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The Reaction of Diphenyltin(IV) or Triphenyltin(IV) Chloride with 3,4,5-Trimethoxybenzoyl Salicylahydrazone. The Crystal Structure of $Ph_2[(MeO)_3C_6H_2C(O)N_2CHC_6H_4O]Sn$

Zhengkun Yu*

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China

Shenggang Yan

Dalian University of Technology, Dalian 116011, People's Republic of China

Peiju Zheng and Jian Chen

Fudan University, Shanghai 200433, People's Republic of China

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ABSTRACT

The title complex has been synthesized by the reaction of diphenyltin(IV) or triphenyltin(IV) chloride with 3,4,5-trimethoxybenzoyl salicylahydrazone and characterized by ^1H, ^{13}C, ^{119}Sn NMR, and IR spectral studies. An X-ray analysis shows that the ligand is tridentate and approximately planar and the central tin atom is in a distorted five-coordinate trigonal bipyramidal geometry. The complex crystallizes in the monoclinic space group C2/c with $a = 29.194(4)$, $b = 10.117(1)$, $c = 22.524(3)$ Å, $\beta = 124.44(2)°$, $V = 5486.5(8)$ Å^3, $Z = 8$. The Sn–C bond lengths are 2.123(9) and 2.116(7) Å, and the bond length between the tin atom and the coordinating nitrogen atom (Sn–N bond) is 2.152(6) Å. The C–Sn–C bond angle and the bond angle between the tin atom and the two axially positioned oxygen atoms are 129.1(1) and 156.17(9)°, respectively. The structure was refined to final $R = 0.056$ and $R_w = 0.074$ for 4145 observed reflections with $I > 3\sigma(I)$.

INTRODUCTION

The tin atoms in organotin(IV) complexes can invariably coordinate to the potential donor atoms, e.g., oxygen, sulfur, or nitrogen atoms, but to a great extent the coordinating ability of these ligating atoms is related to the structures of the target complexes. The molecular structures of some five-coordinate triorganotin(IV) complexes containing these ligating atoms have been extensively studied [1–4], but articles on the structures of five-coordinate diorganotin(IV) compounds have been occasionally presented [5–8]. Using 3,4,5-trimethoxybenzoyl salicylahydrazone (**1**) as the ligand, we synthesized the complex (**2a**, $R = {}^n$Bu) with the structure shown in Scheme 1 through its condensation with di-*n*-butyltin(IV) oxide [8].

Recently, we used the reaction of the same ligand

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*To whom correspondence should be addressed.

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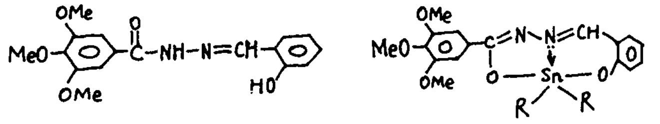

(1) (2)

SCHEME 1

(1) with diphenyltin(IV) dichloride in the presence of a tertiary base tri-*n*-butylamine to cause the diphenyltin unit to bind with the ligand to permit the first structural study of the five-coordinate diphenyltin(IV) complex (**2b**, *R* = Ph). Beyond expectation, when using triphenyltin(IV) chloride as the organotin reagent to prepare a triphenyltin(IV) complex of the same ligand, we obtained the same complex (**2b**) through the disproportionation of the triphenyltin(IV) reagent, which is very different from the reported disproportionation reactions of organotin(IV) compounds [9].

RESULTS AND DISCUSSION

The elemental analyses, IR, NMR spectra, and melting points of the products obtained from these two organotin(IV) chlorides show that the reaction of 3,4,5-trimethoxybenzoyl salicylahydrazone with diphenyltin(IV) dichloride or triphenyltin(IV) chloride formed the same complex (**2b**, *R* = Ph). Maybe the steric hindrance between the ligand and triphenyltin(IV) unit is too great to form a stable triorganotin(IV) complex, so that one phenyl group leaves the triphenyltin unit to bind with one enol-form hydrogen atom or one phenol-form hydrogen atom to result in the stable complex (**2b**). These reactions did not occur in the absence of the tertiary amine. The amine neutralized hydrogen chloride from the reactions to make the reactions proceed smoothly.

IR Spectra

The IR spectrum of the complex (**2b**) is compared with that of the ligand (1) and then the absorptions assigned (Table 1). The free ligand present in the keto form (Scheme 1) is capable of undergoing keto-enol tautomerism, so it may coordinate with a metal atom in either of these two forms, depending on the experimental conditions [8,10]. The IR data of the complex are assigned as follows: (a) The absorptions in the region 3660–3380 cm^{-1} (O–H, N–H) and at 3170 cm^{-1} (N–H) and 1653 cm^{-1} (C=O) in the spectrum of the free ligand disappear from the spectrum of the complex. (b) A new strong band at 1608 cm^{-1} is assigned to the stretching vibration mode of the new C=N bond in the complex. The new band at 1543 cm^{-1} is attributed to the stretching vibration of the conjugated group >C=N–N=C< [11], which means that the nitrogen atom in the HC=N group affords its lone electron pair to form a coordinate bond to the central tin atom. (c) The weak band at 2632 cm^{-1} for the intramolecular hydrogen bond O–H····N in the free ligand is absent in the spectrum of the complex. (d) The new bands at 690 cm^{-1} (m), 575 cm^{-1} (w), and 496 cm^{-1} (m) reveal the formation of Sn–O, Sn–N, and Sn–C bonds in the complex. Therefore, we can infer that the ligand (1) binds to the tin atom in the complex by means of either the phenolic- or enolic-oxygen atom through its deprotonation.

NMR Spectra

The chemical shifts of hydrogen and carbon atoms in the complex are assigned by comparison with those of the ^1H and ^{13}C NMR spectra of the free ligand (1) and complex (**2a**) [8]. The ^1H resonance of the N=C–H group is at the lowest field (δ 8.95). Those of OMe and the aromatic protons can be easily assigned. The ^1H resonances of the N=C–H group and the aromatic protons and the ^{13}C resonances of the complex shift to a lower field than those corresponding ^1H resonances and ^{13}C resonances of the complex (**2a**), which indicates that the approximate conjugate system may conjugate more effectively due to the formation of five- and six-membered rings and the introduction of two phenyl groups that can disperse the electron density on the tin atom. The ^{13}C resonances at the lowest field (δ 167.17, 161.31) are assigned to the carbon atoms of the conjugate

TABLE 1 IR Data and NMR Chemical Shifts of the Complex $Ph_2[(MeO)_3C_6H_2C(O)N_2CHC_6H_4O]Sn$

IR data (cm^{-1})

3070w	3050w	3000w	2940m	2830w	1608s	1589s	1543s	1502s
1467s	1450m	1410m	1388s	1363s	1300s	1226s	1128s	1001m
906m	860m	836m	733s	690m	575w	496m		

NMR chemical shifts δ

^1H NMR: 8.95(s, 1 × H) 7.93(m, 4 × H) 7.60(s, 2 × H) 7.45(m, 10 × H) 3.94(s, 6 × H) 3.82(s, 3 × H)

^{13}C NMR: 167.17 161.31 153.14 139.10 136.22(6 × C) 135.43 134.29 130.56(2 × C) 128.90(6 × C) 128.44 122.12 117.60 116.88 105.17(2 × C) 60.95 56.37(2 × C)

^{119}Sn NMR: −5.88

>C = N–N = C<. Those of the two phenyl groups appear at 136.22 and 128.90, respectively. The resonances of OMe groups appear at the highest field (56.37, 60.95), those of other aromatic carbons in the region 105.17–153.14. The ^{119}Sn NMR spectrum of the complex shows a single ^{119}Sn resonance (−5.88), which also indicates that the ^{119}Sn resonance is shifted downfield because of the previously discussed ring effect and because the complex is possibly present in the form of a monomer in the solution. The spin–spin coupling constant $^{1}J(^{119}Sn–^{13}C)$ is 543 Hz, which is in the range of a five-coordinate organotin(IV) compound [12]. Although the reports on ^{119}Sn NMR chemical shifts of diphenyltin(IV) compounds are very few [13], we can infer that the tin atom is five-coordinate in the solution according to its IR and NMR data. In the light of the preceding discussion, we can suggest that the complex has the molecular structure shown in Scheme 1.

X-Ray Crystallography

The perspective drawing of $Ph_2[(MeO)_3C_6H_2C(O)N_2CHC_6H_4O]Sn$ is shown in Figure 1. Eight molecules of the complex are present in a unit cell. To our knowledge, the unit cell of $Z = 8$ for organotin(IV) complexes is very particular and seldom has been reported [14]. In the solid state, the title complex is present in the form of a discrete monomer. From Figure 1 and the crystal data (Tables 2 and 3), it can be seen that 3,4,5-trimethoxybenzoyl salicylahydrazone is a tridentate and approximately planar ligand. The tin atom forms five- and six-membered rings with the ligand. The tin atom has a distorted trigonal bipyramidal coordination with the two oxygen atoms [O(1), O(2)] occupying the axial positions, two carbon atoms of the phenyl groups [C(21), C(31)], and one nitrogen atom [N(1)] occupying the approximate equatorial positions. This arrangement is in accordance with that in which more electronegative ligating atoms occupy the axial positions in the complexes containing a five-coordinate tin atom [15]. The bond distance of the Sn–O(2) bond is longer than that of the Sn–O(1) bond, which is attributed to the greater steric hindrance of one phenyl group to the O(2) atom than that of the other phenyl group to the O(1) atom [O(1)–Sn–C(31) angle (99.1(2)°) > O(2)–Sn–C(21) angle (91.3(2)°)]. The distance of the C(B)–O(2) bond is comparable to that of the C(11)–O(1) bond, the bond length of Sn–N(1) to that of the Sn–O(1), Sn–O(2), Sn–C(21), or Sn–C(31) bond. These results show that the C = O double bond in the free ligand is changed into a C–O single bond, and the N(1) atom affords its lone electron pair to form a strong coordinate bond to the central tin atom. The length of the C(B)–N(2) bond is almost equal to that of the C(A)–N(1) bond, which means that C(B)–N(2) is also a double bond and the ligand is present in the form of the enol in the complex. According to the orientation of the two phenyl groups, it seems that one of the phenyl groups [C(31), C(32), C(33), C(34), C(35), C(36)] is deshielded to some extent by the other phenyl group, the bonds of C(31)–C(32) [1.42(1) Å], C(34)–C(35) [1.41(1) Å], and C(35)–C(36) [1.42(1) Å] are lengthened more than other C–C bonds [1.37(2)–1.39(1) Å] in the same phenyl group. The two axial oxygen atoms are not in the precise positions of the [O(1)–Sn–O(2) angle, 156.17(9)°]. The lower value of the C(21)–Sn–C(31) angle [129.1(1)°] is in the range of C–Sn–C angles for com-

TABLE 2 Crystal Data and Refinement Details for the Complex

Formula	$C_{29}H_{26}N_2O_5Sn$
Mol. wt.	601.2
Crystal size (mm)	0.3 × 0.2 × 0.2
Crystal system	Monoclinic
Space group	*C2/c*
a (Å)	29.194(4)
b (Å)	10.117(1)
c (Å)	22.524(3)
β (°)	124.44(2)
V (Å³)	5486.5(8)
Z	8
D_c (g cm^{-3})	1.46
μ (M_0 K_α) (cm^{-1})	9.71
F(000)	2432
2θ range (°)	0–50
Scan mode	ω–2θ
Scan width (°)	0.65 ± 0.35 tan θ
Reflections collected	6236
Independent reflections	5988
Observed reflections for $I > 3\sigma(I)$	4145
R	0.056
R_w	0.074
GOF	6.91
$(\Delta/\sigma)_{max}$	0.03
Residual ρ_{max} (eÅ^{-3})	0.65

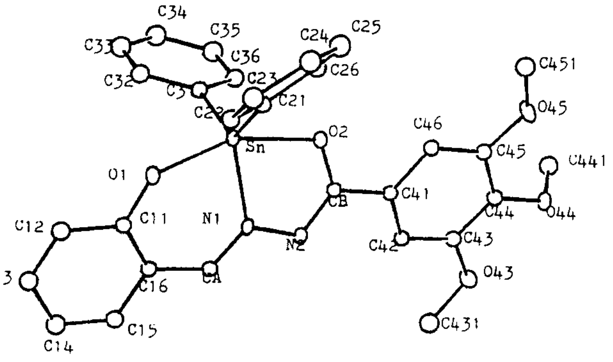

FIGURE 1 Molecular structure of the complex $Ph_2[(MeO)_3C_6H_2C(O)N_2CHC_6H_4O]_2$.

TABLE 3 Selected Bond Lengths (Å) and Angles (°) for the Complex

Sn–O(1)	2.068(7)	Sn–O(2)	2.128(6)	Sn–N(1)	2.152(6)
Sn–C(21)	2.123(9)	Sn–C(31)	2.116(7)	O(1)–C(11)	1.33(1)
O(2)–C(B)	1.308(9)	N(1)–N(2)	1.395(9)	N(1)–C(A)	1.29(1)
N(2)–C(B)	1.30(1)	C(B)–C(41)	1.48(1)	C(A)–C(16)	1.46(1)
C(21)–C(22)	1.39(1)	C(21)–C(26)	1.40(2)	C(22)–C(23)	1.38(1)
C(23)–C(24)	1.40(2)	C(24)–C(25)	1.36(2)	C(25)–C(26)	1.41(2)
C(31)–C(32)	1.42(1)	C(31)–C(36)	1.39(1)	C(32)–C(33)	1.39(1)
C(33)–C(34)	1.37(2)	C(34)–C(35)	1.41(1)	C(35)–C(36)	1.42(1)

O(1)–Sn–O(2)	156.17(9)	O(1)–Sn–N(1)	84.62(9)
O(1)–Sn–C(21)	94.4(2)	O(1)–Sn–C(31)	99.1(2)
O(2)–Sn–N(1)	73.24(8)	O(2)–Sn–C(21)	91.3(2)
O(2)–Sn–C(31)	95.2(2)	N(1)–Sn–C(21)	125.1(2)
N(1)–Sn–C(31)	105.2(2)	C(21)–Sn–C(31)	129.1(1)
Sn–O(1)–C(11)	130.5(2)	Sn–O(2)–C(B)	114.3(2)
Sn–N(1)–N(2)	116.8(2)	Sn–N(1)–C(A)	128.1(3)
N(2)–N(1)–C(A)	114.5(3)	N(1)–N(2)–C(B)	111.0(3)
O(2)–C(B)–N(2)	124.5(3)	N(1)–C(A)–C(16)	125.1(3)
O(1)–C(11)–C(16)	124.4(3)	C(A)–C(16)–C(11)	124.6(3)
Sn–C(21)–C(22)	120.7(2)	Sn–C(21)–C(26)	119.8(2)
Sn–C(31)–C(32)	120.1(2)	Sn–C(31)–C(36)	120.0(2)

plexes containing tridentate ligands [16]. The preceding discussion reveals that the tin atom lies in a distorted trigonal bipyramidal environment.

EXPERIMENTAL

Triphenyltin(IV) chloride was purchased from Aldrich and used without further purification. Dried analytical grade solvents were used in all experiments. The ligand (1) was prepared as previously described [8]. Diphenyltin(IV) dichloride was synthesized by the disproportionation reaction of equimolar amounts of Ph_4Sn and $SnCl_4$ [17]. Other reagents were used as supplied.

IR spectra were recorded using KBr discs on a Digilab FTS-20E spectrometer in the range 4000–400 cm^{-1}. ^{1}H NMR spectra were recorded on an EM-360 spectrometer in $(D_3C)_2CO$ with Me_4Si as the internal standard, ^{13}C NMR in $CDCl_3$ on a Varian XL-200 spectrometer, and ^{119}Sn NMR in $CHCl_3$ on a Varian FT-80A NMR spectrometer operating at 27.4 MHz. Chemical shifts were reported in δ units from internal chloroform (77.05 for ^{13}C) and from external 33% Me_4Sn in C_6H_6 for ^{119}Sn. Microanalyses (C, H, N) were determined by the Element Analysis Group of the Shanghai Institute of Organic Chemistry (China). Tin was estimated as SnO_2 [18].

Preparation of the Complex from Ph_2SnCl_2

To a mixture of 0.18 g (0.5 mmol) Ph_2SnCl_2, 0.17 g (0.5 mmol) 3,4,5-trimethoxybenzoyl salicylahydrazone and 0.56 g (2.9 mmol) of ^{n}Bu$_3$N was added 30 mL (v/v, 1/1) of benzene and chloroform successively at room temperature. The solid was quickly dissolved with stirring. The mixture was stirred for 30 minutes and then filtered. All solvent was removed from the filtrate under reduced pressure to leave a yellow crystalline solid. The desired complex was obtained through the recrystallization of the crude product from ethanol/benzene (6/1, v/v) in 86% yield, m.p. 171–172°C. Anal. found for complex (**2b**): C, 58.03; H, 4.41; N, 4.69, Sn, 19.60. $C_{29}H_{26}N_2O_5Sn$ calc.: C, 57.88; H, 4.32; N, 4.66; Sn, 19.74%.

Preparation of the Complex from Ph_3SnCl

Ph_3SnCl 0.20 g (0.5 mmol), 0.17 g (0.5 mmol) 3,4,5-trimethoxybenzoyl salicylahydrazone, and 0.30 g (1.5 mmol) of ^{n}Bu$_3$N were added to 30 mL (1/1, v/v) of benzene/chloroform. The mixture was stirred at ca. 40°C for about 1 hour and then filtered. The procedure for the isolation of the product was analogous to the case of Ph_2SnCl_2. A yellow crystalline solid was collected from the recrystallization of the crude product in ethanol (in 82% yield), m.p. 171–172°C. Anal. found for the product: C, 58.26; H, 4.45; N, 4.53; Sn, 17.60. The expected complex $C_{35}H_{32}N_2O_5Sn$ calc., C, 61.88; H, 4.71; N, 4.12; Sn, 17.49%.

X-Ray Crystallography

A yellow single crystal of the title complex for X-ray diffraction study was grown in ethanol/benzene (1/1, v/v) or in ethanol by slow evaporation of the solvent at room temperature. Diffraction measurements were made on a Enraf-Nonius CAD4 diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å) at room temperature. With a suitable single crystal of approximate dimensions 0.3 × 0.2 × 0.2 mm^3, a total of 5988 independent reflections was collected in the range of $0° < 2\theta < 50°$ using ω-2θ scan mode. The correction of LP and absorption was applied to the reflection data. Table 2 lists the crystal data of the complex and Table 3 the selected bond lengths and angles.

Structure solution by the MULTAN(86) method revealed the metal atom coordination, and subsequent difference Fourier method yielded positions of all remaining atoms. Some non-H atoms with anisotropic thermal parameters and others with isotropic thermal parameters were refined by the full-matrix least-squares technique. Refinement converged at $R = 0.056$ and $Rw = 0.074$ *for 4145 observed reflections with* $I > 3\sigma(I)$ of 5988 unique ones. A final difference Fourier map exhibited no significant peaks greater than 0.65 $e/\text{Å}^3$. Scattering factors were taken from the International Tables for X-ray crystallography (1974). All computations were performed on a Micro VAX-II with SDP-PLUS and ORTEP programs.

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