C(6)	0.1602 (2)	0.5759 (8)	0.3814 (4)	0.050 (5)
C(7)	0.1858 (2)	0.6781 (8)	0.4435 (5)	0.048 (5)
O(3)	0.1886 (2)	0.6659 (7)	0.5260 (3)	0.072 (5)
O(4)	0.2060 (2)	0.7892 (6)	0.3939 (3)	0.057 (3)
C(8)	0.2302 (3)	0.9080 (11)	0.4437 (7)	0.085 (7)

Table IV. Positional Parameters and Equivalent Isotropic Thermal Parameters for Hbpb

atom	*x/a*	*y/b*	*z/c*	U_{eq}, Å^2
N(11)	0.6038 (2)	0.0462 (4)	0.1183 (2)	0.049 (2)
N(12)	0.6562 (2)	0.1364 (3)	0.0577 (2)	0.043 (2)
C(11)	0.7145 (2)	0.2375 (5)	0.1057 (3)	0.059 (3)
H(11)	0.7576 (26)	0.2992 (59)	0.0684 (24)	0.088 (15)
C(12)	0.7002 (3)	0.2120 (5)	0.1987 (3)	0.071 (3)
H(12)	0.7309 (22)	0.2507 (54)	0.2487 (26)	0.079 (12)
C(13)	0.6316 (3)	0.0923 (5)	0.2030 (3)	0.062 (3)
H(13)	0.6045 (18)	0.0430 (47)	0.2542 (24)	0.061 (11)
B	0.6440 (3)	0.1217 (6)	−0.0492 (3)	0.055 (3)
H(1)	0.7088 (18)	0.1356 (44)	−0.0820 (20)	0.060 (10)
H(2)	0.6114 (18)	−0.0079 (49)	−0.0653 (22)	0.059 (10)
N(21)	0.5825 (2)	0.2778 (4)	−0.0844 (2)	0.045 (2)
N(22)	0.4965 (2)	0.2565 (4)	−0.1007 (2)	0.047 (2)
H(1N)	0.4652 (23)	0.1408 (53)	−0.0994 (29)	0.089 (13)
C(21)	0.4610 (3)	0.4150 (5)	−0.1261 (3)	0.059 (3)
H(21)	0.4005 (23)	0.4218 (47)	−0.1420 (22)	0.066 (11)
C(22)	0.5251 (3)	0.5418 (5)	−0.1265 (3)	0.064 (3)
H(22)	0.5173 (24)	0.6727 (57)	−0.1409 (27)	0.097 (14)
C(23)	0.5995 (3)	0.4527 (5)	−0.1004 (3)	0.060 (3)
H(23)	0.6594 (21)	0.4875 (45)	−0.0915 (20)	0.057 (10)

for 1 and 2 are presented in Tables II and III, respectively.

For the crystal of Hbpb, the initial structure was found by using the direct-methods program MULTAN 80.[22] This gave a starting set of atomic positions for four nitrogen atoms. The program system SHELX 76 was used to locate other atoms. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located from the difference maps and refined with isotropic temperature factors. The final positional and isotropic thermal parameters for Hbpb are given in Table IV.

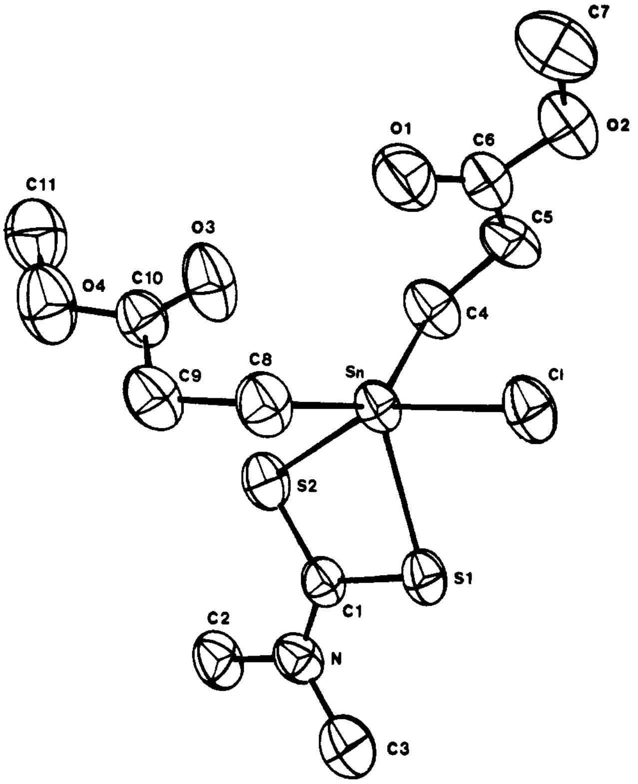

Figure 1. ORTEP drawing of 1 with thermal ellipsoids shown at the 50% probability level.

Table V. Selected Bond Distances (Å) and Angles (deg) for 1 and 2

1		2	
Sn–Cl	2.502 (1)	Sn–Cl	2.504 (2)
Sn–S(1)	2.510 (1)	Sn–N(11)	2.182 (6)
Sn–S(2)	2.691 (1)	Sn–N(21)	2.310 (5)
Sn–C(4)	2.140 (5)	Sn–C(1)	2.136 (6)
Sn–C(8)	2.137 (4)	Sn–O(1)	2.745 (6)
S(1)–C(1)	1.753 (5)	Sn–C(5)	2.134 (6)
S(2)–C(1)	1.714 (5)	B–N(12)	1.555 (9)
N–C(1)	1.298 (6)	B–N(22)	1.549 (9)
N–C(2)	1.460 (7)	N(21)–N(22)	1.351 (7)
N–C(3)	1.460 (6)		
S(1)–Sn–Cl	85.3 (0)	N(11)–Sn–Cl	85.5 (2)
S(2)–Sn–Cl	151.1 (0)	N(21)–Sn–Cl	167.6 (1)
S(2)–Sn–S(1)	68.6 (0)	N(21)–Sn–N(11)	82.1 (2)
C(4)–Sn–Cl	97.9 (1)	C(1)–Sn–Cl	94.2 (2)
C(4)–Sn–S(1)	113.0 (1)	C(1)–Sn–N(11)	102.3 (2)
C(4)–Sn–S(2)	93.3 (1)	C(1)–Sn–N(21)	89.2 (2)
C(8)–Sn–Cl	92.0 (1)	O(1)–Sn–Cl	97.3 (1)
C(8)–Sn–S(1)	109.9 (1)	O(1)–Sn–N(11)	170.9 (2)
C(8)–Sn–S(2)	95.9 (1)	O(1)–Sn–N(21)	95.1 (2)
C(8)–Sn–C(4)	136.5 (2)	O(1)–Sn–C(1)	68.9 (2)
		C(5)–Sn–Cl	91.2 (2)
		C(5)–Sn–N(11)	111.3 (3)
		C(5)–Sn–N(21)	92.5 (2)
		C(5)–Sn–C(1)	146.3 (2)
		C(5)–Sn–O(1)	77.4 (2)
		N(12)–B–N(22)	107.0 (5)

Results and Discussion

Description of the Crystal Structures for 1 and 2. The molecular structure and labeling scheme of 1 are shown in Figure 1. The selected bond distances and angles are collected in Table V. The local geometry around the tin atom is that of a trigonal bipyramid with S(2) and Cl in the apical positions and S(1), C(8), and C(4) in the equatorial positions. The least-squares plane through the trigonal arrangement (S(1), C(8), C(4)) shows that the tin atom is displaced by only 0.0938 Å out of the plane toward S(2) (Table SX). The trigonal bipyramid is distorted, as is seen from the axial S(2)–Sn–Cl angle (154.1 (<1)°) partially resulting from the typical small bite angle (68.6 (<1)°) of the dtc ligand. The bond distances of Sn–S(1) (2.510 (1) Å) and Sn–S(2) (2.691 (1) Å) are proximate to the known Sn–S distances (Sn–S(1) = 2.535 (3) Å; Sn–S(2) = 2.635 (3) Å; Sn–S(3) = 2.540 (3) Å; Sn–S(4) = 2.599 (3) Å) in $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)_2Cl$[23] and are com-

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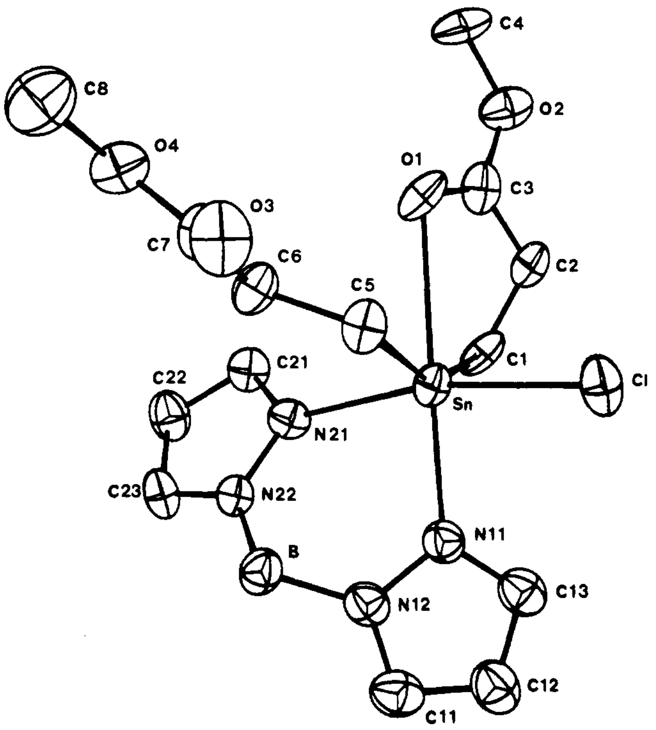

Figure 2. ORTEP drawing of 2 with thermal ellipsoids shown at the 50% probability level.

parable with the typical anisobidentate lengths in most mono- and dialkyltin dithiocarbamate compounds.[24-29] The axial Sn-S(2) bond (2.691 (1) Å) is longer than the corresponding equatorial Sn-S(1) bond (2.510 (1) Å). Similarly, the apical Sn-Cl distance (2.502 (1) Å), which is similar to the axial distance (2.54 Å) in the [$(CH_3)_2SnCl_3]^-$ ion,[30] is longer than the equatorial bond (2.32 Å) in the same ion. The interesting aspect of the structure of 1 is that the two carbonyl groups are no longer coordinated to the tin atom (Sn-O(1) = 3.154 (6) Å; Sn-O(3) = 2.942 (5) Å), in contrast to its starting compound $(CH_3OOCCH_2CH_2)_2SnCl_2$, which includes two five-membered chelate rings via carbonyl oxygen-to-tin coordination (Sn-O(1) = 2.520 (4) Å; Sn-O(3) = 2.524 (4) Å).[8] The Sn-O(3) distance (2.942 (5) Å) in 1 is comparable to that of the dative Sn-O(2) bond (2.95 Å) in tricyclohexyltin(IV) acetate,[31] which is not counted as a coordinative interaction, and it may be not regarded as a bonding interaction from its IR and ^{119}Sn NMR spectra, which will be shown later. This result shows that the dtc ligand acts as a good electron-donating group increasing the electron density on the tin atom, probably due to an additional π-electron flow from the nitrogen to the sulfur atom via in-plane delocalization of the π-orbital system. Thus, the overall geometry around the tin atom of 1 is similar to that of the simple dimethyl analogue $Me_2Sn(S_2CNMe_2)Cl$.[32]

The molecular geometry of 2 is depicted in Figure 2, where the atomic numbering scheme is defined. The selected bond distances and angles appear in Table V. Figure 2 shows a molecule consisting of six- and five-membered rings formed by the bidentate bpb ligand and the intramolecular carbonyl oxygen-to-tin coordination, respectively. The local geometry around the tin atom approximates to a distorted octahedral arrangement with Cl and N(21) in trans position (Cl-Sn-N(21) = 167.6 (1)°). The atoms of N(11), C(5), O(1), C(1), and Sn form a perfect plane (Table SX). The bpb ligand bonded in anisobidentate fashion (Sn-N(11) = 2.182 (6) Å; Sn-N(21) = 2.310 (5) Å) in 2 is similar to that (2.164 (5), 2.339 (5) Å) of the dimethyl analogue $Me_2Sn(bpb)Cl$.[33] The bpb ligand is essentially puckered in a shallow boat form to provide a suitable bite angle while tetrahedral angles at the boron atom are maintained. A feature of particular interest in 2 is the intramolecular Sn-O(1) interaction of one of the ester groups in contrast to 1. The Sn-O(1) bond (2.745 (6) Å) is proximate to the Sn-O bond of (*cis*-3-(benzyloxy)cyclohexyl)halogenodimethyltin (2.72 (2) Å)[34] and (2-carbomethoxy-1,4-cyclohexadien-1-yl)trimethyltin (2.78 (3) Å).[35] However, the distance is longer than the corresponding dative bonds of the starting material $(CH_3OOCCH_2CH_2)_2SnCl_2$ (2.520 (2), 2.524 (4) Å),[8] reflecting a weaker coordination. The angle C(1)-Sn-C(5) (146.3 (3)°) is splayed out compared to that (137.7 (3)°) of the dimethyl analogue, and the dihedral angle (53.49 (35)°) between the two pyrazolyl planes is considerably smaller than the corresponding angle (61°)[33] in the less crowded molecule of the dimethyl analogue probably owing to the Sn-O(1) interaction.

The important difference between the molecular structures of 1 and 2 is in the behavior of the ester group bonded to the tin atom, reflecting the coordination nature of organotin compounds. In other words, in contrast to 1 in which no carbonyl-to-tin coordination is allowed, the presence of the carbonyl-to-tin coordination in 2 with the bulkier bpb ligand (vs dtc ligand) clearly indicates that the electronic effect is dominant in the determination of the coordination structure of organotin compounds, as pointed out earlier.[36,37]

Spectroscopic Properties of 1 and 2. The infrared spectra of 1 and 2 recorded on KBr disks and in chloroform solutions (4000–400 cm^{-1}) indicate that their coordination structures are essentially retained in solution. Among the stretching modes, the ν(CO) bands in the region 1650–1750 cm^{-1} are known to depend on the nature of carbonyl-to-metal bonding.[9,38,39] The ν(CO) bands of 1 both in the solid state (1725 cm^{-1}) and in solution (1723 cm^{-1}) are in the same region as that of the uncoordinated ester group illustrated in $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)_2Cl$ (1724 cm^{-1}), for instance, which indicates the nonchelating nature of the ester group both in the solid state[23] and in solution.[40] In contrast to 1, the appearance of two strong bands in the IR spectrum of 2 with a separation value more than 40 cm^{-1} both in the solid state (1737, 1689 cm^{-1}) and in so-

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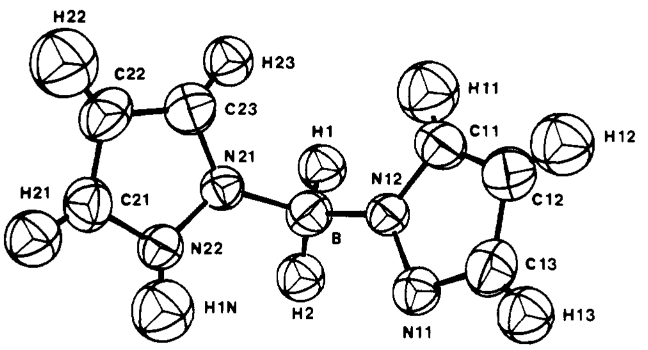


Figure 3. ORTEP drawing of Hbpb with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and angle (deg): B–N(12), 1.540 (4); B–N(21), 1.568 (5); N(11)–N(12), 1.351 (3); N(21)–N(22), 1.335 (3); N(12)–C(11), 1.345 (3); N(21)–C(23), 1.338 (4); N(12)–B–N(21), 109.7 (3).

lution (1730, 1689 cm^{-1}) indicates coexistence of coordinated and uncoordinated carbonyl groups in **2** in both states. However, the coordinated carbonyl stretching band in **2** exhibits a considerable blue shift from that (1652 cm^{-1}) of $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)Cl_2$,[40] indicating a weaker coordination, as is seen in the Sn–O bond length (2.745 (6) Å) of its crystal structure.

It is well-known that the ^{119}Sn chemical shift $\delta(^{119}Sn)$ moves upfield in proportion to the coordination number of tin atom in the organotin(IV) compounds with ligands of similar donating atoms.[36,41–46] The $\delta(^{119}Sn)$ value of **1** (−258.6 ppm) is approximately the same as that of the known five-coordinated analogue $(t\text{-}Bu)_2Sn(S_2CNMe_2)Cl$ (−224 ppm).[36] However, the remarkable upfield shift of the $\delta(^{119}Sn)$ value of **2** (−255.4 ppm) compared with that of the pentacoordinated dimethyl analogue $Me_2Sn(bpb)Cl$ (−181.7 ppm)[33] implies that the tin atom in **2** is hexacoordinated and its coordination number is retained even in solution, consistent with the above-mentioned X-ray (Figure 2) and IR data.

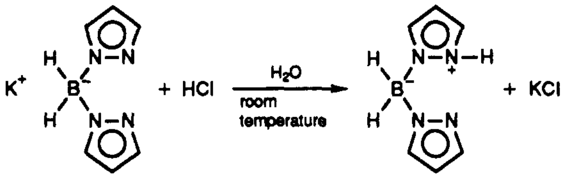
Reaction of 1 and 2 with Sodium Sulfide. The reaction of **1** with sodium sulfide in a 2:1 mole ratio results in the known products $[(CH_3OOCCH_2CH_2)_2SnS]_3$[20,47] and $(CH_3OOCCH_2CH_2)_2Sn(S_2CNMe_2)_2$[10] via an intermolecular migration of the dtc ligand, as shown in reaction 1. When

$$6(CH_3OOCCH_2CH_2)_2Sn(dtc)Cl + 3Na_2S \xrightarrow[\text{room temperature}]{CHCl_3/H_2O} [(CH_3OOCCH_2CH_2)_2SnS]_3 + 3(CH_3OOCCH_2CH_2)_2Sn(dtc)_2 + 6NaCl \quad (1)$$

this reaction is carried out at −20 °C, the same products are obtained. In contrast, the reaction of **2** with sodium sulfide in a 2:1 mole ratio does not afford the corresponding products but gave instead of the $(bpb)_2Sn$ analogue a new N-protonated zwitterion Hbpb along with the same trimeric sulfide. Half of the reactant **2** remained unreacted in the solution. In fact, the equimolar reaction of **2** with sodium sulfide resulted in the same products without unreacted starting material, as shown in reaction 2.

$$3(CH_3OOCCH_2CH_2)_2Sn(bpb)Cl + 3Na_2S \xrightarrow[\text{room temperature}]{CHCl_3/H_2O} [(CH_3OOCCH_2CH_2)_2SnS]_3 + 3Hbpb + 3NaCl + 3NaOH \quad (2)$$

Therefore, it seems certain that the reactions of the compounds **1** and **2** with sodium sulfide proceed by different routes, which will not be discussed in this paper. The new zwitterionic species Hbpb was investigated by elemental analysis and X-ray structure determination (Figure 3). Even though a large number of pyrazabole derivatives have been studied,[48–52] to our knowledge, Hbpb is the first N-protonated dihydrobis(pyrazolyl)borate zwitterion. The local geometry around the boron atom in the zwitterion is nearly tetrahedral, and the bond lengths and angles are of normal values. The proton source seems to be water from the solvent. This zwitterion could be prepared more simply by the reaction (eq 3) of K(bpb) with hydrochloric acid.



(3)

On the other hand, $(CH_3OOCCH_2CH_2)_2Sn(bpb)_2$ could not be prepared even by the reaction of $(CH_3OOCCH_2CH_2)_2SnCl_2$ with K(bpb), but instead, only the mono-bpb analogue **1** was obtained, probably due to the bulky bpb ligand. Thus, the products in the reactions involving the bpb ligand seem to be controlled by the bulkiness of the ligand.

In conclusion, the maintenance of the Sn–O(1) bond in **2** with the bulkier bpb ligand in contrast to **1** with the dtc ligand may be ascribed to the inductive effect of the coordinating atoms of the ligand, and thus, the inductive factor seems to be preferentially responsible for the coordination structure of the organotin compounds. On the other hand, the reactions of **1** and **2** with sodium sulfide seem to be controlled by the bulkiness of the chelating ligands.

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Supplementary Material Available: Tables of anisotropic thermal parameters (Tables SI, SV, and SXI) and bond distances and angles (Tables SII, SVI, and SXII) for **1**, **2**, and Hbpb, dihedral angles for **2** (Table SVII), and least-squares planes for **1** and **2** (Table SX) (8 pages); tables of structure factors (Tables SIV, SIX, and SXIII) for **1**, **2**, and Hbpb (25 pages). Ordering information is given on any current masthead page.

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