

Vol. 19, No. 6 Jun., 2003

研究简报 Í 具有 S…S、S…Cl 作用的一维链状有机锡化合物 氯代二苄基锡哌啶荒酸酯的合成、表征及晶体结构 尹汉东* 王传华 马春林 £ 勇 (聊城大学化学系,聊城 252059) 关键词: 二苄基锡衍生物 哌啶荒酸 合成 晶体结构 分类号: 0614.12

Synthesis, Characterization and Crystal Structure of the S…S and S…Cl Interaction One-Dimensional Chain Complex Chlorodibenzyltin Dithiopiperidylcarbamate

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The chlorodibenzyltin dithiopiperidylcarbamate was synthesized by the reaction of dibenzyltin dichloride with dithiopiperidylcarbamate and was characterized by elemental analysis, IR and ¹H NMR. The crystal structure was determined by X-ray single crystal diffraction. The crystallographic data are as follows: monoclinic, space group $P2_1$, a = 0.63464(13) nm, b = 1.9110(4) nm, c = 0.87367(17) nm, $\beta = 97.67(3)^\circ$, Z = 2, V = 1.0501(4) nm³, $D_c = 1.571$ g \cdot cm⁻³, $\mu = 1.546$ mm⁻¹, F(000) = 500, R = 0.0209, wR = 0.0381 [$I \ge 2\sigma(I)$]. The structures consist of discrete molecules containing five-coordinate tin atoms in a seriously distorted trigonal bipyramidal configuration. The molecules are packed in the unit cell in one-dimensional chain complex through a weak interaction between the chlorine atom, the sulfur atom and one of the other sulfurs of an adjacent molecule. CCDC: 180034.

Keywords: denzyltin derivative dithiopiperidylcarbamate synthesis crystal structure

Organotin (IV) complexes were widely used as biocides, fungicides and in industry as homogeneous catalysts^[1-5]. More recently, pharmaceutical properties of alkyltin (IV) complexes with N, N-dialkyl dithiocarbamate ligands have been investigated for their antitumour activity^[6-8]. Crystallographic studies have revealed that the coordination at the tin atom depends not only on the factors such as R-radical stereochemistry, but also on whether the 1, 1-dithiolates behave as monodentate or bidentate ligands and on whether the complexes are monomeric or oligomeric. In order to investigate the of relationship between the biological activity and structure, we report the synthesis and the crystal structure of the novel chlorodibenzyltin (IV) complex with dithiopiperidylcarbamate ligand.

收稿日期:2002-11-20。收修改稿日期:2003-03-25。

国家自然科学基金资助项目(No. 20271025),教育部骨干教师基金资助项目(No.)和山东省自然科学基金资助项目(No. Z2001B02)。

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1 Experiment Section

1.1 Gerenal Procedures

The reaction was carried out under nitrogen atmosphere by using the standard Schlenk techniques. The solvent was dried over phosphorus (V) oxide and prior to use. IR spectra were recorded with a Nicolet-460 spectrophotometer, samples were as KBr discs. ¹H NMR spectra were recorded on Jeol-FX-90Q NMR spectrometer, chemical shifts are given in ppm relative to Me₄Si in CDCl₃ solvent. Elemental analyses were performed in a PE-2400 II elemental analyzer, Tin was estimated as SnO₂.

1.2 Synthesis of Chlorodibenzyltin (V) Complex with Dithiopiperidylcarbamate Ligand

Anhydrous sodium of dithiopiperidylcarbamate (1. 0mmol) was added to 20mL dichloromethane solution of (PhCH₂)₂SnCl₂ (1. 0mmol) and stirred for 10h at 30°C. The precipitated salts were removed by filtration and the filtrate was concentrated to about 5mL under reduced pressure. Ether (5mL) and hexane (5mL) were added to this solution. Immediately a precipitate was formed. The product was recrystallized from dichloromethane-ether-hexane to give a colorless crystal. Yield 0. 457 g (92%), m. p. 148~150°C. Anal. Found(%): C, 48.24; H, 4.79; N, 2.80; (%) for $C_{20}H_{24}ClNS_2Sn$: C, Sn, 23.76. Calc. 48.37; H, 4.87; N, 2.90; Sn, 23.76. UV(CHCl₃) λ_{max} : 221, 248, 280. IR(KBr, cm⁻¹): ν (C-N) 1503; $\nu_{as}(CSS)$ 1154; $\nu_{s}(CSS)$ 1012; $\nu(Sn-C)$ 563; ν (Sn-S) 448. ¹H NMR(CHCl₃): 7.06 ~ 7.28 (10H, m, Ph-H), 3. 76(4H, t, J = 6.90 Hz, NCH₂), 3. 16 $(4H, t, J_{Sn-H} = 80.99Hz, CH_2Sn), 1.62(6H, m, CH_2).$

1.3 Crystallographic Measurements

Crystals of (PhCH₂) $_2$ SnClS₂CNC₅H₁₀ are colorless prisms. C₂₀H₂₄ClNS₂Sn, $M_r = 496.66$. A single crystal having approximate dimensions 0. 40 × 0. 30 × 0. 3mm³ was mounted in a glass capillary. All measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo K α (0. 071073nm) radiation. The data were collected at temperature of 293(2)K to maximum θ value of 25. 03°. The crystal structure belongs to monoclinic, space group $P2_1$, a = 0.63464(13) nm, b = 1.9110(4) nm, c = 0.87367(17) nm, $\beta = 97.67(3)^\circ$, Z = 2, V = 1.0501(4) nm³, $D_c = 1.571$ g \cdot cm⁻³, $\mu = 1.546$ 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 = 0.0209 and wR = 0.0381 for $3274(R_{int} = 0.0171)$ independent reflections with $I \ge 2\sigma(I)$. In the final difference map, the residuals are $310e \cdot$ nm⁻³ and $-237e \cdot$ nm⁻³, respectively.

CCDC: 180034.

2 Results and Discussion

2.1 IR, UV and ¹H NMR Spectra

The assignment of IR bands of this complex has been made by comparison it with the IR spectra of related dibenzyltin (\mathbb{W}) complex with dithiopiperidylcarbamate ligand, sodium dithiopiperidylcarbamate and dibenzyltin dichloride. A new absorption band appears at 448cm⁻¹ which is the characteristic vibrations of Sn-S bond formed^[7].

One obvious feature of the IR spectra is the similarity of the stretching bands arising from the dithiopiperidylcarbamate ligand. The relatively high value (1503cm⁻¹) for ν (C-N) is similar to that reported for analogous tin complexes^[7-9]. It is suggested that the dithiopiperidylcarbamate ligand of this complex is linked to Sn atom in a bidentate fashion.

In IR spectra, the important bands arise from $\nu(CS_2)$ asym and $\nu(CS_2)$ sym appear at 1154cm⁻¹ and 1012cm⁻¹, respectively. The $\Delta\nu$ value [$\nu(CS_2)_{asym} - \nu(CS_2)_{asym}$] is 142cm⁻¹, which is much smaller than the $\Delta\nu^*$ for the R₂NCS₂R'^[10], but is larger than the $\Delta\nu'$ for the corresponding sodium dithiopiperidylcarbamate. This shows that the dithiopiperidylcarbamate group of complex is coordinated to tin atom in an anisobidentate fashion^[11].

The ¹H NMR spectra of complex show that the chemical shifts of the protons on the benzyl group of the complex exhibit two signals, one at about $7.06 \sim 7.28$ ppm as multiplet, and the other at 3.16 ppm as

triplet which is caused by the tin (¹¹⁹Sn)-hydrogen couplings and the spin-spin coupling constant is $J_{\text{Sn-H}} =$ 80. 99Hz. The proton signal of methylene connecting directly with nitrogen appears at δ 3. 76ppm. They shift downfields 0. 5ppm as compared with that of the salts of analogous acid. It is shown that the coordinated dithiocarbamate group is more electronegative than the one of no coordination^[11].

In UV spectra of the complex, it can be seen that the band 1 at $\lambda_{max} = 221$ nm which belongs to a strong absorption, is a K band due to $\pi - \pi^*$ transition of dithiocarbamate N-C-S. The band 2 at $\lambda_{max} = 248$ nm which belongs to a medium absorption due to $\pi - \pi^*$ transition of S-C-S radical is a hypsochromic shift about 17nm as compared with that of the analogous acid^[10]. The band 3 at $\lambda_{max} = 280$ nm which belongs to a weak absorption is attributed to electron-transfer transition $n - \pi^*$ in CS₂ radical, which exhibits a hypsochromic shift by 34nm, too, as compared with the corresponding band of salt of the dithiocarbamate acid.

2. 2 Molecular structure of

(PhCH₂)₂SnClS₂CNC₅H₁₀

The selected bond distances and angles for $(PhCH_2)_2SnClS_2CNC_3H_{10}$ are given in Table 1. The molecular structure of $(PhCH_2)_2SnClS_2CNC_5H_{10}$ is depicted in Fig. 1. The tin atom is five-coordinate $[Sn(1)-S(1) \ 0.24634(10) \text{ nm}, Sn(1)-S(2) \ 0.26612(10) \text{ nm}, Sn(1)-Cl(1) \ 0.24952(10) \text{ nm}, Sn(1)-C(11) \ 0.2150(3) \text{ nm}, Sn(1)-C(21) \ 0.2143(4) \text{ nm}]$, with a distorted trigonal bipyramid. An additional feature is noted in this structure, there are a close intermolecular Sn…Cl interaction of 0.3536nm (the sum of the Van der Waals radii for Sn and Cl of 0.370nm). The structure is thus described as a one-dimensional chain polymer through a

Sn(1)-C(11)	0.2150(3)	Sn(1)-S(2)	0.26612(10)	S(1)-C(1)	0.1742(3)
Sn(1)-C(21)	0.2143(4)	Sn(1)- $Cl(1)$	0.24952(10)	S(2)-C(1)	0.1700(4)
Sn(1)-S(1)	0.24634(10)	N(1)-C(1)	0.1320(4)	S(1)S(2A)	0.355
N(1)-C(6)	0.1474(7)	N(1)-C(2)	0.1476(4)	$Cl(1)\cdots S(2A)$	0.3536
C(21)-Sn(1)-C(11)	120. 84(15)	S(1)-Sn(1)-Cl(1)	86. 56(3)	C(1)-S(1)-Sn(1)	88.90(12)
C(21)-Sn(1)-S(1)	113.29(11)	C(21)-Sn(1)-S(2)	97.97(11)	C(1)-S(2)-Sn(1)	83.43(12)
C(11)-Sn(1)-S(1)	125. 19(10)	C(11)-Sn(1)-S(2)	93.92(10)	C(12)-C(11)-Sn(1)	112.5(2)
C(21)-Sn(1)-Cl(1)	95.42(11)	S(1)-Sn(1)-S(2)	70.00(3)	C(22)-C(21)-Sn(1)	113.2(2)
C(11)-Sn(1)-Cl(1)	96.06(11)	Cl(1)-Sn(1)-S(2)	156. 12(3)	S(2)-C(1)-S(1)	117.57(19)
C(1)-N(1)-C(6)	124.2(3)	C(1)-N(1)-C(2)	122.8(3)	C(6)-N(1)-C(2)	111.8(3)
N(1)-C(1)-S(1)	119.2(3)	N(1)-C(1)-S(2)	123.2(3)	$Cl(1)\cdots S(2A)\cdots S(1)$	131.3(6)





Fig. 1 Molecular structure of chlorodibenzyltin dithiopiperidylcarbamate with 50% probability level of the thermal elipsoids



Fig. 2 Projection of the unit cell along the c axis

weak interaction between the chlorine atom, the sulfur atom and one of the other sulfurs of an adjacent molecule. This interaction is very weak so that the deviation from the common structural type is minimal. This phenomenon was not observed in the complexes 'Bu₂SnCl(S₂CNEt₂), Ph₂SnCl(S₂CNEt₂)^[13] and Ph₂SnCl ['Pr(xan)]^[14]. The reason may be that the R groups have much larger positional resistence in the ligands of these complexes.

The geometry is loosely based on a trigonal bipyramid, with atom C(11), S(1) and C(21) occupying equatorial positions. As an indication, the sum of the equatorial angles (359. 32°) at the tin atom by the two coordinated carbon atoms and one sulfur atom $[C(21)-Sn(1)-C(11) 120, 84(15)^{\circ}, C(21)-Sn(1)-S$ (1) 113. 29(11)°, C(11)-Sn(1)-S(1) 125. 19(10)°] deviates at most by 0. 68° from the 360°, it shows that the atoms C(11), S(1), C(24) and Sn(1) are almost 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 70.00(3)°], the S(2) atom cannot exactly occupy the corresponding trans axial position of the trigonal bipyramid, and the angle Cl(1)-Sn(1)-S(2) is 156. 12(3)°.

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