Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 3111–3117
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and spectroscopic properties of diorganotin(IV) complexes of 2-quinaldate and crystal structures of $(4\text{-}FC_6H_4CH_2)_2Sn(2\text{-quin})_2 \cdot 2CH_3CN$ and $\{[(2\text{-}ClC_6H_4CH_2)_2SnCl(2\text{-quin})]_2 \cdot CH_3OH\}_n$

Han Dong Yin *, Qi Bao Wang, Sheng Cai Xue

Department of Chemistry, Liaocheng University, Liaocheng 252059, China

Received 14 February 2005; revised 25 March 2005; accepted 25 March 2005
Available online 13 May 2005

Abstract

Twelve diorganotin(IV) complexes of 2-quinaldate $R_2Sn(2\text{-quin})_2$ and $R_2SnCl(2\text{-quin})$ have been synthesized by dealkyltion reactions of 2-quinaldic acid (2-quinH) with $(R_3Sn)_2O$ (R = $PhCH_2$ **1**, 2-$ClC_6H_4CH_2$ **2**, 2-$FC_6H_4CH_2$ **3**, 4-$FC_6H_4CH_2$ **4**, 4-$CNC_6H_4CH_2$ **5,** Ph **6**, 2,4-$Cl_2C_6H_3CH_2$ **7**) and R_3SnCl (R = 2-$ClC_6H_4CH_2$ **8**, 4-$ClC_6H_4CH_2$ **9**, 2-$FC_6H_4CH_2$ **10**, 4-$FC_6H_4CH_2$ **11**, $PhCH_2$ **12**), and all the complexes have been characterized by elemental analysis, IR and multinuclear NMR (^1H, ^{13}C, ^{119}Sn) spectroscopies. The structures of $(4\text{-}FC_6H_4CH_2)_2Sn(2\text{-quin})_2 \cdot 2CH_3CN$ (**4**) and $\{[(2\text{-}ClC_6H_4CH_2)_2Sn(2\text{-quin})Cl]_2 \cdot CH_3OH\}_n$ (**8**) have been determined by X-ray diffraction. Studies show that complex **4** is a monomer with the central tin atom six-coordinated in a skew-trapezoidal-bipyramidal geometry and complex **8** is a one-dimensional polymer with the tin atom six-coordinated. Studies also show that the nitrogen atoms of the 2-quin ligand are coordinating to the tin atoms for all of the 12 complexes.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Organotin complex; 2-Quinaldic acid; Synthesis; Crystal structure

1. Introduction

Organotin(IV) complexes are widely used as biocides, fungicides and as homogeneous catalysts in industry [1–5]. Recently, pharmaceutical properties of organotin complexes with carboxylic acid have been investigated for their antitumor activity [6–9]. In general, the biocidal activity of organotin complexes is greatly influenced by the structure of the complex and the coordination number at the tin atoms [8–12]. Previous papers [5,13–15] have reported the synthesis and X-ray crystal structure determinations of several organotin complexes with carboxylic acids in which the R′ group has an additional potential donor atom (e.g., N, O and S) available for coordinating to tin, and that have led to new structural modes of the organotin derivatives. We have previously reported several unexpected products of organotin(IV) complexes with pyridinylcarboxylic acids [14,15], which can be assigned to dealkylation reactions as can be seen in the literature [16–19]. As an extension of this study, we synthesized another 12 diorganotin complexes of 2-quinaldate by two quite different methods. Studies show that whichever reaction we selected the final products are diorganotin complexes 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. All the complexes have been characterized by elemental analyses, IR and NMR (^1H, ^{13}C

* Corresponding author. Tel.:/fax: +866358239121.
E-mail address: handongyin@sohu.com (H.D. Yin).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.03.046

and ^{119}Sn) spectra, and the results of this study are reported herein.

2. Experimental

2.1. Materials and methods

Triorganotin(IV) chloride and bis(triorganotin)(IV) oxide were prepared by the methods described in the literature [20]. The melting points were obtained with Kolfer micro melting point apparatus and uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs 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.

2.2. Syntheses of complexes

2.2.1. $(PhCH_2)_2Sn(2\text{-}quin)_2$ (**1**)

To a stirred solution of 2-quinaldic acid (0.692 g, 4.0 mmol) in benzene was added $[(PhCH_2)_3Sn]_2O$ (0.799 g, 1.0 mmol). The mixture was heated under reflux for 6–7 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: 87.52%, m.p. 183–185 °C. Anal. Calc. for $C_{34}H_{26}N_2O_4Sn$: C, 63.28; H, 4.06; N, 4.34; Sn, 18.40. Found: C, 63.43; H, 4.12; N, 4.31; Sn, 18.37%. ^{1}H NMR ($CDCl_3$): δ 8.77 (d, 2H, H-3), 8.46 (d, 2H, H-4), 8.27 (d, 2H, H-9), 8.11 (d, 2H, H-6), 7.98 (dd, 2H, H-8), 7.85 (dd, 2H, H-7), 6.24-7.25 (m, 10H, Ph–H), 2.96 (s, 4H, J_{Sn-H} = 87 Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 174 (COO), 149, 147, 135, 128, 128, 126, 125, 125, 122, 121, 117, 115, 109 (Ar–C), 30 (CH_2Ar, $^{1}J_{Sn-C}$ = 728 Hz). ^{119}Sn NMR ($CDCl_3$): δ −262. IR (KBr): υ_{asym}(OCO), 1669 cm^{-1}; υ_{sym}(OCO), 1321 cm^{-1}; υ(Sn–C), 582 cm^{-1}; υ(Sn–N), 490 cm^{-1}; υ(Sn–O), 469 cm^{-1}.

2.2.2. $(2\text{-}Cl\ C_6H_4CH_2)_2Sn(2\text{-}quin)_2 \cdot CH_2Cl_2$ (**2**)

The synthesis procedure of complex **2** was similar to complex **1**. The resulting solid was recrystallized from dichloromethane and *n*-hexane to give colorless crystals. Yield: 78.5%, m.p. 200–202 °C. Anal. Calc. for $C_{35}H_{26}Cl_5N_2O_4Sn$: C, 50.37; H, 3.14; N, 3.36; Sn, 14.22. Found: C, 49.86; H, 3.03; N, 3.42; Sn, 14.20%. ^{1}H NMR ($CDCl_3$): δ 8.84 (d, 2H, H-3), 8.44 (d, 2H, H-4), 8.28 (d, 2H, H-9), 8.04 (d, 2H, H-6), 7.95 (dd, 2H, H-8), 7.78 (dd, 2H, H-7), 6.55–7.45 (m, 8H, Ar–H), 3.02 (s, 4H, J_{Sn-H} = 80 Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 172 (COO), 152, 147, 136, 132, 130, 128, 127, 126, 125, 125, 124, 122, 120, 117, 115 (Ar–C), 31 (CH_2Ar, $^{1}J_{Sn-C}$ = 775 Hz). ^{119}Sn NMR ($CDCl_3$): δ −278. IR (KBr): υ_{asym}(OCO), 1671 cm^{-1}; υ_{sym}(OCO), 1329 cm^{-1}; υ(Sn–C), 545 cm^{-1}; υ(Sn–N), 474 cm^{-1}; υ(Sn–O), 452 cm^{-1}.

2.2.3. $(2\text{-}FC_6H_4CH_2)_2Sn(2\text{-}quin)_2$ (**3**)

The synthesis procedure of complex **3** was similar to complex **1**. The resulting solid was recrystallized from dichloromethane and *n*-hexane to give colorless crystals. Yield: 84.3%, m.p. 189–191 °C. Anal. Calc. for $C_{34}H_{24}F_2N_2O_4Sn$: C, 59.94; H, 3.53; N, 4.13; Sn, 17.42. Found: C, 60.21; H, 3.61; N, 4.08; Sn, 17.50%. ^{1}H NMR ($CDCl_3$): δ 8.78 (d, 2H, H-3), 8.45 (d, 2H, H-4), 8.29 (d, 2H, H-9), 8.07 (d, 2H, H-6), 7.96 (dd, 2H, H-8), 7.80 (dd, 2H, H-7), 6.210–7.46 (m, 8H, Ar–H), 2.98 (s, 4H, J_{Sn-H} = 81 Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 172 (COO), 152, 147, 136, 131, 129, 128, 126, 126, 125, 124, 123, 122, 121, 119, 113 (Ar–C), 33 (CH_2Ar, $^{1}J_{Sn-C}$ = 763 Hz). ^{119}Sn NMR ($CDCl_3$): δ −276. IR (KBr): υ_{asym}(OCO), 1666 cm^{-1}; υ_{sym}(OCO), 1325 cm^{-1}; υ(Sn–C), 523 cm^{-1}; υ(Sn–N), 498 cm^{-1}; υ(Sn–O), 459 cm^{-1}.

2.2.4. $(4\text{-}FC_6H_4CH_2)_2Sn(2\text{-}quin)_2 \cdot 2CH_3CN$ (**4**)

The synthesis procedure of complex **4** was similar to complex **1**. The resulting solid was recrystallized from acetonitrile to give colorless crystals. Yield: 83.7%, m.p. 211–213 °C. Anal. Calc. for $C_{38}H_{30}F_2N_4O_4Sn$: C, 59.79; H, 3.96; N, 7.34; Sn, 15.55. Found: C, 59.56; H, 3.88; N, 7.41; Sn, 15.51%. ^{1}H NMR ($CDCl_3$): δ 8.72 (d, 2H, H-3), 8.45 (d, 2H, H-4), 8.30 (t, 2H, H-9), 8.09 (d, 2H, H-6), 8.01 (dd, 2H, H-8), 7.83 (dd, 2H, H-7), 6.24–7.41 (m, 8H, Ar–H), 2.99 (s, 4H, J_{Sn-H} = 82 Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 174 (COO), 155, 146, 132, 130, 129, 128, 126, 126, 125, 124, 123, 122, 118 (Ar–C), 32 (CH_2Ar, $^{1}J_{Sn-C}$ = 734 Hz). ^{119}Sn NMR ($CDCl_3$): δ −273. IR (KBr): υ_{asym}(OCO), 1669 cm^{-1}; υ_{sym}(OCO), 1321 cm^{-1}; υ(Sn–C), 543 cm^{-1}; υ(Sn–N), 483 cm^{-1}; υ(Sn–O), 455.

2.2.5. $(4\text{-}CNC_6H_4CH_2)_2Sn(2\text{-}quin)_2$ (**5**)

The synthesis procedure of complex **5** was similar to complex **1**. The resulting solid was recrystallized from dichloromethane and *n*-hexane to give colorless crystals. Yield: 81.9%, m.p. 203–205 °C. Anal. Calc. for $C_{36}H_{24}N_4O_4Sn$: C, 62.19; H, 3.48; N, 8.06; Sn, 17.07. Found: C, 62.37; H, 3.45; N, 8.11; Sn, 17.22%. ^{1}H NMR ($CDCl_3$): δ 8.79 (d, 2H, H-3), 8.45 (d, 2H, H-4), 8.30 (d, 2H, H-9), 8.09 (d, 2H, H-6), 8.01 (dd, 2H, H-8), 7.83 (dd, 2H, H-7), 6.24–7.22 (m, 8H, Ar–H), 2.99 (s, 4H, J_{Sn-H} = 85 Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 171 (COO), 152, 137, 131, 130, 129, 128, 126, 126, 125, 124, 123, 122, 118 (Ar–C), 115 (CN), 32 (CH_2Ar, $^{1}J_{Sn-C}$ = 739 Hz). ^{119}Sn NMR ($CDCl_3$): δ −289. IR (KBr): υ_{asym}(OCO), 1648 cm^{-1}; υ_{sym}(OCO), 1383 cm^{-1}; υ(Sn–C), 538 cm^{-1}; υ(Sn–N), 496 cm^{-1}; υ(Sn–O), 455 cm^{-1}.

*2.2.6. $Ph_2Sn(2\text{-quin})_2$ (**6**)*

The synthesis procedure of complex **6** was similar to complex **1**. The resulting solid was recrystallized from acetonitrile to give colorless crystals. Yield: 87.52%, m.p. 217–219 °C. Anal. Calc. for $C_{32}H_{22}N_2O_4Sn$: C, 62.27; H, 3.59; N, 4.54; Sn, 19.23. Found: C, 62.14; H, 3.67; N, 4.43; Sn, 19.28%. ^{1}H NMR ($CDCl_3$): δ 8.81 (d, 2H, H-3), 8.57 (d, 2H, H-4), 8.32 (d, 2H, H-9), 8.21 (d, 2H, H-6), 8.01 (dd, 2H, H-8), 7.93 (dd, 2H, H-7), 6.80–7.67 (m, 10H, Ph–H). ^{13}C NMR ($CDCl_3$): δ 172 (COO), 148, 147, 135, 130, 130, 128, 126, 125, 125, 123, 122, 121, 117 (Ar–C, $^1J_{Sn-C}$ = 631 Hz). ^{119}Sn NMR ($CDCl_3$): δ −312. IR (KBr): υ_{asym}(OCO), 1667 cm^{-1}; υ_{sym}(OCO), 1335 cm^{-1}; υ(Sn–C), 496 cm^{-1}; υ(Sn–N), 483 cm^{-1}; υ(Sn–O), 457 cm^{-1}.

*2.2.7. $(2,4\text{-}Cl_2C_6H_3CH_2)_2Sn(2\text{-quin})_2$ (**7**)*

The synthesis procedure of complex **7** was similar to complex **1**. The resulting solid was recrystallized from acetonitrile to give colorless crystals. Yield: 84.3%, m.p. 174–176 °C. Anal. Calc. for $C_{34}H_{22}Cl_4N_2O_4Sn$: C, 52.15; H, 2.83; N, 3.58; Sn, 15.16. Found: C, 52.39; H, 2.96; N, 3.47; Sn, 15.31%. ^{1}H NMR ($CDCl_3$): δ 8.77 (d, 2H, H-3), 8.52 (d, 2H, H-4), 8.33 (d, 2H, H-9), 8.15 (d, 2H, H-6), 7.95 (dd, 2H, H-8), 7.89 (dd, 2H, H-7), 6.53–7.62 (m, 6H, Ar–H), 2.98 (s, 4H, J_{Sn-H} = 81 Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 172 (COO), 150, 147, 136, 132, 130, 128, 127, 126, 125, 125, 124, 122, 120, 120, 118 (Ar–C), 34 (CH_2Ar, $^1J_{Sn-C}$ = 784 Hz). ^{119}Sn NMR ($CDCl_3$): δ −284. IR (KBr): υ_{asym}(OCO), 1671 cm^{-1}; υ_{sym}(OCO), 1347 cm^{-1}; υ(Sn–C), 573 cm^{-1}; υ(Sn–N), 486 cm^{-1}; υ(Sn–O), 463 cm^{-1}.

*2.2.8. $\{[(2\text{-}ClC_6H_4CH_2)_2SnCl(2\text{-quin})]_2 \cdot CH_3OH\}_n$ (**8**)*

To a stirred solution of 2-quinaldic acid (0.173 g, 1.0 mmol) and Et_3N (1.2 mmol) in benzene was added $(2\text{-}ClC_6H_4CH_2)_3SnCl$ (0.531 g, 1.0 mmol). The mixture was heated under reflux for 1.5 h and the solvent was removed by evaporation in vacuo. The crude adduct was recrystallized from methanol. Yield: 67.1%, m.p. 179–181 °C. Anal. Calc. for $C_{49}H_{40}Cl_6N_2O_5Sn_2$: C, 49.58; H, 3.40; N, 2.36; Sn, 20.00. Found: C, 49.42; H, 3.37; N, 2.41; Sn, 20.14%. ^{1}H NMR ($CDCl_3$): δ 8.49 (d, 2H, H-3), 8.41 (d, 2H, H-4), 8.10 (d, 2H, H-9), 7.85 (d, 2H, H-6), 7.76 (dd, 2H, H-8), 7.68 (dd, 2H, H-7), 6.87–7.43 (m, 8H, Ar–H), 3.12 (s, 4H, J_{Sn-H} = 88 Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 173 (COO), 152, 147, 136, 131, 129, 128, 126, 126, 125, 124, 122, 122, 121, 120, 118 (Ar–C), 31 (CH_2Ar, $^1J_{Sn-C}$ = 697 Hz). ^{119}Sn NMR ($CDCl_3$): δ −297. IR (KBr): υ_{asym}(OCO), 1625 cm^{-1}; υ_{sym}(OCO), 1454 cm^{-1}; (Sn–C), 559 cm^{-1}; υ(Sn–N), 499 cm^{-1}; υ(Sn–O), 453 cm^{-1}.

*2.2.9. $(4\text{-}ClC_6H_4CH_2)_2SnCl(2\text{-quin}) \cdot CH_2Cl_2$ (**9**)*

The method of synthesis of the complex **9** was similar as described for **8**. The resulting solid was recrystallized from dichloromethane to give colorless crystals. Yield: 70%, m.p. 202–203 °C. Anal. Calc. for $C_{25}H_{20}Cl_5NO_2Sn$: C, 45.33; H, 3.04; N, 2.11; Sn, 17.92. Found: C, 45.28; H, 3.17; N, 2.13; Sn, 17.74%. ^{1}H NMR ($CDCl_3$): 8.50 (1H, d, H-3), 8.45 (1H, d, H-4), 8.20 (1H, d, H-9), 7.90 (d, 2H, H-6), 7.81 (dd, 2H, H-8), 7.73 (dd, 2H, H-7), 6.77-7.46 (8H, m, Ar–H), 3.13 (s, 4H, J_{Sn-H} = 85 Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 173 (COO), 152, 147, 132, 134, 129, 127, 126, 125, 124, 122, 122, 121, 118 (Ar–C), 31 (CH_2Ar, $^1J_{Sn-C}$ = 680 Hz). ^{119}Sn NMR δ −295. IR (KBr): υ_{as}(OCO), 1615 cm^{-1}; υ_s(OCO), 1427 cm^{-1}; υ(Sn–C), 548 cm^{-1}; υ(Sn–N), 480 cm^{-1}; υ(Sn–O), 457 cm^{-1}.

*2.2.10. $(2\text{-}FC_6H_4CH_2)_2SnCl(2\text{-quin})$ (**10**)*

The method of synthesis of the complex **10** was similar as described for **8**. The resulting solid was recrystallized from dichloromethane and *n*-hexane to give colorless crystals. Yield: 76.8%, m.p. 183–185 °C. Anal. Calc. for $C_{24}H_{18}ClF_2NO_2Sn$: C, 52.94; H, 3.33; N, 2.57; Sn, 21.80. Found: C, 53.26; H, 3.41; N, 2.51; Sn, 21.96%. ^{1}H NMR ($CDCl_3$): δ 8.58 (1H, d, H-3), 8.49 (1H, d, H-4), 8.18 (1H, d, H-9), 7.90 (d, 2H, H-6), 7.85 (dd, 2H, H-8), 7.70 (dd, 2H, H-7), 6.34–7.43 (m, 8H, Ar–H), 3.15 (s, 4H, J_{Sn-H} = 88 Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 173 (COO), 152, 147, 136, 131, 130, 128, 126, 126, 125, 124, 123, 122, 121, 119, 113 (Ar–C), 32 (CH_2Ar, $^1J_{Sn-C}$ = 682 Hz). ^{119}Sn NMR ($CDCl_3$): δ −296. IR (KBr): υ_{asym}(OCO), 1610 cm^{-1}; υ_{sym}(OCO), 1436 cm^{-1}; υ(Sn–C), 536 cm^{-1}; υ(Sn–N), 493 cm^{-1}; υ(Sn–O), 451 cm^{-1}.

*2.2.11. $(4\text{-}FC_6H_4CH_2)_2SnCl(2\text{-quin})$ (**11**)*

The method of synthesis of the complex **11** was similar as described for **8**. The resulting solid was recrystallized from acetonitrile to give colorless crystals. Yield: 80.3%, m.p. 193–195 °C. Anal. Calc. for $C_{24}H_{18}ClF_2NO_2Sn$: C, 52.94; H, 3.33; N, 2.57; Sn, 21.80. Found: C, 52.87; H, 3.40; N, 2.63; Sn, 21.59%. ^{1}H NMR ($CDCl_3$): δ 8.61 (1H, d, H-3), 8.45 (1H, d, H-4), 8.21 (1H, d, H-9), 7.93 (d, 2H, H-6), 7.85 (dd, 2H, H-8), 7.68 (dd, 2H, H-7), 6.27–7.43 (m, 8H, Ar–H), 3.02 (s, 4H, J_{Sn-H} = 89 Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 173 (COO), 153, 147, 135, 131, 129, 128, 126, 126, 125, 124, 123, 122, 118 (Ar–C), 32 (CH_2Ar, $^1J_{Sn-C}$ = 672 Hz). ^{119}Sn NMR ($CDCl_3$): δ −283. IR (KBr): υ_{asym}(OCO), 1617 cm^{-1}; υ_{sym}(OCO), 1425 cm^{-1}; υ(Sn–C), 538 cm^{-1}; υ(Sn–N), 486 cm^{-1}; υ(Sn–O), 450.

*2.2.12. $(PhCH_2)_2SnCl(2\text{-quin})$ (**12**)*

The method of synthesis of the complex **12** was similar as described for **8**. The resulting solid was recrystallized from acetonitrile to give colorless crystals. Yield: 80.5%, m.p. 187–188 °C. Anal. Calc. for $C_{24}H_{20}ClNO_2Sn$: C, 56.68; H, 3.96; N, 2.75; Sn, 23.34. Found: C, 56.55; H, 4.02; N, 2.60; Sn, 23.61%. ^{1}H NMR ($CDCl_3$): δ 8.69 (1H, d, H-3), 8.46 (1H, d, H-4), 8.21

Table 1
Crystallographic data of complexes **4** and **8**

	4	**6**
Empirical formula	$C_{38}H_{30}F_2N_4O_4Sn$	$C_{49}H_{40}Cl_6N_2O_5Sn_2$
M	763.35	1186.91
T (K)	298(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	10.071(5)	12.613(13)
b (Å)	23.682(13)	20.10(2)
c (Å)	14.626(8)	20.33(2)
β (°)	99.912(7)	103.865(17)
V (Å$^{3)}$	3436(3)	5005(9)
Z	4	4
D_{calc} (Mg m^{-3})	1.475	1.575
$F(000)$	1544	2360
μ (mm^{-1})	0.801	1.365
Reflections collected	17790	24414
Unique data	6057	8422
Data/restraints/parameters	6057/18/466	8422/134/589
Maximum/minimum transmission	0.7561, 0.6763	0.6046, 0.5428
GOF	1.055	0.874
R_1, $wR_2[I > 2\sigma(I)]$	0.0348, 0.0778	0.0669, 0.1302
R_1, wR_2 (all data)	0.0517, 0.0845	0.1495, 0.1609
Largest difference peak, hole (e Å^{-3})	0.358, −0.811	0.854, −0.413

(1H, d, H-9), 7.85 (d, 2H, H-6), 7.72 (dd, 2H, H-8), 7.64 (dd, 2H, H-7), 6.46-7.32 (m, 10H, Ph–H), 2.94 (s, 4H, J_{Sn-H} = 87 Hz, $SnCH_2$). ^{13}C NMR ($CDCl_3$): δ 172 (COO), 150, 148, 135, 128, 128, 126, 125, 124, 122, 121, 117, 115, 110 (Ar–C), 31 (CH_2Ar, $^1J_{Sn-C}$ = 658 Hz). ^{119}Sn NMR ($CDCl_3$): δ −285. IR (KBr): υ_{asym}(O-CO), 1615 cm^{-1}; υ_{sym}(OCO), 1430 cm^{-1}; υ(Sn–C), 587 cm^{-1}; υ(Sn–N), 483 cm^{-1}; υ(Sn–O), 465 cm^{-1}.

2.3. X-ray crystallography

Crystallographic data and refinement details are given in Table 1. All X-ray crystallographic data were collected on a Bruker smart-1000 CCD diffractometer with graphite monochromated Mo Kα (0.71073 Å) radiation and the φ–ω scan technique. The structures were solved by direct method and difference Fourier map using SHELXL-97 program, and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically.

3. Results and discussion

3.1. Syntheses

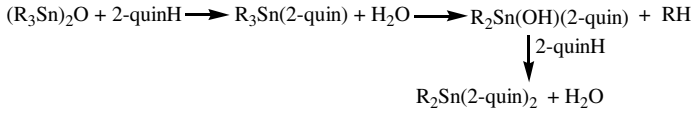
We treated $(R_3Sn)_2O$ and 2-quinH in a 1:2 stoichiometry in benzene and hoped to get triorganotin complexes of 2-quinaldate. To our surprise, dealkylation reaction occurs and as a result we have obtained 12 diorganotin(IV) complexes of 2-quinaldate. We assumed that it may result from the steric bulk of the 2-quin ligand as have studied in the previous report [14–19], in order to confirm our assumption we have done further research by devising another reaction shown in Scheme 1. Studies show that whichever reaction we selected the final products are diorganotin complexes of 2-quinaldate, which strongly indicates that the coordination number at 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 or $Et_3N \cdot HCl$ facilitates the dealkyltion reaction. Based on these studies, we raised possible mechanisms for all of the 12 complexes, which are shown in Scheme 1.

3.2. IR and NMR studies

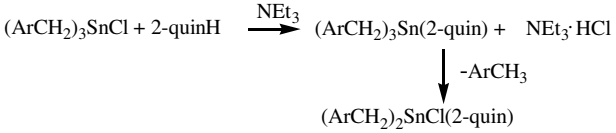
The infrared spectra of diorganotin(IV) complexes with carboxylic acid have been recorded and some important assignments are shown above. The Δv ($v_{as}(CO_2) - v_s(CO_2)$) value is used to determine the nature of bonding of carboxylate to tin(IV) complexes according to the previous report [21]. It is generally believed that the difference in Δv between asymmetric $v_{asym}(CO_2)$ and symmetric $v_{sym}(CO_2)$ absorption frequencies below 200 cm^{-1} for the bidentate carboxylate moiety, but greater than 200 cm^{-1} for the unidentate carboxylate moiety [22]. Study shows that the values of Δv of the complex **1**–**7** are between 265 and 348 cm^{-1} and this strongly indicate that these complexes adopt unidentate carboxylate structure [23,24]. The value of Δv of complexes **8**–**12** are 171–194 cm^{-1}, and this shows that complexes **8**–**12** adopt the bidentate carboxylate, which accords with the result of the X-ray diffraction study for complex **8**. Compared with the free ligand the new occurrence of the bands in the region of 474 and 499 cm^{-1} for all the 12 complexes were assigned to the Sn–N vibrations, which provides prove for the existence of Sn–N bonds for all of the 12 complexes, and the bands in the region of 450 and 469 cm^{-1} were assigned to the Sn–O vibrations according to the literature [14,15].

Chemical shifts $\delta(^1H)$ and $\delta(^{13}C)$ inherent to ligand atoms and organic radicals bound to Sn in complexes **1**–**12** are assigned by comparison with the spectra of the free ligand, 2-quinaldic acid as well as of the complex $[R_2SnCl_2(2\text{-quin})]^-(HNEt_3)^+$ [24]. Signal integrations indicate the stoichiometry $R_2Sn(2\text{-quin})_2$ and $R_2SnCl(2\text{-quin})$.

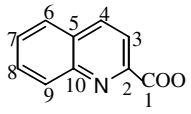
The ^1H NMR of complexes **1**–**5**, and **7**–**12** show that the chemical shifts of the protons of methylene on the benzyl group exhibit signals about 2.94–3.15 ppm as single with ^{119}Sn satellites, the coupling constant J_{Sn-H} is equal 80–89 Hz. The signals at 7.48–8.84 ppm as mutipliplicity for all the 12 complexes are assigned to the



R= $PhCH_2$ **1**, 2-$ClC_6H_4CH_2$ **2,** 2-$FC_6H_4CH_2$ **3**, 4-$FC_6H_4CH_2$ **4**, 4-$CNC_6H_4CH_2$ **5,** Ph **6**, 2,4-$Cl_2C_6H_3CH_2$ **7**;



Ar=2-$ClC_6H_4CH_2$ **8**, 4-$ClC_6H_4CH_2$ **9**, 2-$FC_6H_4CH_2$ **10**, 4-$FC_6H_4CH_2$ **11**, $PhCH_2$ **12**



2-quin

Scheme 1.

protons of 2-quin ligand, which is shifting slightly to the low field compared with the free ligand.

In the ^{13}C NMR spectra of complexes **1**–**12**, 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 complexes **1**–**12**, which could be interpreted in terms of Sn–N interactions.

Previous studies show that for most methyl derivatives there have a relationship between the $^1J(^{119}Sn–^{13}C)$ values and the Me–Sn–C angle [25,26], on this base we assumed that there must some relationship between benzyltin derivatives and the C–Sn–C angle. The sequence of the $^1J(^{119}Sn–^{13}C)$ values for complexes **1**–**7** is **7** > **2** ≈ **3** > **5**≈ **4** > **1** > **6**, which accords to the sequences of the stereo-constraints, 2,4-$Cl_2C_6H_3CH_2$ > 2-$ClC_6H_4CH_2$ ≈ 2-$FC_6H_4CH_2$ > 4-$CNC_6H_4CH_2$ ≈ 4-$FC_6H_4CH_2$ > $C_6H_4CH_2$ > Ph, so does complexes **8**–**12**.

It is reported that in the alkyltin carboxylates, four-coordinate tin has $\delta(^{119}Sn)$ values range from +200 to −60 ppm, five-coordinate tin from −90 to −190 ppm, and six-coordinate tin from −200 to −400 ppm [27]. On this base, the ^{119}Sn NMR values for complexes **1**–**7** in the region −262 and −312 ppm as one broad sharp signal indicate that in solution the tin atoms of these complexes are six-coordinate, which suggest that the Sn–N interaction probably survives in solution as well in the solid state. The ^{119}Sn NMR values for complexes **8**–**12** in the region −283 and −297 ppm also show that both the Sn–N interaction and the intermolecular Sn–O interaction survive in solution. And their structures are similar to those diorganotin complexes of 2-quinaldate that have been reported [13].

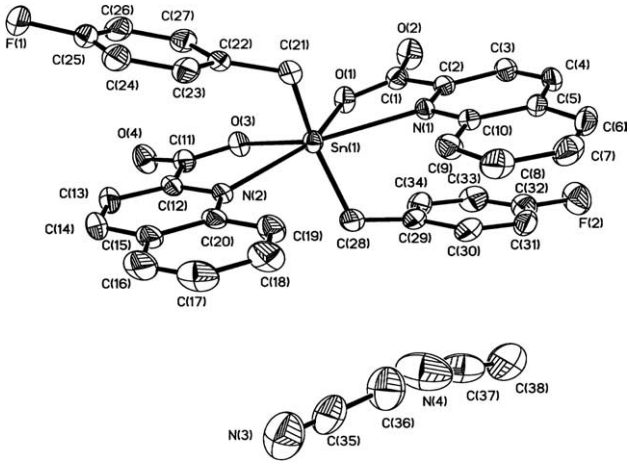


Fig. 1. Molecular structure of complex **4**.

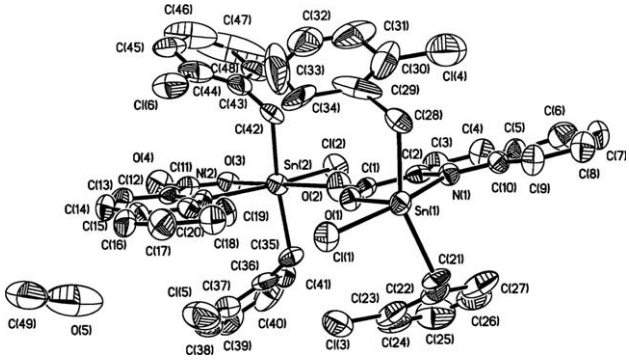


Fig. 2. Molecular structure of complex **8**.

3.3. Structural studies

The crystal structure and unit cell of complexes **4** and **8** are shown in Figs. 1 and 2, respectively, and the one-dimensional chain work of complex **8** is shown in Fig. 3. All hydrogen atoms have been omitted for the purpose of clarity. Tables 2 and 3, respectively, list selected bond lengths and angles for complexes **4** and **8**.

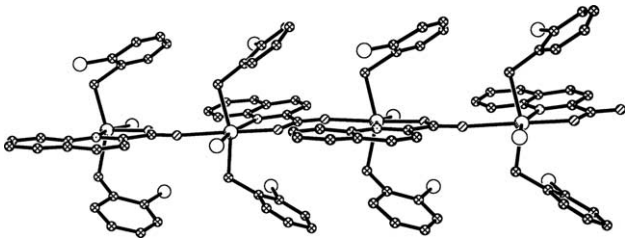


Fig. 3. One-dimensional chain work of complex **8**.

Table 2
Selected bond distances (Å) and angles (°) for complex **4**

Sn(1)–O(3)	2.086(2)	N(1)–C(2)	1.325(4)
Sn(1)–O(1)	2.090(2)	N(1)–C(10)	1.366(4)
Sn(1)–C(21)	2.152(3)	N(2)–C(12)	1.320(4)
Sn(1)–C(28)	2.159(3)	N(2)–C(20)	1.366(4)
Sn(1)–N(2)	2.505(3)	O(1)–C(1)	1.292(4)
Sn(1)–N(1)	2.516(2)	O(2)–C(1)	1.221(4)
F(1)–C(25)	1.371(4)	O(3)–C(11)	1.303(4)
F(2)–C(32)	1.368(4)		
O(3)–Sn(1)–O(1)	77.94(9)	C(21)–Sn(1)–N(1)	81.79(10)
O(3)–Sn(1)–C(21)	103.43(11)	C(28)–Sn(1)–N(1)	87.21(11)
O(1)–Sn(1)–C(21)	99.80(11)	N(2)–Sn(1)–N(1)	140.77(8)
O(3)–Sn(1)–C(28)	99.96(12)	C(21)–Sn(1)–N(2)	86.14(11)
O(1)–Sn(1)–C(28)	101.40(11)	C(28)–Sn(1)–N(2)	85.74(11)
C(21)–Sn(1)–C(28)	151.15(14)	O(3)–Sn(1)–N(1)	148.19(8)
O(3)–Sn(1)–N(2)	70.99(8)	O(1)–Sn(1)–N(1)	70.26(9)
O(1)–Sn(1)–N(2)	148.89(8)		

Table 3
Selected bond distances (Å) and angles (°) for complex **8**

Sn(1)–O(1)	2.097(6)	Sn(2)–O(3)	2.107(6)
Sn(1)–C(28)	2.174(9)	Sn(2)–C(35)	2.146(9)
Sn(1)–C(21)	2.177(9)	Sn(2)–C(42)	2.153(9)
Sn(1)–O(4A)	2.434(7)	Sn(2)–N(2)	2.394(7)
Sn(1)–Cl(1)	2.436(3)	Sn(2)–O(2)	2.421(7)
Sn(1)–N(1)	2.462(7)	Sn(2)–Cl(2)	2.454(3)
O(1)–Sn(1)–C(28)	100.0(3)	C(35)–Sn(2)–O(2)	79.8(3)
O(1)–Sn(1)–C(21)	101.0(3)	C(42)–Sn(2)–O(2)	80.2(3)
C(28)–Sn(1)–C(21)	154.9(4)	N(2)–Sn(2)–O(2)	107.9(2)
O(1)–Sn(1)–O(4A)	175.0(3)	O(3)–Sn(2)–Cl(2)	90.0(2)
C(28)–Sn(1)–O(4A)	79.1(3)	C(35)–Sn(2)–Cl(2)	95.2(3)
C(21)–Sn(1)–O(4A)	81.1(4)	C(42)–Sn(2)–Cl(2)	95.4(3)
O(1)–Sn(1)–Cl(1)	89.62(17)	N(2)–Sn(2)–Cl(2)	163.50(18)
C(28)–Sn(1)–Cl(1)	98.0(3)	O(2)–Sn(2)–Cl(2)	88.62(17)
C(21)–Sn(1)–Cl(1)	95.8(3)	O(3)–Sn(2)–C(35)	100.0(3)
O(4A)–Sn(1)–Cl(1)	85.7(2)	O(3)–Sn(2)–C(42)	100.3(3)
O(1)–Sn(1)–N(1)	72.6(2)	C(35)–Sn(2)–C(42)	157.1(4)
C(28)–Sn(1)–N(1)	86.9(3)	O(3)–Sn(2)–N(2)	73.5(3)
C(21)–Sn(1)–N(1)	86.3(4)	C(35)–Sn(2)–N(2)	88.4(3)
O(4A)–Sn(1)–N(1)	112.1(3)	C(42)–Sn(2)–N(2)	87.2(3)
Cl(1)–Sn(1)–N(1)	162.18(18)	O(3)–Sn(2)–O(2)	178.6(3)

*3.3.1. Structures of $[(4\text{-F-PhCH}_2)_2\text{Sn}(2\text{-quin})_2]\cdot 2(CH_3CN)$ (**4**) and $\{[(2\text{-Cl-PhCH}_2)_2\text{Sn}(2\text{-quin})\text{Cl}]_2\cdot(CH_3OH)\}_n$ (**8**)*

Complex **4** is a monomer as can be seen in Fig. 1. In the structure of the complex, the tin atom forms four primary bonds: two to the *p*-fluorobenzyl carbon atoms, and two to the oxygen atoms of two carboxylates. In addition, there exists a coordination interaction between tin and nitrogen atoms. The Sn–N bond length 2.516(2) Å for Sn(1)–N(1) and 2.505(3) Å for Sn(1)–N(2) is similar to that of the corresponding distances found in $Me_2Sn(2\text{-quin})_2$ (2.594(3), 2.473(4) Å) and $Cy_2Sn(2\text{-pic})_2(OH_2)\cdot MeOH$ (2.550(3), 2.495(3) Å) [13], it is longer than that of found in $Me_2Sn(2\text{-quin})_2$ showing above, but it is much shorter than the sum of the van der Waals radii of tin and nitrogen, 3.74 Å [28]. The two 2-quin ligands are bidentate coordinating to the tin atom using one carboxylate oxygen atom and the nitrogen atom, thus providing five-membered chelate rings with bite angles of 70.26(9)° for O(1)–Sn(1)–N(1) and 70.99(8)° for O(3)–Sn(1)–N(2). Thus the geometry at tin becomes skew-trapezoidal-bipyramidal with two *p*-fluorobenzyl carbon atoms in axial sites and two oxygen atoms and two nitrogen atoms occupying the equatorial position. The sum of the angles subtended at tin atom in the trigonal plane is 359.96°, so that the Sn(1), O(1), O(3), N(1) and N(2) atoms are in the same plane, and the mean deviation for these atoms from the plane is ±0.0112 Å.

Study shows that in this complex there exists intermolecular non-bonding F···F interaction similar to that of the Cl···Cl interaction in our previous report [29]. The F···F bond distance is 2.877 Å, which is considerably shorter than the sum of the van der Waals radii of twice the fluorin atoms and should be considered as weak non-bonding interaction [28], thus the complex become a weakly-bridged one-dimensional chain polymer as can be seen in Fig. 2.

While complex **8** is a polymer with the structural unit containing two distinct tin atoms with small differences in bond lengths and bond angles as shown in Fig. 2, both of the tin atoms are six-coordinate axially by two oxygen atoms and equatorially by one chlorine atom, one nitrogen atom and two tin-bound *o*-chlorobenzyl carbon atoms. The carboxylate groups are bidentate with one each oxygen atom to the intramolecular and the intermolecular tin atoms, thus the complex becomes a one-dimensional chain polymer as shown in Fig. 3.

The Sn–O bond distances 2.097(6) Å for Sn(1)–O(1), 2.434(7) Å for Sn(1)–O(4A), 2.107(6) Å for Sn(2)–O(3) and 2.421(7) Å for Sn(2)–O(2) are similar to that of the corresponding distances found in $[^n\text{Bu}_3\text{Sn}(\text{O-COCH}_2\text{C}_8\text{H}_5\text{N-3})]_n$ [30]. The Sn–Cl bond lengths are 2.436(3) Å for Sn(1)–Cl(1) and 2.454(3) Å for Sn(2)–Cl(2) lie in the range of the normal covalent radii 2.37–2.60 Å [31]. The bond angles 175.0(3) Å for O(1)–Sn(1)–O(4A) and 178.6(3) Å for O(3)–Sn(2)–O(2) indicate that the geometry at both tin atoms become distorted octahedral. The sum of the angles subtended at Sn(1) and Sn(2) atoms in the equatorial plane are 367° and 366.2°, respectively, which shows that the Sn(1), Cl(1), C(21), C(28) and the Sn(2), Cl(2), C(42), C(35)

atoms are almost co-planar. The mean deviations from the plane are ±0.3259 and ±0.3035 Å. Studies show that the dihedral angels formed by the two planes is 6.6°, and this indicates that the above eight atoms also are almost in the same plane.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 250004 for complex **4** and CCDC No. 228447 for complex **8**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

We acknowledge the National Natural Foundation PR China (20271025) and the Shandong Province Science Foundation (L2003B01), and the state Key Laboratory of Crystal Materials, Shandong University, PR China.

References

[1] B. Jousseaume, V. Guillou, N. Noiret, M. Pereyre, J.M. France, J. Organomet. Chem. 450 (1993) 97.
[2] A.G. Davies, P.J. Smith, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, vol. 2, Pergamon Press, Oxford, 1982, p. 519.
[3] J.A. Zubita, J.J. Zuckerman, Inorg. Chem. 24 (1987) 251.
[4] G.K. Sandhu, R. Gupta, S.S. Sandhu, R.V. Parish, Polyhedron 4 (1985) 81.
[5] C.S. Parulekar, V.K. Jain, T.K. Das, A.R. Gupta, B.F. Hoskins, E.R.T. Tiekink, J. Organomet. Chem. 372 (1989) 193.
[6] M. Gielen, A.M. Khloufi, M. Biesmans, R. Kayser, Appl. Organometal. Chem. 7 (1993) 201.
[7] S. Wilson, L. Dzon, A. Reed, M. Pruitt, M.M. Whalen, Appl. Organometal. Chem 19 (2004) 554.
[8] M. Gielen, Appl. Organometal. Chem. 16 (2002) 481.
[9] M. Gielen, M. Biesemans, R. Willem, Appl. Organometal. Chem. 19 (2005) 440.
[10] K.C. Molloy, T.G. Purcell, E. Hahn, H. Schumann, J.J. Zuckerman, Organometallics 5 (1986) 85.
[11] K.C. Molloy, K. Quill, I.W. Nowell, J. Chem. Soc., Dalton Trans. (1987) 101.
[12] R.R. Holmes, Acc. Chem. Res. 22 (1989) 190;
J. Otera, T. Yano, R. Owawara, Organometallics 5 (1986) 1167.
[13] D. Dakternieks, A. Duthie, D.R. Smyth, C.P.D. Stapleton, E.R.T. Tiekink, Organometallics 22 (2003) 4599.
[14] H.D. Yin, C.H. Wang, Y. Wang, C.L. Ma, J.X. Shao, Chem. J. Chin. Univ. 24 (2003) 68.
[15] H.D. Yin, C.H. Wang, C.L. Ma, H.X. Fang, Chin. J. Chem. 21 (2003) 452.
[16] K.C.K. Swamy, M.A. Said, S. Nagabrahmanandachari, D.M. Poojary, J. Chem. Soc., Dalton Trans. (1998) 1645.
[17] V. Chandrasekhar, V. Bhaskar, A. Steiner, S. Zacchini, Organometallics 21 (2002) 4528.
[18] V. Chandrasekhar, S. Nagendran, K. Gopal, A. Steiner, S. Zacchini, Chem. Commun. (2003) 862.
[19] T.S. Basu Baul, K.S. Singh, A. Lycka, M. Holcapek, A. Linden, J. Organomet. Chem. 690 (2005) 1581.
[20] (a) K. Sisido, Y. Takeda, Z. Kinugawa, J Am. Chem. Soc. 82 (1960) 434;
(b) Q.L. Xie, X.H. Xu, D.K. Zhang, Acta Chim. Sinica 50 (1992) 508.
[21] B.Y.K. Ho, J.J. Zuckerman, Inorg. Chem. 12 (1973) 1552.
[22] X.N. Fang, X.Q. Song, Q.L. Xie, J. Organomet. Chem. 619 (2001) 43.
[23] S.P. Narula, S.K. Bharadwaj, Y. Sharda, D.C. Povey, G.W. Smith, J. Organomet. Chem. 430 (1992) 167.
[24] H.D. Yin, Q.B. Wang, S.C. Xue, J. Organomet. Chem. 690 (2005) 831.
[25] T.P. Lockhart, W.F. Manders, Inorg. Chem. 25 (1986) 892.
[26] J. Holecek, A. Lycka, Inorg. Chim. Acta 118 (1986) L15.
[27] S.G. Eoh, S.H. Ang, J.P.D. Declercq, Polyhedron 16 (1997) 3729.
[28] A. Bondi, J. Phys. Chem. 68 (1964) 441.
[29] H.D. Yin, M. Hong, Chin. Inorg. Chem. 20 (2004) 297.
[30] Q.L. Xie, X.K. Yao, R.J. Wang, Z.G. Zhang, J.M. Hu, Acta Chim. Sinica 49 (1991) 723.
[31] F.H. Allen, S.A. Bellard, M.D. Brice, B.A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B.G. Hummelink-Peters, O. Kennard, W.D.S. Motherwell, J.R. Rogers, D.G. Watson, Acta Crystallogr., Sect. B 35 (1979) 2331.