Chinese Chemical Letters Vol. 16, No. 2, pp 193-196, 2005
http://www.imm.ac.cn/journal/ccl.html

Synthesis and Structural Characterization of Some Diorganotin Complexes of N-(3, 5-Dibromosalicylidene)-α-amino Acid and their Diphenyltin Dichloride Adducts

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Abstract: The title complexes, $R'_2Sn(3,5\text{-}Br_2\text{-}2\text{-}OC_6H_2CH{=}NCHRCOO)$, and their diphenyltin dichloride adduct, $R'_2Sn(3,5\text{-}Br_2\text{-}2\text{-}OC_6H_2CH{=}NCHRCOO)\bullet SnPh_2Cl_2$, were synthesized and characterized by elemental analysis, IR, ^1H and ^{13}C NMR and X-ray single crystal diffraction. The structural features of the compounds were described.

Keywords: Diorganotin complexes, molecular adduct, crystal structure, α-amino acid Schiff base.

The organotin complexes with Schiff base derived from α-amino acid continue to receive attention owing to their structural feature and biological properties, especially antitumour activities[1-5]. Studies[2,4] have shown that the diorganotin complexes with salicylidene-α-amino acid or (2-hydroxynaphthalidene)-α-amino acid Schiff bases are the isolated monomeric, with the tin atom in a distorted trigonal bipyramid and the carboxylate moiety in the tridentate ligand in unidentate mode. Thus the free carbonyl oxygen can coordinate a second Sn-containing species and form the molecular adducts. In this paper, we report the synthesis and structural characterization of some diorganotin complexes of N-(3,5-dibromosalicylidene)-α-amino acid and their 1:1 molecular adducts with diphenyltin dichloride, a novel dinuclear organotin compounds. The reaction equations were as follows:

$$R'_2SnCl_2 + 3,5\text{-}Br_2\text{-}2\text{-}HOC_6H_2CH{=}NCHRCOOK \longrightarrow \underset{\mathbf{1}}{R'_2Sn(3,5\text{-}Br_2\text{-}2\text{-}OC_6H_2CH{=}NCHRCOO)}$$

$$\mathbf{1} + Ph_2SnCl_2 \longrightarrow \underset{\mathbf{2}}{R'_2Sn(3,5\text{-}Br_2\text{-}2\text{-}OC_6H_2CH{=}NCHRCOO)\bullet SnPh_2Cl_2}$$

R = H, Me, *i*-Pr, *i*-Bu, *s*-Bu, Bz; R′= *n*-Bu, Cy, Ph.

Experimental

Preparation of ligand: Monopotassium salt of N-(3,5-dibromosalicylidene)-α-amino acid was prepared by the condensation reaction of potassium salt of α-amino acid with 3,5-di-

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bromosalicylaldehyde in a 50% ethanolic solution at 60 °C.

Preparation of complexes **1**: Into 30 mL dry benzene, 2 mmol Et_3N, 1.5 mmol ligand and 1.5 mmol diorganotin dichloride in 30 mL dry benzene were dropped. The mixture was refluxed for 3 h, and then filtered. The yellow filtrate was concentrated in a rotary evaporator. The yellow product obtained was recrystallized from chloroform-hexane (1:1, v/v). The results were listed in **Table 1**[6].

Preparation of adducts **2:** A dry benzene solution of Ph_2SnCl_2 (0.69 g, 2.0 mmol) was added dropwise to hot benzene solution of the complex **1** (2 mmol). The reaction mixture was refluxed for 2 h, and excess solvent was removed under reduced pressure. The yellow solid thus obtained was washed several times with hot hexane and recrystallized from chloroform solution. The results were shown in **Table 2**[7].

Table 1 The yield (%) and melting point (°C) of complexes **1**

No.	R	R′	mp	yield	No.	R	R′	mp	yield
1a	H	*n*-Bu	128-9	54	**1i**	*i*-Bu	*n*-Bu	112-4	57
1b	H	Ph	146-7	70	**1k**	*i*-Bu	Ph	136-7	70
1c	H	Cy	155-6	62	**1l**	*i*-Bu	Cy	185-6	47
1d	Me	*n*-Bu	44-5	56	**1m**	*s*-Bu	*n*-Bu	136-8	56
1e	Me	Ph	122-3	67	**1n**	*s*-Bu	Ph	182-3	60
1f	Me	Cy	178-9	53	**1o**	Bz	*n*-Bu	108-9	77
1g	*i*-Pr	*n*-Bu	115-6	73	**1p**	Bz	Ph	119-20	75
1h	*i*-Pr	Ph	218-9	60	**1q**	Bz	Cy	206-7	70
1i	*i*-Pr	Cy	190-1	69					

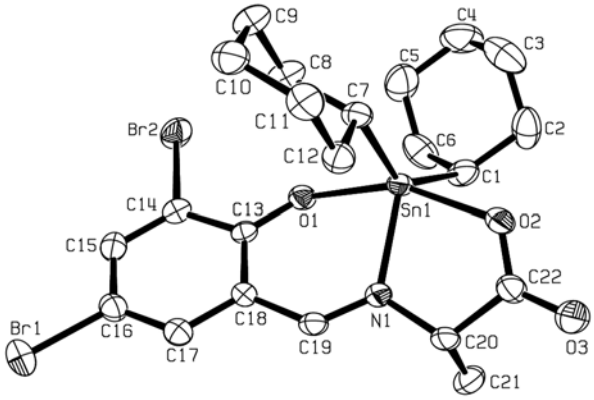
Table 2 The yield (%) and melting point (°C) of adducts **2**

No.	R	R′	mp	yield	No.	R	R′	mp	yield
2a	H	Ph	174-6	50	**2c**	*i*-Pr	Ph	194-5	48
2b	Me	Ph	165-6	46	**2d**	Bz	Ph	125-6	62

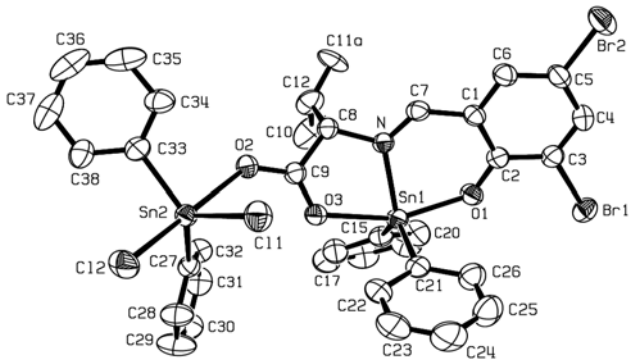
Results and Discussion

Compared the free ligand, the $\nu_{as}(CO_2)$ and ν(C=N) of the complexes **1** shifted to low frequencies, which indicate that the carboxyl oxygen and the imino nitrogen atoms were coordinated to the tin atom[2,4]. The magnitude of $\Delta\nu(CO_2)$ (ν_{as}-ν_s >210 cm^{-1}) showed the unidentate bonding through the carboxylate moiety[2,8]. A medium intensity band of ν(Sn–O) was at around 550 cm^{-1}. In complexes **2**, the $\nu_{as}(CO_2)$ vibration shifted further to lower wavenumbers, confirming the interaction of Ph_2SnCl_2 with the carbonyl oxygen atom of complexes **1**. The appearance of spin-spin coupling between the azomethine proton and the tin nucleus (^3J(SnN=CH) = ~45 Hz) further confirmed the presence of nitrogen-tin coordination in all complexes. The δ_C values of carbonyl C=O in **1** downfield shifted ($\Delta\delta$ = ~0.5) compared with that in **2** due to the coordination of carbonyl to tin.

Figure 1 Molecular structure of **1f** and **2c**



1f



2c

The results of X-ray single crystal diffractions of **1f** and **2c** are completely in agreement with these of spectral analysis (see **Figure 1**)[9]. In complex **1f**, the coordination geometry about tin atom is a distorted trigonal bipyramid with two cyclohexyl groups (C1 and C7) and the imino N1 atom in equatorial positions and a unidentate carboxyl group oxygen O2 and a phenoxide O1 atom in axial sites (O1–Sn–O2 = 154.94(13)°). The tin atom lies in the ligand plane and forms a five-membered and a six-membered chelate ring with ligand. The complex **2** is a monomeric 1:1 donor-acceptor dinuclear tin compound. Each of the two tin atoms, Sn1 and Sn 2, has a five-coordination geometry in a distorted trigonal bipyramidal arrangement. The two phenyl groups (C15, C21) and imino nitrogen take up the equatorial positions, while the carboxyl oxygen O1 and phenoxide O3, take up the axial sites (O1–Sn1–O3 = 157.37(11)°) around the Sn1 atom. The Sn2 atom is surrounded by the carbonyl O2 and Cl2 along the axial direction (O2–Sn2–Cl2 = 171.14(9)°) while the second Cl1 atom and the C27 and C33 of two phenyl form the equatorial plane.

The primary antimicrobial test showed that these complexes possess moderate bactericidal activities. For example, the minimum inhibitory concentration of complex

2c against *Escherichia coli, Staphylococcus aureus, Bacillus subtilis, and Bacillus aerogenens* is 25, 50, 25, 125 μg/mL, respectively.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 20173050).

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6. Selected analytical and spectral data: Compound **1o**, Anal. Calcd. for $C_{24}H_{29}Br_2NO_3Sn$: C, 43.81, H, 4.44, N, 2.13. Found: C, 43.53, H, 4.199, N, 2.01%. IR (KBr) ν: 1673 ($(COO)_{as}$), 1608 (C=N), 1379 ($(COO)_s$), 549 (Sn–O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, δ ppm): 0.83 (t, 3H, *J* = 7.3 Hz, CH_3), 0.96 (t, 3H, *J* = 7.3 Hz, CH_3), 1.26-1.74 (m, 12H, $2CH_2CH_2CH_2Sn$), 3.02 (dd, 1H, *J* = 9.3, 13.9 Hz, $CHHC_6H_5$), 3.55 (dd, 1H, *J* = 3.7, 13.9 Hz, $CHHC_6H_5$), 4.21 (dd, 1H, *J* = 3.7, 9.3 Hz, *J* (^{119}Sn-^1H) = 39.8 Hz, CH), 6.88 (d, 1H, *J* = 2.4 Hz, H-2 in $Br_2C_6H_2$), 7.09-7.11 (m, 2H, *o*-H in C_6H_5), 7.28-7.31 (m, 3H, *m*-H + *p*-H in C_6H_5), 7.39 (s, 1H, *J*(^{119}Sn-^1H) = 43.4 Hz, N = CH), 7.79 (d, 1H, *J* = 2.4 Hz, H-4 in $Br_2C_6H_2$). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 172.86 (C=O), 171.36 (CH=N), 163.76, 141.98, 136.09, 118.30, 118.14, 107.41 ($Br_2C_6H_2$), 134.98, 130.34, 129.39, 127.96 (C_6H_5), 70.46 (=NCH), 42.02 ($CH_2C_6H_5$), 27.07 (CH_2CH_2Sn), 26.84 (CH_2CH_2Sn), 26.78 ($CH_2CH_2CH_2Sn$), 26.72 ($CH_2CH_2CH_2Sn$), 22.56 [*J*($^{119/117}Sn$-^{13}C) = 591.8/ 565.6 Hz, CH_2Sn], 22.36 [*J*($^{119/117}Sn$-^{13}C) = 588.4/560.6 Hz, CH_2Sn], 13.82 (CH_3), 13.65 (CH_3)
7. Selected analytical and spectral data: Compound **2b**, Anal. Calcd. for $C_{34}H_{27}Br_2Cl_2NO_3Sn_2$: C, 42.29, H, 2.82, N, 1.45. Found: C, 41.93, H, 2.79, N, 1.31%. IR (KBr) ν: 1612 ($(COO)_{as}$), 1431 ($(COO)_s$), 564 (Sn-O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, δ ppm): 1.55 (d, 3H, *J* = 7.3 Hz, CH_3), 4.31 (q, 1H, *J* = 7.2 Hz, *J*(^{119}Sn-^1H) = 39.6 Hz, CHN), 7.31 (d, 1H, *J* = 2.4 Hz, H-2 in $Br_2C_6H_2$), 7.37-7.42 (m, 3H, *m*-H + *p*-H in C_6H_5), 7.48-7.50 (m, 3H, *m*-H + *p*-H in C_6H_5), 7.53-7.57 (m, 6H, *m*-H + *p*-H in C_6H_5), 7.72-7.74 (m, 4H, *J* ($^{119/117}Sn$-^1H) = 91.4/79.4 Hz, *o*-H in C_6H_5), 7.80-7.83 (m, 2H, *J* (^{119}Sn-^1H) = 80.2 Hz, *o*-H in C_6H_5), 7.95 (d, 1H, *J* = 2.4 Hz, H-4 in $Br_2C_6H_2$), 7.97-7.99 (m, 2H, *J* ($^{119/117}Sn$-^1H) = 90.9/78.4 Hz, *o*-H in C_6H_5), 8.28 (s, 1H, *J*(^{119}Sn-^1H) = 55.2 Hz, N = CH). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 173.84 (C=O), 171.08 (CH=N), 163.54, 142.61, 136.51, 118.87, 118.77, 108.54 ($Br_2C_6H_2$), 136.70 (*i*-C), 136.58 (*o*-C), 131.53, 131.43 (*p*-C), 129.60 (*J*(^{119}Sn-^{13}C) = 91.0 Hz), 129.50 (*J*(^{119}Sn-^{13}C) = 94.0 Hz, *m*-C) (ph), 136.83 (*i*-C), 135.36 (*J*(^{119}Sn-^{13}C) = 62.5 Hz, *o*-C), 132.04 (*J*(^{119}Sn-^{13}C) = 16.7 Hz, *p*-C), 129.96 (*J*(^{119}Sn-^{13}C) = 83.5 Hz, *m*-C) (ph_2SnCl_2), 64.67 (=NCH), 22.54 (CH_3)
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9. Crystal structure determinations of **1f** and **2c**: Intensity data were collected at 293 K on a Rigaku RAXIS-RAPID diffractometer. The crystal data were as follows: **1f**, $C_{22}H_{29}Br_2NO_3Sn$, Monoclinic, Space group $P2_1/c$, a = 16.0018(14), b = 10.3245(10), c = 15.4417(17) Å, β = 109.846(6)°, V = 2399.6(4) $Å^3$, Z = 4, R = 0.0378, *w*R = 0.0832. **2c**, $C_{36}H_{31}Br_2Cl_2NO_3Sn_2$, triclinic, space group *P*-1, a = 12.0476(5), b = 12.3358(4), c = 14.1244(5) Å, α = 79.597(2), β = 79.604(2), γ = 64.512(2)°, V = 1851.16(12) $Å^3$, Z = 2, R = 0.0346, *w*R = 0.0810.

Received 12 January, 2004