Structure of Dicyclohexyltin(IV) Complexes

Bull. Korean Chem. Soc., Vol. 10, No. 4, 1989 343

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Synthesis and Properties of Dicyclohexyltin(IV) Complexes. Structure of Cy₂Sn(S₂CNMe₂)₂

Ok - Sang Jung, Min Jung Kim, Jong Hwa Jeong, and Youn Soo Sohn*

Division of Chemistry, Korea Advanced Institute of Science & Technology, Seoul 136 - 791

Dicyclohexyltin(IV) complexes Cy_2SnX (X = O, S, $(Me_2NCS_2)_2$) have been prepared and characterized by means of elemental analysis, cryoscopic data, and IR spectroscopy. X-ray structure determination for $Cy_2Sn(S_2CNMe_2)_2$ (monoclinic; P2/c; a = 8.992(1), b = 6.688(1), c = 19.453(2) Å, β = 96.556(7) ; R = 0.041) has shown that the molecule is C_2-symmetric with both dithiocarbamate ligands bonding in anisobidentate mode and the local geometry around the hexacoordinate Sn(IV) atom is a distorted octahedral arrangement with the two cyclohexyl groups in trans position. The physical and chemical properties measured suggest polymeric and trimeric structures for Cy_2SnO and Cy_2SnS, respectively.

Introduction

Numerous dimethyltin(IV) and di-*t*-butyltin(IV) complexes have been investigated in order to understand the steric and inductive effects of organic ligands in their tin complexes. Physicochemical studies indicated that dimethyltin oxide is polymeric[1] while di-*t*-butyltin oxide is cyclotrimeric[2,3]. Dimethyltin sulfide has been found to be a 6-membered cyclic trimer[4,5] whereas di-*t*-butyltin sulfide is a 4-membered cyclic dimer[6]. Furthermore, X-ray crystallographic studies have shown that the coordination geometry of Me₂Sn(S₂CNMe₂)₂ is a distorted octahedral arrangement[7] in contrast to the distorted trigonal-bipyramidal structure of (*t*-

Bu)₂Sn(S₂CNMe₂)₂[8]. Thus it appears that there is a remarkable difference between Me₂Sn(IV) and (*t*-Bu)₂Sn(IV) complexes in chemical behavior. However, dicyclohexyltin(IV) complexes, median in bulkiness and inductive effect between dimethyltin(IV) and di-*t*-butyltin(IV) complexes, are surprisingly less well evaluated than their dimethyltin(IV) and di-*t*-butyltin counter parts although a few cyclohexyltin(IV) complexes were recently reported by the authors[9]. In an effort to understand the behavior of dicyclohexyltin(IV) complexes, we have prepared Cy₂SnX (X = O, S, (Me₂NCS₂)₂) and discussed in terms of their physicochemical evidences together with the crystal structure of Cy₂Sn(S₂CNMe₂)₂.

Table 1. Crystal Parameters and Experimental Details for Cy$_2$Sn-(S$_2$CNMe$_2$)$_2$

Formula	C$_{18}$H$_{34}$N$_2$S$_4$Sn
Formula weight	525.41
Crystal system	Monoclinic
Space group	P2/c
a, b, c(Å)	8.992(1), 6.668(1), 19.453(2)
β(deg.)	96.556(7)
V(Å^3)	1162(1)
Z	2
d_{cal}(g cm^{-3})	1.50
Crystal size(mm)	0.33 × 0.42 × 0.50
μ(cm^{-1})	26.89
Radiation	Mo-K$_\alpha$(λ = 0.71073 Å)
Scan method	w–2θ
Data collected	h, $\pm k$, $\pm l$, 1$\leq$$\theta$$\leq$26
No. of unique observation	2654
No. of unique data $I>3\sigma(I)$	1892
No. of parameters refined	114
Over determination ratio	16.60
$R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$	0.0413
$R_G = (\Sigma|F_o - F_c|^2/\Sigma F_o^2)^{1/2}$	0.0603

Experimental

Dicyclohexyltin dibromide was from commercial source (Alfa Chemicals) and used without further purification. Sodium N,N-dimethyldithiocarbamate was prepared in the standard manner[10]. All solvents were either used directly from freshly opened bottles or dried prior to use. Chemical analyses were carried out by the Chemical Analysis Laboratory at KAIST. The molecular weight was measured cryoscopically in benzene using a Cryette A Automatic Cryoscope. The IR spectra in the 4000–400 cm^{-1} region were measured on KBr pellet with an Analect fx-6160 FT-IR spectrophotometer. The ^{1}H-NMR spectra were recorded on ⋅ JEOL JNM DMX 60 spectrometer.

Preparation of Dicyclohexyltin oxide. Cy$_2$SnBr$_2$ (2.22

g, 5 mmol) in 50 ml of water was mixed with NaOH (0.4 g, 10 mmol) in 20 ml of water, and the mixture was stirred at room temperature for 1 hour. The resultant precipitate was filtered, washed with cold ethyl ether and then dried in vacuum for several hours resulting in a white solid product (1.35 g, 90% yield). m.p.>220 °C. Anal. Calcd. for C$_{12}$H$_{22}$OSn: C, 47.89; H, 7.37. Found: C, 46.98; H, 7.20.

Preparation of Dicyclohexyltin Sulfide. A solution of Na$_2$S·9H$_2$O (1.20 g, 5 mmol) dissolved in 50 ml of water was added dropwise to an equimolar solution of Cy$_2$SnBr$_2$ (2.22 g, 5 mmol) in 50 ml of chloroform, and the resulting solutions were stirred at room temperature for 1 hour. The chloroform layer was separated and evaporated to produce a white solid. Recrystallization of the crude product from chloroform-petroleum ether (1:1) at 0 °C gave a crystalline solid (1.27 g, 80% yield). m.p. 193–194 °C. Anal. Calcd. C$_{12}$H$_{22}$SSn: C, 45.46; H, 6.99. Found: C, 45.38; H, 6.89. M. W. measured: 920.06 (theory for (Cy$_2$SnS)$_3$: 951.18). ^{1}H-NMR (CDCl$_3$): δ(ppm) = 1.0–2.5(m).

Preparation of Cy$_2$Sn(S$_2$CNMe$_2$)$_2$. This compound was prepared by the previous procedure[9].

Crystallographic Analyses of Cy$_2$Sn(S$_2$CNMe$_2$)$_2$. All the crystallographic data were obtained by using an Enraf-Nonius CAD4 diffractometer with graphite monochromated molybdenum radiation (λ(K$_{\alpha 1}$) = 0.70930, λ(K$_{\alpha 2}$) = 0.71359 Å) at ambient temperature of 23 ± 2 °C. A single crystal recrystallized from chloroform-petroleum ether solvent pair was glued to the interior of a thin walled glass capillary which was then sealed. Preliminary diffractometric investigation indicated monoclinic system and centrosymmetry from the intensities of Friedel pairs ($I_{hkl} = I_{\bar{h}\bar{k}\bar{l}}$). From the systematic absence $h0l$ for $l = 2n + 1$, $00l$ for $l = 2n + 1$, the space group was uniquely determined as P2/c (No. 13)[11]. The cell constants were determined by the least squares refinement of the diffraction geometry for 25 intense reflections having 10$\leq$ $\theta$$\leq$13. Crystal parameters and procedural information corresponding to data collection are given in Table 1. The structure was solved by use of the conventional heavy atom method and difference Fourier techniques and refined by means of full matrix least squares procedures using SHELX-76, a system of computer program for X-ray structure determination[12]. The non-hydrogen atoms were refined

Table 2. Fractional Atomic Coordinates and Anisotropic Thermal Parameters for Cy$_2$Sn(S$_2$CNMe$_2$)$_2$

ATOM	X/A	Y/B	Z/C	K^*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn	0.0000	0.7429(1)	0.2500	0.5	0.0309(3)	0.0291(4)	0.0263(3)	0.0000	-0.0016(2)	0.0000
S1	0.0807(2)	0.6150(3)	0.1159(1)	1.0	0.0524(12)	0.0277(10)	0.0390(10)	-0.0053(8)	0.0106(9)	-0.0001(9)
S2	0.0785(2)	1.0273(3)	0.1728(1)	1.0	0.0528(11)	0.0268(9)	0.0230(9)	-0.0029(8)	0.0103(8)	-0.0004(9)
C1	0.1189(8)	0.8629(12)	0.1075(4)	1.0	0.0319(37)	0.0324(39)	0.0320(37)	-0.0036(32)	0.0014(30)	0.0052(32)
N	0.1757(7)	0.9364(10)	0.0529(3)	1.0	0.0402(34)	0.0364(36)	0.0313(31)	0.0001(27)	0.0072(26)	0.0032(29)
C2	0.2214(11)	1.1476(13)	0.0479(5)	1.0	0.0658(59)	0.0344(47)	0.0593(54)	0.0080(41)	0.0210(46)	-0.0072(43)
C3	0.2029(10)	0.8100(13)	-0.0061(4)	1.0	0.0608(52)	0.0440(49)	0.0314(38)	-0.0046(34)	0.0141(36)	0.0086(40)
C11	0.2296(8)	0.6584(12)	0.2888(4)	1.0	0.0271(35)	0.0368(41)	0.0364(38)	0.0042(33)	-0.0057(29)	0.0021(31)
C12	0.2890(9)	0.8098(12)	0.3436(4)	1.0	0.0381(42)	0.0349(44)	0.0554(50)	-0.0040(37)	-0.0145(37)	-0.0027(34)
C13	0.4551(9)	0.7630(15)	0.3705(5)	1.0	0.0379(42)	0.0441(49)	0.0797(62)	0.0028(51)	-0.0168(41)	-0.0014(44)
C14	0.4693(10)	0.5479(15)	0.3988(5)	1.0	0.0457(49)	0.0534(57)	0.0586(55)	0.0045(46)	-0.0122(41)	0.0055(43)
C15	0.4098(10)	0.3965(14)	0.3429(5)	1.0	0.0441(47)	0.0457(51)	0.0641(57)	-0.0018(45)	-0.0077(42)	0.0108(42)
C16	0.2444(9)	0.4428(12)	0.3143(5)	1.0	0.0401(44)	0.0304(41)	0.0587(52)	0.0008(38)	-0.0106(38)	0.0055(35)

*Occupancy of the Atom.

Structure of Dicyclohexyltin(IV) Complexes
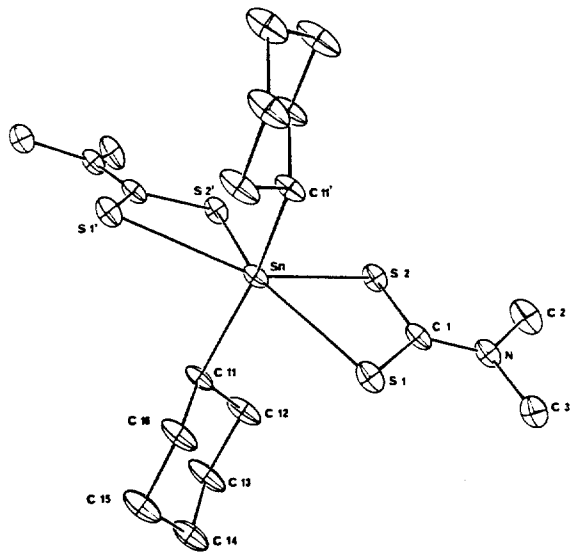
Bull. Korean Chem. Soc., Vol. 10, No. 4, 1989 345

Figure 1. An ORTEP drawing and atom–labeling scheme of Cy_2Sn-$(S_2CNMe_2)_2$.

Table 3. Bond Distances(Å) and Angle(°) for $Cy_2Sn(S_2CNMe_2)_2$

Atom	Distance	Atom	Angle
Sn–S(1)	2.914(2)	S(2)–Sn–S(1)	65.3(1)
Sn–S(2)	2.571(2)	C(11)–Sn–S(1)	84.9(2)
Sn–C(11)	2.190(7)	C(11)–Sn–S(2)	94.6(2)
S(1)–C(1)	1.705(8)	C(11)–Sn–C(11)'	150.1(1)
S(2)–C(1)	1.749(7)	S(2)–Sn–S(2)'	84.9(1)
C(1)–N	1.326(9)	S(1)–Sn–S(1)'	146.3(1)
N–C(2)	1.477(10)	S(1)–Sn–S(2)'	148.5(1)
N–C(3)	1.469(9)	C(1)–S(1)–Sn	82.7(3)
C(11)–C(12)	1.523(10)	C(1)–S(2)–Sn	93.0(3)
C(12)–C(13)	1.557(10)	S(2)–C(1)–S(1)	118.7(4)
C(13)–C(14)	1.540(13)	N–C(1)–S(1)	122.5(6)
C(14)–C(15)	1.537(13)	N–C(1)–S(2)	118.7(6)
C(11)–C(16)	1.532(11)	C(2)–N–C(1)	122.9(7)
C(15)–C(16)	1.557(11)	C(3)–N–C(1)	121.8(7)
		C(3)–N–C(2)	115.3(6)
		C(12)–C(11)–Sn	108.1(5)
		C(16)–C(11)–Sn	113.5(5)
		C(16)–C(11)–C(12)	113.0(6)
		C(13)–C(12)–C(11)	110.3(7)
		C(14)–C(13)–C(12)	110.2(7)
		C(15)–C(14)–C(13)	110.7(7)
		C(16)–C(15)–C(14)	111.4(7)
		C(15)–C(16)–C(11)	110.1(7)

anisotropically and hydrogen atoms were omitted from the refinement. The final error indices were $R = 0.041$, $R_G = 0.060$. Final coordinates and thermal parameters are listed in Table 2.

Results and Discussion

Structure of $Cy_2Sn(S_2CNMe_2)_2$. The molecular geometry and labeling scheme for the title complex is shown in Figure 1. Bond distances and angles are tabulated in Table 3.

Table 4. Relevant IR Bands of Cy_2SnX

Compds.	ν(C–H), cm^{-1}	δ(CH$_2$), cm^{-1}	ν(Sn–C), cm^{-1}
X = O	2923(vs), 2847(vs)	1442(vs)	661(w)
X = S	2920(vs), 2845(vs)	1443(vs)	655(w)
X = (S$_2$CNMe$_2$)$_2$	2923(vs), 2846(vs)	1442(vs)	590(w)

vs = very strong ; w = weak

The molecular geometry shows 2–fold axis that is through the Sn atom bisecting the angles of C(11)–Sn–C(11)', S(2)–Sn–S(2)', and S(1)–Sn–S(1)', simultaneously. The complex is a discrete molecule that consists of two 4–membered chelate rings by the bidentate dithiocarbamate ligands, and thus the Sn is 6–coordinate with S(1), S(2), S(1)', and S(2)' in equatorial positions and C(11), C(11)' in axial positions in a distorted octahedral arrangement similar to the structure of dimethyltin(IV) analogs $Me_2Sn(S_2CNR_2)_2$ (R = Me[7], Et[13]). The bidentate dithiocarbamate ligands are bonded to tin atom in the anisobidentate manner: Sn–S(1) and Sn–S(2) distances of 2.914(2) and 2.571(2) Å, respectively, are similar to those of 2.954(7) and 2.497(8) Å in $Me_2Sn(S_2CNMe_2)_2$[7]. The typical small bite angle (65.3(1)°) of the dithiocarbamate ligand is in part responsible for the distortion from the octahedral geometry. However, the bonding fashion of dithiocabamate ligands in the present complex is different from that of $(t-Bu)_2Sn(S_2CNMe_2)_2$ in which one of the dithiocarbamate ligand acts as an anisobidentate while the other is a monodentate[8].

The most interesting structural feature of the present compound is that the axial bond angle C(11)–Sn–C(11)' is 150.14° implying that the two cyclohexyl groups are almost in trans position. The Me–Sn–Me angle, 136.0°, in the dimethyltin (IV) analog $Me_2Sn(S_2CNMe_2)_2$[7], is intermediate[14] between cis and trans, and in the diphenyltin(IV) compound Ph_2Sn-$(S_2CNEt_2)_2$ the phenyl group are essentially in cis position (C–Sn–C = 101.4°). The increase in the R–Sn–R bond angle from R = phenyl to cyclohexyl groups may be explained in terms of bulkiness of the organic groups bonded to tin atom. Considering the van der Waals radii of those cyclic groups perpendicular to their ring, methyl group may be regarded to be intermediate between phenyl and cyclohexyl groups.

Comparison of the hexacoordinate structure of the present dicyclohexyltin(IV) dithiocarbamate with the five coordinate structure of t-butyltin(IV) analog $(t-Bu)_2Sn(S_2CNMe_2)$[8] results in an important implication concerning the coordination chemistry of organotin(IV) dithiocarbamate complexes. Since many six coordinate $(t-Bu)_2Sn(IV)$ complexes[16] with the t-butyl groups in trans position like the present dicyclohexyltin(IV) complex are known even if t-butyl group is bulkier than the cyclohexyl group, it may be concluded that the five coordination instead of six in the di-t-butyltin(IV) analog is ascribed to the electronic effect of t-butyl group rather than to its steric effect, as was previously suggested by the authors[9].

The bond distance of Sn–C(11) (2.190(7) Å) in the present dithiocarbamate complex is slightly longer than that (2.132 (8) Å) in Cy_2SnBr_2[17], presumably due to lower acidity of the tin atom in the 6–coordinate than in the 4–coordinate complexes.

Physical and Spectroscopic Properties of Dicyclo-

hexyltin Complexes. Dicyclohexyltin oxide is insoluble in all solvents and stable up to high temperature ($>220\,°C$). Such properties suggest that the coordinative association is preserved in the dicyclohexyltin oxide, as in the structure of dimethyltin oxide[1]. On the other hand, dicyclohexyltin sulfide is soluble in common organic solvents such as benzene, acetone, chloroform and dimethyl sulfoxide, and is a colorless crystalline solid with sharp melting point ($193–194\,°C$). In particular, cryoscopic measurement in benzene indicates that dicyclohexyltin sulfide is trimeric. The IR bands of the complexes relevant to their molecular structures listed in Table 4 show the expected values.

Among the stretching modes, ν(Sn–C) band is known to depend on the structure[18,19]. The red shift of the ν(Sn–C) mode of $Cy_2Sn(S_2CNMe_2)_2$ compared to that of dicyclohexyltin oxide and dicyclohexyltin sulfide may be ascribed to decrease of Lewis acidity of the tin atom by hexa–coordination.

The physical and chemical properties of dicyclohexyltin (IV) complexes are in accordance with those of dimethyltin complexes in the solid state and in solution.

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Tl – Tl Interactions in Tl Dimer Investigated by Relativistic and Nonrelativistic EHT Calculations

Yoon Sup Lee* and Youngkyu Do

Department of Chemistry, Korea Advanced Institute of Science and Technology Seoul 960 – 650.

Interactions between Tl atoms for the Tl dimer are studied by relativistic and nonrelativistic EHT methods. Relativistic bond weakening for the Tl dimer is qualitatively explained by comparing orbital energies from relativistic and nonrelativistic calculations. It is also shown that significant overlap exists, especially for 6p orbitals, at the internuclear distance larger than 4 Å, implying that Tl – Tl interaction is not just the electrostatic interaction in the recently discovered dimeric thallacarborane.

Introduction

Diatomic Tl_2 is one of the favorite molecules in elucidating relativistic bond weakening because the inclusion of spin-orbit effects results in substantial decrease of calculated dissociation energies.[1-3] Bond weakening for Tl_2 ground state is attributed to the requirement to form a hybrid of $6p_{1/2}$ and $6p_{3/2}$ atomic spinors in order to produce an analog of bonding σ molecular orbital. The hybridization costs energy

since the atomic Tl is in $^2P_{1/2}$ ground state which is essentially the configuration of one $6p_{1/2}$ open shell electron. From the above argument, we may expect that this weakening might be expainable in the orbital interaction level.

In this report, we employ simple EHT method[4] to study relativistic effects. We utilize existing programs for the relativistic[5] and nonrelativistic[4] EHT calculations.

Most previous calculations on Tl_2 are based upon relativistic effective core potentials.[1,2] The results from the pre-