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# Synthesis, Structural Characterization, and Biological Studies of Six- and Five-Coordinate Organotin(IV) Complexes with the Thioamides 2-Mercaptobenzothiazole, 5-Chloro-2-mercaptobenzothiazole, and 2-Mercaptobenzoxazole

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Organotin(IV) complexes with the formulas $[(C_6H_5)_3Sn(mbzt)]$ (**1**), $[(C_6H_5)_3Sn(cmbzt)]$ (**3**), and $[(C_6H_5)_2Sn(cmbzt)_2]$ (**4**) (Hmbzt = 2-mercaptobenzothiazole and Hcmbzt = 5-chloro-2-mercaptobenzothiazole) have been synthesized and characterized by elemental analysis; FT-IR, Raman, $^1H$, $^{13}C$, and $^{119}Sn$ NMR, and Mössbauer spectroscopic techniques; and X-ray crystallography at various temperatures. The crystal structures of complexes **1**, **3**, and **4** were determined by X-ray diffraction at room temperature [295(1) or 293(2) K]. The complexes $[(C_6H_5)_3Sn(mbzo)]$ (**2**) and $[(n\text{-}C_4H_9)_2Sn(cmbzt)_2]$ (**5**) (Hmbzo = 2-mercaptobenzoxazole) were synthesized by new improved methods, and their structures were determined at low temperature [100(1) K] and compared to those solved at room temperature. Comparison with $\{(CH_3)_2Sn(cmbzt)_2]\}$ (**6**), already reported, was also attempted. The influence of temperature on the geometry of the complexes is discussed. In the cases of complexes **1**–**3**, three carbon atoms from phenyl groups and one sulfur atom and one nitrogen atom from thione ligands form a tetrahedrally distorted trigonal-bipyramidal geometry around the five-coordinate tin(IV) ion. In complexes **4**–**6**, two carbon atoms from aryl groups and two sulfur atoms and two nitrogen atoms from thione ligands form a distorted tetrahedral geometry, tending toward octahedral, around the six-coordinate tin(IV) ions, with *trans*-$C_2$, *cis*-$N_2$, and *cis*-$S_2$ configurations. Although the C–Sn and S–Sn bond distances are found to be constant in compounds **1**–**6**, their N–Sn bond lengths vary significantly (from 2.635 to 3.078 Å), with the longer distances found in the cases of five-coordinate complexes **1**–**3**.

## 1. Introduction

The study of organotin compounds has been a matter of interest for several decades.[1,2] Organotin compounds such as stannoxanes have been studied for their catalytic activity in many organic processes including the formation of urethanes from alcohols and isocyanates, of acetals from alcohols and ketones, of esters from acids and alcohols, and of esters from esters and alcohols during transesterification processes,[3−6] and dimeric polar distannoxanes often show better catalytic activity than monomers in nonpolar solvents.[7] Organotin compounds are also commercially used as indus-

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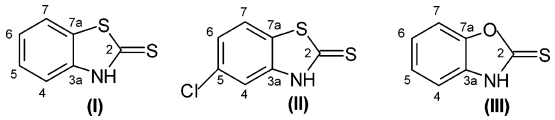
trial and agricultural biocides because of their antifungal properties.[8,9] Recently, diorganotin compounds have been investigated for their antitumor activity.[10]

Interest in the chemistry of heterocyclic thiones arises from their wide range of applications in analytical chemistry, medicine, and biology as biocides.[11−15] A number of organotin compounds with thiolates have been synthesized and studied for their biocidal[16] and antitumor[17] activities, and their catalytic activity in regio- and stereoselective syntheses of both $\gamma$-diketones and $\alpha,\beta$-dihydroxy ketones[18,19] has also been reported. Although many organotin compounds containing a single tin atom with pyrimidine-2-thiolate or pyridine-2-thiolate moieties have been structurally characterized,[20−30] there are very few reports on the synthesis of organotin compounds containing other thioles.

Organotins were also proposed to interact with the high-affinity site of ATPase (histidine only) and the low-affinity site of ATPase and hemoglobins (histidine and cysteine).[31] On the other hand, it is well-known that the interaction of heavy metals with free sulfhydryl groups in proteins, causing distortion of the protein structure, is one of the proposed mechanisms of metal-induced cell death.[32] These results

**Chart 1**




prompted us to investigate the correlation between enzyme inhibition by organotin compounds and their antitumor activity. Lipoxygenase (LOX) is an enzyme that takes part in the metabolism of arachidonic acid. LOX catalyzes the oxidation of arachidonic acid to leukotrienes and prostaglandines, in an essential mechanism for cell life.[33] Prostaglandins, the final products formed from the metabolism of arachidonic acid, contribute to tumorigenesis, acting as angiogenesis factors.[34a] Linoleic acid, on the other hand, discovered in beef and dairy products, was found to be a potential mutagen inhibitor.[34b]

In this study, the synthesis and characterization of the new complexes $[(C_6H_5)_3Sn(mbzt)]$ (**1**), $[(C_6H_5)_3Sn(cmbzt)]$ (**3**), and $[(C_6H_5)_2Sn(cmbzt)_2]$ (**4**), where Hmbzt is 2-mercaptobenzoxazole (**I**) and Hcmbzt is 5-chloro-2-mercaptobenzothiazole (**II**) (Chart 1), are reported. These compounds, together with the known complexes $[(C_6H_5)_3Sn(mbzo)]$ (**2**)[35a] [Hmbzo = 2-mercaptobenzoxazole (**III**)], $[(n\text{-}C_4H_9)_2Sn(cmbzt)_2]$ (**5**),[35b] and $[(CH_3)_2Sn(cmbzt)_2]$ (**6**),[10b] were used in experiments correlating their structures at variable temperatures and their LOX inhibitory activities. Such inhibition might be the cause of the antitumor action of tin antitumor complexes.

## 2. Results and Discussion

**(I) General Aspects.** Organotin(IV) complexes **1**, **2**, **5**, and **6** were synthesized by reacting a methanolic solution of organotin chloride $R_{4-n}SnCl_n$ with an aqueous solution of the appropriate thioamide containing an equimolar amount of potassium hydroxide, as shown in eq 1.

$$R_{4-n}SnCl_n + nHL \xrightarrow[KOH]{MeOH,\ H_2O} R_{4-n}SnL_n + nKCl + nH_2O \quad (1)$$

$n = 1$, R = $C_6H_5-$ and HL = Hmbzt (**1**), Hbzo (**2**)

$n = 2$, HL = Hcmbzt and R = $n\text{-}C_4H_9-$ (**5**), $CH_3-$ (**6**)

Compounds **3** and **4** were prepared by direct reaction of diphenyltin oxide $[(C_6H_5)_2SnO]$ or triphenyltin hydroxide with 5-chloro-2-mercaptobenzothiazole (eqs 2 and 3).

$$(C_6H_5)_3SnOH + Hcmbzt \xrightarrow{bz} (C_6H_5)_3Sn(cmbzt)\ (\mathbf{3}) + H_2O \quad (2)$$

$$(C_6H_5)_2SnO + 2Hcmbzt \xrightarrow{bz} (C_6H_5)_2Sn(cmbzt)_2\ (\mathbf{4}) + H_2O \quad (3)$$


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**Table 1.** Characteristic Vibration Bands ($cm^{-1}$) in Infrared Spectra of Complexes or Ligands

| | | | thioamide | | | | infrared | | Raman | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| molecule | $\nu$(NH) | $\nu$(CH) | I | II | III | IV | $\nu$(Sn−S) | $\nu$(Sn−N) | $\nu$(Sn−S) | $\nu$(Sn−N) | ref(s) |
| Hmbzt | 3112 br | – | 1497 | 1320 | 1013 | 938 | – | – | – | – | 10b, 11 |
| **1** | – | 3059−3048 | 1419 | 1306 | 1009 | 927 | 381 | 264, 206 | 341 | 263 | this work |
| Hmbzo | 3236 br | – | 1507 | 1246 | 1007 | 744 | – | – | – | – | 11 |
| **2** | – | 3059−2049 | 1490 | 1239 | 995 | 743 | 392 vw | 262, 203 | – | 267 | this work |
| Hmcbzt | 3090 br | – | 1504 | 1313 | 1040 | 918 | – | – | – | – | 10b |
| **3** | – | 3061 | 1419 | 1295 | 995 | 910 | 386 | 254, 209 | 349 | 274, 251 | this work |
| **4** | – | | | | | | | | | | |

**Table 2.** $^{119}$Sn Mössbauer Spectroscopic Data for Complexes **1**−**6**

| complex | temp (K) | IS (mm $s^{-1}$) | $\Delta E_q$ (mm $s^{-1}$) | area (%) | IS (mm $s^{-1}$) | $\Delta E_q$ (mm $s^{-1}$) | area (%) |
|---|---|---|---|---|---|---|---|
| **1** | 80 | 1.37 | 1.88 | 100 | | | |
| **2** | 80 | 1.34 | 1.96 | 82 | 1.34 | 2.37 | 18 |
| | 93 | 1.34 | 1.99 | 90 | 1.30 | 2.42 | 10 |
| | 100 | 1.34 | 1.97 | 89 | 1.34 | 2.50 | 11 |
| | 114 | 1.34 | 1.99 | 93 | 1.34 | 2.37 | 7 |
| | 120 | 1.32 | 2.02 | 100 | | | |
| | 140 | 1.33 | 2.24 | 100 | | | |
| | 180 | 1.30 | 2.02 | 100 | | | |
| **3** | 80 | 1.35 | 1.88 | 55 | 1.29 | 1.98 | 45 |
| **4** | 80 | 1.45 | 2.75 | 55 | 1.39 | 2.61 | 45 |
| **5** | 80 | 1.57 | 2.95 | 62 | 1.64 | 3.10 | 38 |
| | 95 | 1.42 | 2.96 | 43 | 1.67 | 3.02 | 57 |
| | 110 | 1.47 | 2.92 | 40 | 1.66 | 3.02 | 60 |
| | 120 | 1.46 | 2.89 | 30 | 1.64 | 3.03 | 70 |
| | 140 | 1.47 | 2.95 | 61 | 1.76 | 2.99 | 39 |
| **6** | 85 | 1.479 | 3.00 | 79 | 1.31 | 2.80 | 11 |

All complexes are air-stable powders. Crystals of compounds **1**−**3**, **5**, and **6** that were suitable for X-ray analysis were obtained by slow evaporation of diethyl ether/methanol/acetonitrile solutions, whereas crystals of **4** were grown from a chloroform/toluene solution.

**(II) Spectroscopy. (a) Vibrational Spectroscopy.** Characteristic infrared bands of the complexes and the ligands are listed in Table 1.

The IR spectra of the complexes show distinct vibrational bands at 1410−1490 and 1305−1240 $cm^{-1}$ that can be assigned to $\nu$(CN) vibrations (thioamide I and II bands) and bands at 1020−995 and 930−740 $cm^{-1}$ that can be attributed to $\nu$(CS) vibrations (thioamide III and IV bands). No bands due to $\nu$(NH) or $\nu$(SH) vibrations are observed in the IR spectra of the complexes, indicating deprotonation of all ligands. Thioamide bands are shifted to lower frequencies in the complexes, supporting sulfur donation and deprotonation of the ligands as well. The bands at 500−600 $cm^{-1}$ can be assigned to the antisymmetric and symmetric vibrations of Sn−C bonds, whereas the bands at 380−395 $cm^{-1}$ are attributed to $\nu$(Sn−S) vibrations.[10b,16] The bands at 265−245 and 205−195 $cm^{-1}$ are assigned to the $\nu$(Sn−N) bond vibrations. Sn−S and Sn−N vibrations are also Raman-active.[36] Thus, the bands at 240−270 $cm^{-1}$ in the Raman spectra of complexes **1**−**6** are due to $\nu$(Sn−N), whereas those at 340−390 $cm^{-1}$ are assigned to $\nu$(Sn−S) (Table 1).

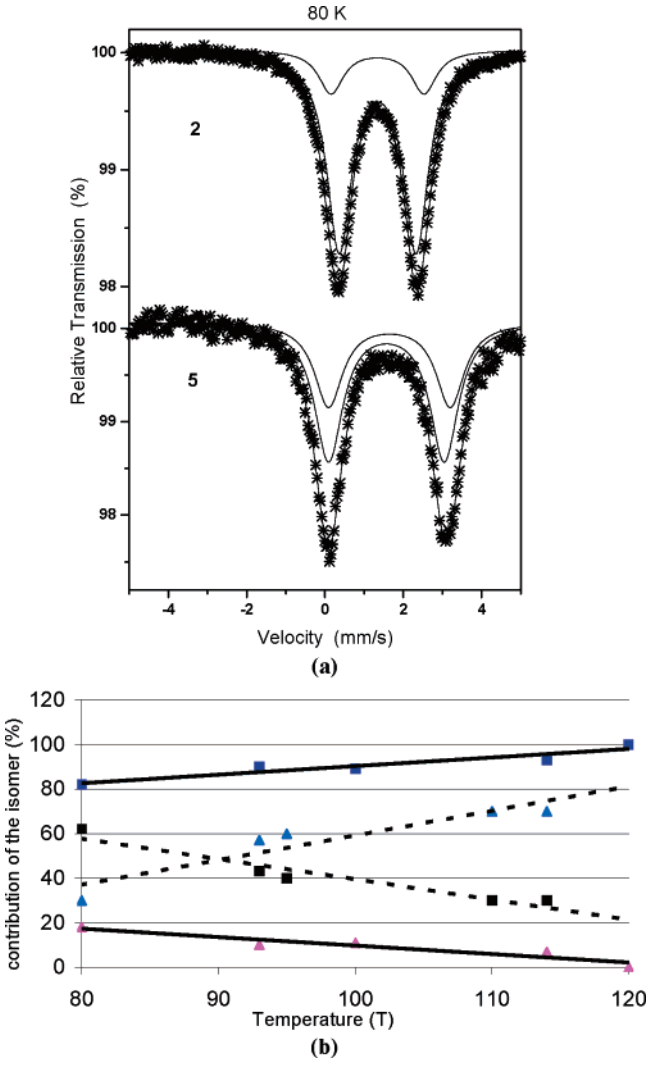


**Figure 1.** (a) $^{119}$Sn Mössbauer spectra of **2** and **5**. (b) Contributions (%) of the isomers versus temperature (K) for complexes **2** (—) and **5** (– – –).

**(b) $^{119}$Sn Mössbauer Spectroscopy.** Solid-state $^{119}$Sn Mössbauer spectroscopic data of complexes **1**−**6** are reported in Table 2, and typical spectra of **2** and **5** are shown in Figure 1a.

The spectra of the complexes consist of two symmetric Lorentzian doublets (Table 2). The occurrence of two symmetric Lorentzians indicates the possible formation of two structural isomers in the cases of complexes **2**−**6**.[10b,29,37] The presence of two structural isomers was confirmed by

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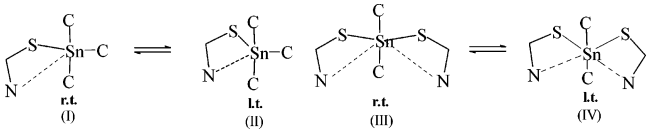
**Scheme 1.** Bonding Environments around the Tin Atoms of Complexes **2**−**6** Found by $^{119}$Sn Mössbauer Spectroscopy




X-ray analysis for compound **1** as well (see sections on crystal structures), which was not observed in the $^{119}$Sn Mössbauer spectra because of the small amount of sample. It is noticeable that, at temperatures above 120 K, complex **2** shows only one isomer whereas, at lower temperatures, two isomers are observed in the relative proportions reported in Table 2. The structures of complexes **4**−**6** are distorted octahedral, as their $\Delta E_q$ values lie in the range of 2.60−3.10 mm s$^{-1}$ (Table 2), similar to those of other *trans*-$R_2Sn(L)_2$ (R = alkyl, L = thioamide) complexes.[10b,29,37] Complexes **1**−**3**, on the other hand, have trigonal-bipyramidal structures with $\Delta E_q$ = 1.88−2.50 mm s$^{-1}$, as expected.[10b,29,37] In all complexes **1**−**6**, Sn is in the 4+ oxidation state, having isomer shift (IS) values between 1.29 and 1.67 mm s$^{-1}$.[10b,29,37] Thus, two isomers with different Sn−N distances can be postulated (Scheme 1) for all complexes, with relative abundances calculated from the spectra (Table 2). These are constantly shown in the Mössbauer spectra. A decrease in temperature leads to shortening of the Sn−N bond distances in the case of complexes **1**−**3** by increasing of the proportion of isomer **II** (Scheme 1). In the case of complexes **4**−**6**, an increase in temperature leads to more symmetric geometries by tending to equalize the two Sn−N distances (Scheme 1; see also sections on crystal structures). Figure 1b shows the percent contributions of the isomers for complexes **2** and **5** at various temperatures. It is also important to note that the proportion of the two isomers is almost 60:40 for compound **4** according to the Mössbauer and X-ray crystal structure results (see sections on crystal structure).

**(c) $^{119}$Sn NMR Spectroscopy.** The coordination of Sn can also be estimated through $\delta$($^{119}$Sn) values by fingerprinting.[29,38] It has been reported that the $\delta$($^{119}$Sn) values (in ppm) for $R_2Sn(IV)$ and $R_3Sn(IV)$ complexes with five-coordinate Sn vary from +25 to −329 ppm. From $\delta$($^{119}$Sn) values recorded in $^{119}$Sn NMR spectra of complexes **1** (−262.7 ppm) and **3** (−216.0 and −233.8 ppm), it appears that the tin(IV) ion is five-coordinate in these complexes. The presence of two signals in the case of complex **3** is due to the two isomers (see sections on $^{119}$Sn Mössbauer spectroscopy and crystal structure) in which the Sn−C bond distance varies significantly (Table 3). The occurrence of one signal in the $^{119}$Sn NMR spectra of complex 1 might be due to the overlapping of the signals for the two isomers (see sections on crystal structure), where Sn−C bond distances are much closer than in **3** (Table 3).

**(III) Crystal and Molecular Structures. (A) Crystal Structures of [$(C_6H_5)_3$Sn(mbzt)] (1), [$(C_6H_5)_3$Sn(mbzo)]**

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for Triorganotin(IV) Complexes **1**−**3** Measured at Room Temperature [295(1) or 293(2)] or Low Temperature [100(1) K], with esd's in Parentheses

| complex **1** at 295(1) K | | | | complex **2** | | | | complex **3** at 293(2) K | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| isomer A | | isomer B | | 295(1) K | | 100(1) K | | isomer A | | isomer B | |
| Bond Lengths (Å) | | | | | | | | | | | |
| Sn1A−S2A | 2.4540(15) | Sn1B−S2B | 2.4625(14) | Sn1−S12 | 2.4661(13) | Sn1−S12 | 2.4699(9) | Sn1−S1 | 2.458(3) | Sn2−S3 | 2.456(3) |
| Sn1A−N3A | 2.945(4) | Sn1B−N3B | 2.898(4) | Sn1−N11 | 3.078(4) | Sn1−N11 | 3.067(3) | Sn1−N8 | 3.007(4) | Sn1−N34 | 3.010(3) |
| Sn1A−C31A | 2.126(4) | Sn1B−C31B | 2.135(4) | Sn1−C21 | 2.120(4) | Sn1−C21 | 2.131(3) | Sn1−C15 | 2.119(11) | Sn2−C27 | 2.133(10) |
| Sn1A−C21A | 2.126(4) | Sn1B−C21B | 2.146(4) | Sn1−C31 | 2.140(4) | Sn1−C31 | 2.140(3) | Sn1−C1 | 2.118(10) | Sn2−C47 | 2.152(9) |
| Sn1A−C41A | 2.149(4) | Sn1B−C41B | 2.143(4) | Sn1−C41 | 2.153(5) | Sn1−C41 | 2.148(3) | Sn1−C21 | 2.144(10) | Sn2−S3 | 2.151(10) |
| C2A−S2A | 1.724(6) | C2B−S2B | 1.747(5) | S12−C12 | 1.736(5) | S12−C12 | 1.742(3) | S1−C7 | 1.718(11) | S3−C33 | 1.736(11) |
| Angles (deg) | | | | | | | | | | | |
| C31A−Sn1A−C21A | 114.42(17) | C31B−Sn1B−C21B | 106.64(17) | S12−Sn1−C21 | 109.25(12) | S12−Sn1−C21 | 108.78(9) | C15−Sn1−C1 | 110.7(4) | C27−Sn2−C47 | 111.5(4) |
| C31A−Sn1A−C41A | 108.19(17) | C31B−Sn1B−C41B | 118.24(16) | S12−Sn1−C31 | 110.80(13) | S12−Sn1−C31 | 110.50(10) | C15−Sn1−C21 | 109.7(4) | C27−Sn2−C41 | 120.3(4) |
| C21A−Sn1A−C41A | 107.75(16) | C21B−Sn1B−C41B | 105.39(17) | S12−Sn1−C41 | 98.21(12) | S12−Sn1−C41 | 98.47(9) | C1−Sn1−C21 | 107.1(4) | C47−Sn2−C41 | 107.4(4) |
| C31A−Sn1A−S2A | 112.83(11) | C31B−Sn1B−S2B | 114.84(11) | C21−Sn1−C31 | 117.58(18) | C21−Sn1−C31 | 118.54(13) | C15−Sn1−S1 | 118.0(3) | C27−Sn2−S3 | 107.5(3) |
| C21A−Sn1A−S2A | 113.63(13) | C21B−Sn1B−S2B | 98.33(13) | C21−Sn1−C41 | 108.70(18) | C21−Sn1−C41 | 107.36(14) | C1−Sn1−S1 | 111.7(3) | C47−Sn2−S3 | 98.1(4) |
| C41A−Sn1A−S2A | 98.53(14) | C41B−Sn1B−S2B | 110.83(13) | C31−Sn1−C41 | 110.56(18) | C31−Sn1−C41 | 111.29(13) | C21−Sn1−S1 | 98.4(3) | C41−Sn2−S3 | 109.8(3) |
| C31A−Sn1A−N3A | 81.21(14) | C31B−Sn1B−N3B | 85.93(14) | N11−Sn1−C21 | 76.70(14) | N11−Sn1−C21 | 76.70(10) | C15−Sn1−N8 | 85.25(1) | C27−Sn2−N34 | 83.02(4) |
| C21A−Sn1A−N3A | 86.20(15) | C21B−Sn1B−N3B | 157.43(14) | N11−Sn1−C31 | 87.02(15) | N11−Sn1−C31 | 86.45(10) | C1−Sn1−N8 | 83.67(4) | C47−Sn2−N34 | 155.39(3) |
| C41A−Sn1A−N3A | 156.80(16) | C41B−Sn1B−N3B | 83.82(15) | N11−Sn1−C41 | 154.54(14) | N11−Sn1−C41 | 155.11(10) | C21−Sn1−N8 | 155.86(2) | C41−Sn2−N34 | 79.59(4) |

(38) (a) Otera, J.; Kusaba, A.; Hinoishi, T. and Kawasaki, Y. *J. Organomet. Chem.* **1982**, *228*, 223. (b) Otera, J. *J. Organomet. Chem.* **1981**, *221*, 57.

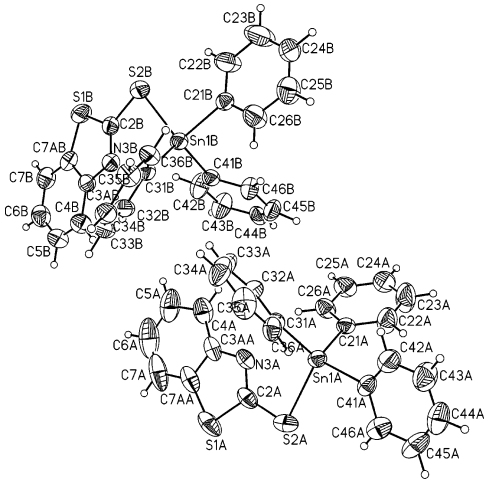



**Figure 2.** ORTEP diagram of a molecule of **1** measured at 273 K, together with the atom numbering scheme. There are two independent molecules per unit cell.

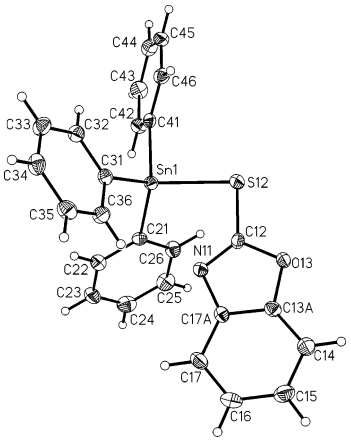



**Figure 3.** ORTEP diagram of a molecule of **2** measured at 100 K, together with the atom numbering scheme. There is only one independent molecule per unit cell.

**(2), and [(C$_6$H$_5$)$_3$Sn(cmbzt)] (3).** The structures of complexes **1**−**3** were solved by X-ray diffraction at room temperature [295(1) or 293(2) K]. The crystal structure of **2** was also determined at 100(1) K. Although the structure of compound **2** at room temperature has already been reported,[35a] it was repeated here, only for comparison, both at room temperature [295(1) K] and at low temperature [100(1) K]. The results of the structure determination compare well with the Mössbauer spectral findings. ORTEP diagrams of complexes **1**−**3** are shown in Figures 2−4, respectively. Selected bond distances and angles are reported in Table 3.

The structures of compounds **1**−**3** consist of a deprotonated thioamide ligand bonded to a [Ph$_3$Sn(IV)] moiety through the sulfur atom. A weak Sn−N interaction complete the coordination sphere around the metal center. The geometry around the Sn atom is distorted trigonal-bipyramidal, the equatorial plane being defined from the two carbons of phenyl groups and the sulfur atoms. According to Reedijk et al.,[39] the geometry around tin atoms can be characterized by the value of $\tau = (\beta - \alpha)/60$,[39] where $\beta$ is

(39) Addison, A. W.; Nageswara Rao, T.; Reedijk, J.; Van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.

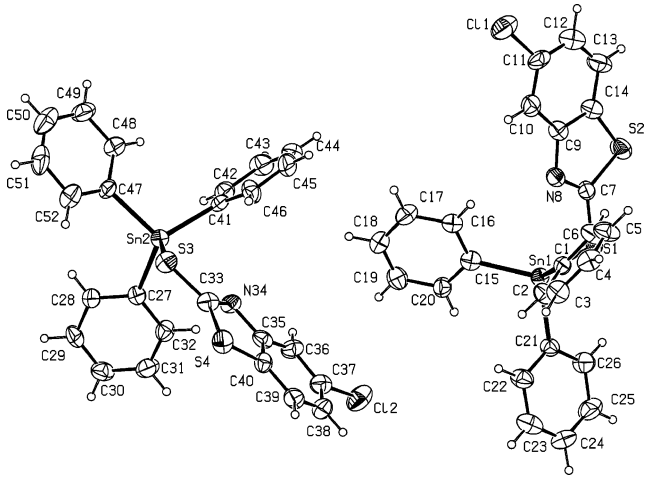



**Figure 4.** ORTEP diagram of a molecule of **3** measured at 293 K, together with the atom numbering scheme. There are two independent molecules per unit cell.

the largest of the basal angles around the tin atoms. For **1A**, it is C41A−Sn1A−N3A = 156.80(16)°; for **1B**, it is C21B−Sn1B−N3B = 157.43(14)°; for **2**[295(1) K], it is N11−Sn1−C41 = 154.54(14)°; for **2**[100(1) K], it is N11−Sn1−C41 = 155.11(10)°; for **3A**, it is C21−Sn1−N8 = 155.86(2)°, and for **3B**, it is C47−Sn2−N34 = 155.39(3)°. The second largest of the basal angles around the tin atoms, $\alpha$, for **1A** is C31A−Sn1A−C21A = 114.42(17)°; for **1B**, it is C31B−Sn1B−C41B = 118.24(16)°; for **2**(295 K), it is C21−Sn1−C31 = 117.58(18)°; for **2**(100 K), it is C21−Sn1−C31 = 118.54(13)°; for **3A**, it is C15−Sn1−S1 = 118.0(3)°; and for **3B**, it is C27−Sn2−C41 = 120.3(4)°. The angle values $\alpha = \beta = 180°$ correspond to a square-pyramidal geometry, and the value of $\alpha = 120°$ corresponds to a perfectly trigonal-pyramidal geometry. Thus, the $\tau$ value is equal to zero for a perfect square pyramid and unity for a perfect trigonal pyramid.[39,40] The calculated $\tau$ values for the complexes are as follows: **1A**, 0.71; **1B**, 0.65; **2**(295 K), 0.62; **2**(100 K), 0.61; **3A**, 0.63; and **3B**, 0.58. These values indicate a highly distorted trigonal-bipyramidal arrangement around tin atoms with one carbon from a phenyl group and the nitrogen from the thioamide in the axial positions and two carbon atoms from two phenyl groups and the sulfur in the plane positions.

The Sn−S bond lengths are in the range of 2.45−2.47 Å (Table 3) and are independent of the type of ligand and the temperature of the measurement. However, the Sn−N bonds vary significantly from 2.90 to 3.08 Å depending on the ligand [**1A**, Sn1A−N3A = 2.945(4) Å; **1B**, Sn1B−N3B = 2.898(4) Å; **2**(295 K), Sn1−N11 = 3.078(4) Å; **3A**, Sn1−N8 = 3.007(4) Å; and **3B**, Sn1−N34 = 3.010(3) Å]. They are also affected by temperature, being Sn1−N11 = 3.078(4) Å for **2**(295 K) and Sn1−N11 = 3.067(3) Å for **2**(100 K). The values of the Sn−N bond distances found in complexes **1**−**3** are comparable to those found in [(C$_6$H$_{10}$)$_3$Sn(mbzt)][35b] (Sn−N = 3.055 Å). In {[(C$_6$H$_5$)$_3$Sn]$_2$(mna)·[(CH$_3$)$_2$CO]},[10b,c] however, the Sn−N distance was found to be significantly shorter [2.711(2) Å]. It is noteworthy that complex **2** shows only one isomer at both temperatures by X-ray diffraction.

**(B) Crystal Structures of [(C$_6$H$_5$)$_2$Sn(cmbzt)$_2$] (4) and [(*n*-C$_4$H$_9$)$_2$Sn(cmbzt)$_2$] (5).** The structures of complexes **4**

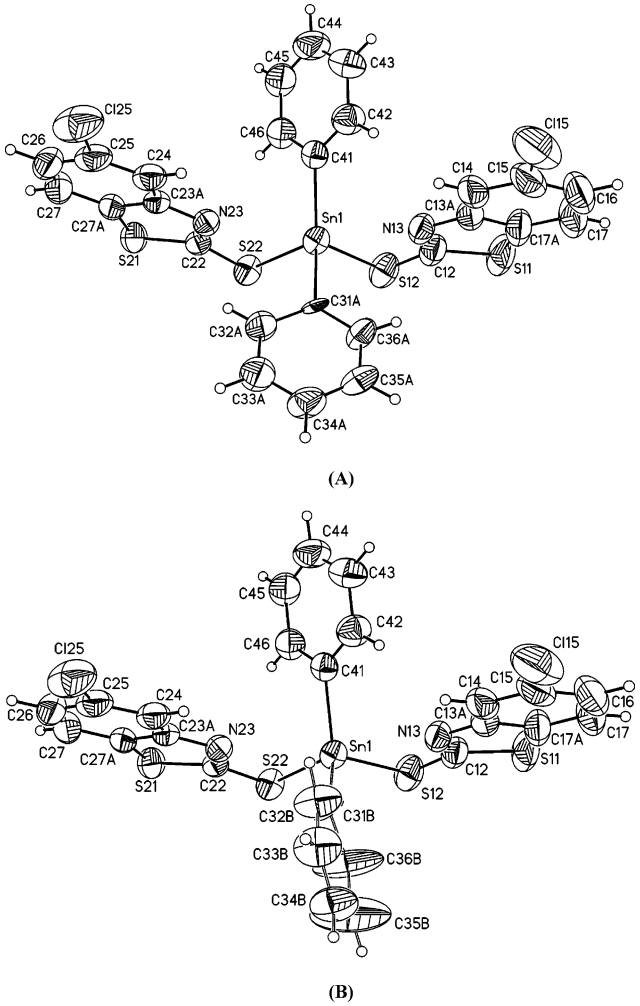



**Figure 5.** ORTEP diagram of a molecule of **4** measured at 293 K, together with the atom numbering scheme. The molecule exists in two different conformations (**4A** and **4B**) that are statistically distributed over the same sites (in a 60:40 ratio). The difference is in the orientation of C31−C36 phenyl ring.

and **5** were solved by X-ray diffraction at room temperature [295(1) or 293(2) K]. The crystal structure of **5** was also determined at 100(1) K. The structure of compound **5**, already reported at room temperature,[35b] was also repeated here, for comparison, at both room temperature [295(1) K] and low temperature [100(1) K]. The results of the structure determination also compare well with the Mössbauer spectral findings. ORTEP diagrams of complexes **4** and **5** are shown in Figures 5 and 6, respectively. Selected bond distances and angles are reported in Table 4.

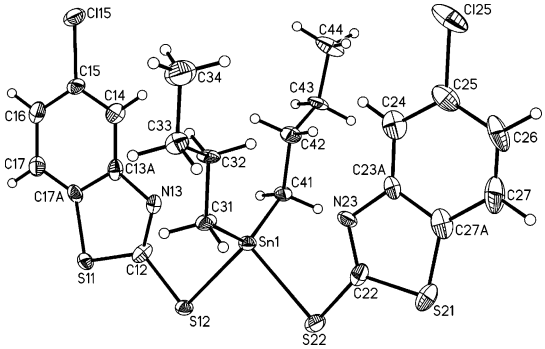



**Figure 6.** ORTEP diagram of a molecule of **5** measured at 100 K, together with the atom numbering scheme. There is only one independent molecule per unit cell.

Compounds **4** and **5** are covalent monomers in the solid state with a distorted octahedral geometry around the metal ion. Thus, two trans aryl groups are bonded to the tin atom [Sn1−C41 = 2.137(2) Å, Sn1−C31A = 2.23(2) Å for isomer **4A**; Sn1−C41 = 2.137(2) Å, Sn1−C31B = 1.98(3) Å for isomer **4B**; Sn1−C10 = 2.132(7) Å, Sn1−C20 = 2.143(7) Å for complex **5**(293 K); and Sn1−C31 = 2.145(7) Å, Sn1−C41 = 2.161(8) Å for complex **5**(100 K)]. Two deprotonated thioamide ligands are also bonded to the tin atom via sulfur [Sn1−S12 = 2.4947(7) Å, Sn1−S22 = 2.5020(7) Å in **4A** and **4B**; Sn1−S2 = 2.4885(16) Å, Sn1−S3 = 2.515(2) Å in **5**(293 K); and Sn1−S12 = 2.5042(19) Å, Sn1−S22 = 2.5286(19) Å in **5**(100 K)]. The octahedral geometry is completed by Sn−N interactions between the nitrogen atoms of the ligands and the metal center [Sn1−N13 = 2.653(2) Å, Sn1−N23 = 2.7718(18) Å in **4**; Sn1−N1 = 2.783(9) Å, Sn1−N2 = 2.789(10) Å in **5**(293 K); and Sn1−N13 = 2.748(7) Å, Sn1−N23 = 2.766(7) Å in **5**(100 K)]. These Sn−N bond interactions are stronger for the octahedral arrangement than for trigonal-bipyramidal complexes **1**−**3**. Increasing the temperature makes the geometry

**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for Triorganotin(IV) Complexes **4** and **5** Measured at Room Temperature [295(1) K] or Low Temperature [100(1) K], with esd's in Parentheses

| complex **4** at 295(1) K | | | | complex **5** | | | |
|---|---|---|---|---|---|---|---|
| isomer A | | isomer B | | 293(2) K | | 100(1) K | |
| Bond Lengths (Å) | | | | | | | |
| Sn1−S12 | 2.4947(7) | Sn1−S12 | 2.4947(7) | Sn1−S2 | 2.4885(16) | Sn1−S12 | 2.5042(19) |
| Sn1−S22 | 2.5020(7) | Sn1−S22 | 2.5020(7) | Sn1−S3 | 2.515(2) | Sn1−S22 | 2.5286(19) |
| Sn1−N13 | 2.653(2) | Sn1−N13 | 2.653(2) | Sn1−N1 | 2.783(9) | Sn1−N13 | 2.748(7) |
| Sn1−N23 | 2.7718(18) | Sn1−N23 | 2.7718(18) | Sn1−N2 | 2.789(10) | Sn1−N23 | 2.766(7) |
| Sn1−C41 | 2.137(2) | Sn1−C41 | 2.137(2) | Sn1−C10 | 2.132(7) | Sn1−C31 | 2.145(7) |
| Sn1−C31A | 2.23(2) | Sn1−C31B | 1.98(3) | Sn1C20 | 2.143(7) | Sn1−C41 | 2.161(8) |
| C12−S12 | 1.720(3) | C12−S12 | 1.720(3) | S2−C12 | 1.719(7) | S12−C12 | 1.746(7) |
| C22−S22 | 1.728(2) | C22−S22 | 1.728(2) | S3−C15 | 1.708(8) | S22−C22 | 1.747(9) |
| Angles (deg) | | | | | | | |
| C41−Sn1−C31A | 137.7(5) | C41−Sn1−C31B | 129.8(7) | S2−Sn1−S3 | 90.68(6) | S12−Sn1−S22 | 91.00(6) |
| C31A−Sn1−S12 | 105.1(5) | C31B−Sn1−S12 | 112.4(8) | C10−Sn1−S2 | 105.70(19) | S12−Sn1−C31 | 104.8(2) |
| C31A−Sn1−S22 | 103.9(6) | C31B−Sn1−S22 | 106.9(10) | C20−Sn1−S2 | 108.72(19) | S12−Sn1−C41 | 108.2(2) |
| C41−Sn1−S12 | 106.02(6) | C41−Sn1−S12 | 106.02(6) | C10−Sn1−S3 | 105.5(2) | S22−Sn1−C31 | 104.87(19) |
| C41−Sn1−S22 | 104.51(7) | C41−Sn1−S22 | 104.51(7) | C20−Sn1−S3 | 108.12(19) | S22−Sn1−C41 | 108.66(19) |
| S12−Sn1−S22 | 89.23(3) | S12−Sn1−S22 | 89.23(3) | C10−Sn1−C20 | 130.8(3) | C31−Sn1−C41 | 131.8(3) |

more symmetrical, leading to almost equal Sn−N bonds by lengthening some Sn−N bond distances (Scheme 1).

The C−S−Sn−S torsion angles found in complexes **4** and **5** [S22−Sn1−S12−C12 = −179.5° for **4**, S2−Sn1−S3−C15 = −176.6° for **5**(293 K), and S22−Sn1−S12−C12 = 178.4° for **5**(100 K)] indicate the almost coplanar arrangement of the N, C, Sn, and S atoms. Thus, the conformation around the tin atom is *trans*-$C_2$, *cis*-$N_2$, *cis*-$S_2$. The values of the C−Sn−C angles [C41−Sn1−C31A = 137.7(5)° in **4A**, C41−Sn1−C31B = 129.8(7)° in **4B**, C10−Sn1−C20 = 130.8(3)° in **5**(293 K), and C31−Sn1−C41 = 131.8(3)° in **5**(100 K)] imply distortion of the octahedral structure, in agreement with the Mössbauer results (vide infra).

**(IV) Biological Studies.** As has already been reported,[41] complexes **3**−**6** exhibit an effect on the catalytic transformation reaction of oleic acid to hyperoxo-oleic acid that increases from the dimethyltin(IV) to the di-*n*-butyltin(IV) and to the diphenyltin(IV) (**6** < **5** < **4**) derivative. The diphenyltin(IV) complex, on the other hand, shows stronger catalytic activity than the coresponding triphenyltin complex (**3** < **4**). It was proposed that the formation of reactive radials R• and/or [$R_nSnL_{4-n}$]• could cause the initiation of the chain radical oxidation of the substrate.[41]

It was further shown that the inhibition of LOX decreased significantly in the presence of complexes **1**−**6**, in the order **6** ≈ **5** < **4** or **1** < **2** < **3**, with both series being more active than *cis*-platinum. Between the tri- (**3**) and diphenyltin(IV) (**4**) complexes of Hcmbzt ligand, complex **4** showed stronger inhibitory activity (**4** > **3**). The same order was also found to be valid for the antitumor activities of these complexes against sarcoma cells (mesenchymal tissue) from the Wistar rat and polycyclic aromatic hydrocarbon (PAH, benzo[*a*]-pyrene) carcinogenesis.[41]

## 3. Conclusions

New organotin(IV) complexes with the thioamides 2-mercaptobenzothiazole (Hmbzt), 5-chloro-2-mercaptobenzothiazole (Hcmbzt), and 2-mercaptobenzoxazole (Hmbzo) were prepared and characterized crystallographically in this study, with the aim of comparing the possible effects on the geometry of the final products of the electronegativity of the heteroatoms present in the ligands and the steric effects of the R groups. The triorganotin complexes can be described with a tetrahedrally distorted trigonal-bipyramidal geometry around tin(IV) ion, and the corresponding di-organotin derivatives with a distorted tetrahedral toward an octahedral geometry. Although the Sn−S bond distances were found to be almost stable (2.45−2.53 Å) in complexes **1**−**5** regardless of both the geometry or the ligand used, the Sn−N bond distances varied significantly from 2.63 to 3.08 Å and it was found to depend on the geometry around tin(IV). Thus, in the case of triorganotin **1**−**3** derivatives, the Sn−N distance is found between 2.90 and 3.08 Å and in diorganotin complexes **4**−**6** between 2.63 and 2.81 Å possibly for steric reasons. In the triorganotin complexes, the longest such distance measured was for complex **2** (3.08 Å), where the presence of the electronegative oxygen atom decreases the relative negative charge of the nitrogen atom, thus increasing the Sn−N distance. In diorganotin complexes **4**−**6**, the Sn−N distance varied from 2.65 Å in **4** to 2.79 Å in **5** and 2.81 Å in **6**. In general, this order reflects the donor capacity of the ligand around tin(IV), being methyl < *n*-butyl < phenyl, with the shortest Sn−N distance observed with complex **4**.

Solid-state $^{119}$Sn Mössbauer spectroscopy and X-ray crystallography also showed the formation of two structural isomers in the solid state. For all of the complexes prepared, the isomers differ in the bond distance around the metal center (See Tables 3 and 4). In the case of complex 3, $^{119}$Sn NMR spectroscopy can distinguish between the two isomers in DMSO-$d_6$ solutions, where the variations of Sn−C bond distances differ the most, as was also revealed by its X-ray crystal structure (Table 3).

X-ray crystallography of **2** and **5** at room temperature (295 or 293 K) and low temperature (100 K) showed that, at higher temperatures, a lengthening of the Sn−N distance occurs. The Sn−S bond distances, however, show the opposite trend, decreasing at higher temperature in the case of complex **5**.

X-ray crystallography showed the presence of two isomers at room temperature in complexes **1**, **3**, and **4**.

Finally, variable-temperature $^{119}$Sn Mössbauer spectroscopy showed that two isomeric forms for each compound exist in the solid state, with proportions that vary with temperature. Thus, two isomers can also be postulated for compounds **2**, **5**, and **6** according to their Mössbauer spectra, although the crystals used might only contain one isomer.

## 4. Experimental Section

**Materials and Instruments.** All solvents used were of reagent grade, and thioamides and organotin chlorides (Aldrich, Merck) were used with no further purification. Diphenyltin oxide was prepared by reacting diphenyltin dichloride with potassium hydroxide as described previously.[1,2,18] Elemental analyses for C, H, N, and S were carried out with a Carlo Erba EA model 1108 instrument. Infrared spectra in the range of 4000−370 $cm^{-1}$ were obtained from KBr disks. Far-infrared spectra in the range of 400−50 $cm^{-1}$ were obtained from polyethylene disks with a Perkin-Elmer Spectrum GX FT-IR spectrometer. A Jasco UV/vis/NIR V 570 series spectrophotometer was used to obtain electronic absorption spectra. The $^1$H NMR spectra were recorded on a Bruker AC 250, 400 MHFT NMR instrument in $CDCl_3$ or DMSO-$d_6$ solutions. Chemical shifts $\delta$ are reported in ppm using $^1$H TMS as an internal reference. $^{119}$Sn Mössbauer spectra were collected at various sample temperatures (85−150 K), with a constant-acceleration spectrometer equipped with a $CaSnO_3$ source kept at room temperature. The calibration of the spectrometer was carried out with a $^{57}$Co source and an Fe absorber at room temperature. The line widths were very close to the natural width (0.28 mm/s). The content of the tin samples was calculated to be approximately 4 mg Sn in the 2-$cm^2$ area of the sample holder. Micro-FT-Raman measurements were

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(41) Xanthopoulou, M. N.; Hadjikakou, S. K.; Hadjiliadis, N.; Milaeva, E. R.; Gracheva, J. A.; Tyurin, V. Y.; Kourkoumelis, N.; Christoforidis, K. C.; Metsios, A. K.; Charalabopoulos, K.; Karkabounas, S. 2006, manuscript submitted.

**Table 5.** Crystal Data and the Structure Refinement Details for the Complexes **1**, **2**, and **5**

| | **1** | **2**[295(1) K] | **2**[100(1) K] | **3** | **4** | **5**[293(2) K] | **5**[100(1) K] |
|---|---|---|---|---|---|---|---|
| empirical formula | $C_{25}H_{19}NS_2Sn$ | $C_{25}H_{19}NOSSn$ | $C_{25}H_{19}NOSSn$ | $C_{25}H_{18}ClNS_2Sn$ | $C_{26}H_{16}Cl_2N_2S_4Sn$ | $C_{22}H_{24}Cl_2N_2S_4Sn$ | $C_{22}H_{24}Cl_2N_2S_4Sn$ |
| fw | 516.22 | 500.16 | 500.16 | 550.70 | 674.24 | 634.26 | 634.26 |
| temperature (K) | 295(1) | 295(1) | 100(1) | 293(2) | 295(1) | 293(2) | 100(1) |
| cryst syst | monoclinic | monoclinic | monoclinic | triclinic | triclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $Cc$ | $Cc$ | $P_1$ | $P_1$ | $P2_1/c$ | $P2_1/n$ |
| $a$, Å | 12.458(3) | 8.6369(6) | 8.6228(9) | 10.987(3) | 9.9270(7) | 10.6948(10) | 10.589(2) |
| $b$, Å | 11.442(2) | 38.582(3) | 38.042(4) | 12.793(4) | 11.6737(9) | 31.203(3) | 31.416(4) |
| $c$, Å | 31.685(6) | 6.8784(7) | 6.8084(8) | 16.819(4) | 12.5560(9) | 8.0881(7) | 8.004(2) |
| $\alpha$, deg | 90 | 90 | 90 | 86.96(2) | 71.508(6) | 90 | 90 |
| $\beta$, deg | 91.91(3) | 100.640(8) | 101.466(10) | 87.41(2) | 83.149(6) | 100.361(8) | 100.27(2) |
| $\gamma$, deg | 90 | 90 | 90 | 78.57(2) | 75.536(6) | 90 | 90 |
| $V$, Å$^3$ | 4514.0(16) | 2252.7(3) | 2188.8(4) | 2312.4(11) | 1334.91(17) | 2655.1(4) | 2620.0(9) |
| $Z$ | 8 | 4 | 4 | 2 | 2 | 4 | 4 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.519 | 1.475 | 1.518 | 1.582 | 1.678 | 1.587 | 1.608 |
| $\mu$, mm$^{-1}$ | 1.3 | 1.2 | 1.3 | 1.4 | 1.5 | 1.5 | 1.5 |
| R1, wR2 [$I > 2\sigma(I)$] | 0.0455, 0.0985 | 0.0313, 0.0775 | 0.0240, 0.0586 | 0.0727, 0.2188 | 0.0306, 0.0558 | 0.0664, 0.2064 | 0.0483, 0.1429 |

carried out using near-infrared laser radiation ($Nd^{3+}$:YAG, 1064.1 nm). FT-Raman spectra (2.6 cm$^{-1}$ resolution) were recorded on a Bruker IFS-88 FT-IR/FRA-105 Raman module fitted with a Ge proprietary detector and coupled via two 1.0-m photooptic cables to a Nikon Optiphot-II optical microscope equipped with a Nikon 20X, super-long-range objective. Near-IR laser radiation was directed onto the sample through the objective and collected along the same optical pathway in a 180° backscattering mode. Samples were measured as solid powders dispersed on a glass slide.

**Preparation of Complexes [$(C_6H_5)_3$Sn(mbzt)] (1), [$(C_6H_5)_3$Sn(mbzo)] (2), [($n$-$C_4H_9)_2$Sn(cmbzt)$_2$] (5), and [$(CH_3)_2$Sn(cmbzt)$_2$] (6).** Compound **6** was prepared according to the method described previously.[10b] Complexes **1**, **2**, and **5** were synthesized as follows: A suspension of the appropriate thioamide (2-mercaptobenzothiazole, 0.167 g, 1 mmol for **1**; 2-mercaptobenzoxazole, 0.151 g, 1 mmol for **2**, 5-chloro-2-mercaptobenzothiazole, 0.403 g, 2 mmol for **5**) in distilled water (8 cm$^{-3}$) was treated with a solution of 1 N KOH (1 cm$^{-3}$, 1 mmol for **1** and **2** and 2 cm$^{-1}$, 2 mmol for **5**). A clear solution was then formed. Afterward, a methanolic (3 cm$^{-3}$) solution of organotin(IV) chloride [$(C_6H_5)_3$SnCl, 0.385 g, 1 mmol for **1** and **2**; ($n$-$C_4H_9)_2SnCl_2$ and 0.304 g, 1 mmol for **5**) were added. A white precipitate formed immediately that was filtered off after the mixture had been stirred for 3 h. The precipitate was then washed with 5 mL of cold distilled water and dried in vacuo over silica gel. Crystals of complexes **1**, **2**, and **5** suitable for X-ray analysis were formed by slow evaporation of a diethyl ether/methanol/acetonitrile (6:1:1) solution for **2** and **5** and a methanol solution for **1**.

**1.** Yield 56%, mp 88−90 °C. Elemental analysis: found C 58.75, H 2.95, N 2.70, S 12.11%; calcd for $C_{25}H_{19}NS_2Sn$ C 58.17, H 3.71, N 2.71, S 12.42%. $^1$H NMR (ppm): 7.11 (t, $J^3$ = 7.4 Hz), 7.24 (t, $J^3$ = 7.6 Hz), 7.39 (br), 7.48 (d, $J^3$ = 10.8 Hz), 7.60 (d, $J^3$ = 7.8 Hz), 7.77 (s, $J^2$ $^{119}$Sn−H = 58.5 Hz) (DMSO-$d_6$). $^{13}$C NMR (ppm): 150.88, 142.72, 136.60, 136.24, 135.88, 135.01, 129.2, 128.60, 128.0, 125.89, 123.35, 120.90, 117.93 (DMSO-$d_6$).

**2.** Yield 60%, mp 92−94 °C. Elemental analysis of the crystals: found C 60.96, H 4.02, N 2.84, S 6.39%; calcd for $C_{25}H_{19}NOSSn$ C 60.04, H 3.83, N 2.80, S 6.41%. $^1$H NMR (ppm): 8.35 (t), 7.97−7.70 (br), 7.44 (br), 7.25 (dd, $J^3$ = 6.85 Hz, $J^4$ = 2.2 Hz), 7.14 (td, $J^3$ = 6.6 Hz, $J^4$ = 3.0 Hz), 7.10−6.94 (m) (DMSO-$d_6$). $^{13}$C NMR (ppm): 150.47, 142.72, 141.02, 136.88, 136.02, 135.66, 129.16, 128.54, 123.34, 122.02, 114.74, 108.53 (DMSO-$d_6$).

**5.** Yield 30%, mp 120−123 °C. Elemental analysis of the crystals: found C 41.80, H 3.45, N 4.34, S 19.69%; calcd for $C_{22}H_{24}Cl_2N_2S_4Sn$ C 41.70, H 3.80, N 4.40, S 20.20%. $^1$H NMR (ppm): 8.25 (s), 7.68 (d, $J^3$ = 9.0 Hz), 7.32 (d, $J^3$ = 6.0 Hz), 1.58 (br), 1.28 (br), 0.85 (br) (DMSO-$d_6$). $^{13}$C NMR (ppm): 190.38, 143.14, 131.92, 124.19, 123.30, 112.57, 30.48, 26.23, 18.74, 13.71 (DMSO-$d_6$).

**6.** Yield 55%, mp 220−221 °C. Elemental analysis: found C 33.55, H 2.03, N 5.08, S 22.13%; calcd for $C_{16}H_{14}Cl_2N_2OS_4Sn$ C 33.83, H 2.48, N 4.93, S 22.57%. $^1$H NMR: 7.66 (d, $J^3$ = 8.4 Hz), 7.29 (dd, $J^3$ = 6.5, $J^4$ = 1.9 Hz), 7.24 (d, $J^3$ = 2.0 Hz), 0.63 (br) (DMSO-$d_6$), 7.67 (d, $J^4$ = 1.8 Hz), 7.59 (d, $J^3$ = 8.5 Hz), 7.25 (d, $J^3$ = 8.5, $J^4$ = 1.9 z), 1.30 (s, $J^2$ $^{119/117}$Sn−H = 75.0, 28.71 Hz) ($CDCl_3$). $^{13}$C NMR (ppm): 174.5, 152.5, 135.8, 133.0, 125.1, 122.5, 119.8, 9.3 ($CDCl_3$); 190.78, 131.80, 129.10, 124.06, 123.22, 114.24, 112.45, 6.61 (DMSO-$d_6$).

**Preparation of Complexes [$(C_6H_5)_3$Sn(cmbzt)] (3) and [$(C_6H_5)_2$Sn(cmbzt)$_2$] (4).** A mixture of triphenyltin(IV) hydroxide ($C_{24}H_{16}OSn$, 0.366 g, 1 mmol) for **3** or diphenyltin(IV) oxide [$(C_6H_5)_2SnO$, 0.144 g, 0.5 mmol] for **4** with 5-chloro-2-mercaptobenzothiazole (0.202 g, 1 mmol) was suspended in 30 cm$^3$ of benzene in a 100-mL spherical flask. The flask was fitted with a Dean−Stark moisture trap, and the reaction mixture was refluxed for 24 h. The solution was filtered, and the clear filtrate was concentrated to dryness using a rotary evaporator. Crystals of **3** and **4** suitable for X-ray analysis were formed by slow evaporation of a diethyl ether/methanol/acetonitrile solution for **3** and a chloroform solution for **4**.

**3.** Yield 55%, mp 118−119 °C. Elemental analysis: found C 57.14, H 3.39, N 2.47, S 12.09%; calcd for $C_{25}H_{18}ClNS_2Sn$ C 54.50, H 3.30, N 2.50, S 11.60%. $^1$H NMR (ppm): 7.86 (d, $J^3$ = 6.3 Hz, $J^2$ $^{119}$Sn−H = 60.1 Hz), 7.61 (d, $J^3$ = 8.4 Hz), 7.49 (d, $J^4$ = 1.8 Hz), 7.40 (br), 7.14 (dd, $J^3$ = 8.4, $J^4$ = 1.9 Hz) (DMSO-$d_6$). $^{13}$C NMR (ppm): 153.9, 142.9, 136.6, 136.3, 135.9, 134.9, 130.3, 129.2, 128.6, 122.9, 128.13, 121.9, 118.3 (DMSO-$d_6$).

**4.** Yield 41%, mp 221−224 °C. Elemental analysis: found C 47.02, H 2.36, N 4.00, S 21.06%; calcd for $C_{26}H_{18}Cl_2N_2S_4Sn$ C 46.30, H 2.40, N 4.10, S 19.00%. $^{13}$C NMR (ppm): 190.90, 146.1, 142.7, 142.6, 131.89, 128.5, 128.4, 124.16, 123.4, 123.3, 112.1 (DMSO-$d_6$).

**Crystallography.** Intensity data for the colorless crystals of **1**−**5** were collected on a KUMA KM4CCD four-circle diffractometer[42a]

(42) (a) *KUMA KM-4CCD User Manual*; KUMA Diffraction: Wroclaw, Poland, 1999. (b) *CrysAlis, Program for Reduction of the Data from KUMA CCD Diffractometer*; KUMA Diffraction: Wroclaw, Poland, 1999. (c) Blessing, R. H. *J. Appl.Crystallogr.* **1989**, *22*, 396. (d) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (e) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

with a CCD detector, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were determined by a least-squares fit.[42b] All data were corrected for Lorentz and polarization effects and absorption.[42b,c]

The structure was solved by direct methods with SHELXS97[42d] and refined by full-matrix least-squares procedures on $F^2$ with SHELXL97.[42e] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located at calculated positions and refined using a riding model with isotropic thermal parameters fixed at 1.2 times the $U_{eq}$ value of the appropriate carrier atom. Significant crystal data are reported in Table 5. Supplementary data are available from CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail: deposit@ccdc.cam.ac.uk), upon request, quoting the deposition numbers CCDC 605961−605966 for complexes **1**, **2**(100 K), **2**(293 K), **4**, **5**(100 K), and **5**(293 K), respectively, as well as CCDC 606444 for compound **3**.

**Biological Tests.** These have been described in detail elsewhere.[41]

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