

Syntheses and Crystal Structures of Benzyltin(IV) Derivatives of 2-Mercaptobenzothiazole

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The complexes (PhCH₂)₂Sn(MBT)₂ (**2**) and (PhCH₂)₃Sn(MBT) (**3**) (HMBT: 2-mercaptobenzothiazole) have been synthesized and characterized by elemental analyses, and IR, ¹H, ¹³C, ¹¹⁹Sn NMR spectrometries and X-ray diffraction. Studies on the crystal structures of **2** and **3** show that HMBT acts as bidentate ligand through chelation of N and S atoms. Complex **2** contains a six-coordinate tin atom with the axial angle C(15)-Sn(1)-C(22) 129.6(2)°. And the tin environment of complex **3** is a distorted *cis*-trigonal bipyramid with C(8)-Sn(1)-N(1) 158.80°.

Keywords crystal structure, benzyltin(IV) derivative, 2-mercaptobenzothiazole

Introduction

Metal thiolato complexes have been extensively investigated because of their ability to adopt various nuclearities and their relevance in biological science, since they form the inorganic part of the biologically active centers of some metalloproteins and enzymes.¹⁻³ Recently, attention has been paid to the coordination chemistry of heterocyclic thiol/thione donors, which can give potential access to new compounds with unusual structures and reactivities,⁴ such as 2-mercaptobenzothiazole (HMBT) and the related mercaptans.

2-Mercaptobenzothiazole (HMBT) ligand may exist in two tautomeric forms of **1a** and **1b** (Figure 1), but crystallographic study shows that thione form **1b** is preferred (the crystal structure of HMBT **1** was shown in following figure). Correspondingly, at least four possible bonding modes, as shown in Figure 2, between ligand and tin are conceivable. Coordination with the exocyclic sulfur in **A** can be found in every kind of tetrahedral monomeric structures.⁵ Coordination with only the endocyclic nitrogen in **B** is not common for tin compounds, but it is often found for zinc derivatives.⁶ Chelation by both thiol-S and hetero-S atoms in **C** is unknown to our knowledge, but N, S chelation in **D** is commonly observed in dialkyltin compounds.⁷

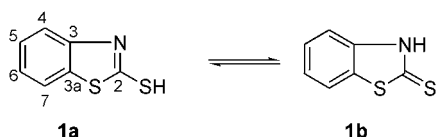


Figure 1 Thiol **1a** and thione **1b** tautomeric forms of the title ligand.

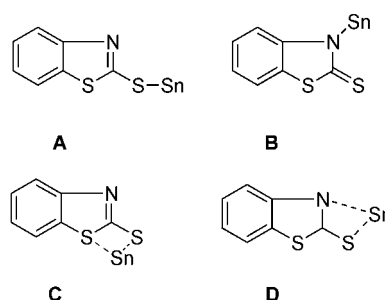


Figure 2 Possible modes of coordination of the title ligand to tin.

In order to investigate the structural and active patterns of HMBT further, we chose dibenzyltin dichloride and tribenzyltin chloride to react with HMBT. In this paper, we report the syntheses of the complexes (PhCH₂)₂Sn(MBT)₂ (**2**) and (PhCH₂)₃Sn(MBT) (**3**), which were characterized by elemental analyses, and IR, ¹H, ¹³C, ¹¹⁹Sn NMR spectrometries, as well as X-ray crystallography. The reactions are shown in Scheme 1.

Experimental

Physical measurements

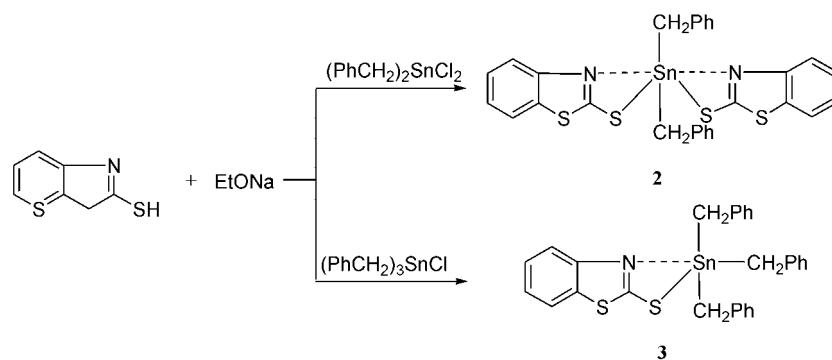
Tribenzyltin chloride and 2-mercaptobenzothiazole were commercially available, and used without further purification. Dibenzyltin dichloride was prepared by a standard method reported in the literature.⁸ The melting points were obtained with a Kofler micro melting point apparatus and were uncorrected. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ¹H, ¹³C and ¹¹⁹Sn

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Scheme 1



NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300, 75.3 and 111.9 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified. ^{13}C spectra are broadband proton decoupled. The chemical shifts were reported in ppm with respect to the references and were stated relative to external tetramethylsilane (TMS) for ^1H and ^{13}C NMR, and to neat tetramethyltin for ^{119}Sn NMR. Elemental analyses were performed with a PE-2400II apparatus.

Syntheses

NaMBT The reaction was carried out under nitrogen atmosphere. A reaction mixture of HMBT (0.400 g, 2.50 mmol) and EtONa (0.17 g, 2.50 mmol) in dry ethanol (20 mL) was stirred for 2 h in a flask at room temperature. The solution was gradually removed by evaporation under vacuum until a solid product was obtained. Yield 90%. m.p. >300 °C. ^{13}C NMR (CDCl_3) δ : 122.5 (C7), 124.1 (C4), 126.2 (C6), 126.9 (C5), 134.6 (C3), 154.3 (C3a), 172.6 (C2); IR ν : 1632 (C=N), 753 (s, C—S) cm^{-1} . Anal. calcd for $\text{C}_7\text{H}_4\text{S}_2\text{NNa}$: C 44.44, H 2.11, N 6.98; found C 44.56, H 2.11, N 6.98.

Dibenzyl bis(MBT)tin(IV) (2) A reaction mixture of $(\text{PhCH}_2)_2\text{SnCl}_2$ (0.372 g, 1 mmol) and NaMBT (0.378 g, 2 mmol) in ethanol (20 mL) was refluxed in a Schlenk flask under nitrogen for 10 h. After being cooled down to room temperature, the pale yellow solution was gradually removed by evaporation under vacuum until a solid product was obtained. The suitable crystal was recrystallized from benzene-hexane. Yield 71%. m.p. 180—182 °C. ^1H NMR (CDCl_3) δ : 7.06—7.51 (m, 18H), 3.54—3.26 (m, $^2J_{\text{SnH}}=70$ Hz, 4H, $\text{CH}_2\text{-Ph}$); ^{13}C NMR (CDCl_3) δ : 35.7 ($\text{CH}_2\text{-Ph}$, $^1J^{117,119}_{\text{SnC}}=375.3, 392.9$ Hz), 122.1 (C7), 123.6 (C4), 123.5 (C6), 121.9 (C5), 128.1 ($^4J_{\text{SnC}}=31$ Hz, *m*-C), 128.7 ($^5J_{\text{SnC}}=25$ Hz, *p*-C), 125.8 ($^3J_{\text{SnC}}=48$ Hz, *o*-C), 134.1 (C3), 136.4 ($^2J_{\text{SnC}}=34$ Hz, *i*-C), 152.0 (C3a), 173.1 (C2); ^{119}Sn NMR (CDCl_3) δ : -219.3; IR ν : 1539 (C=N), 753 (s, C—S); 340, 290 ν_{as} , $\nu_{\text{s}}(\text{Sn—C})$; 309 (m, Sn—S) cm^{-1} . Anal. calcd for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{S}_4\text{Sn}$: C 53.09, H 3.50, N 4.42;

found C 53.10, H 3.52, N 4.40.

Tribenzyl (MBT)tin(IV) (3) A reaction mixture of $(\text{PhCH}_2)_3\text{SnCl}$ (0.427 g, 1 mmol) and NaMBT (0.189 g, 1 mmol) in ethanol (20 mL) was refluxed in a Schlenk flask under nitrogen for 10 h. After being cooled down to room temperature, the white solution was gradually removed by evaporation under vacuum until a solid product was obtained. The suitable crystal was recrystallized from benzene-hexane. Yield 85%. m.p. 95—97 °C. ^1H NMR (CDCl_3) δ : 6.89—7.15 (m, 19H), 2.86—3.15 (m, $^2J_{\text{SnH}}=64$ Hz, 6H, $\text{CH}_2\text{-Ph}$); ^{13}C NMR (CDCl_3) δ : 24.7 ($\text{CH}_2\text{-Ph}$, $^1J^{117,119}_{\text{SnC}}=62.1, 64.6$ Hz), 122.3 (C7), 123.8 (C4), 123.7 (C6), 122.3 (C5), 128.0 ($^4J_{\text{SnC}}=31$ Hz, *m*-C), 128.8 ($^5J_{\text{SnC}}=25$ Hz, *p*-C), 124.9 ($^3J_{\text{SnC}}=48$ Hz, *o*-C), 134.3 (C3), 139.1 ($^2J_{\text{SnC}}=34$ Hz, *i*-C), 152.6 (C3a), 172.8 (C2); ^{119}Sn NMR (CDCl_3) δ : -88.9; IR ν : 1539 (C=N), 753 (s, C—S), 340, 290 ν_{as} , $\nu_{\text{s}}(\text{Sn—C})$, 310 (m, Sn—S) cm^{-1} . Anal. calcd. for $\text{C}_{28}\text{H}_{25}\text{NS}_2\text{Sn}$: C 60.23, H 4.51, N 2.51; found C 60.22, H 4.49, N 2.53.

X-ray crystallography

The X-ray analyses were determined on a Bruker SMART CCD 1000 diffractometer. Correction for semi-empirical absorption from equivalents was applied, and the structure was solved by direct methods and refined by a full-matrix least squares procedure based on F^2 using the SHELXL-97 program system. All non-H atoms were included in the model at their calculated positions. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included.

The crystal data and refinement details are given in Table 1 and selected bond distances and angles in Table 2. Fractional atomic coordinates and their isotropic equivalent displacement coefficients are listed in Table 3 and Table 4 for complexes 2 and 3 respectively. The labeling of the atoms of HMBT (1) and corresponding complexes 2 and 3 are shown in Figures 3, 4 and 5 respectively.

Table 1 Experimental data for the X-ray diffraction studies of **1**, complexes **2** and **3**

Compounds	1	2	3
Chemical formula	C ₇ H ₅ NS ₂	C ₂₈ H ₂₂ N ₂ S ₄ Sn	C ₂₈ H ₂₅ NS ₂ Sn
Formula weight	167.24	633.41	528.30
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /nm	0.8028(3)	0.8870(2)	1.4730(5)
<i>b</i> /nm	0.6000(2)	1.1062(3)	1.0438(4)
<i>c</i> /nm	1.5385(5)	1.4790(4)	1.7289(6)
<i>α</i> /(°)	90	93.165(4)	90
<i>β</i> /(°)	100.750(5)	94.170(2)	104.822(5)
<i>γ</i> /(°)	90	107.515(4)	90
<i>V</i> /nm ³	0.7281(4)	1.3757(6)	2.5699(15)
<i>D_c</i> /(g·cm ⁻³)	1.526	1.529	1.443
<i>Z</i>	4	2	4
<i>F</i> (000)	344	636	1128
Crystal size/mm ³	0.50×0.40×0.40	0.50×0.30×0.20	0.25×0.15×0.10
<i>θ</i> range/(°)	2.68 to 25.03	1.39 to 25.03	1.62 to 23.36
Absorption/mm ⁻¹	0.641	1.252	1.172
Reflections	3636/1726	6464/4724	11008/3722
collected/unique	[<i>R</i> _{int} =0.0219]	[<i>R</i> _{int} =0.00244]	[<i>R</i> _{int} =0.0561]
Goodness-of-fit on <i>F</i> ²	1.059	0.983	0.881
<i>R</i> indices (all data)	<i>R</i> ₁ =0.410, <i>wR</i> ₂ =0.0827	<i>R</i> ₁ =0.0719, <i>wR</i> ₂ =0.1460	<i>R</i> ₁ =0.0876, <i>wR</i> ₂ =0.0513
Largest diff. peak and hole/(e·nm ⁻³)	156 and -246	709 and -602	702 and -364

Table 2 Selected bond lengths (nm) and angles (°) of **1**, complexes **2** and **3**

Complex 1		Complex 2		Complex 3	
N(1)—C(1)	0.1343(3)	Sn(1)—C(15)	0.2159(6)	Sn(1)—C(22)	0.2141(6)
N(1)—C(2)	0.1385(3)	Sn(1)—C(22)	0.2161(6)	Sn(1)—C(15)	0.2142(6)
S(1)—C(1)	0.1740(2)	Sn(1)—S(4)	0.24984(18)	Sn(1)—C(8)	0.2164(6)
S(1)—C(3)	0.1740(2)	Sn(1)—S(2)	0.25019(18)	Sn(1)—S(2)	0.24631(15)
S(2)—C(1)	0.1660(2)	Sn(1)—N(1)	0.2892(18)	Sn(1)—N(1)	0.2902(5)
		Sn(1)—N(2)	0.2696(18)	S(2)—C(1)	0.1731(5)
		S(2)—C(1)	0.1729(7)	S(1)—C(1)	0.1755(5)
		S(4)—C(8)	0.1727(7)	S(1)—C(7)	0.1737(5)
C(1)-N(1)-C(2)	16.76(18)	C(15)-Sn(1)-C(22)	129.6(2)	C(22)-Sn(1)-C(15)	115.0(3)
C(1)-S(1)-C(3)	92.42(9)	C(15)-Sn(1)-S(4)	110.63(17)	C(22)-Sn(1)-C(8)	109.1(3)
N(1)-C(1)-S(2)	127.68(16)	C(22)-Sn(1)-S(4)	108.02(18)	C(15)-Sn(1)-C(8)	111.3(3)
N(1)-C(1)-S(1)	109.12(15)	C(15)-Sn(1)-S(2)	107.83(19)	C(22)-Sn(1)-S(2)	105.3(2)
S(2)-C(1)-S(1)	123.19(12)	C(22)-Sn(1)-S(2)	103.60(17)	C(15)-Sn(1)-S(2)	114.92(19)
N(1)-C(2)-C(7)	127.07(19)	S(4)-Sn(1)-S(2)	89.39(6)	C(8)-Sn(1)-S(2)	100.02(19)
N(1)-C(2)-C(3)	111.97(18)	C(15)-Sn(1)-N(1)	78.86(7)	S(2)-Sn(1)-N(1)	59.05(3)
		C(22)-Sn(1)-N(1)	84.82(7)	C(8)-Sn(1)-N(1)	158.80(3)
		S(2)-Sn(1)-N(1)	59.25(18)	C(15)-Sn(1)-N(1)	78.10(3)
		S(4)-Sn(1)-N(1)	148.42(8)	C(22)-Sn(1)-N(1)	81.94(2)
		C(15)-Sn(1)-N(2)	82.94(8)	N(1)-C(1)-S(2)	123.7(4)
		C(22)-Sn(1)-N(2)	88.38(8)	N(1)-C(1)-S(1)	115.6(4)
		S(2)-Sn(1)-N(2)	150.75(8)	S(2)-C(1)-S(1)	120.6(3)
		S(4)-Sn(1)-N(2)	61.42(9)	C(3)-C(2)-N(1)	124.9(6)

Table 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{nm}^2 \times 10$) for complex **2**

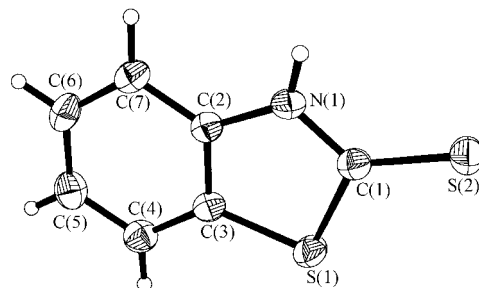
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Sn(1)	11237(1)	8864(1)	7363(1)	56(1)
N(1)	9786(6)	6378(5)	7979(4)	64(1)
N(2)	10987(7)	11109(5)	6864(3)	63(1)
S(1)	11432(3)	5002(2)	8637(1)	85(1)
S(2)	12887(2)	7477(2)	7811(1)	73(1)
S(3)	13270(2)	13070(2)	6543(1)	79(1)
S(4)	13713(2)	10584(2)	7122(1)	71(1)
C(1)	11245(8)	6325(6)	8117(4)	60(2)
C(2)	8687(8)	5323(6)	8297(4)	63(2)
C(3)	7056(9)	5111(7)	8248(5)	82(2)
C(4)	6107(11)	4002(9)	8600(5)	93(2)
C(5)	6810(14)	3138(9)	8969(7)	110(3)
C(6)	8464(14)	3344(8)	9034(6)	107(3)
C(7)	9389(9)	4466(7)	8681(5)	73(2)
C(8)	12528(8)	11517(6)	6837(4)	63(2)
C(9)	10272(9)	12031(6)	6619(4)	66(2)
C(10)	8635(9)	11867(8)	6605(5)	81(2)
C(11)	8135(12)	12883(10)	6323(6)	99(3)
C(12)	9240(15)	14020(9)	6079(6)	103(3)
C(13)	10849(13)	14176(7)	6114(6)	92(2)
C(14)	11350(9)	13159(6)	6397(4)	69(2)
C(15)	10220(7)	9356(6)	8559(4)	65(2)
C(16)	11459(7)	10327(6)	9211(4)	55(2)
C(17)	11600(8)	11628(6)	9218(4)	62(2)
C(18)	12678(9)	12492(7)	9847(5)	75(2)
C(19)	13668(9)	12091(8)	10463(5)	77(2)
C(20)	13568(9)	10825(8)	10433(5)	76(2)
C(21)	12462(8)	9919(7)	9823(4)	68(2)
C(22)	10082(7)	8010(6)	6045(4)	61(2)
C(23)	8344(7)	7920(6)	5926(4)	56(2)
C(24)	7855(9)	8890(7)	5581(5)	74(2)
C(25)	6244(11)	8789(9)	5486(6)	92(2)
C(26)	5116(10)	7728(10)	5743(6)	98(3)
C(27)	5599(10)	6760(10)	6087(7)	104(3)
C(28)	7186(9)	6839(7)	6189(5)	80(2)

Results and discussion

In the IR spectra of **1**, the ligand exhibits a broad band in the 2800—2600 cm^{-1} region,⁹ which is a typical N—H stretching, and the absorption at 1210 cm^{-1} has been assigned to $\nu(\text{C}=\text{S})$.¹⁰ The appearance of $\nu(\text{C}=\text{S})$ and N—H stretching indicated that HMBT exists as thione form of **1b**. In previous report,¹¹ the tin(IV) chloride stretching frequencies in the di- and tri-

Table 4 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{nm}^2 \times 10$) for Complex **3**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Sn(1)	10198(1)	8830(1)	1514(1)	63(1)
N(1)	9008(3)	6964(4)	482(2)	63(1)
S(1)	9378(1)	6120(1)	-813(1)	71(1)
S(2)	10469(1)	8243(1)	211(1)	69(1)
C(1)	9576(4)	7118(4)	30(3)	60(2)
C(2)	8358(4)	6010(5)	179(3)	63(2)
C(3)	7657(5)	5625(7)	515(4)	90(2)
C(4)	7064(5)	4660(8)	164(5)	105(2)
C(5)	7152(5)	4082(7)	-526(5)	96(2)
C(6)	7825(5)	4463(6)	-876(4)	83(2)
C(7)	8443(4)	5431(5)	-525(3)	61(2)
C(8)	11255(5)	10302(6)	1883(4)	76(2)
C(9)	12115(4)	9968(5)	1655(4)	69(2)
C(10)	12799(5)	9163(6)	2114(4)	73(2)
C(11)	13593(5)	8849(7)	1880(4)	83(2)
C(12)	13737(5)	9302(7)	1180(5)	89(2)
C(13)	13075(6)	10096(7)	714(5)	91(2)
C(14)	12290(6)	10427(6)	952(4)	82(2)
C(15)	8822(4)	9552(7)	1461(4)	76(2)
C(16)	8831(3)	10668(6)	1994(4)	61(2)
C(17)	9011(4)	10507(8)	2812(4)	88(2)
C(18)	9035(6)	11556(11)	3289(5)	116(3)
C(19)	8858(6)	12749(10)	2983(7)	117(3)
C(20)	8693(6)	12912(8)	2192(6)	112(3)
C(21)	8669(5)	11884(8)	1700(4)	86(2)
C(22)	10601(6)	7179(7)	2257(4)	84(2)
C(23)	10159(5)	7142(5)	2931(4)	63(2)
C(24)	9306(6)	6554(6)	2838(5)	94(2)
C(25)	8895(8)	6527(10)	3475(8)	156(5)
C(26)	9293(12)	7061(14)	4175(9)	201(11)
C(27)	10137(10)	7643(12)	4260(8)	163(6)
C(28)	10574(7)	7702(7)	3657(5)	98(2)

**Figure 3** Crystal structure of **1**. Probability ellipsoids drawn at 30%.

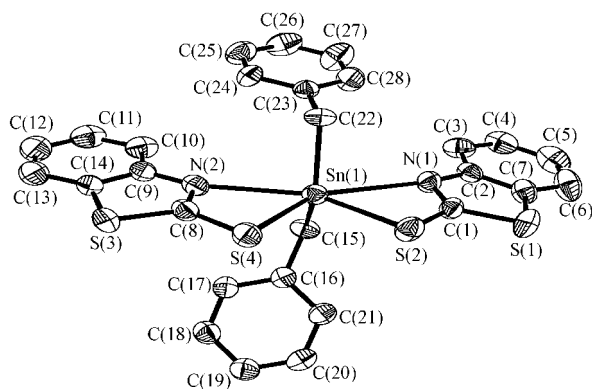


Figure 4 Crystal structure of complex **2**. Probability ellipsoids drawn at 30%.

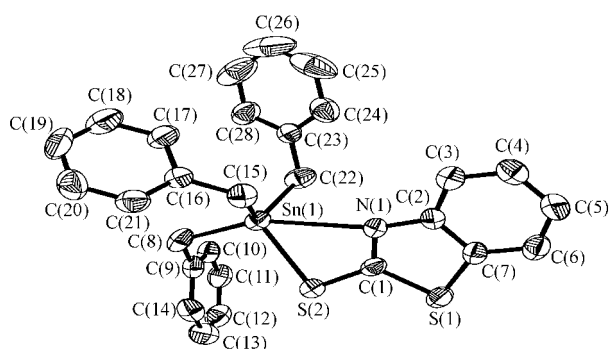


Figure 5 Crystal structure of complex **3**. Probability ellipsoids drawn at 30%.

chloroorganotin(IV) derivatives fall as strong or medium broad bands in the range $220\text{--}320\text{ cm}^{-1}$. But this band is absent in the spectra of complexes **2** and **3**, indicating the complete substituent for chlorine atoms. The frequencies $\nu(\text{Sn—S})$ appearing at 309 cm^{-1} for **2** and 310 cm^{-1} for **3**, agree with those detected for some organotin(IV)-sulfur derivatives.^{12,13} The $\nu(\text{C=N})$ band, occurring at 1539 cm^{-1} , is considerably shifted towards lower frequencies with respect to that of the free ligand. The stretching frequency is lowered owing to the displacement of electron density from the nitrogen to the tin atom, which resulted in the weakening of the C=N bond as reported in the literature,^{14,15} and confirmed the coordination of the heterocyclic nitrogen to the tin. The appearance of Sn—S and C=N bonds indicated the bonding mode in these complexes as **D**.

In the ^{13}C NMR spectra of these two complexes **2** and **3**, chemical shifts are quite similar to those of the parent ligand. Only a small shift in the positions of hetero-carbon atoms (C—S) is seen, which may be due to the deshielding of the carbon atoms upon deprotonation of the thiol group and coordination through sulfur atom.¹⁶

Only single ^{119}Sn chemical shift was observed for each of the compounds, $\delta -219.3$ for complex **2** and $\delta -88.9$ for **3**. The chemical shifts for complex **2** is

somewhat different from the values, $\delta 300\text{--}500$, expected for the six-coordinated tin(IV) compounds.¹⁷ The single value for complex **3** is similar to the that of $\text{Ph}_3\text{Sn}(\text{MBT})$, $\delta -91.4$, which is between the values of 4- and 5-coordinated triorganotin.⁵ Both complexes **2** and **3** are accounted for undergoing sufficiently fast exchanges on the NMR timescale to result in average values only being observed.

X-ray structure of HMBT (**1**)

In order to confirm the form of HMBT as free ligand in the solid state, we recrystallized it from benzene and obtained the crystal suitable for X-ray diffraction. The crystal structure of HMBT (**1**) is shown in Figure 3. The C—S bond length in the free ligand, $0.1660(2)\text{ nm}$, is shorter than the C=S double bond 0.1681 nm in thioureas.¹⁸ So it was concluded that free HMBT exists as thione form **1b**, which is consistent with the IR data in the literatures reported previously.^{19, 20}

X-ray structure of the complex **2**

In complex **2**, the chlorine atoms of benzyltin compounds were substituted by sulfur anions completely, as seen in Figure 4. Compared to products of reactions of HMBT with dibutyltin dichloride and diphenyltin dichloride,^{21,22} though the stereo-constraint of PhCH_2 is larger than *n*-Bu, it is not large enough to effect the replacement of the second chlorine atom of chloroorganotin compounds. It seems that only R groups with more large stereo-constraints such as Ph would inhibit the complete substituent.

Complex **2** contains a six-coordinate tin atom. Two carbon atoms [C(15) and C(22)] and two sulfur atoms [S(2) and S(4)] are covalently linked to the metal. The valence extension is performed via the nitrogen atoms of the benzothiazole ring [N(1) and N(2) atoms]. Two chelating nitrogen atoms occupy *cis* positions, as in the case of the sulfur atoms.

Compared with the C—S bonds (0.1660 nm) of free ligand, the corresponding bonds in complex **2** ($0.1729(7)\text{ nm}$, $0.1727(7)\text{ nm}$) are much longer. They are similar and approach to the 0.175 nm generally accepted for the C—S(sp^2) single bond.²³ So it was concluded that, in complex **2**, the double bond has shifted to C=N and C—S exists as single bond. Consequently, the form of HMBT has turned into thiol tautomer.

The Sn—S bond lengths, $0.24984(18)\text{ nm}$, $0.25019(18)\text{ nm}$ for **2**, are a little longer than the sum of the covalent radii (0.242 nm),²⁴ which may be due to the bidentate functions of the HMBT. To perform valence extension, it requires the nitrogen atoms to be close enough to tin atom. But the S and N equatorial donor atoms belong to the same moiety, and their positions are fixed and the S—Sn—N angles can only admit very little deformation. So the Sn—S bonds stretch a little to meet the requirement of Sn—N valence extension. Concerning the Sn—N distances, $0.2892(18)\text{ nm}$, $0.2696(18)\text{ nm}$ for **2**, both of them lie between the sums of the covalent radii and van der Waals radii of Sn and N atoms (0.215

and 0.374 nm).²⁵ They are totally in agreement with the valence extension of the metal atom.^{26,27} The nature of Sn—S, Sn—N and C—S bonds show that HMBT bonds to tin as the same mode of **D**.

In the structure of complex **2**, the sum of angles between the tin atom and the equatorial atoms [S(2), S(4), N(1), and N(2)] is 359.68°, which approaches the value of 360°, indicating that these atoms are almost in the same plane. But the axial angle C(15)-Sn(1)-C(22) 129.6(2)° is departed from the ideal value of 180°, reflecting the great distortion of octahedron geometry.

X-ray structure of the complex **3**

In complex **3**, as seen in Figure 5, the chlorine atoms of benzyltin compounds were substituted by sulfur anion. Compared to complex **2**, though the number of benzyl groups increased to three, their stereo-constraints could not inhibit the substituent procedure yet. This reflects the ionic nature of chloroorganotin compounds.

Complex **3** contains a five-coordinate tin atom. Three carbon atoms [C(8), C(15), C(22)] and one sulfur atom [S(2)] are covalently linked to the metal. Similar to complex **2**, the valence extension is still performed via the nitrogen atom of the benzothiazole ring [N(1)].

The C—S bond of complex **3**, 0.1731(5) nm, is even longer than that in complex **2**, so the C—S bond exists as single bond and the form of HMBT is thiol tautomer. The Sn—S and the Sn—N bonds, 0.24631(15) nm and 0.2902(5) nm, are a little shorter and longer than the corresponding bonds of complex **2**, respectively, indicating that the effects of bidentate ligand decreased. But the nature of Sn—S, Sn—N and C—S bonds show that, in complex **3**, HMBT bonds to tin as the same mode of **D** as in complex **2**.

In the structure of complex **3**, the sum of angles between the tin atom and the equatorial atoms [S(2), C(15) and C(22)] 335.22°, and the axial angle C(8)-Sn(1)-N(1) 158.80(3)° has differences from the ideal values, reflecting the distortion of trigonal bipyramidal geometry.

Supplementary materials

Crystallographic data (excluding structure factors) for the structure analysis of compounds **1**, **2** and **3** have been deposited in the Cambridge Crystallographic Data Center, with CCDC no. 192496, 192497 and 183608. 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>).

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