

Synthesis, Characterization and Crystal Structure of Chlorodibenzyltin(IV) Complex with Dithiomorpholinocarbamate Ligand

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Chlorodibenzyltin(IV) complex with dithiomorpholinocarbamate ligand was synthesized by the reaction of dibenzyltin dichloride with dithiomorpholinocarbamate in 1:1 stoichiometry. The complex was characterized by elementary analysis, UV, IR and ^1H NMR spectra. The crystal structure was determined by X-ray single crystal diffraction study. The crystallographic data are as follows: triclinic, space group $P\bar{1}$, $a = 0.8723(2)$ nm, $b = 1.099(2)$ nm, $c = 1.1036(3)$ nm, $\alpha = 86.498(4)^\circ$, $\beta = 89.697(5)^\circ$, $\gamma = 82.807(5)^\circ$, $Z = 2$, $V = 1.0479(4)$ nm 3 , $D_c = 1.580$ g/cm $^{-3}$, $\mu = 1.553$ mm $^{-1}$, $F(000) = 500$, $R_1 = 0.0442$, $wR_2 = 0.0974$. The crystal consists of discrete molecules containing five-coordinate tin atoms in a distorted trigonal bipyramidal configuration. The molecules are packed in the unit cell in one-dimensional chain structure through a weak interaction between the chlorine atom and sulfur atom, the sulfur atom and one of the sulfurs of an adjacent molecule.

Keywords chlorodibenzyltin(IV) complex, dithiomorpholinocarbamate, crystal structure, S...S and S...Cl interactions

Introduction

Organotin(IV) complexes were widely used as biocides, fungicides and in industry as homogeneous catalysts.¹⁻⁶ More recently, pharmaceutical properties of alkyltin(IV) complexes with *N,N*-dialkyl dithiocarbamate ligands have been investigated for their antitumour activity.^{7,8} In order to explore the relationships between biological activity and structure, we report the synthesis and the crystal structure of novel chlorodibenzyltin(IV)

complex with dithiomorpholinocarbamate ligand.

Experimental

General procedures

The reaction was carried out under nitrogen atmosphere with use of standard Schlenk techniques. The solvent was dried over phosphorus(V) oxide prior to use. IR spectra were recorded on a Nicolet-460 spectrophotometer, samples were as KBr discs. ^1H NMR spectra were recorded on a Jeol-FX-90Q NMR spectrometer, and chemical shifts are given in δ relative to Me_4Si in CDCl_3 solvent. Elemental analysis was performed in a Yanaco M-3 elemental analyzer. Tin was estimated as SnO_2 .

Synthesis of chlorodibenzyltin(IV) complex with dithiomorpholinocarbamate ligand

Anhydrous sodium dithiomorpholinocarbamate (1.0 mmol) was added to 20 mL of dichloromethane solution of $(\text{PhCH}_2)_2\text{SnCl}_2$ (1.0 mmol) and stirring for 10 h at 30 $^\circ\text{C}$. The precipitated salts were removed by filtration and the filtrate was concentrated to about 5 mL under reduced pressure. Ether (5 mL) and hexane (5 mL) were added to this solution. Immediately precipitate was formed. The product was recrystallized from dichloromethane-ether-hexane to give a colorless crystal 0.444 g, yield 89%, m.p. 140—142 $^\circ\text{C}$; UV-vis (CHCl_3) λ_{max} : 222, 253,

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286 nm; $^1\text{H NMR}$ (CHCl_3 , 90 Hz) δ : 7.08—7.23 (m, 10H, Ph-H), 3.81 (t, $J = 7.46$ Hz, 4H, NCH_2), 4.03 (t, $J = 7.46$ Hz, 4H, OCH_2), 3.12 (t, $J_{\text{Sn-H}} = 81.06$ Hz, 4H, CH_2Sn); IR (KBr) ν : 1498 (s, C—N), 1158, 1026 (s, CS_2), 562 (m, Sn—C), 452 (s, Sn—S) cm^{-1} . Anal. calcd for $\text{C}_{19}\text{H}_{22}\text{ClNOS}_2\text{Sn}$: C 45.77, H 4.45, N 2.81, Sn 23.80; found C 45.52, H 4.37, N 2.77, Sn 23.95.

Crystallographic measurements

Crystals of $(\text{PhCH}_2)_2\text{SnClS}_2\text{CNC}_4\text{H}_8\text{O}$ ($\text{C}_{19}\text{H}_{22}\text{ClNOS}_2\text{Sn}$, M_r 498.64) are colorless prisms. A single crystal having approximate dimensions of 0.25 mm \times 0.20 mm \times 0.20 mm was mounted in a glass capillary. All measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo $K\alpha$ ($\lambda = 0.071073$ nm) radiation. The data were collected at temperature of 293(2) K to maximum θ value of 25.02°. The crystal structure belongs to triclinic, space group $P\bar{1}$, $a = 0.8723(2)$ nm, $b = 1.099(2)$ nm, $c = 1.1036(3)$ nm, $\alpha = 86.498(4)^\circ$, $\beta = 89.697(5)^\circ$, $\gamma = 82.807(5)^\circ$, $Z = 2$, $V = 1.0479(4)$ nm³, $D_c = 1.580$ g/cm⁻³, $\mu = 1.553$ mm⁻¹, $F(000) = 500$. The structure was solved by direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined by full-matrix least-squares calculation to $R_1 = 0.0442$ and $wR_2 = 0.0974$ for 2642 observed reflections with $I > 2\sigma(I)$. In the final difference map, the residuals are 7.16×10^2 and -9.52×10^2 e/nm³, respectively.

Results and discussion

IR, UV and $^1\text{H NMR}$ spectra

The assignments of IR bands of these complexes have been made by comparison with the IR spectra of related dibenzyltin(IV) complex with dithiomorpholinocarbamate ligand, sodium dithiomorpholinocarbamate and dibenzyltin dichloride. A new absorption band appears at 452 cm^{-1} which is the characteristic vibrations of Sn—S bond.⁷

One obvious feature of the IR spectra is the similarity to the stretch bands arising from the dithio-piperidyl-carbamate ligand. The relatively high value (1498 cm^{-1})

for $\nu(\text{C}\cdots\text{N})$ is similar to that reported for analogous tin complexes.^{8,9} This suggests that the dithiomorpholinocarbamate ligand of this complex is linked to Sn atom in a bidentate fashion.

In IR spectra, the important bands arising from $\nu_{\text{as}}(\text{CS}_2)$ and $\nu_{\text{s}}(\text{CS}_2)$ appear at 1158 and 1026 cm^{-1} , respectively. The $\Delta\nu [\nu_{\text{as}}(\text{CS}_2) - \nu_{\text{s}}(\text{CS}_2)]$ is 132 cm^{-1} , which much smaller than the $\Delta\nu^*$ for the $\text{R}_2\text{NCS}_2\text{R}'$,¹⁰ but larger than the $\Delta\nu'$ for the corresponding sodium dithiomorpholinocarbamate.¹¹ This shows that the dithiomorpholinocarbamate group of the complex was coordinated to tin atom in an anisobidentate fashion.¹²

$^1\text{H NMR}$ spectra of the complex show that the chemical shifts of the protons on the benzyl group of the complex exhibit two signals in range of δ 7.08—7.23 as multiplet, and δ 3.12 as triplet which is caused by the tin (^{119}Sn)-hydrogen couplings (the spin-spin coupling constant $J_{\text{Sn-H}} = 81.06$ Hz). The proton signal of methylene connected directly with nitrogen appears at δ 3.81. They shift downfields δ 0.6 as compared with that of the salts of appropriate acid. It is shown that the coordinated dithiocarbamate group is more electronegative than in case of no coordination.¹¹

In UV-vis spectra of the complex it can be seen that the band at $\lambda_{\text{max}} = 222$ nm which belongs to strong absorption, is a K band due to $\pi\text{-}\pi^*$ transition of dithiocarbamate $\text{N}\cdots\text{C}\cdots\text{S}$. The band at $\lambda_{\text{max}} = 253$ nm which belongs to medium absorption due to $\pi\text{-}\pi^*$ transition of $\text{S}\cdots\text{C}\cdots\text{S}$ radical is a hypsochromic shift about 14 nm as compared with that of the appropriate acid.¹¹ The band at $\lambda_{\text{max}} = 286$ nm which belongs to a weak absorption is attributed to electron-transfer transition $n\text{-}\pi^*$ in CS_2 radical, which exhibits a hypsochromic shift by 32 nm, too, as compared with the corresponding band of salt of dithiocarbamic acid.

Molecular structure of $(\text{PhCH}_2)_2\text{SnClS}_2\text{CNC}_4\text{H}_8\text{O}$

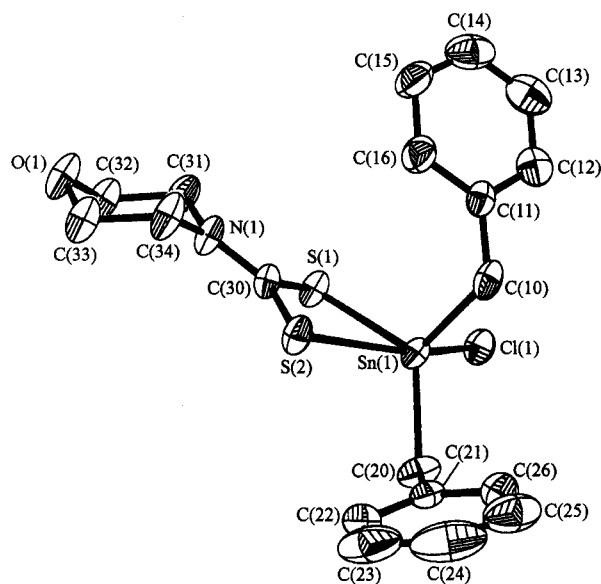
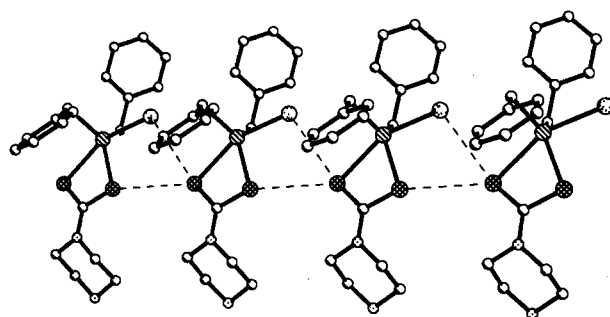
The selected bond distances and angles for $(\text{PhCH}_2)_2\text{SnClS}_2\text{CNC}_4\text{H}_8\text{O}$ are given in Table 2. The molecular structure of $(\text{PhCH}_2)_2\text{SnClS}_2\text{CNC}_4\text{H}_8\text{O}$ is depicted in Fig. 1. The tin atom is five-coordinated [$\text{Sn}(1)\text{—S}(1)$ 0.2466(2) nm, $\text{Sn}(1)\text{—S}(2)$ 0.2725(2) nm, $\text{Sn}(1)\text{—Cl}(1)$ 0.2441(2) nm, $\text{Sn}(1)\text{—C}(20)$ 0.2152(6) nm, $\text{Sn}(1)\text{—C}(10)$ 0.2154(6) nm], with a

Table 1 Atomic coordinates ($\times 10^4$) and isotropic equivalent displacement parameters ($\text{nm}^2 \times 10^5$)

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)	2788(1)	2494(1)	7372(1)	49(1)	C(20)	649(7)	3494(6)	7933(7)	74(2)
S(1)	3117(2)	1363(1)	5507(1)	59(1)	C(21)	817(7)	4809(5)	8013(5)	54(2)
S(1)	2964(2)	4071(1)	5388(1)	60(1)	C(22)	274(8)	5677(8)	7100(7)	80(2)
Cl(1)	2702(2)	566(2)	8577(1)	70(1)	C(23)	473(14)	6910(10)	7190(11)	125(4)
O(1)	4321(6)	2787(4)	1054(4)	81(1)	C(24)	1189(13)	7210(10)	8180(15)	130(5)
N(1)	3988(6)	2683(4)	3589(4)	61(1)	C(25)	1719(9)	6438(10)	9040(10)	107(3)
C(10)	4933(7)	2969(5)	8050(5)	60(2)	C(26)	1534(8)	5225(7)	8971(6)	75(2)
C(11)	6345(7)	2222(5)	7615(5)	53(2)	C(30)	3414(7)	2722(5)	4696(5)	49(1)
C(12)	7150(8)	1330(6)	8370(7)	71(2)	C(31)	4359(9)	1544(6)	2940(5)	71(2)
C(13)	8453(10)	637(7)	7988(9)	91(2)	C(32)	3775(9)	1745(6)	1676(5)	76(2)
C(14)	8974(10)	789(9)	6846(11)	101(3)	C(33)	3890(9)	3860(6)	1661(6)	79(2)
C(15)	8208(10)	1655(9)	6063(7)	93(3)	C(34)	4464(9)	3771(6)	2924(5)	75(2)
C(16)	6887(8)	2392(7)	6452(6)	76(2)					

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for $(\text{PhCH}_2)_2\text{SnClS}_2\text{CNC}_4\text{H}_8\text{O}$

Sn(1)—C(20)	0.2152(6)	Sn(1)—S(2)	0.27249(16)	S(1)—C(30)	0.1741(6)
Sn(1)—C(10)	0.2154(6)	Sn(1)—Cl(1)	0.24408(16)	O(1)—C(32)	0.1431(7)
Sn(1)—S(1)	0.24664(16)	N(1)—C(30)	0.1319(7)	S(1)⋯S(2A)	0.2954
O(1)—C(33)	0.1403(8)	S(2)—C(30)	0.1711(6)	Cl(1)⋯S(2A)	0.3487
C(20)—Sn(1)—C(10)	119.1(2)	S(1)—Sn(1)—Cl(1)	90.18(6)	C(30)—S(1)—Sn(1)	89.32(18)
C(20)—Sn(1)—S(1)	124.6(2)	C(20)—Sn(1)—S(2)	91.8(2)	C(30)—S(2)—Sn(1)	81.73(19)
C(10)—Sn(1)—S(1)	112.87(16)	C(10)—Sn(1)—S(2)	90.40(16)	C(11)—C(10)—Sn(1)	115.0(4)
C(20)—Sn(1)—Cl(1)	99.71(19)	S(1)—Sn(1)—S(2)	69.28(5)	C(21)—C(20)—Sn(1)	110.4(4)
C(10)—Sn(1)—Cl(1)	98.68(17)	Cl(1)—Sn(1)—S(2)	159.45(5)	S(2)—C(30)—S(1)	118.0(3)
N(1)—C(30)—S(1)	119.7(4)	C(30)—N(1)—C(31)	124.3(5)	Cl(1)⋯S(2A)⋯S(1)	132.5(4)

**Fig. 1** Molecular structure of chlorodibenzyltin dithiomorpholinocarbamate.**Fig. 2** Perspective view showing the one-dimensional S⋯S and S⋯Cl interactions network of the compound.

distorted trigonal bipyramid. An additional feature was noted in this structure, however, that being the presence of a close intermolecular S⋯Cl interaction of 0.3487 nm (the sum of the Van Der Waals radii for S and Cl of 0.397 nm)¹³ and S⋯S interaction of 0.2954 nm (the sum of the Van Der Waals radii for S and S of 0.370

nm)¹⁴, the structure was thus described as a one-dimensional chain organotin complex through a weak interaction between the chlorine atom and sulfur atom, and between the sulfur atom and one of the sulfurs of an adjacent molecule. The interaction is very weak so that the deviation from the common structural type is minimal. This phenomenon was not observed in the complexes ^tBu₂SnCl(S₂CNEt₂), Ph₂SnCl(S₂CNEt₂)¹⁵ and Ph₂SnCl [ⁱPr(xan)].¹⁶ The reason may be that R has much larger room resistance, in the ligands of these complexes.

The geometry is approximately based on a trigonal bipyramid, with atom C(20), S(1) and C(10) occupying equatorial positions. As an indication of the sum of the equatorial angles (356.57°) at the tin atom by the two coordinated carbon atoms and one sulfur atom [C(10)-Sn(1)-S(1) 112.87(16)°, C(20)-Sn(1)-S(1) 124.6(2)°, C(20)-Sn(1)-C(10) 119.1(2)°] deviates at most by 3.43° from the 360°, so the atoms C(20), S(1), C(10) and Sn(1) are not in a same plane. The Cl atom occupies approximately one apical position of the trigonal bipyramid. Conversely, due to the constraint of the chelate [the angle [S(1)-Sn(1)-S(2)] is not 90° but only 69.28(5)°], the S(2) atom cannot exactly occupy the corresponding trans axial position of the trigonal bipyramid, the angle Cl(1)-Sn(1)-S(2) being 159.45(5)°.

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