Heteroatom Chemistry
Volume 17, Number 2, 2006

Synthesis and Characterization of Dimeric Organotin Compounds {[$(ArCH_2)_2$ Sn(2-quin)]$_2$O}$_2$ and Crystal Structure of {[(2-*Cl*$C_6H_4CH_2)_2$Sn(2-quin)]$_2$O}$_2$

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Received 26 June 2005; revised 29 September 2005

ABSTRACT: *Ten new dimeric organotin compounds {[$(ArCH_2)_2$ Sn(2-quin)]$_2$O}$_2$ (Ar = Ph* **1**, *2-ClC_6H_4* **2**, *3-ClC_6H_4* **3**, *4-ClC_6H_4* **4**, *2-FC_6H_4* **5**, *3-FC_6H_4* **6**, *4-FC_6H_4* **7**, *4-BrC_6H_4* **8**, *4-CNC_6H_4* **9**, *2,4-$Cl_2C_6H_3$* **10***) have been synthesized by dealkylation reactions of 2-quinH with [$(ArCH_2)_3Sn]_2O$, and their structures have been characterized by elemental analysis, IR and NMR (^{1}H, ^{13}C, ^{119}Sn) spectroscopies. The structures of {[(2-Cl$C_6H_4CH_2)_2$Sn(2-quin)]$_2$O}$_2$* **2** *have been determined by X-ray diffraction. Studies show that compound* **2** *has a tetranuclear, centrosymmetric dimeric structure, with the endo-cyclic tin atom five-coordinated and the exo-cyclic tin atom six coordinated. Studies also show that the nitrogen atoms of the 2-quin ligand are coordinating to the tin atom for all the ten compounds.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:152–159, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20194

INTRODUCTION

Tetranuclear dimeric organotin compounds are a kind of interesting organotin oxo clusters and have attracted considerable attention during the last several decades in view of their unique structural features [1–5] as well as biological activities [6,7] and in homogenous catalysis [8,9]. In the solid state, they contain characteristic $Sn_4O_2X_2Y_2$ structural motifs with staircase or ladder arrangements, a planar four-membered Sn_2O_2 ring and, generally, five- or six-coordination around the tin atom [1,10,11]. Furthermore, among main group organometallics, organotin compounds demonstrate considerably higher anti-cancer activity in vitro as well as lower toxicity than the known *cis*-platin [12,13]. Studies on organotin(IV) derivatives containing carboxylate ligands with additional donor atom, such as nitrogen have revealed new structural types which may lead to compounds with different activity [14–17]. For example, [^{n}Bu$_2$Sn(2-pic)$_2$(H$_2$O)] [14], Me$_2$Sn(2-quin)$_2$[15], and Cy$_2$Sn(2-pic)$_2$(H$_2$O)·MeOH [15] have special structure, owing to the multidentate nature of the 2-pyridinecarboxylate and 2-quinaldate ligands which utilize both the carboxylate O and the pyridinyl or quinolinyl N atoms to coordinate to tin atom. We have previously reported several unexpected products of organotin(IV) compounds with pyridinylcarboxylic acids [18,19], which can be assigned to dealkylation reactions as can be seen in the literature [20–23]. As an extension of this

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Contract grant sponsor: National Natural Foundation, People's Republic of China.
Contract grant number: 20771025.
Contract grant sponsor: Shandong Province Science Foundation.
Contract grant number: L2003B01.

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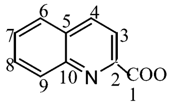


2-quin

SCHEME 1

study, we synthesized another 10 dimeric organotin compounds $\{[(ArCH_2)_2Sn(2\text{-}quin)]_2O\}_2$ (Ar = Ph **1**, 2-ClC_6H_4 **2**, 3-ClC_6H_4 **3**, 4-ClC_6H_4 **4**, 2-FC_6H_4 **5**, 3-FC_6H_4 **6**, 4-FC_6H_4 **7**, 4-BrC_6H_4 **8**, 4-CNC_6H_4 **9**, 2,4-$Cl_2C_6H_3$ **10**). Studies show that whichever reaction we selected the final products are diorganotin compounds of 2-quinaldate, which strongly indicates that the steric bulk of the ligand 2-quin plays a significant role in controlling the coordination geometry at tin regardless of the nature of the tin-bound R groups. The structural formula is shown in Scheme 1. All the compounds have been characterized by elemental analyses, IR and NMR (^{1}H, ^{13}C, and ^{119}Sn) spectra, and the results of this study are reported herein.

EXPERIMENTAL

Materials and Methods

Organotin(IV) oxides were commercially available and used without further purification. The melting points were obtained with Kolfer micromelting point apparatus and were uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr disks and sodium chloride optics. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Mercury Plus-400 NMR spectrometer; chemical shifts were given in ppm relative to Me_4Si and Me_4Sn in $CDCl_3$ solvent. Elemental analyses were performed in a PE-2400 II elemental analyzer.

Syntheses of Compounds **1–10**

$\{[(PhCH_2)_2Sn(2\text{-}quin)]_2O\}_2$ **1**. 2-Quinaldic acid (0.346 g, 2.0 mmol) was added to a benzene solution of $[(PhCH_2)_3Sn]_2O$ (0.799 g, 1.0 mmol). The mixture was heated under reflux with stirring for 8 h, and the solvent was removed by evaporation in vacuo. The crude adduct was recrystallized from dichloromethane and *n*-hexane to give colorless crystals. Yield 87.5%, mp 222–223°C. Anal. Found: C, 59.70; H, 4.11; N, 3,02; Sn, 24.48. Calcd for $C_{96}H_{80}N_4O_{10}Sn_4$: C, 59.92; H, 4.19; N, 2.91; Sn, 24.67. ^{1}H NMR ($CDCl_3$): δ 8.74 (br, 4H, H-3), 8.52 (br, 4H, H-4), 8.30 (br, 4H, H-9), 8.13 (br, 4H, H-6), 7.87 (m, 4H, H-8), 7.80 (m, 4H, H-7), 6.75–7.40 (m, 40H, Ph-H), 2.91 (s, 8H, $J_{Sn-H} = 78$ Hz, $SnCH_2$), 3.17 (s, 8H, $J_{Sn-H} = 87$ Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 174.25 (COO), 149.50, 148.14, 135.85, 128.43, 128.30, 126.58, 125.57, 125.24, 122.28, 121.46, 117.60, 115.12, 109.21 (Ar-C), 30.79, 33.23 (CH_2Ar, $^1J(^{119}Sn\text{–}^{13}C) = 590, 831$ Hz). ^{119}Sn NMR ($CDCl_3$): δ −181.43, −224.45. IR (KBr): $\nu_{asym}(CO_2)$, 1572, 1654 cm^{-1}; $\nu_{sym}(CO_2)$, 1321, 1402 cm^{-1}; ν(Sn—O—Sn), 643 cm^{-1}; ν(Sn—C), 568 cm^{-1}; ν(Sn—N), 476 cm^{-1}; ν(Sn—O), 465 cm^{-1}.

$\{[(2\text{-}ClC_6H_4CH_2)_2Sn(2\text{-}quin)]_2O\}_2\cdot 8H_2O$ **2**. The method of synthesis of compound **2** was similar as described for **1**. The resulting solid was recrystallized from 95% ethanol to give colorless crystals. Yield 75.3%, mp 230–232°C. Anal. Found: C, 49.31; H, 3.71; N, 2.43; Sn, 20.21. Calcd for $C_{96}H_{88}Cl_8N_4O_{18}Sn_4$: C, 49.19; H, 3.78; N, 2.39; Sn, 20.26. ^{1}H NMR ($CDCl_3$): δ 8.87 (br, 4H, H-3), 8.42 (br, 4H, H-4), 8.28 (br, 4H, H-9), 8.00 (br, 4H, H-6), 7.93 (m, 4H, H-8), 7.78 (m, 4H, H-7), 6.59–7.45 (m, 32H, Ph-H), 3.04 (s, 8H, $J_{Sn-H} = 79$ Hz, $SnCH_2$), 3.22 (s, 8H, $J_{Sn-H} = 86$ Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 173.26 (COO), 152.41, 147.50, 136.74, 132.62, 130.43, 128.49, 127.60, 126.15, 125.75, 125.33, 124.61, 122.36, 120.47, 117.43, 115.37 (Ar-C), 31.26, 34.21 (CH_2Ar, $^1J(^{119}Sn\text{–}^{13}C) = 615, 854$ Hz). ^{119}Sn NMR ($CDCl_3$): δ – 180.37, −226.30. IR (KBr): $\nu_{asym}(CO_2)$, 1579, 1671 cm^{-1}; $\nu_{sym}(CO_2)$, 1406, 1329 cm^{-1}; ν(Sn—O—Sn), 630 cm^{-1}; ν(Sn—C), 569 cm^{-1}; ν(Sn–N), 467 cm^{-1}; ν(Sn—O), 442 cm^{-1}.

$\{[(3\text{-}ClC_6H_4CH_2)_2Sn(2\text{-}quin)]_2O\}_2$ **3**. The method of synthesis of compound **3** was similar as described for **1**. The resulting solid was recrystallized from dichloromethane and *n*-hexane to give colorless crystals. Yield 71.5%, mp 244–246°C. Anal. Found: C, 52.58; H, 3.42; N, 2.41; Sn, 21.45. Calcd for $C_{96}H_{72}Cl_8N_4O_{10}Sn_4$: C, 52.41; H, 3.30; N, 2.55; Sn, 21.58. ^{1}H NMR ($CDCl_3$): δ 8.85 (br, 4H, H-3), 8.46 (br, 4H, H-4), 8.32 (br, 4H, H-9), 8.02 (br, 4H, H-6), 7.90 (m, 4H, H-8), 7.81 (m, 4H, H-7), 6.94–7.60 (m, 32H, Ph-H), 3.03 (s, 8H, $J_{Sn-H} = 80$ Hz, $SnCH_2$), 3.25 (s, 8H, $J_{Sn-H} = 89$ Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 174.13 (COO), 152.32, 149.10, 136.35, 133.54, 130.13, 128.52, 128.04, 126.85, 125.88, 125.21, 124.54, 123.18, 121.56, 117.64, 115.89 (Ar-C), 31.43, 34.52 (CH_2Ar, $^1J(^{119}Sn\text{–}^{13}C) = 608, 843$ Hz). ^{119}Sn NMR ($CDCl_3$): δ −181.76, −229.34. IR (KBr): $\nu_{asym}(CO_2)$, 1583, 1680 cm^{-1}; $\nu_{sym}(CO_2)$, 1410, 1331 cm^{-1}; ν(Sn—O—Sn), 635 cm^{-1}; ν(Sn—C), 562 cm^{-1}; ν(Sn—N), 463 cm^{-1}; ν(Sn—O), 448 cm^{-1}.

$\{[(4\text{-}ClC_6H_4CH_2)_2Sn(2\text{-}quin)]_2O\}_2$ **4**. The method of synthesis of compound **4** was similar as described

for **1**. The resulting solid was recrystallized from dichloromethane and *n*-hexane to give colorless crystals. Yield 72.5%, mp 249–251°C. Anal. Found: C, 52.58; H, 3.35; N, 2.51; Sn, 21.27. Calcd for $C_{96}H_{72}Cl_8N_4O_{10}Sn_4$: C, 52.41; H, 3.30; N, 2.55; Sn, 21.58. ^{1}H NMR ($CDCl_3$): δ 8.83 (br, 4H, H-3), 8.47 (br, 4H, H-4), 8.32 (br, 4H, H-9), 8.04 (br, 4H, H-6), 7.86 (m, 4H, H-8), 7.70 (m, 4H, H-7), 6.36–7.41 (m, 32H, Ph-H), 2.98 (s, 8H, $J_{Sn\text{—}H} = 79$ Hz, $SnCH_2$), 3.18 (s, 8H, $J_{Sn\text{—}H} = 85$ Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 172.32 (COO), 152.87, 147.41, 132.15, 129.65, 128.73, 127.42, 126.44, 125.21, 124.54, 122.68, 122.11, 121.43, 118.72 (Ar-C), 31.17, 34.02 (CH_2Ar, $^1J(^{119}Sn\text{–}^{13}C) = 611$, 842 Hz). ^{119}Sn NMR ($CDCl_3$): $\delta - 181.76$, −225.78. IR (KBr): $\nu_{asym}(CO_2)$, 1567, 1680 cm^{-1}; $\nu_{sym}(CO_2)$, 1391, 1325 cm^{-1}; ν(Sn—O—Sn), 637 cm^{-1};ν(Sn—C), 556 cm^{-1}; ν(Sn—N), 471 cm^{-1}; ν(Sn—O), 450 cm^{-1}.

{[(2-FC$_6$H$_4$CH$_2$)$_2$Sn(2-quin)]$_2$O}$_2$ **5**. The method of synthesis of compound **5** was similar as described for **1**. The resulting solid was recrystallized from dichloromethane and *n*-hexane to give colorless crystals. Yield 75.4%, mp 197–198°C. Anal. Found: C, 55.37; H, 3.48; N, 2.72; Sn, 23.08. Calcd for $C_{96}H_{72}F_8N_4O_{10}Sn_4$: C, 55.75; H, 3.51; N, 2.72; Sn, 22.95. ^{1}H NMR ($CDCl_3$): δ 8.65 (br, 4H, H-3), 8.37 (br, 4H, H-4), 8.18 (br, 4H, H-9), 7.96 (br, 4H, H-6), 7.83 (m, 4H, H-8), 7.75 (m, 4H, H-7), 6.34–7.41 (m, 32H, Ph-H), 2.92 (s, 8H, $J_{Sn\text{—}H} = 76$ Hz, $SnCH_2$), 3.17 (s, 8H, $J_{Sn\text{—}H} = 84$ Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 172.96 (COO), 152.28, 147.60, 136.93, 132.38, 130.51, 128.45, 127.68, 125.97, 125.46, 125.01, 124.43, 122.47, 120.31, 117.56, 115.40 (Ar-C), 31.04, 33.79 (CH_2Ar, $^1J(^{119}Sn\text{–}^{13}C) = 622$, 865 Hz). ^{119}Sn NMR ($CDCl_3$): δ −179.89, −224.32. IR (KBr): $\nu_{asym}(CO_2)$, 1570, 1682 cm^{-1}; $\nu_{sym}(CO_2)$, 1400, 1325 cm^{-1}; ν(Sn—O—Sn), 637 cm^{-1}; ν(Sn—C), 561 cm^{-1}; ν(Sn—N), 472 cm^{-1}; ν(Sn—O), 450 cm^{-1}.

{[(3-FC$_6$H$_4$CH$_2$)$_2$Sn(2-quin)]$_2$O}$_2$ **6**. The method of synthesis of compound **6** was similar as described for **1**. The resulting solid was recrystallized from dichloromethane and *n*-hexane to give colorless crystals. Yield 74.8%, mp 209–210°C. Anal. Found: C, 55.80; H, 3.42; N, 2.80; Sn, 22.74. Calcd for $C_{96}H_{72}F_8N_4O_{10}Sn_4$: C, 55.75; H, 3.51; N, 2.72; Sn, 22.95. ^{1}H NMR ($CDCl_3$): δ 8.70 (br, 4H, H-3), 8.41 (br, 4H, H-4), 8.12 (br, 4H, H-9), 7.88 (br, 4H, H-6), 7.92 (m, 4H, H-8), 7.78 (m, 4H, H-7), 6.83–7.58 (m, 32H, Ph-H), 2.97 (s, 8H, $J_{Sn\text{—}H} = 78$ Hz, $SnCH_2$), 3.25 (s, 8H, $J_{Sn\text{—}H} = 88$ Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 174.02 (COO), 153.05, 148.34, 136.69, 133.12, 130.88, 129.45, 128.34, 125.83, 126.06, 125.47, 124.83, 122.12, 120.87, 117.43, 115.87 (Ar-C), 31.87, 34.18 (CH_2Ar, $^1J(^{119}Sn\text{–}^{13}C) = 612$, 845 Hz). ^{119}Sn NMR ($CDCl_3$): δ −181.36, −228.43. IR (KBr): $\nu_{asym}(CO_2)$, 1575, 1684 cm^{-1}; $\nu_{sym}(CO_2)$, 1406, 1327 cm^{-1}; ν(Sn—O—Sn), 645 cm^{-1}; ν(Sn—C), 558 cm^{-1}; ν(Sn—N), 472 cm^{-1}; ν(Sn—O), 453 cm^{-1}.

{[(4-FC$_6$H$_4$CH$_2$)$_2$Sn(2-quin)]$_2$O}$_2$ **7**. The method of synthesis of compound **7** was similar as described for **1**. The resulting solid was recrystallized from acetonitrile to give colorless crystals. Yield 80.7%, mp 213–215°C. Anal. Found: C, 55.83; H, 3.43; N, 2.80; Sn, 23.11. Calcd for $C_{96}H_{72}F_8N_4O_{10}Sn_4$: C, 55.75; H, 3.51; N, 2.72; Sn, 22.95. ^{1}H NMR ($CDCl_3$): δ 8.79 (br, 4H, H-3), 8.40 (br, 4H, H-4), 8.23 (br, 4H, H-9), 8.00 (br, 4H, H-6), 7.92 (m, 4H, H-8), 7.69 (m, 4H, H-7), 6.45–7.38 (m, 32H, Ph-H), 2.97 (s, 8H, $J_{Sn\text{—}H} = 79$ Hz, $SnCH_2$), 3.21 (s, 8H, $J_{Sn\text{—}H} = 85$ Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 172.80 (COO), 153.03, 147.37, 132.2, 129.56, 128.81, 127.57, 126.24, 125.18, 124.49, 122.75, 122.24, 121.50, 118.94 (Ar-C), 31.87, 34.72 (CH_2Ar, $^1J(^{119}Sn\text{–}^{13}C) = 606$, 830 Hz). ^{119}Sn NMR ($CDCl_3$): δ −187.13, −225.38. IR (KBr): $\nu_{asym}(CO_2)$, 1576, 1675 cm^{-1}; $\nu_{sym}(CO_2)$, 1333, 1405 cm^{-1}; ν(Sn—O—Sn), 642 cm^{-1}; ν(Sn—C), 552 cm^{-1}; ν(Sn—N), 469 cm^{-1}; ν(Sn—O), 457 cm^{-1}.

{[(4-NCC$_6$H$_4$CH$_2$)$_2$Sn(2-quin)]$_2$O}$_2$·3H$_2$O **8**. The method of synthesis of compound **8** was similar as described for **1**. The resulting solid was recrystallized from 95% ethanol to give colorless crystals. Yield 75.4%, mp 260–261°C. Anal. Found: C, 57.31; H, 3.44; N, 8.00; Sn, 22.18. Calcd for $C_{104}H_{78}N_{12}O_{13}Sn_4$: C, 57.02; H, 3.38; N, 7.82; Sn, 22.10. ^{1}H NMR ($CDCl_3$): δ 8.64 (br, 4H, H-3), 8.40 (br, 4H, H-4), 8.27 (br, 4H, H-9), 8.11 (br, 4H, H-6), 7.91 (m, 4H, H-8), 7.75 (m, 4H, H-7), 6.27–7.25 (m, 32H, Ph-H), 2.98 (s, 8H, $J_{Sn\text{—}H} = 77$ Hz, $SnCH_2$), 3.18 (s, 8H, $J_{Sn\text{—}H} = 86$ Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 173.20 (COO), 152.76, 137.53, 131.21, 130.34, 129.11, 128.32, 126.65, 126.54, 125.87, 124.30, 123.01, 122.85, 112.21 (Ar-C), 115.32 (CN), 32.03, 32.25 (CH_2Ar, $^1J(^{119}Sn\text{–}^{13}C) = 627$, 869 Hz). ^{119}Sn NMR ($CDCl_3$): δ −193.36, −231.43. IR (KBr): $\nu_{asym}(CO_2)$, 1564, 1643 cm^{-1}; $\nu_{sym}(CO_2)$, 1357, 1401 cm^{-1}; ν(Sn—O—Sn), 647; ν(Sn—C), 555 cm^{-1}; ν(Sn—N), 470 cm^{-1}; ν(Sn—O), 451 cm^{-1}.

{[(4-BrC$_6$H$_4$CH$_2$)$_2$Sn(2-quin)]$_2$O}$_2$ **9**. The method of synthesis of compound **9** was similar as described for **1**. The resulting solid was recrystallized from dichloromethane and *n*-hexane to give colorless crystals. Yield 77.3%, mp 278–279°C. Anal.

TABLE 1 Crystallographic Data of Compound **2**

Empirical formula	$C_{96}H_{88}Cl_8N_4O_{18}Sn_4$	Z	1
Formula weight	2344.06	Calculated density (mg m^{-3})	1.464
Temperature (K)	298(2)	F(0 0 0)	1172
Wavelength (Å)	0.71073	Crystal size (mm)	0.51 × 0.38 × 0.21
Crystal system	Triclinic	Scan range θ (°)	2.15–25.03
Space group	$P\bar{1}$	Limiting indices	
Unit cell dimensions		h	−11 to 13
a (Å)	10.959(8)	k	−14 to 18
b (Å)	15.161(11)	l	−20 to 19
c (Å)	16.853(12)	Total/unique/R_{int}	13188/9079/0.0402
α(°)	106.291(10)	Goodness-of-fit on F^2	0.998
β(°)	97.292(11)	μ (mm^{-1})	1.191
γ(°)	91.722(11)	R_1/wR_2	0.0523/0.1243
Volume (Å^3)	2660(3)	ρ_{max}/ρ_{min}(e Å^{-3})	1.209/−0.666

Found: C, 45.32; H, 2.81; N, 2.25; Sn, 18.45. Calcd for $C_{96}H_{72}Br_8N_4O_{10}Sn_4$: C, 45.12; H, 2.84; N, 2.19; Sn, 18.58. ^{1}H NMR ($CDCl_3$): δ 8.76 (br, 4H, H-3), 8.41 (br, 4H, H-4), 8.25(br, 4H, H-9), 7.88 (br, 4H, H-6), 7.72 (m, 4H, H-8), 7.57 (m, 4H, H-7), 6.58–7.54 (m, 32H, Ph-H), 2.95 (s, 8H, $J_{Sn\text{–}H} = 78$ Hz, $SnCH_2$), 3.14 (s, 8H, $J_{Sn\text{–}H} = 82$ Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 172.12 (COO), 152.23, 147.54, 132.01, 129.70, 128.32, 127.76, 126.48, 125.23, 124.34, 122.55, 122.21, 121.76, 118.17 (Ar-C), 31.32, 34.11 (CH_2Ar, $^1J(^{119}Sn\text{–}^{13}C) = 618$, 870 Hz). ^{119}Sn NMR ($CDCl_3$): $\delta - 183.54$, −224.90. IR (KBr): $\nu_{asym}(CO_2)$, 1571, 1667 cm^{-1}; $\nu_{sym}(CO_2)$, 1400, 1320 cm^{-1}; ν(Sn—O—Sn), 641 cm^{-1}; ν(Sn—C), 552 cm^{-1}; ν(Sn—N), 465 cm^{-1}; ν(Sn—O), 446 cm^{-1}.

$\{[(2,4\text{-}Cl_2C_6H_3CH_2)_2Sn(2\text{-quin})]_2O\}_2$ **10**. The method of synthesis of compound **10** was similar as described for **1**. The resulting solid was recrystallized from dichloromethane and *n*-hexane to give colorless crystals. Yield 68.9%, mp 178–179°C. Anal. Found: C, 46.55; H, 2.71; N, 2.20; Sn, 19.38. Calcd for $C_{96}H_{64}Cl_{16}N_4O_{10}Sn_4$: C, 46.58; H, 2.61; N, 2.26; Sn, 19.18. ^{1}H NMR ($CDCl_3$): δ 8.88 (br, 4H, H-3), 8.63 (br, 4H, H-4), 8.40 (br, 4H, H-9), 8.15 (br, 4H, H-6), 8.03 (m, 4H, H-8), 7.75 (m, 4H, H-7), 6.34–7.38 (m, 24H, Ph-H), 3.11 (s, 8H, $J_{Sn\text{–}H} = 78$ Hz, $SnCH_2$), 3.30 (s, 8H, $J_{Sn\text{–}H} = 86$ Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 173.54 (COO), 152.65, 148.11, 136.65, 132.81, 130.25, 129.02, 127.87, 126.65, 125.67, 125.50, 124.01, 122.27, 120.40, 117.80, 115.54 (Ar-C), 32.13, 34.84 (CH_2Ar, $^1J(^{119}Sn\text{–}^{13}C) = 603$, 836 Hz). ^{119}Sn NMR ($CDCl_3$): δ −181.13, −226.84. IR (KBr): $\nu_{asym}(CO_2)$, 1565, 1657 cm^{-1}; $\nu_{sym}(CO_2)$, 1404, 1340 cm^{-1}; ν(Sn—O—Sn), 637 cm^{-1}; ν(Sn—C), 565 cm^{-1}; ν(Sn—N), 462 cm^{-1}; ν(Sn—O), 448 cm^{-1}.

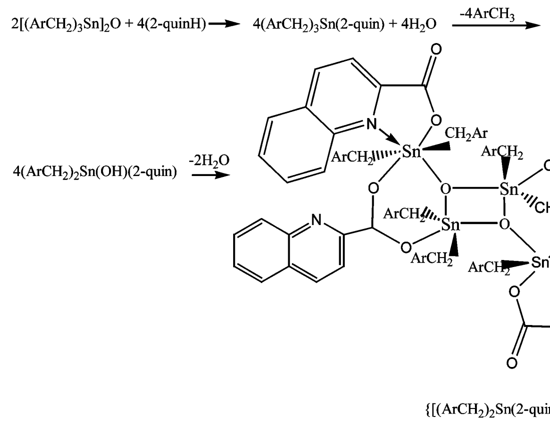
X-ray Crystallography

Crystallographic data and refinement details are given in Table 1. All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer. A criterion of observability was used for the solution and refinement. The structure was solved by a direct method and refined by a full-matrix least-squares procedure based on F^2 using the SHELXL-97 program system. All data were collected at 298(2) K using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation and the φ–ω scan technique. The positions of the rest nonhydrogen atoms were determined from successive Fourier syntheses. The hydrogen atoms were placed in the geometrically calculated positions and allowed to ride on their respective parent atoms.

RESULTS AND DISCUSSION

Syntheses

We treated $(R_3Sn)_2O$ and 2-quinH in a 1:2 stoichiometry in benzene and hoped to get triorganotin complexes of 2-quinaldate. To our surprise, dealkylation reaction occurs and as a result we have obtained 10 dimeric diorganotin(IV) compounds $\{[(ArCH_2)_2Sn(2\text{-quin})]_2O\}_2$ (Ar = Ph **1**, 2-ClC_6H_4 **2**, 3-ClC_6H_4 **3**, 4-ClC_6H_4 **4**, 2-FC_6H_4 **5**, 3-FC_6H_4 **6**, 4-FC_6H_4 **7**, 4-BrC_6H_4 **8**, 4-CNC_6H_4 **9**, 2,4-$Cl_2C_6H_3$ **10**). We assumed that it may result from the steric bulk of the 2-quin ligand as have studied in the previous report [18–23]; in order to confirm our assumption we have done further research by devising another reaction shown in Scheme 2. Studies show that whichever reaction we selected, the final products are diorganotin compounds of 2-quinaldate, which strongly indicates that the coordination number at



Ar= Ph **1**, 2-ClC_6H_4 **2**, 3-ClC_6H_4 **3**, 4-ClC_6H_4 **4**, 2-FC_6H_4 **5**, 3-FC_6H_4 **6**, 4-FC_6H_4 **7**,
4-BrC_6H_4 **8**, 4-CNC_6H_4 **9**, 2,4-$Cl_2C_6H_3$ **10**

SCHEME 2

tin is dominated by the 2-quin ligand. And studies also show that the structure of the molecule have something to do with the reaction conditions and tin-bound R groups. The existence of H_2O facilitates the dealkylation reaction. Based on our previous studies [18,19], we raised possible mechanisms for all the 10 compounds, which are shown in Scheme 2.

IR and NMR Studies

The infrared spectra of compounds **1–10** have been recorded and some important assignments are shown above. The free acid shows a broad O–H absorption at 3000–2500 cm^{-1}, which is absent in the spectra of the eight title compounds, showing the deprotonation of the COOH groups during the reactions. In compounds **1–10**, the Sn—C absorption band occur at 552–568 cm^{-1} region. The band in 442–465 cm^{-1} are assigned to the stretching mode of the Sn—O linkage. In these compounds, the strong bands in the 630–647 cm^{-1} are attributed to ν(Sn—O—Sn) indicating a Sn—O—Sn link [11,20]. Compared with the free ligand, the new occurrence of the bands in the region of 462–476 cm^{-1} for all the eight compounds were assigned to the Sn—N vibrations, which provides prove for the existence of Sn—N bonds for all the eight compounds [17].

The $\Delta\nu$ ($\nu_{as}(CO_2)$–$\nu_s(CO_2)$) value is used to determine the type of bonding between metal and carboxyl group [21]. It is generally believed that the difference in $\Delta\nu$ between asymmetric $\nu_{asym}(CO_2)$ and symmetric $\nu_{sym}(CO_2)$ absorption frequencies below 200 cm^{-1} for the bidentate carboxylate moiety, but greater than 200 cm^{-1} for the unidentate carboxylate moiety [20,24]. In compounds **1–10**, the presence of two values for each of $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ indicates that there are two different types of carboxylate groups. The two bands which occur at 1643–1682 cm^{-1} and 1565–1583 cm^{-1} were assigned to $\nu_{as}(CO_2)$, while the bands at 1320–1340 cm^{-1} and 1400–1410 cm^{-1} were assigned to $\nu_s(CO_2)$. The magnitudes of $\Delta\nu^1$ ($\nu_{as}(CO_2)^1 - \nu_s(CO_2)^1$) and $\Delta\nu^2$ ($\nu_{as}(CO_2)^2 - \nu_s(CO_2)^2$) for compounds **1–10** are 275–357 cm^{-1} and 163–176 cm^{-1}, respectively, which indicate the presence of bidentate and monodentate carboxylate groups in these compound [16,25].

The ^1H NMR spectra of compounds **1–10** show that the chemical shifts of the protons of methylene bounded to tin atom ($ArCH_2Sn$) exhibit two signals at the region 2.91–3.30 ppm as singlet signal having satellite signals indicates that there are two different types of tin atoms, which is caused by tin (^{119}Sn)–hydrogen coupling. And the spin–spin coupling constant J_{Sn-H} are equal to 76–80 and 82–89 Hz, which would be in agreement with the decrease of the s-character of the C(Bz)–Sn bonds on going from five- to six-coordination. The signals at 7.69–8.88 as multiplicity for all the 10 compounds are assigned to the protons of 2-quin ligand, which is shifting slightly to the low field compared with 2-quinH.

Compounds **1–10** generally show broad signals for the protons of 2-quin ligands, shifted to low field with respect to the value for 2-quinH, which could be interpreted in terms of the Sn ← N interaction. This finding may be consistent with previous studies, which suggest that only quinoline and pyridine type N atoms, present in the carboxylate R′ group, coordinate to Sn [15–17].

The ^{13}C NMR data for the compounds **1–10** are consistent with a dimeric tetraorganostannoxane structure. Although at least two different types of carboxylate groups are present, only single resonances are observed for the CO_2 group in the ^{13}C spectra. The possible reason is that the exchange of 2-quin ligands is faster than NMR time-scale. The $^1J_{Sn-C}$ values for compounds **1–10** are 590–626 and 831–870 Hz, similar to be that of the dimeric organotin compound $\{[^nBu_2Sn(2\text{-}Py)]_2O\}_2$ [26].

In the ^{13}C NMR spectra of compounds **1–10**, parameters $\delta(^{13}C)$ for ligand atoms, as wall as CO_2, correspond to data reported for $[R_2SnCl_2(2\text{-}quin)]^-(HNEt_3)^+$ [27]; moreover, broad signals occur for ligand atoms in compounds **1–10**, which further suggest the occurrence of two different types of 2-quin species.

In the ^{13}C NMR spectra of compounds **1–10**, chemical shifts are similar to the free ligands. The ^{13}C NMR data show a slightly downfield shift of all carbon resonances compared with the free ligand in compounds **1–10**, which could be interpreted in terms of the Sn ← N interaction.

The ^{119}Sn NMR spectroscopic data are very useful for determining the coordination number of tin, its molecular geometry, and stereochemistry. In the dialkyltin carboxylates, four-coordinate tin has $\delta(^{119}Sn)$ values ranging from about +200 to −60 ppm, five-coordinate tin from −90 to −190 ppm, and six-coordinate tin from −210 to −400 ppm [28].

The ^{119}Sn NMR spectra of all the 10 compounds (**1–10**) display two well-separated resonances as is observed for dicarboxylato tetraorganodistannoxanes, indicating dimeric structures in solution [11,29–31]. The low- and high-field resonances observed for these compounds are attributed to the exo-cyclic and endo-cyclic tin atoms, respectively [32]. Of these two signals, the low field signal is broad, which may be due to the "wagging motion" of the exo-cyclic tin atoms in solution [3,33]. The ^{119}Sn NMR data for compounds **1–10** indicate that two signals appear at −180.37 to −193.36 ppm and −226.84 to −231.43 ppm, showing that there are two nonequivalent tin atoms in each molecule, and suggest that the coordination number of two tin atoms should be five and six, respectively. The values of the ^{119}Sn chemical shift indicate that bonding should be similar to each other of the compounds **1–10**.

Structural Studies of {[(2-Cl-PhCH$_2$)$_2$Sn(2-quin)]$_2$O·8H$_2$O}$_2$ 2

The molecular structure and unit cell of compound **2** are shown in Figs. 1 and 2, respectively. All hydrogen atoms have been omitted for the purpose of clarity. Table 2 lists selected bond lengths and angles for compound **2**.

The molecule of compound **2** possesses a tetranuclear centrosymmetric dimeric structure, which is presented in Fig. 2. The endo-cyclic Sn—O distances in Sn_2O_2 core, 2.141 and 2.016 Å, are slightly shorter than that of the corresponding distances found in the literature [11,26,34]. In the title structure, the four 2-quin ligands are divided into two different types according to their coordinating fashion. Two of them are bidentate and connect with each of exo- and endo-cyclic tin atoms by using both oxygen atoms of the carboxylate, whereas the other two are bidentate and both connected to the exo-cyclic tin atoms by using one carboxylate oxygen atom and the nitrogen atom.

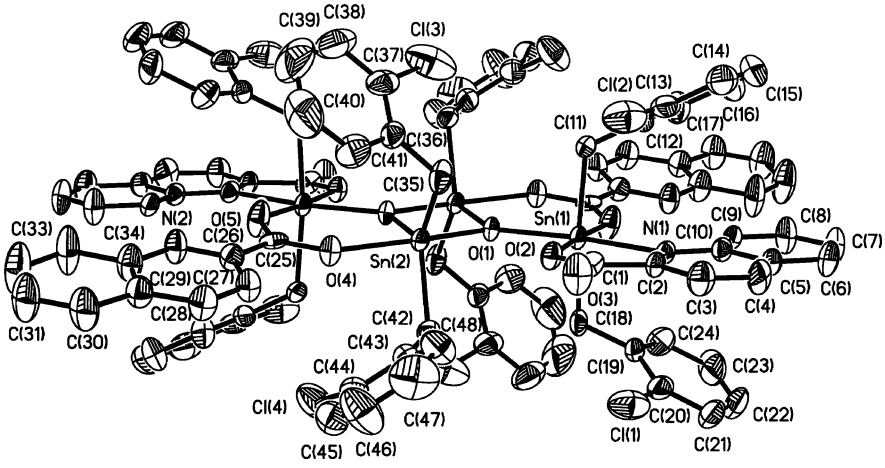


FIGURE 1 Molecular structure of compound **2**. Displacement ellipsoids are drawn at 30% probability.

TABLE 2 Selected Bond Distances (Å) and Angles (°) for Compound **2**

Bond distance (Å)			
Sn(1)—O(1)	2.103(4)	Sn(2A)—O(1)	2.016(4)
Sn(1)—O(2)	2.116(5)	Sn(1A)—O(5)	2.223(6)
Sn(1)—C(18)	2.137(8)	O(2)—C(1)	1.294(9)
Sn(1)—C(11)	2.157(7)	O(3)—C(1)	1.211(9)
Sn(1)—O(5A)	2.223(6)	O(4)—C(25)	1.319(9)
Sn(1)—N(1)	2.399(6)	O(5)—C(25)	1.232(8)
Sn(2)—O(1A)	2.016(4)	N(1)—C(2)	1.299(9)
Sn(2)—O(1)	2.141(4)	N(1)—C(10)	1.366(9)
Sn(2)—C(42)	2.148(7)	N(2)—C(26)	1.311(9)
Sn(2)—C(35)	2.149(8)	N(2)—C(34)	1.379(10)
Sn(2)—O(4)	2.255(5)	C(25)—C(26)	1.429(10)
Sn(2)—O(2)	3.208(5)		
Bond angle (°)			
O(1)—Sn(1)—O(2)	85.00(17)	C(42)—Sn(2)—O(4)	85.5(2)
O(1)—Sn(1)—C(18)	92.7(2)	C(35)—Sn(2)—O(4)	88.5(3)
O(2)—Sn(1)—C(18)	95.4(3)	O(1A)—Sn(2)—O(2)	136.39(15)
O(1)—Sn(1)—C(11)	90.5(2)	O(1)—Sn(2)—O(2)	60.57(14)
O(2)—Sn(1)—C(11)	96.1(3)	C(42)—Sn(2)—O(2)	76.1(2)
C(18)—Sn(1)—C(11)	168.3(3)	C(35)—Sn(2)—O(2)	67.3(2)
O(1)—Sn(1)—O(5A)	98.96(18)	O(4)—Sn(2)—O(2)	132.60(12)
O(2)—Sn(1)—O(5A)	175.70(19)	Sn(2A)—O(1)—Sn(1)	129.7(2)
C(18)—Sn(1)—O(5A)	82.8(3)	Sn(2A)—O(1)—Sn(2)	103.76(18)
C(11)—Sn(1)—O(5A)	85.6(3)	Sn(1)—O(1)—Sn(2)	126.3(2)
O(1)—Sn(1)—N(1)	157.80(19)	O(1)—Sn(2)—C(42)	97.0(2)
O(2)—Sn(1)—N(1)	72.8(2)	O(1A)—Sn(2)—C(35)	119.4(3)
C(18)—Sn(1)—N(1)	90.7(2)	O(1)—Sn(2)—C(35)	101.0(3)
C(11)—Sn(1)—N(1)	90.5(2)	C(42)—Sn(2)—C(35)	122.9(4)
O(5A)—Sn(1)—N(1)	103.2(2)	O(1A)—Sn(2)—O(4)	90.87(18)
O(1A)—Sn(2)—O(1)	76.24(18)	O(1)—Sn(2)—O(4)	166.58(17)
O(1A)—Sn(2)—C(42)	117.4(3)		

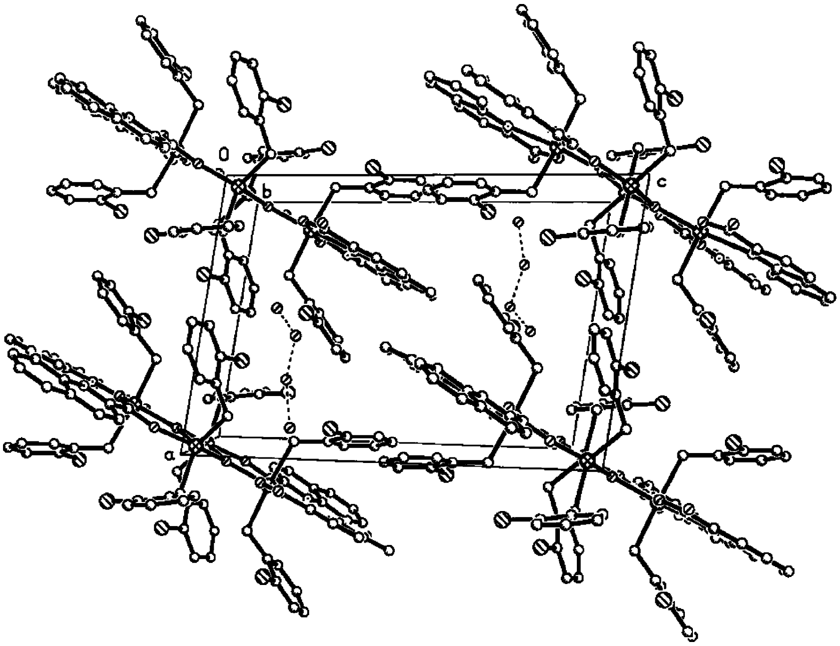


FIGURE 2 Projection of compound **2**.

The exo-cyclic tin atom Sn(1) is six-coordinate in an octahedral geometry axially by two carboxylic oxygen atoms and equatorially by one bridging oxygen atom of the Sn_2O_2 core, two tin-bound *o*-chlorobenzyl carbon atoms, and one nitrogen atom. The bond length 2.399(6) Å for Sn(1)—N(1) is much shorter than that of $Me_2Sn(2\text{-quin})_2$, 2.594(3), 2.473(4) Å [15]. The Sn—O bond lengths Sn(1)—O(1), Sn(1)—O(2), and Sn(1)—O(5A) are 2.103(4), 2.116(5), and 2.223(6) Å, respectively, which are similar to the corresponding distances found in the compound $[^nBu_2SnOC(O)C_6H_4NO_2\text{-}o]_2O$ [25]. The sum of the bond angles O(1)—Sn(1)—C(18) 92.7(2)°, C(18)—Sn(1)—N(1) 90.7(2)°, C(11)—Sn(1)—N(1) 90.5(2)°, and O(1)—Sn(1)—C(11) 90.5(2)° is 364.4°, which shows that the Sn(1), O(1), N(1), C(11), and C(18) atoms are coplanar. Study shows that the mean deviation for the five atoms from the plane is ±0.2757 Å. Thus, the coordination at Sn(1) atom should best be described as a slightly distorted octahedral geometry. The endo-cyclic tin atom Sn(2) is five coordinated in a distorted trigonal bipyramidal geometry as indicted by the axial bond angle O(1)—Sn(2)—O(4) 166.58(17)°, which deviates from linear angle 180°. The O(1A), C(35), and C(42) atoms occupy the equatorial positions with the bond angles 117.4(3)° for O(1A)—Sn(2)—C(42), 119.4(3)° for O(1A)—Sn(2)—C(35), and 122.9(4)° for C(35)—Sn(2)—C(42) and the sum of these angles is 359.7°, which shows that the Sn(2), O(1A), C(35), and C(42) atoms are in the same plane. The mean deviation for the four atoms from the plane is ±0.0241 Å.

In the molecular structure of compound **2**, there are eight H_2O molecules as can be seen in Fig. 2, and studies show that hydrogen bonds exist between these water molecules.

ACKNOWLEDGMENTS

We acknowledge the state Key Laboratory of Crystal Materials, Shandong University, PR China for support.

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