

Synthesis, Spectroscopic Properties and Crystal Structures of Dibenzyltin(IV) Dithiobenzoate and Chlorodibenzyltin(IV) Thiobenzoate

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Two dibenzyltin(IV) complexes with thiobenzoate ligand, $(\text{PhCH}_2)_2\text{Sn}(\text{SOCPh})_2$ (**1**) and $(\text{PhCH}_2)_2\text{Sn}(\text{Cl})\text{SOCPh}$ (**2**), have been synthesized by the reaction of dibenzyltin(IV) dichloride with thiobenzoic acid in the presence of organic base Et_3N and characterized by IR, ^1H NMR spectroscopy and elemental analysis. Their crystal structures were determined by X-ray single crystal diffraction analysis. In the crystals of **1**, the tin atom is six-coordinated in a distorted octahedron configuration. In the crystals of **2**, the molecular packing in unit cell reveals that the two adjacent molecules are symmetrically linked to each other to form a dimer with intermolecular $\text{Sn}\cdots\text{Cl}$ distances of 0.3591(2) nm and the tin atom is five-coordinated in a distorted trigonal bipyramid configuration.

Keywords dibenzyltin(IV) complex, thiobenzoate, synthesis, crystal structure

Introduction

Organotin complexes of carboxylic acid are widely used as biocides, fungicides, and in industry as homogeneous catalysts. More recently, pharmaceutical properties of organotin complexes of carboxylic acid have been investigated for their antitumour activity.¹⁻⁴ Crystallographic studies have revealed that the structures of organotin complexes of carboxylic acid are dependent on both the nature of the allyl (or aryl) substituent bound to the tin atom and the type of carboxylate ligands.⁵⁻¹⁰ In order to allow exploration of relationship between biological activity and structure, a number of investigations of such molecules have been reported in recent years. In our recent work, the organotin(IV) complexes of heterocyclic carboxylic acid³⁻¹⁰ were synthesized, and their structure and biological activities were also studied. Up to now, the dibenzyltin complexes with thiocarboxylic acid have not been reported previously. As an extension of our studies of organotin complexes of carboxylic acid, herein we report two organotin complexes with thiocarboxylic acid, $(\text{PhCH}_2)_2\text{Sn}(\text{SOCPh})_2$ (**1**) and $(\text{PhCH}_2)_2\text{Sn}(\text{Cl})\text{SOCPh}$ (**2**).

Experimental

General procedure

IR spectra were recorded on a Nicolet-460 spectrophotometer, as KBr discs. ^1H NMR spectra were recorded on a Jeol-FX-90Q NMR spectrometer and the

chemical shifts are given relative to Me_4Si in CDCl_3 . Elemental analyses were performed on a PE-2400-II elemental analyzer, and tin was estimated as SnO_2 . X-ray measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated $\text{Mo K}\alpha$ ($\lambda=0.071073$ nm) radiation.

Synthesis of dibenzyltin(IV) complexes with thiobenzoate ligand

$(\text{PhCH}_2)_2\text{Sn}(\text{SOCPh})_2$ (1**)** The preparation of complex **1** was carried out under nitrogen atmosphere. $(\text{PhCH}_2)_2\text{SnCl}_2$ (1.0 mmol of), PhCOSH (2.0 mmol) and Et_3N (2.2 mmol) were added to 20 cm^3 of dry benzene and stirred for 12 h at 80 °C. The precipitated salts were removed by filtration and the filtrate was concentrated to 5 cm^3 under reduced pressure. Hexane (5 cm^3) was added to this solution. Precipitate was formed immediately. The products were recrystallized from dichloromethane-hexane to give colorless crystals 0.43 g, yield 75%, m.p. 145—147 °C; ^1H NMR (CDCl_3 , 90 MHz) δ : 7.11—8.05 (m, 20H, C_6H_5), 3.22 (t, $J_{\text{Sn-H}}=81.0$ Hz, 4H, CH_2Sn); IR (KBr) ν : 3060, 3022, 2922, 2850, 1590, 1213, 924, 547, 458 cm^{-1} . Anal. calcd for $\text{C}_{28}\text{H}_{24}\text{O}_2\text{S}_2\text{Sn}$: 575.28, C 58.46, H 4.20, S 11.15, Sn 20.63; found C 58.74, H 4.35, S 11.09, Sn 20.82.

$(\text{PhCH}_2)_2\text{Sn}(\text{Cl})\text{SOCPh}$ (2**)** The preparation of complex **2** was carried out under nitrogen atmosphere. $(\text{PhCH}_2)_2\text{SnCl}_2$ (1.0 mmol), PhCOSH (1.0 mmol) and Et_3N (1.1 mmol) were added to 20 cm^3 of dry benzene and stirred for 12 h at 80 °C. The precipitated salts were

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removed by filtration and the filtrate was concentrated to 5 cm³ under reduced pressure. Hexane (5 cm³) was added to this solution. Precipitate was formed immediately. The products were recrystallized from dichloro-methane-hexane to give colorless crystals 0.36 g, yield 76%, m.p. 102—104 °C; ¹H NMR (CDCl₃, 90 MHz) δ : 7.18—8.21 (m, 15H, C₆H₅), 3.27 (t, $J_{\text{Sn-H}}=81.3$ Hz, 4H, CH₂Sn); IR (KBr) ν : 3058, 3025, 2934, 2856, 1604, 1218, 930, 528, 451 cm⁻¹. Anal. calcd for C₂₁H₁₉ClOSn: C 473.56, H 53.26, S 6.77, Sn 25.06; found C 53.01, H 4.30, S 6.49, Sn, 25.41.

Crystallographic measurements and Structure analysis

The colorless crystals having approximate dimensions of 0.30 mm × 0.2 mm × 0.20 mm (**1**) and 0.40 mm × 0.3 mm × 0.30 mm (**2**) were mounted in a fiber, respectively. All measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo K α ($\lambda=0.071073$ nm) radiation. The two structures were solved by direct method and difference Fourier maps using SHELXL-97 program and refined by full-matrix least-squares on F^2 (Table 1). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically.

Results and discussion

Synthesis and properties

Complexes **1** and **2** are soluble in organic solvents such as benzene, methylene dichloride, chloroform, THF and DMSO. These solvents must be prepared under water-free condition because dibenzyltin dichloride is water-sensitive in solvent, otherwise, no tin-containing thiobenzoate complexes were formed, but dibenzyltin oxide could be detected.

IR spectra of complexes

The assignment of IR bands of these complexes has been made by comparison with the IR spectra of related dibenzyltin complexes, thiobenzoate, and dibenzyltin dichloride. A new absorption band appears at 458 and 451 cm⁻¹ which is the characteristic vibrations of Sn—S bond formed.^{11,12} Three strong absorption bands at 1590, 1604; 1213, 1218; and 924, 930 cm⁻¹, which are assigned to ν (C—O), ν (C-phenyl), and ν (C—S) of thiobenzoxy ligands respectively, are in correspondence with the reported data.^{13,14} It can be deduced that complexes **1** and **2** contain thiobenzoxy as ligands.

Molecular structure of complex 1

The molecular structure and packing in the unit cell are shown in Figures 1 and 2, respectively. Table 2 gives

Table 1 Crystallographic data of complexes **1** and **2**

| | 1 | 2 |
|--|--|--|
| Molecular formula | C ₂₈ H ₂₄ O ₂ S ₂ Sn | C ₂₁ H ₁₉ ClOSSn |
| Formular weight | 575.28 | 473.56 |
| Crystal system | Triclinic | Monoclinic |
| Space group | <i>P1</i> | <i>P2₁/c</i> |
| Unit cell dimensions | | |
| <i>a</i> /nm | 0.5734(4) | 1.4950(5) |
| <i>b</i> /nm | 1.2193(8) | 0.5999(2) |
| <i>c</i> /nm | 2.7446(18) | 2.3238(8) |
| α (°) | 95.483(10) | 90 |
| β (°) | 95.974(10) | 107.481(6) |
| γ (°) | 90.074(10) | 90 |
| <i>V</i> /nm ³ | 1.899(2) | 1.9878(11) |
| <i>Z</i> | 3 | 4 |
| <i>D</i> _{cal} /(g•cm ⁻³) | 1.510 | 1.582 |
| <i>F</i> (000) | 2610 | 944 |
| Scan range θ (°) | 1.50 ≤ θ ≤ 25.02 | 1.43 ≤ θ ≤ 25.03 |
| Total/unique/ <i>R</i> _{int} | 9862/7955/0.0336 | 9633/3496/0.0752 |
| μ /mm ⁻¹ | 3.590 | 1.530 |
| <i>R</i> ₁ / <i>wR</i> ₂ | 0.0398/0.0479 | 0.0479/0.0856 |
| ρ _{max} and ρ _{min} /(e•nm ⁻³) | 5.67 × 10 ² and -4.87 × 10 ² | 7.86 × 10 ² and -4.63 × 10 ² |

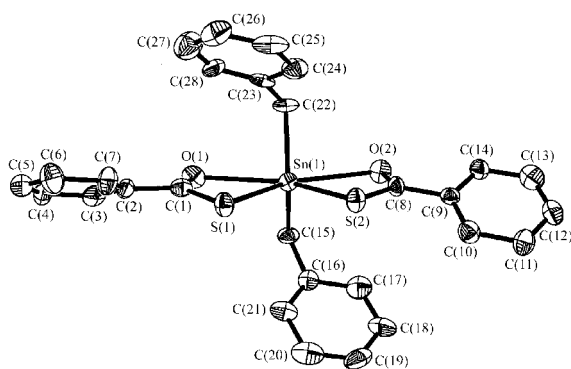


Figure 1 Molecular structure of $(\text{PhCH}_2)_2\text{Sn}(\text{SOCPPh})_2$ (**1**).

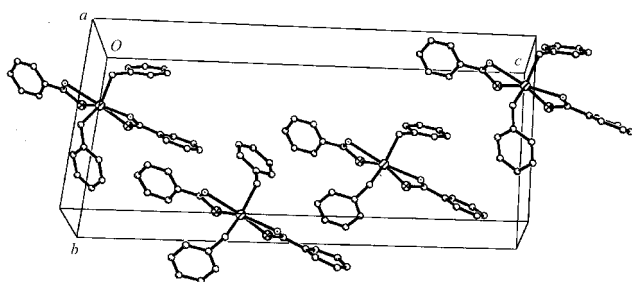


Figure 2 Molecular packing in the unit cell for $(\text{PhCH}_2)_2\text{Sn}(\text{SOCPPh})_2$ (**1**).

the atomic coordinates and equivalent isotropic thermal parameters. The selected bond lengths and angles are given in Table 3. The unit cell contains three independent molecules. In fact a computer fitting of molecules **A**, **B**, and **C** shows only very marginal difference in the bond lengths and angles. One of the three molecules is represented in Figure 1 with its numbering scheme. The tin atom is six-coordinated with lengths, Sn(1)—C(22) 0.2142(7) nm, Sn(1)—C(15) 0.2148(9) nm, Sn(1)—S(2) 0.2467(3) nm, Sn(1)—S(1) 0.2471(3) nm, Sn(1)—O(2) 0.2731(3) nm, Sn(1)—O(1) 0.2708(3) nm, and in a distorted octahedron configuration. From Figure 1 it can be seen that the Sn atom exists in the center of a skew-trapezoidal plane defined by the two S atoms and two O atoms derived from two chelating thiobenzoate ligands. The two remaining ligands are the organic substituents which lie above and under the plane. The thiobenzoate ligands chelate the Sn center with unequal Sn—O and Sn—S bond distances, and the longer C—S bond distances associated with the shorter Sn—S bonds (Table 3).

The geometry is loosely based on an octahedron, with atoms S(1), O(1), S(2), and O(2) occupying the equatorial positions. The sum of the equatorial angles (360.4°) at the tin atom by the four coordinated sulfur and oxygen atoms [S(1)—Sn(1)—O(1) $60.6(4)^\circ$, S(2)—Sn(1)—S(1) $89.0(5)^\circ$, S(2)—Sn(1)—O(2) $60.4(5)^\circ$, O(1)—Sn(1)—O(2) $150.4(2)^\circ$] deviates at most by -0.4° from the 360° , indicating that the atoms S(1), O(1), S(2), O(2), and Sn(1) are almost in the same plane.

Table 2 Atomic coordinates ($\times 10^4$) and thermal parameters ($\text{nm}^2 \times 10^5$) for complex **1**

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} | Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} |
|-------|-----------|----------|----------|------------------------|-------|----------|----------|----------|------------------------|
| Sn(1) | 1830(2) | 1741(1) | 3449(1) | 43(1) | C(36) | 4010(18) | 4142(10) | -644(5) | 52(4) |
| Sn(2) | 5069(1) | 5221(1) | 347(1) | 49(1) | C(37) | 3420(20) | 3708(9) | -1169(5) | 56(3) |
| Sn(3) | 8173(1) | 8259(1) | 6551(1) | 49(1) | C(38) | 1308(16) | 3930(8) | -1433(4) | 67(3) |
| O(1) | 3467(13) | 2811(7) | 4331(3) | 62(3) | C(39) | 887(19) | 3535(10) | -1914(4) | 79(3) |
| O(2) | 2595(13) | 667(7) | 2566(3) | 59(3) | C(40) | 2420(20) | 2860(9) | -2143(5) | 70(4) |
| O(3) | 6624(15) | 6262(8) | 1220(4) | 67(3) | C(41) | 4400(17) | 2661(12) | -1873(7) | 92(6) |
| O(4) | 6131(12) | 4258(7) | -485(3) | 65(3) | C(42) | 5010(20) | 3052(10) | -1394(5) | 59(3) |
| O(5) | 10039(13) | 9226(7) | 7384(3) | 65(3) | C(43) | 6562(13) | 6637(7) | 94(3) | 59(3) |
| O(6) | 8850(15) | 7178(8) | 5667(4) | 65(3) | C(44) | 4892(18) | 7124(10) | -267(5) | 50(4) |
| S(1) | -953(4) | 2452(2) | 4030(1) | 55(1) | C(45) | 4900(20) | 6909(12) | -774(6) | 67(4) |
| S(2) | -1530(4) | 1032(2) | 2869(1) | 54(1) | C(46) | 3280(20) | 7303(10) | -1091(5) | 87(4) |
| S(3) | 2262(4) | 5857(2) | 944(1) | 60(1) | C(47) | 1520(20) | 7952(9) | -932(5) | 80(4) |
| S(4) | 1836(4) | 4586(2) | -285(1) | 56(1) | C(48) | 1420(18) | 8189(8) | -448(5) | 73(3) |
| S(5) | 5576(4) | 8903(2) | 7187(1) | 56(1) | C(49) | 3081(19) | 7791(7) | -120(4) | 66(3) |
| S(6) | 4765(4) | 7627(2) | 5956(1) | 59(1) | C(50) | 6672(13) | 3832(7) | 643(3) | 60(3) |
| C(1) | 1440(15) | 2870(11) | 4439(5) | 49(4) | C(51) | 5025(19) | 2861(10) | 566(5) | 54(4) |
| C(2) | 1000(18) | 3347(8) | 4950(3) | 47(3) | C(52) | 3380(18) | 2713(9) | 875(4) | 64(3) |
| C(3) | 2630(20) | 4062(12) | 5221(6) | 69(5) | C(53) | 1727(18) | 1866(10) | 776(4) | 77(3) |

Continued

| Atom | x | y | z | U_{eq} | Atom | x | y | z | U_{eq} |
|-------|-----------|----------|---------|----------|-------|----------|-----------|---------|----------|
| C(4) | 2270(20) | 4485(11) | 5696(5) | 63(4) | C(54) | 1867(19) | 1104(9) | 383(5) | 82(3) |
| C(5) | 360(20) | 4154(10) | 5887(4) | 73(3) | C(55) | 3560(20) | 1228(9) | 77(4) | 85(4) |
| C(6) | -1250(20) | 3456(10) | 5628(4) | 78(4) | C(56) | 5113(18) | 2079(12) | 183(6) | 62(4) |
| C(7) | -971(17) | 3052(9) | 5162(4) | 67(3) | C(57) | 8113(19) | 9292(11) | 7548(5) | 52(4) |
| C(8) | 476(19) | 603(10) | 2450(5) | 42(3) | C(58) | 8010(18) | 9776(9) | 8059(4) | 48(3) |
| C(9) | -525(15) | 144(7) | 1949(4) | 46(3) | C(59) | 9870(20) | 10444(11) | 8299(6) | 73(4) |
| C(10) | -2689(16) | 414(8) | 1742(4) | 63(3) | C(60) | 9850(20) | 10857(10) | 8783(5) | 64(4) |
| C(11) | -3450(20) | 35(10) | 1258(4) | 78(4) | C(61) | 8010(19) | 10605(10) | 9027(5) | 72(4) |
| C(12) | -2100(20) | -690(10) | 1010(4) | 75(4) | C(62) | 6208(19) | 9948(9) | 8814(5) | 91(4) |
| C(13) | -20(20) | -987(11) | 1232(6) | 73(4) | C(63) | 6239(16) | 9571(8) | 8333(4) | 59(3) |
| C(14) | 880(20) | -570(11) | 1697(5) | 59(4) | C(64) | 6770(20) | 7144(11) | 5550(5) | 47(4) |
| C(15) | 3261(14) | 3137(7) | 3151(3) | 57(3) | C(65) | 5859(18) | 6681(7) | 5047(4) | 52(3) |
| C(16) | 1470(18) | 3627(11) | 2825(5) | 53(4) | C(66) | 3697(16) | 6938(8) | 4822(4) | 66(3) |
| C(17) | 1250(20) | 3311(12) | 2308(6) | 73(5) | C(67) | 3010(20) | 6554(9) | 4334(4) | 77(4) |
| C(18) | -520(20) | 3680(9) | 2004(5) | 94(4) | C(68) | 4480(19) | 5866(9) | 4090(4) | 78(4) |
| C(19) | -2180(20) | 4302(10) | 2189(5) | 91(4) | C(69) | 6570(20) | 5565(11) | 4321(6) | 78(5) |
| C(20) | -2120(20) | 4644(9) | 2676(5) | 86(4) | C(70) | 7340(20) | 5960(11) | 4768(6) | 59(4) |
| C(21) | -256(18) | 4265(8) | 2988(4) | 64(3) | C(71) | 9471(14) | 9672(7) | 6253(3) | 62(3) |
| C(22) | 3556(14) | 361(7) | 3750(3) | 58(3) | C(72) | 7940(20) | 10631(10) | 6328(5) | 51(3) |
| C(23) | 2059(19) | -98(10) | 4098(5) | 50(3) | C(73) | 5930(19) | 10769(9) | 6023(4) | 69(3) |
| C(24) | 156(19) | -814(8) | 3899(4) | 66(3) | C(74) | 4437(19) | 11610(10) | 6116(5) | 83(4) |
| C(25) | -1344(19) | -1145(9) | 4231(5) | 85(4) | C(75) | 4980(20) | 12384(9) | 6519(5) | 84(3) |
| C(26) | -950(20) | -826(11) | 4711(5) | 96(4) | C(76) | 6950(20) | 12262(10) | 6820(4) | 94(4) |
| C(27) | 950(18) | -162(11) | 4905(5) | 98(4) | C(77) | 8410(20) | 11384(9) | 6746(6) | 71(5) |
| C(28) | 2340(20) | 170(13) | 4570(5) | 77(5) | C(78) | 9920(14) | 6847(7) | 6803(3) | 60(3) |
| C(29) | 4590(20) | 6300(11) | 1344(5) | 59(4) | C(79) | 8650(18) | 6340(10) | 7160(5) | 45(3) |
| C(30) | 4283(18) | 6802(8) | 1853(4) | 50(3) | C(80) | 6663(18) | 5691(8) | 7017(4) | 68(3) |
| C(31) | 2326(17) | 6556(8) | 2079(4) | 60(3) | C(81) | 5300(20) | 5287(9) | 7356(5) | 75(3) |
| C(32) | 2170(20) | 6925(10) | 2556(5) | 81(4) | C(82) | 5890(18) | 5526(9) | 7835(5) | 90(4) |
| C(33) | 3820(18) | 7610(9) | 2798(4) | 74(3) | C(83) | 7870(20) | 6171(9) | 7998(5) | 90(4) |
| C(34) | 5720(20) | 7916(11) | 2595(6) | 79(4) | C(84) | 9120(20) | 6577(12) | 7653(5) | 65(4) |
| C(35) | 6010(20) | 7460(12) | 2109(6) | 63(5) | | | | | |

Table 3 Selected bond distances (nm) and angles ($^{\circ}$) for complex 1

| | Molecule A | Molecule B | Molecule C |
|-------------|------------|------------|------------|
| Sn(1)—C(22) | 0.2142(7) | 0.2111(8) | 0.2130(8) |
| Sn(1)—C(15) | 0.2148(9) | 0.2133(9) | 0.2141(9) |
| Sn(1)—S(2) | 0.2467(3) | 0.2474(3) | 0.2485(3) |
| Sn(1)—S(1) | 0.2471(3) | 0.2486(3) | 0.2482(3) |
| Sn(1)—O(2) | 0.2731(3) | 0.2642(2) | 0.2585(3) |
| Sn(1)—O(1) | 0.2708(3) | 0.2581(2) | 0.2690(2) |
| O(1)—C(1) | 0.1229(11) | 0.1247(12) | 0.1233(12) |
| O(2)—C(8) | 0.1224(12) | 0.1253(11) | 0.1199(12) |

Continued

| | Molecule A | Molecule B | Molecule C |
|-------------------|------------|------------|------------|
| S(1)—C(1) | 0.1723(12) | 0.1691(12) | 0.1713(11) |
| S(2)—C(8) | 0.1755(11) | 0.1724(13) | 0.1748(12) |
| O(1)-Sn(1)-O(2) | 150.4(2) | 146.2(2) | 147.2(2) |
| S(1)-Sn(1)-O(1) | 60.6(4) | 59.4(1) | 61.3(3) |
| S(1)-Sn(1)-O(2) | 149.7(2) | 153.1(2) | 151.1(2) |
| S(2)-Sn(1)-O(1) | 149.3(5) | 151.3(2) | 152.4(4) |
| S(2)-Sn(1)-O(2) | 60.4(5) | 61.3(4) | 59.4(4) |
| C(15)-Sn(1)-O(1) | 84.3(2) | 81.1(4) | 83.3(5) |
| C(15)-Sn(1)-O(2) | 83.3(5) | 83.4(3) | 85.2(4) |
| C(22)-Sn(1)-O(1) | 83.2(3) | 83.3(5) | 83.4(4) |
| C(22)-Sn(1)-O(2) | 84.5(7) | 83.4(3) | 80.4(5) |
| C(22)-Sn(1)-C(15) | 130.1(3) | 130.9(3) | 131.2(3) |
| C(22)-Sn(1)-S(2) | 107.9(2) | 109.0(2) | 106.3(2) |
| C(15)-Sn(1)-S(2) | 107.3(2) | 106.0(2) | 108.3(2) |
| C(22)-Sn(1)-S(1) | 107.2(2) | 104.1(2) | 108.4(2) |
| C(15)-Sn(1)-S(1) | 107.5(2) | 108.2(2) | 104.0(3) |
| S(2)-Sn(1)-S(1) | 89.0(5) | 91.7(1) | 91.8(2) |
| C(1)-S(1)-Sn(1) | 87.8(4) | 88.1(4) | 85.5(4) |
| C(8)-S(2)-Sn(1) | 88.1(4) | 85.9(4) | 87.6(4) |
| C(16)-C(15)-Sn(1) | 110.5(7) | 110.9(6) | 111.6(6) |
| C(23)-C(22)-Sn(1) | 109.2(6) | 110.7(6) | 111.9(6) |
| O(1)-C(1)-C(2) | 119.0(11) | 117.4(10) | 118.0(11) |
| O(1)-C(1)-S(1) | 123.0(10) | 121.2(10) | 121.0(10) |
| C(2)-C(1)-S(1) | 118.0(8) | 119.2(8) | 120.0(9) |
| O(2)-C(8)-C(9) | 121.6(10) | 119.2(10) | 119.1(10) |
| O(2)-C(8)-S(2) | 121.6(10) | 121.0(10) | 121.8(10) |
| C(9)-C(8)-S(2) | 116.8(8) | 119.9(9) | 119.3(9) |

Molecular structure of complex 2

The molecular structure and packing in the unit cell are shown in Figure 3 and Figure 4. Table 4 gives the atomic coordinates and equivalent isotropic thermal

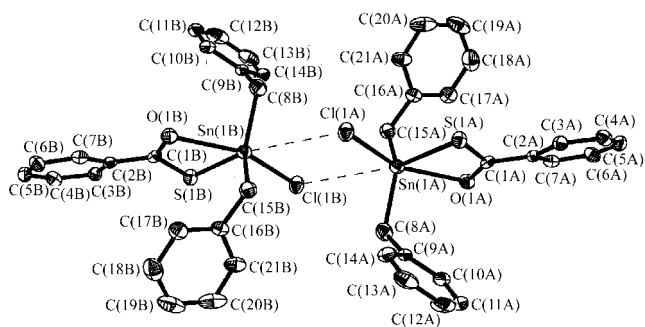


Figure 3 Dimer structure of $(\text{PhCH}_2)_2\text{Sn}(\text{Cl})\text{SOCPh}$ (**2**).

parameters. The selected bond lengths and angles are listed in Table 5.

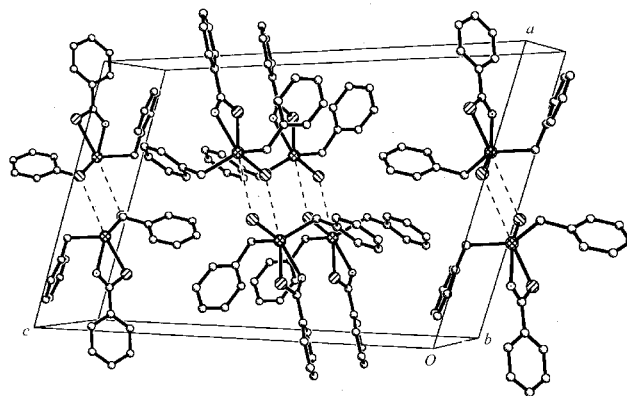


Figure 4 Molecular packing in the unit cell for $(\text{PhCH}_2)_2\text{Sn}(\text{Cl})\text{SOCPh}$ (**2**).

Table 4 Atomic coordinates ($\times 10^4$) and thermal parameters ($\text{nm}^2 \times 10^5$) for complex **2**

| Atom | x | y | z | U_{eq} | Atom | x | y | z | U_{eq} |
|-------|----------|----------|---------|-----------------|-------|----------|-----------|---------|-----------------|
| Sn(1) | 6537(1) | 8788(1) | 5640(1) | 50(1) | C(10) | 6591(6) | 6920(17) | 7288(5) | 65(3) |
| O(1) | 7898(3) | 6337(9) | 6108(2) | 60(1) | C(11) | 6784(7) | 7550(30) | 7867(6) | 92(4) |
| S(1) | 8005(1) | 10591(3) | 6206(1) | 58(1) | C(12) | 6441(10) | 9460(30) | 8015(6) | 110(6) |
| Cl(1) | 5782(1) | 12369(3) | 5335(1) | 68(1) | C(13) | 5925(9) | 10790(20) | 7592(7) | 86(4) |
| C(1) | 8456(5) | 7860(12) | 6302(3) | 46(2) | C(14) | 5715(6) | 10200(16) | 7003(5) | 64(3) |
| C(2) | 9448(5) | 7494(12) | 6595(3) | 42(2) | C(15) | 6612(7) | 7613(17) | 4788(4) | 69(3) |
| C(3) | 10027(5) | 9124(13) | 6956(3) | 51(2) | C(16) | 7466(6) | 8303(14) | 4650(3) | 52(2) |
| C(4) | 10953(6) | 8685(16) | 7224(4) | 58(2) | C(17) | 8239(8) | 6997(18) | 4753(4) | 72(3) |
| C(5) | 11336(6) | 6716(17) | 7128(4) | 62(2) | C(18) | 9020(9) | 7760(30) | 4603(5) | 106(4) |
| C(6) | 10788(6) | 5141(17) | 6772(4) | 60(2) | C(19) | 9007(11) | 9770(40) | 4338(6) | 120(6) |
| C(7) | 9861(6) | 5480(13) | 6510(3) | 51(2) | C(20) | 8230(12) | 11080(20) | 4234(5) | 107(4) |
| C(8) | 5766(7) | 7480(20) | 6205(5) | 71(3) | C(21) | 7494(8) | 10356(18) | 4391(4) | 76(3) |
| C(9) | 6037(5) | 8208(13) | 6838(3) | 46(2) | | | | | |

Table 5 Selected bond distances (nm) and angles ($^\circ$) for complex **2**

| | | | |
|--------------------|------------|--------------------|-----------|
| Sn(1)—C(8) | 0.2138(10) | Sn(1)—S(1) | 0.2447(2) |
| Sn(1)—C(15) | 0.2138(9) | Sn(1)—O(1) | 0.2481(5) |
| Sn(1)—Cl(1) | 0.2431(2) | Sn(1)—Cl(1A) | 0.3591(2) |
| O(1)—C(1) | 0.1228(7) | S(1)—C(1) | 0.1760(7) |
| C(8)-Sn(1)-C(15) | 129.5(4) | C(15)-Sn(1)-S(1) | 110.8(3) |
| C(8)-Sn(1)-Cl(1) | 102.4(3) | Cl(1)-Sn(1)-S(1) | 91.6(7) |
| C(15)-Sn(1)-Cl(1) | 99.8(3) | C(8)-Sn(1)-O(1) | 92.0(3) |
| C(8)-Sn(1)-S(1) | 113.2(3) | C(15)-Sn(1)-O(1) | 86.9(3) |
| S(1)-Sn(1)-O(1) | 62.6(8) | Cl(1)-Sn(1)-O(1) | 154.0(5) |
| Cl(1A)-Sn(1)-S(1) | 164.6(4) | Cl(1A)-Sn(1)-Cl(1) | 73.2(5) |
| Cl(1A)-Sn(1)-O(1) | 132.1(1) | C(8)-Sn(1)-Cl(1A) | 73.8(1) |
| C(15)-Sn(1)-Cl(1A) | 70.1(9) | C(1)-O(1)-Sn(1) | 95.6(4) |
| C(1)-S(1)-Sn(1) | 84.5(3) | C(9)-C(8)-Sn(1) | 117.9(6) |
| C(16)-C(16)-Sn(1) | 113.6(6) | O(1)-C(1)-C(2) | 123.1(7) |
| O(1)-C(1)-S(1) | 117.0(6) | C(2)-C(1)-S(1) | 119.9(6) |

In complex **2**, The tin atom is five-coordinated with lengths: [Sn(1)—S(1) 0.2447(2) nm, Sn(1)—O(1) 0.2481(5) nm, Sn(1)—Cl(1) 0.2431(2) nm, Sn(1)—C(8) 0.2138(10) nm, Sn(1)—C(15) 0.2138(9) nm], in a distorted trigonal bipyramid. An additional feature was noted in this structure, *i.e.* the presence of a short intermolecular Sn \cdots Cl distance of 0.3591(2) nm (the sum of the van der Waals radii for Sn and Cl is 0.397 nm) makes the structure as a weakly-bridged dimer. This interaction is very weak so that the deviation from the common structural type is minimal. This phenomenon was observed in the complexes (PhCH₂)₂SnCl(S₂CNMe₂),¹⁵ but it did not occur in the complexes ^tBu₂SnCl(S₂CNEt₂)¹⁶, Ph₂SnCl(S₂CNEt₂),¹⁶ and Ph₂SnCl[ⁱPr(xan)].¹⁷

The geometry is loosely based on a trigonal bipyramid, with atoms C(8), S(1), and C(15) occupying the equatorial positions. As an indication the sum of the equatorial angles (353.5 $^\circ$) at the tin atom by the two coordinated carbon atoms and one sulfur atom [C(15)-Sn(1)-S(1) 110.8(3) $^\circ$, C(8)-Sn(1)-C(15) 129.5(4) $^\circ$, C(8)-Sn(1)-S(1) 113.2(3) $^\circ$] deviates at most by 6.5 $^\circ$ from 360 $^\circ$, so the atoms S(1), C(8), C(15), and Sn(1) are almost in the same plane. The Cl atom occupies approximately one apical position of the trigonal bipyramid. Conversely, due to the constraint of the chelating ligand [the angle [S(1)-Sn(1)-O(1)] is only 62.6(8) $^\circ$], the O(1) atom can not exactly occupy the corresponding *trans* axial position of the trigonal bipyramid with the angle Cl(1)-Sn(1)-O(1) being 154.0(5) $^\circ$.

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