Tris(pyrazolyl)borate complexes of 3-methoxy-3-oxopropyltin(IV). Crystal structure and properties of $CH_3OOCCH_2CH_2Sn((pz)_3BH)X_2$ (X = Cl, NCS)

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Abstract

(Hydrotris(pyrazolyl)borato)(3-methoxy-3-oxopropyl)tin(IV) compounds, $CH_3OOCCH_2CH_2$-Sn$((pz)_3BH)X_2$ (**1**: X = Cl; **2**: X = NCS), have been prepared and examined. The X-ray crystal structures of **1**·CH_2Cl_2 ($C2/c$; a 20.658(4), b 8.848(1), c 26.485(5) Å, β 109.73(1)°; $Z = 8$; $R = 0.540$) and **2**·C_6H_6 ($P\bar{1}$; a 9.756(1), b 11.783(1), c 13.407(1) Å, α 110.236(9), β 109.647(8), γ 95.842(8)°; $Z = 2$; $R = 0.0463$) shows discrete molecules containing a distorted octahedral tin atom, and a facial tridentate hydrotris(pyrazolyl)borate ligand; the carbonyl oxygen atom of 3-methoxy-3-oxopropyl group is released from the tin atom to accommodate the negative tridentate ligand. The spectral and the cryoscopic data for solid state or in solution are consistent with the crystal structures.

Introduction

Since Trofimenko discovered the potential tridentate ligand, tris(pyrazolyl)borate $((pz)_3BH)$ with nitrogens as the donor atoms [1–3], the chemistry of the moieties has been well established because it is a rare uninegative tridentate ligand and partially because of its histidine-like ligation in transition metal chemistry [4–17]. In addition to the transition metal complexes, recently organotin(IV)poly(pyrazolyl)borates have become interesting not only because of its coordination geometry (the first hexa-coordinated triorganotin(IV)) but also its availability as a useful starting material [18–21].

On the order hand, we have recently prepared and characterized a series of 3-methoxy-3-oxopropyltin(IV) (so-called "estertin") complexes with potential multidentate ligands to extend the coordination chemistry of organotin(IV) compounds [22–25]. The behavior of the carbonyl group in estertin compounds is particularly sensitive to the environment around the tin atom.

In an attempt to explore the chemistry of estertin compounds, we have prepared crystalline materials formulated as $CH_3OOCCH_2CH_2Sn((pz)_3BH)X_2$ $((pz)_3BH =$

hydrotris(pyrazolyl)borate(tpb); X = Cl, NCS). Here we describe the features of the present compounds in terms of their crystal structures and with spectral data.

Experimental

All manipulations and reactions were performed under nitrogen with the use of standard Schlenkware at room temperature. All chemicals were of reagent grade and used without further purification. All the solvents were dried by standard methods before use. Chemical analyses were carried out by the Chemical Analysis Laboratory at KIST. The molecular weights were determined cryoscopically in benzene by use of a Cryette A Automatic Cryoscope. The IR spectra in the 4000–400 cm^{-1} region were measured on KBr disc with an Analect Instrument fx 6160 FT-IR spectrometer. All NMR spectra were recorded in $CDCl_3$ on a Bruker AM-200 operating at 200 MHz(^1H) and 74.63 MHz(^{119}Sn) in pulse mode with Fourier transform at ambient temperature. The chemical shifts determined were relative to internal Me_4Si (^1H) and external Me_4Sn (^{119}Sn) for indicated nuclei.

3-Methoxy-3-oxopropyltin(IV) trichloride [26] and potassium hydrotris(pyrazolyl)borate [1] were prepared by published procedures.

Preparation of $CH_3OOCCH_2CH_2Sn((pz)_3BH)Cl_2$ (1).
A solution of $CH_3OOCCH_2CH_2SnCl_3$ (3.12 g, 10 mmol) in 50 ml of dichloromethane was added dropwise to a stirred suspension of $K(pz)_3BH$ (2.55 g, 10 mmol) in 50 ml of dichloromethane. The cloudy solution was stirred for 2 hours and filtered to remove potassium chloride. All the volatiles were removed under vacuum, to leave a white solid (79% yield). Recrystallization of the white solid from dichloromethane gave a colorless crystal suitable for X-ray crystallography and formulated as $CH_3OOCCH_2CH_2Sn((pz)_3BH)Cl_2 \cdot CH_2Cl_2$ (m.p. 165–166 °C). Anal. Calcd. for $C_{13}H_{17}N_6Cl_2O_2BSn \cdot CH_2Cl_2$: C, 29.26; H, 3.73; N, 14.62. Found: C, 29.20; H, 3.38; N, 14.51. Molecular weight measured: 461 (Calcd. for $C_{13}H_{17}N_6Cl_2O_2BSn$: 489.7). IR (KBr, cm^{-1}): ν(B–H) 2509; ν(CO) 1730. ^1H NMR ($CDCl_3$; δ, ppm): pyrazolyl group (8.17(d),1H; 7.88(d),2H; 7.74(d),2H; 7.63(d),1H; 6.32(t), 2H; 6.25(t),1H; CH_2Cl_2 (5.28(s),2H); CH_3O–(3.71(s),3H); –CH_2– (2.97(t),2H); –CH_2Sn(2.01(t),2H). ^{119}Sn NMR ($CDCl_3$; δ, ppm): −482.4.

Preparation of $CH_3OOCCH_2CH_2Sn((pz)_3BH)(NCS)_2$ (2)
To a solution of **1** (5.75 g, 10 mmol) in 30 ml of acetone was added dropwise KSCN (1.94 g, 20 mmol) in 30 ml of acetone, and the solution was stirred for 2 hours. The solution was filtered to remove potassium chloride, and the solvent was evaporated under vacuum to give a white solid in 85% yield. The white solid was recrystallized from a benzene–petroleum ether (1:1) solution to give a colorless crystal of $CH_3OOCCH_2CH_2Sn((pz)_3BH)(NCS)_2 \cdot C_6H_6$ (m.p. 141–142 °C) suitable for the X-ray diffraction study. Anal. Calcd. for $C_{15}H_{17}N_8O_2S_2BSn \cdot C_6H_6$: C, 41.14; H, 3.78; N, 18.28. Found: C, 40.80; H, 3.50; N, 18.46%. Molecular weight measured: 529 (Calcd. for $C_{15}H_{17}N_8O_2S_2BSn$: 534.9). IR (KBr, cm^{-1}): ν(B–H) 2518; ν(C–N) 2040; ν(C=O) 1731. ^1H NMR ($CDCl_3$; δ, ppm): pyrazolyl group (8.10(d),1H; 8.07(d),2H; 7.78(d),2H; 7.67(d),1H; 6.41(t),2H; 6.37(t),1H); C_6H_6 (7.36(s),6H); CH_3O– (3.80(s),3H); –CH_2– (2.99(t),2H); –CH_2Sn (1.89(t),2H). ^{119}Sn NMR ($CDCl_3$; δ, ppm): −589.5.

Table 1

Crystal and experimental details for $1\cdot CH_2Cl_2$ and $2\cdot C_6H_6$

	$1\cdot CH_2Cl_2$	$2\cdot C_6H_6$
Formula	$C_{13}H_{17}N_6O_2Cl_2BSn\cdot CH_2Cl_2$	$C_{15}H_{17}N_8O_2S_2BSn\cdot C_6H_6$
FW	574.66	613.09
Space group	$C2/c$	$P\bar{1}$
a, b, c (Å)	20.658(4), 8.848(1), 26.485(5)	9.756(1), 11.783(1), 13.407(1)
α, β, γ (deg.)	109.73	110.236(9), 109.647(8), 95.842(8)
V (Å^3)	4557(2)	1319.8(4)
Z	8	2
$d_{cal.}$ (g cm^{-3})	1.67	1.54
Crystal size (mm)	$0.52\times0.60\times0.68$	$0.36\times0.42\times0.50$
μ (cm^{-1})	14.85	10.52
Scan method	$\omega/2\theta$	$\omega/2\theta$
Data collected	$h, k, \pm l, 1\leqslant\theta\leqslant25°$	$h, \pm k, \pm l, 1\leqslant\theta\leqslant25°$
Number of total observations	8854	5482
Number of unique observations $I>3\sigma(I)$	2848	4692
Number of parameters refined	238	286
Largest shift/esd	0.02	0.02
Largest peak (e Å^{-3})	1.51 (0.90 Å from Sn)	1.42 (0.094 Å from Sn)
gof	2.76	0.41
R	0.0540	0.0463
R_w	0.0585	0.0544

Table 2

Positional and equivalent isotropic thermal parameters ^{a} for $1\cdot CH_2Cl_2$

Atom	x	y	z	U_{eq}
Sn	0.2030(0)	0.07481(1)	0.0935(0)	0.040(0)
Cl(1)	0.1577(1)	0.2924(2)	0.0356(1)	0.054(1)
Cl(2)	0.1978(1)	0.1972(3)	0.1734(1)	0.062(2)
N(31)	0.0963(4)	0.0033(8)	0.0768(3)	0.046(5)
N(32)	0.0741(4)	−0.1377(8)	0.0638(3)	0.046(4)
N(21)	0.2211(4)	−0.1507(7)	0.1329(3)	0.043(4)
N(22)	0.1832(4)	−0.2746(7)	0.1096(3)	0.045(4)
N(11)	0.1860(3)	−0.0680(8)	0.0204(3)	0.040(4)
N(12)	0.1536(3)	−0.2035(7)	0.0145(3)	0.037(4)
C(31)	0.0069(5)	−0.1517(12)	0.0581(4)	0.058(7)
C(32)	−0.0147(5)	−0.0106(13)	0.0696(4)	0.063(7)
C(33)	0.0408(5)	0.0840(11)	0.0811(4)	0.056(6)
C(21)	0.2076(6)	−0.3953(10)	0.1417(4)	0.059(7)
C(22)	0.2612(6)	−0.3507(11)	0.1853(4)	0.064(8)
C(23)	0.2682(5)	−0.1961(12)	0.1794(4)	0.059(7)
C(11)	0.1493(4)	−0.2634(10)	−0.0341(3)	0.045(5)
C(12)	0.1820(4)	−0.1674(12)	−0.0580(3)	0.051(6)
C(13)	0.2047(4)	−0.0458(10)	0.0230(4)	0.048(5)
B	0.1228(5)	−0.2633(10)	0.0556(4)	0.047(7)
C(1)	0.3088(4)	0.1146(10)	0.1035(3)	0.041(5)
C(2)	0.3412(6)	0.2580(13)	0.1359(4)	0.066(7)
C(3)	0.3704(6)	0.2281(13)	0.1958(5)	0.070(8)
O(1)	0.3833(6)	0.1036(9)	0.2168(4)	0.104(9)
O(2)	0.3812(5)	0.3551(10)	0.2235(4)	0.099(8)
C(4)	0.4052(9)	0.3393(19)	0.2829(5)	0.111(13)
Cl(1S)	−0.0367(3)	0.2546(6)	0.1769(2)	0.131(2)
Cl(2S)	0.0127(3)	0.4914(7)	0.1263(2)	0.140(2)
C(S)	0.0299(10)	0.3924(25)	0.1886(9)	0.140(7)

^{a} Equivalent isotropic U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

X-Ray diffraction study of $1 \cdot CH_2Cl_2$ *and* $2 \cdot C_6H_6$

All the X-ray crystallographic data were collected by using an Enraf Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ 0.71067 Å) at ambient temperature of 23(2)°C. Each crystal was mounted inside a thin-walled glass capillary, which was sealed as an unstable precaution against moisture and dioxygen. Accurate cell dimensions were obtained from the setting angles of 25 carefully centered reflections, $12 < \theta < 16°$ for $1 \cdot CH_2Cl_2$ and $9 < \theta < 14$ for $2 \cdot C_6H_6$ by a least-squares procedure. During the data collection, three standard reflections monitored after every hour revealed no systematic variation in intensity. All calculations were performed on an IBM 3083 computer using SHELX 76 [27] and atomic scattering factors were supplied by the SHELX system. Crystal data and additional details of data collection and refinement are summarized in Table 1.

Table 3

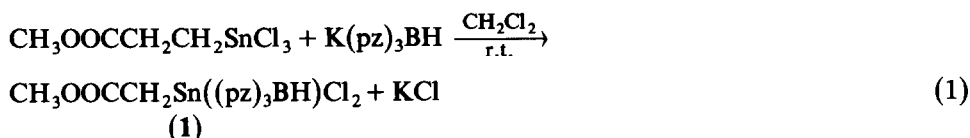Positional parameters and equivalent isotropic thermal parameters for $2 \cdot C_6H_6$

Atom	x	y	z	U_{eq}
Sn	0.2055(0)	0.1585(0)	0.8328(0)	0.047(0)
S(1)	0.0462(5)	0.1961(3)	1.1391(3)	0.226(5)
S(2)	−0.0969(3)	0.4543(2)	0.8257(3)	0.126(2)
N(31)	0.1605(6)	0.1524(5)	0.9763(4)	0.081(4)
C(1)	0.1090(7)	0.1670(5)	1.0398(5)	0.067(4)
N(32)	0.1047(5)	0.3099(4)	0.8370(4)	0.071(3)
C(2)	0.0176(6)	0.3675(5)	0.8337(4)	0.058(3)
C(3)	0.0243(5)	0.0039(5)	0.7061(4)	0.058(3)
C(4)	−0.1326(6)	0.0289(5)	0.6765(5)	0.067(3)
C(5)	−0.1749(5)	0.0815(5)	0.5868(4)	0.057(3)
O(1)	−0.0904(4)	0.1205(4)	0.5522(4)	0.086(3)
O(2)	−0.3187(4)	0.0809(4)	0.5497(3)	0.075(3)
C(6)	−0.3722(7)	0.1225(8)	0.4586(6)	0.096(6)
N(11)	0.3660(5)	0.0362(3)	0.8477(3)	0.052(2)
N(12)	0.5060(4)	0.0710(4)	0.8567(4)	0.056(2)
C(11)	0.5772(6)	−0.0203(5)	0.8590(5)	0.071(3)
C(12)	0.4783(7)	−0.1188(5)	0.8511(5)	0.073(4)
C(13)	0.3483(6)	−0.0798(4)	0.8460(4)	0.062(3)
N(21)	0.3158(4)	0.1984(4)	0.7242(3)	0.051(2)
N(22)	0.4663(4)	0.2171(4)	0.7560(3)	0.054(2)
C(21)	0.5052(6)	0.2544(5)	0.6838(5)	0.066(3)
C(22)	0.3767(6)	0.2591(5)	0.6016(5)	0.067(3)
C(23)	0.2594(6)	0.2222(4)	0.6297(4)	0.054(3)
N(31)	0.4072(5)	0.3005(4)	0.9703(3)	0.053(2)
N(32)	0.5467(5)	0.2998(4)	0.9696(4)	0.054(2)
C(31)	0.6503(7)	0.3928(5)	1.0680(5)	0.074(4)
C(32)	0.5748(8)	0.4518(5)	1.1336(5)	0.079(5)
C(33)	0.4212(7)	0.3947(5)	1.0687(5)	0.071(4)
B	0.5674(6)	0.2043(5)	0.8643(5)	0.058(3)
C(1S)	0.0179(8)	0.4417(7)	0.5739(7)	0.081(2)
C(2S)	0.0299(8)	0.6284(7)	0.5442(7)	0.084(2)
C(3S)	0.0459(8)	0.5674(7)	0.6172(7)	0.083(2)
C(4S)	0.3593(12)	0.4831(10)	0.4397(10)	0.117(3)
C(5S)	0.4017(12)	0.5572(10)	0.5458(10)	0.118(3)
C(6S)	0.4473(13)	0.4182(11)	0.3810(10)	0.132(4)

For crystals $1 \cdot CH_2Cl_2$ and $2 \cdot C_6H_6$, the structures were solved by conventional Patterson method for space group $C2/c$ (No. 15) and $P\bar{1}$ (No. 2) [28], respectively, followed by successive difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters and non-hydrogen atoms of solvated molecules were refined with isotropic thermal parameters. Hydrogen atoms were omitted from the refinement. The final values of the refined positional and equivalent isotropic thermal parameters for $1 \cdot CH_2Cl_2$ and $2 \cdot C_6H_6$ are presented in Tables 2 and 3, respectively.

Results and discussion

Synthesis

The potassium tris(pyrazolyl)borate (tpb) prepared by Trofimenko's procedure [1] was treated with 3-methoxy-3-oxopropyltin trichloride in dichloromethane to give obtain 1 (eq. 1). Reaction of 1 with potassium thiocyanate (KSCN) in the

$$CH_3OOCCH_2CH_2SnCl_3 + K(pz)_3BH \xrightarrow[\text{r.t.}]{CH_2Cl_2}$$

$$CH_3OOCCH_2Sn((pz)_3BH)Cl_2 + KCl \tag{1}$$
$$\textbf{(1)}$$

mole ratio of of $1:2$ gives **2** as identified from chemical analysis and its spectral data (see below).

$$1 + 2KSCN \xrightarrow[\text{r.t.}]{\text{acetone}} CH_3OOCCH_2CH_2Sn((pz)_3BH)(NCS)_2 + 2KCl \tag{2}$$
$$\textbf{(2)}$$
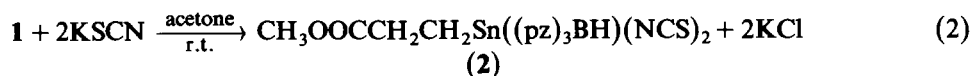
Recrystallization of **1** and **2** from dichloromethane and benzene–petroleum ether, respectively, affords the solvated colorless crystal $1 \cdot CH_2Cl_2$ and $2 \cdot C_6H_6$ which are suitable for X-ray crystallography. In particular, after the solvated molecule had been removed, cryoscopic measurements in benzene showed that both molecules are discrete monomers.

On the other hand, we made several attempts to prepare the family complexes containing two tpb ligands such as $(HB(pz)_3)_2MX_n$ of Ta and Y [10,13,29], but this was not possible, presumably because of the large steric requirement of the tpb ligand. However, Zaidi et al. recently reported the chemical species of $R_2Sn(tpb)_2$ (R = Me, Bu) though with insufficient evidence [20].

Crystal structure description of 1 and 2

The ORTEP drawing and labeling scheme of **1** is presented in Fig. 1. The bond distances and angles are listed in Table 4. The dichloromethane solvate molecule is not included in the molecular structure and does not interact with the parent molecule **1**. The coordination geometry around the tin atom is approximately octahedral with Sn–N(11), Sn–N(21), Sn–N(31), Sn–Cl(1), Sn–Cl(2), and Sn–C(1) bonds. The tpb ligand is bonded to the tin atom in a tridentate fashion (Sn–N(11), 2.237(6); Sn–N(21), 2.225(7); Sn–N(31), 2.191(7) Å) which is essentially facial to provide a suitable bite angle while maintaining a tetrahedral angle at the boron atom. The two chlorine atoms are splayed out to give Cl(1)–Sn–Cl(2) angles (94.3(1)°) with a concomitant closing of the N(21)–Sn–N(31) angle (80.4(3)°) partially resulting in a distortion of the octahedral tin atom. The Sn–N bond lengths
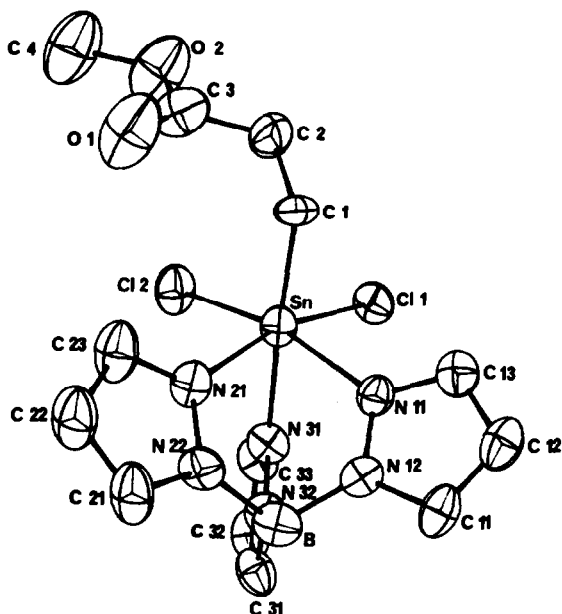
Fig. 1. ORTEP drawing of $CH_3OOCCH_2CH_2Cn((pz)_3BH)Cl_2$(1)·$CH_2Cl_2$ showing 50% probability thermal ellipsoids and the numbering scheme. Dichloromethane solvate molecule has been omitted.

(Sn–N(11), 2.237(6); Sn–N(21), 2.225(7); Sn–N(31), 2.191(7) Å) along with Sn–C(1) (2.140(7) Å) are slightly shorter than those (Sn–N, 2.388(2) Å; Sn–C, 2.165(2) Å) in a trimethyl analogue $Me_3Sn(tpb)$ [18] presumably due to a increase of Lewis acidity of the tin atom by the partial change of donor atoms. The important feature in 1 is that the carbonyl group is released from the tin atom (Sn · · · O(1), 4.04(1) Å) to accommodate the uninegative tridentate bonding mode of the tpb ligand, in sharp contrast to the bidentate dithiocarbamate analogue, $CH_3OOCCH_2CH_2Sn(S_2CN-Me_2)Cl_2$, which includes a five-membered chelate ring via the carbonyl oxygen-to-tin coordination (Sn–O(1), 2.436(6) Å) [22].

The molecular geometry including the numbering scheme of 2 is depicted in Fig. 2. The bond distances and angles are listed in Table 5. The benzene solvate molecule is not included in Fig. 2 since the benzene does not interact with 2. The local geometry around the tin atom is similar to that of 1 except that the NCS group undergoes replacement instead of Cl. Complex 2 exists as a discrete molecule: the shortest intermolecular distance not involving hydrogen atoms is 3.497(9) Å between C(11) and neighboring C(13). In addition, the intermolecular distance between S(1) and Sn is much longer 4.822(4) Å than that found in most organotin(IV) isothio-cyanates, including the intermolecular association between the terminal atom S of the isothiocyanate group and the neighboring Sn [30–33]. That complex 2 exists as discrete molecules may be ascribed to the crowded hexa-coordinated sphere of the tin atom. Though two linkage isomers are possible, the two thiocyanate groups in 2 are bonded to the isothiocyanate mode. The nearly linear N–C–S angles of 175.5(6)° and 175.5(5)° for 2 and the bond lengths of N–C and C–S of the isothiocyanate groups are consistent with those of most isothiocyanatotin(IV) com-

Table 4

Bond distances (Å) and angles (°) for **1**

Sn–Cl(1)	2.442(2)	N(22)–B	1.551(12)
Sn–Cl(2)	2.413(2)	C(21)–C(22)	1.361(14)
Sn–N(31)	2.191(7)	C(22)–C(23)	1.390(14)
Sn–N(21)	2.225(7)	N(11)–N(12)	1.356(9)
Sn–N(11)	2.237(6)	N(11)–C(13)	1.345(11)
Sn–C(1)	2.140(7)	N(12)–C(11)	1.368(10)
N(31)–N(32)	1.333(10)	N(12)–B	1.529(12)
N(31)–C(33)	1.387(11)	C(11)–C(12)	1.366(13)
N(32)–C(31)	1.350(11)	C(12)–C(13)	1.394(13)
N(32)–B	1.564(11)	C(1)–C(2)	1.551(13)
C(31)–C(32)	1.393(15)	C(2)–C(3)	1.517(15)
C(32)–C(33)	1.369(15)	O(1)–C(3)	1.222(13)
N(21)–N(22)	1.368(9)	O(2)–C(3)	1.320(14)
N(21)–C(23)	1.346(11)	O(2)–C(4)	1.489(16)
N(22)–C(21)	1.352(11)		
Cl(2)–Sn–Cl(1)	94.3(1)	B–N(22)–C(21)	130.1(7)
N(31)–Sn–Cl(1)	87.4(2)	N(12)–N(11)–Sn	121.7(5)
N(31)–Sn–Cl(2)	88.1(2)	C(13)–N(11)–Sn	130.6(6)
N(21)–Sn–Cl(1)	165.9(2)	C(13)–N(11)–N(12)	107.6(7)
N(21)–Sn–Cl(2)	92.3(2)	C(11)–N(12)–N(11)	108.9(7)
N(21)–Sn–N(31)	80.4(3)	B–N(12)–N(11)	122.1(6)
N(11)–Sn–Cl(1)	89.3(2)	B–N(12)–C(11)	128.7(7)
N(11)–Sn–Cl(2)	166.4(2)	C(32)–C(31)–N(32)	106.6(9)
N(11)–Sn–N(31)	79.0(2)	C(33)–C(32)–C(31)	106.9(8)
N(11)–Sn–N(21)	81.5(2)	C(32)–C(33)–N(31)	108.6(8)
C(1)–Sn–Cl(1)	96.2(2)	C(22)–C(21)–N(22)	109.2(9)
C(1)–Sn–Cl(2)	99.4(2)	C(23)–C(22–C(21)	105.9(8)
C(1)–Sn–N(31)	171.4(3)	C(22)–C(23)–N(21)	109.1(9)
C(1)–Sn–N(21)	95.0(3)	C(12)–C(11)–N(12)	108.0(8)
C(1)–Sn–N(11)	93.2(3)	C(13)–C(12)–C(11)	106.3(8)
N(32)–N(31)–Sn	123.9(5)	C(12)–C(13)–N(11)	109.1(8)
C(33)–N(31)–Sn	129.6(6)	N(22)–B–N(32)	105.8(7)
C(33)–N(31)–N(32)	106.3(7)	N(12)–B–N(32)	107.2(7)
C(31)–N(32)–N(31)	111.5(7)	N(12)–B–N(22)	106.3(7)
B–N(32)–N(31)	121.2(7)	C(2)–C(1)–Sn	115.7(6)
B–N(32)–C(31)	127.3(8)	C(3)–C(2)–C(1)	112.3(9)
N(22)–N(21)–Sn	121.8(5)	O(1)–C(3)–C(2)	125.5(11)
C(23)–N(21)–Sn	130.7(6)	O(2)–C(3)–C(2)	111.5(10)
C(23)–N(21)–N(22)	107.5(7)	O(2)–C(3)–O(1)	123.0(12)
C(21)–N(22)–N(21)	108.3(7)	C(4)–O(2)–C(3)	116.2(10)
B–N(22)–N(21)	121.7(6)		

plexes [30–33]. The bonding fashion of the tpb ligand in **2** is similar to that in **1** as can be seen from Fig. 1 and Fig. 2. In particular, the carbonyl group in **2** also does not chelate to the tin atom (Sn $\cdots$ O(1), 3.736(5) Å) although an isothiocyanate group has been known to be more electronegative than a chlorine atom [34]. In addition, comparison of the coordination number of **2** with that of $(CH_3)_2Sn(NCS)_2(C_{15}H_{11}N_3)$ [35] reveals additional important information as the coordination of the tin atom: it is six-coordinated in **2** whereas in $(CH_3)_2Sn$-
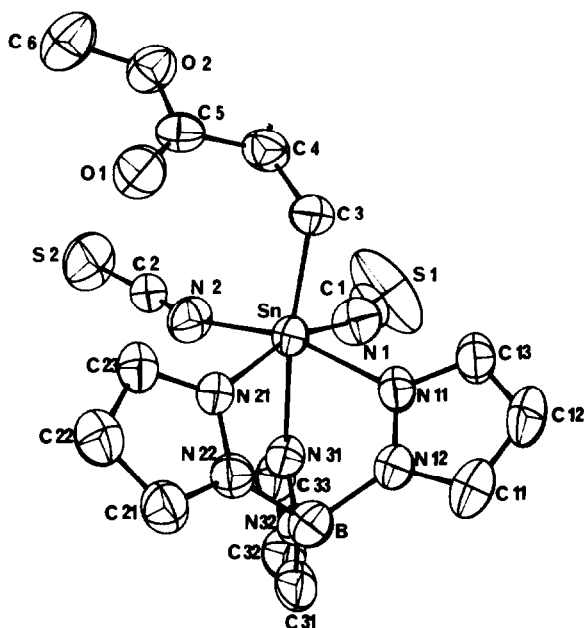
Fig. 2. ORTEP drawing of $CH_3OOCCH_2CH_2Sn((pz)_3BH)(NCS)_2$ (2)·C_6H_6 showing 50% probability thermal ellipsoids and the numbering scheme. Benzene solvate molecule has been omitted.

$(NCS)_2(C_{15}H_{11}N_3)$ it is seven-coordinated probably because of the typical bite angles of terpyridyl group. On the other hand, all the known seven-coordinated organotin(IV) compounds are special cases such as $CH_3Sn(S_2CNMe_2)_3$ [36], CH_3-$Sn(NO_3)_3$ [37], and $(CH_3OOCCH_2CH_2)_2Sn(S_2CNMe_2)_2$ [38], with typical small bite angles. Thus, we suggest that the coordination in organotin compounds showing more than seven-coordination is strongly controlled by the bite angle of potential multidentate ligands as well as appropriate donor atom in contrast to organotin(IV) compounds showing less than six-coordination, in which electronic effects determine the coordination nature, as pointed out earlier [25,39].

Spectroscopic properties

The IR spectra of **1** and **2** show all the expected values consistent with X-ray crystal structures. A strong band at 2509 cm^{-1} (**1**) or 2518 cm^{-1} (**2**) is observed and is readily assigned to ν(B–H) [1]. In particular, the ν(C=O) band (1730 cm^{-1} for **1**; 1731 cm^{-1} for **2**) is in the same region as that of free ester, viz. CH_3OOCCH_3 (1740 cm^{-1}) [40], indicating that each carbonyl group is not coordinated to the tin atom. From the Wada–Okawara criterion [41], a strong and broad band at 2040 cm^{-1} in **2** is strongly indicative of isothiocyanate bonding mode.

Information relevant to coordination number as come from the ^{119}Sn NMR spectra [42–47]. $\delta(^{119}$Sn) = -482.4 ppm of **1** in CDCl$_3$ solution is similar to that (-483.0 ppm) of the known n-Bu analogue, n-BuSn(tpb)Cl$_2$, which includes hexa-coordinated tin atom [21]. The comparison indicates that **1** has a hexa-coordinated tin atom resulting from the free ester group, even in solution. For **2**, $\delta(^{119}$Sn) = -589.5 ppm is more shielded than that of **1**, but lies downfield compared to the chemical shift (-620.5 ppm) of the known six-coordinated Sn(tpb)Cl$_3$ [21]. Thus,

Table 5

Bond distances (Å) and angles (°) for **2**

Sn–N(1)	2.134(5)	C(32)–C(33)	1.404(9)
C(5)–O(1)	1.197(6)	N(31)–C(33)	1.351(7)
C(5)–O(2)	1.320(6)	N(12)–B	1.579(7)
O(2)–C(6)	1.429(8)	N(22)–B	1.525(7)
N(11)–N(12)	1.337(6)	N(32)–B	1.562(7)
N(12)–C(11)	1.342(6)	Sn–N(2)	2.117(4)
C(11)–C(12)	1.382(9)	Sn–C(3)	2.124(5)
C(12)–C(13)	1.380(8)	Sn–N(11)	2.239(4)
N(11)–C(13)	1.352(6)	Sn–N(21)	2.219(4)
N(21)–N(22)	1.354(5)	Sn–N(31)	2.197(4)
N(22)–C(21)	1.333(6)	N(1)–C(1)	1.101(7)
C(21)–C(22)	1.385(8)	C(1)–S(1)	1.594(5)
C(22)–C(23)	1.394(7)	N(2)–C(2)	1.139(7)
N(21)–C(23)	1.339(6)	C(2)–S(2)	1.592(5)
N(31)–N(32)	1.365(6)	C(3)–C(4)	1.534(7)
N(32)–C(31)	1.357(6)	C(4)–C(5)	1.494(7)
C(31)–C(32)	1.385(10)		
N(2)–Sn–N(1)	90.7(2)	C(11)–N(12)–N(11)	110.6(4)
C(3)–Sn–N(1)	95.0(2)	B–N(12)–N(11)	120.7(4)
C(3)–Sn–N(2)	101.7(2)	B–N(12)–C(11)	128.7(4)
N(11)–Sn–N(1)	93.3(2)	C(12)–C(11)–N(12)	107.5(5)
N(11)–Sn–N(2)	165.4(2)	C(13)–C(12)–C(11)	105.7(4)
N(11)–Sn–C(3)	91.9(2)	C(12)–C(13)–N(11)	109.4(5)
N(21)–Sn–N(1)	163.4(2)	N(22)–N(21)–Sn	121.6(3)
N(21)–Sn–N(2)	90.7(2)	C(23)–N(21)–Sn	130.1(3)
N(21)–Sn–C(3)	100.9(2)	C(23)–N(21)–N(22)	107.8(4)
N(21)–Sn–N(11)	81.5(1)	C(21)–N(22)–N(21)	109.4(4)
N(31)–Sn–N(1)	82.9(2)	B–N(22)–N(21)	121.8(4)
N(31)–Sn–N(2)	85.5(2)	B–N(22)–C(21)	128.7(4)
N(31)–Sn–C(3)	172.5(2)	C(22)–C(21)–N(22)	108.6(4)
N(31)–Sn–N(11)	81.1(1)	C(23)–C(22)–C(21)	105.2(4)
N(31)–Sn–N(21)	80.7(2)	C(22)–C(23)–N(21)	109.0(4)
C(1)–N(1)–Sn	160.0(5)	N(32)–N(31)–Sn	122.0(3)
N(1)–C(1)–S(1)	175.5(6)	C(33)–N(31)–Sn	129.4(4)
C(2)–N(2)–Sn	161.2(5)	C(33)–N(31)–N(32)	108.5(4)
N(2)–C(2)–S(2)	175.5(5)	C(31)–N(32)–N(31)	109.3(5)
C(4)–C(3)–Sn	115.9(4)	B–N(32)–N(31)	120.8(4)
C(5)–C(4)–C(3)	114.1(4)	B–N(32)–C(31)	129.9(5)
O(1)–C(5)–C(4)	125.1(5)	C(32)–C(31)–N(32)	107.5(6)
O(2)–C(5)–C(4)	111.7(4)	C(33)–C(32)–C(31)	107.0(5)
O(2)–C(5)–O(1)	123.2(5)	C(32)–C(33)–N(31)	107.7(5)
C(6)–O(2)–C(5)	115.9(4)	N(22)–B–N(12)	108.3(4)
N(12)–N(11)–Sn	121.9(3)	N(32)–B–N(12)	105.8(4)
C(13)–N(11)–Sn	131.2(4)	N(32)–B–N(22)	107.2(4)
C(13)–N(11)–N(12)	106.8(4)		

the coordination number of the tin atom in **2** also seems to be six in solution. Although **1** and **2** have the same hexa-coordinated tin atom in solution, the higher field $\delta(^{119}\text{Sn})$ in **2** than in **1** is presumably because of the partial change in donor atoms bonded to the tin atom.
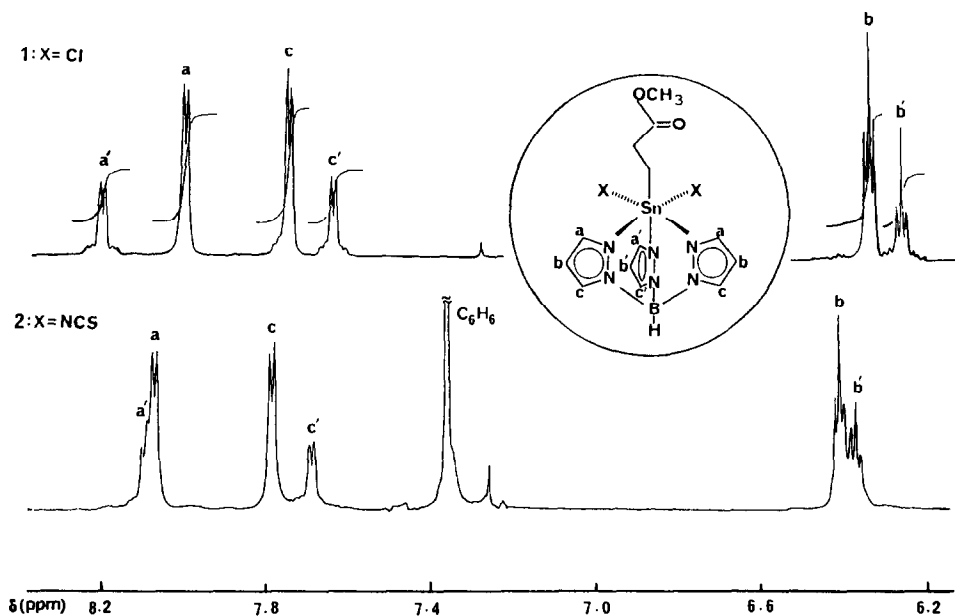
Fig. 3. ^{1}H NMR spectra (200 MHz) of pyrazolyl group in $1 \cdot CH_2Cl_2$ and $2 \cdot C_6H_6$ recorded at ambient temperature of 23(2)° C in $CDCl_3$.

The ^{1}H NMR spectra of pyrazolyl ring in **1** and **2** shown in Fig. 3 indicates two types of pyrazole rings in a 2:1 integration ratio. If it is assumed from the above-mentioned crystal structures for the solid state and $\delta(^{119}Sn)$ in chloroform solution that the tpb ligand in each complex is tridentate, the two types of pyrazole ring signals may be ascribed to the presence of two different groups (**1**: $CH_3OOCCH_2CH_2$, Cl; **2**: $CH_3OOCCH_2CH_2$, NCS) bonded to tin atom. The $H_a' - H_a$ chemical shift difference for **2** is large compared with that of **1** owing to the exchange of Cl for NCS. On the other hand, from our previous result, $\delta(^1H)$ for CH_3O- could also be used to determine the behavior of the ester group bonded to the tin atom. For example, $\delta(^1H)$ 4.0 ppm for CH_3O- in the carbonyl oxygen-to-tin coordinated compound, $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)Cl_2$, is deshielded by approximately 0.3 ppm relative to that ($\delta(^1H)$ 3.7 ppm) in $CH_3OOCCH_2CH_2Sn(S_2CNMe_2)_2Cl$ in which the carbonyl group is not coordinated to the tin atom [22]. Thus, $\delta(^1H)$ 3.71 ppm for **1** and 3.80 ppm for **2** are additional evidence that the carbonyl group is released from the tin atom in solution.

In conclusion, the present estertin(IV) complexes involving tris(pyrazolyl)borate ligand have a hexa-coordinated tin atom, which leaves a free ester group to accommodate the tridentate tpb ligand in the solid and solution state. The structure of **2** suggests that the nature of the coordination of the organotin compounds more than seven-coordination is strongly controlled by the typical bite angle of potential multidentate ligand in addition to appropriate donating atoms.

Acknowledgement

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