

Communication

Synthesis and characterization of ionic organotin compounds $[R_2SnCl_2(2\text{-quin})]^- (HNEt_3)^+$ and crystal structures of $[(2,4\text{-}Cl_2\text{-}C_6H_3CH_2)_2SnCl_2(2\text{-quin})]^- (HNEt_3)^+$

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Abstract

Eight ionic organotin compounds $[R_2SnCl_2(2\text{-quin})]^- (HNEt_3)^+$ have been synthesized by reactions of 2-quinH with R_2SnCl_2 ($R = PhCH_2$ **1**, 2-*Cl*- $C_6H_4CH_2$ **2**, 4-*Cl*- $C_6H_4CH_2$ **3**, 2-*F*- $C_6H_4CH_2$ **4**, 4-*F*- $C_6H_4CH_2$ **5**, 4-*CN*- $C_6H_4CH_2$ **6**, Ph **7**, 2,4- $Cl_2\text{-}C_6H_3CH_2$ **8**) in the presence of organic base NEt_3 , and their structures have been characterized by elemental analysis, IR and multinuclear NMR (1H , ^{13}C , ^{119}Sn) spectroscopies. The structure of $[(2,4\text{-}Cl_2\text{-}C_6H_3CH_2)_2SnCl_2(2\text{-quin})]^- (NEt_3)^+$ (**8**) has been determined by X-ray diffraction study. Studies show that compound **8** has a monomeric structure with the central tin atom six-coordinate in a distorted octahedral configuration and the nitrogen atoms of the 2-quin ligands are coordinating to the tin atom in all the eight compounds.

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Keywords: Ionic organotin compound; 2-Quinaldate; Synthesis; Crystal structure

1. Introduction

Organotin(IV) compounds with carboxylic acid are widely used as biocides, fungicides and in industry as homogeneous catalysts [1–5]. Recently, pharmaceutical properties of organotin esters of carboxylic acid have been investigated for their antitumour activity [6,7]. In general, the biocidal activity of organotin complexes is greatly influenced by the structure of the molecule and the coordination number of the tin atoms [8–10]. Atassi [11] assumed that water-soluble organotin compounds are likely to be more active than compounds soluble only in organic solvents. Therefore we synthesized eight ionic organotin compounds $[R_2SnCl_2(2\text{-quin})]^- (HNEt_3)^+$, whose water solubility under physiological conditions is expected to be improved with respect to

organotin(IV) carboxylate. All the compounds have been characterized by elemental analyses, IR and NMR (1H , ^{13}C and ^{119}Sn) spectra, and the results of this study are reported herein.

2. Experimental

2.1. Materials and methods

Diorganotin(IV) dichlorides were commercially available and used without further purification. The melting points were obtained with Kolfer micro melting point apparatus and were uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. 1H , ^{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.

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Elemental analyses were performed in a PE-2400 II elemental analyzer, and tin was estimated as SnO₂.

2.2. Preparation of the complexes

2-Quinaldic acid (1.0 mmol) and NEt₃ (1.0 mmol) were added to a dichloromethane solution (20 ml) of dialkyltin dichloride (1.0 mmol) and stirred for 1.5 h at 30 °C and then filtered. The filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The solid was recrystallized from acetonitrile to give colorless crystals.

2.2.1. [(PhCH₂)₂SnCl₂(2-quin)]⁻(HNEt₃)⁺ (1)

0.47 g, yield 72%, m.p. 192–194 °C. Anal. Calc. for C₃₀H₃₆Cl₂N₂O₂Sn: C, 55.76; H, 5.62; N, 4.33; Sn, 18.37. Found: C, 55.57; H, 5.72; N, 4.28; Sn, 18.54%. ¹H NMR (CDCl₃): δ 11.15 (s, 1H, HNEt₃), 8.82 (1H, d, *J* = 8 Hz, H-3), 8.50 (1H, d, *J* = 8 Hz, H-4), 8.23 (1H, d, *J* = 7 Hz, H-9), 8.18 (1H, d, *J* = 8 Hz, H-6), 8.01 (1H, dd, *J* = 8, 5 Hz, H-8), 7.76 (1H, dd, *J* = 8, 4 Hz, H-7), 6.75–7.42 (10H, m, Ph-H), 2.91 (4H, d, *J*_{Sn-H} = 84 Hz, SnCH₂), 2.81 (6H, q, *J* = 7 Hz, CH₂), 1.12 (9H, t, *J* = 7 Hz, CH₃). ¹³C NMR (CDCl₃): δ 177.22 (COO), 150.63, 147.68, 136.10, 129.04, 128.47, 126.88, 125.21, 125.35, 122.73, 121.59, 117.64, 115.43, 109.12 (Ar-C), 30.58 (CH₂Ar), 52.24 (NCH₂), 7.53 (CH₃). ¹¹⁹Sn NMR δ -495.43. IR (KBr): ν_{as}(OCO), 1655 cm⁻¹; ν_s(OCO), 1330 cm⁻¹; ν(Sn-C), 575 cm⁻¹; ν(Sn-N), 482 cm⁻¹; ν(Sn-O), 458 cm⁻¹.

2.2.2. [(2-Cl-C₆H₄CH₂)₂SnCl₂(2-quin)]⁻(HNEt₃)⁺ (2)

0.56 g, yield 78%, m.p. 175–176 °C. Anal. Calc. for C₃₀H₃₄Cl₄N₂O₂Sn: C, 50.39; H, 4.79; N, 3.92; Sn, 16.60. Found: C, 50.52; H, 4.71; N, 4.13; Sn, 16.47%. ¹H NMR (CDCl₃): δ 11.13 (s, 1H, HNEt₃), 8.85 (1H, d, *J* = 8 Hz, H-3), 8.44 (1H, d, *J* = 7 Hz, H-4), 8.31 (1H, d, *J* = 8 Hz, H-9), 8.03 (1H, d, *J* = 6 Hz, H-6), 7.91 (1H, dd, *J* = 8, 5 Hz, H-8), 7.80 (1H, dd, *J* = 8, 5 Hz, H-7), 6.55–7.42 (8H, m, Ar-H), 3.02 (4H, d, *J*_{Sn-H} = 84 Hz, SnCH₂), 2.83 (6H, q, *J* = 7 Hz, CH₂), 1.14 (9H, t, *J* = 7 Hz, CH₃). ¹³C NMR (CDCl₃): δ 175.12 (COO), 152.70, 147.54, 136.88, 132.52, 130.54, 128.70, 127.67, 126.22, 125.53, 125.30, 124.64, 122.39, 120.61, 117.35, 115.42 (Ar-C), 31.48 (CH₂Ar), 52.81 (NCH₂), 7.33 (CH₃). ¹¹⁹Sn NMR δ -497.47. IR (KBr): ν_{as}(OCO), 1668 cm⁻¹; ν_s(OCO), 1365 cm⁻¹; ν(Sn-C), 560 cm⁻¹; ν(Sn-N), 490 cm⁻¹; ν(Sn-O), 447 cm⁻¹.

2.2.3. [(4-Cl-C₆H₄CH₂)₂SnCl₂(2-quin)]⁻(HNEt₃)⁺ (3)

0.46 g, yield 65%, m.p. 210–211 °C. Anal. Calc. for C₃₀H₃₄Cl₄N₂O₂Sn: C, 50.39; H, 4.79; N, 3.92; Sn, 16.60. Found: C, 50.65; H, 4.80; N, 3.85; Sn, 16.72%. ¹H NMR (CDCl₃): δ 11.10 (s, 1H, HNEt₃), 8.56 (1H, d, *J* = 8 Hz, H-3), 8.47 (1H, d, *J* = 8 Hz, H-4), 7.91 (1H, d, *J* = 6 Hz, H-9), 7.52–7.79 (3H, m, H-6, H-8 &

H-7), 6.75–7.42 (8H, m, Ar-H), 2.97 (4H, d, *J*_{Sn-H} = 80 Hz, SnCH₂), 2.74 (6H, q, *J* = 7 Hz, CH₂), 1.20 (9H, t, *J* = 7 Hz, CH₃). ¹³C NMR (CDCl₃): δ 171.25 (COO), 153.08, 147.49, 132.10, 129.84, 128.55, 127.34, 126.32, 125.14, 124.77, 122.87, 122.00, 121.51, 118.92 (Ar-C), 31.73 (CH₂Ar), 54.18 (NCH₂), 7.47 (CH₃). ¹¹⁹Sn NMR δ -491.55. IR (KBr): ν_{as}(OCO), 1658 cm⁻¹; ν_s(OCO), 1355 cm⁻¹; ν(Sn-C), 556 cm⁻¹; ν(Sn-N), 485 cm⁻¹; ν(Sn-O), 453 cm⁻¹.

2.2.4. [(2-F-C₆H₄CH₂)₂SnCl₂(2-quin)]⁻(HNEt₃)⁺ (4)

0.49 g, yield 72%, m.p. 184–185 °C. Anal. Calc. for C₃₀H₃₄Cl₂F₂N₂O₂Sn: C, 52.82; H, 5.02; N, 4.11; Sn, 17.40. Found: C, 53.03; H, 5.10; N, 4.22; Sn, 17.57%. ¹H NMR (CDCl₃): δ 11.06 (s, 1H, HNEt₃), 8.83 (1H, d, *J* = 7 Hz, H-3), 8.49 (1H, d, *J* = 8 Hz, H-4), 8.32 (1H, d, *J* = 8 Hz, H-9), 8.02 (1H, d, *J* = 6 Hz, H-6), 7.84 (1H, dd, *J* = 7, 4 Hz, H-8), 7.72 (1H, dd, *J* = 7, 4 Hz, H-7), 6.33–7.44 (8H, m, Ar-H), 2.95 (4H, d, *J*_{Sn-H} = 89 Hz, SnCH₂), 2.78 (6H, q, *J* = 7 Hz, CH₂), 1.16 (9H, t, *J* = 7 Hz, CH₃). ¹³C NMR (CDCl₃): δ 175.10 (COO), 154.22, 145.98, 137.05, 132.34, 130.37, 129.10, 127.34, 125.90, 125.18, 124.79, 123.33, 122.21, 121.43, 120.34, 113.86 (Ar-C), 33.45 (CH₂Ar), 53.15 (NCH₂), 7.38 (CH₃). ¹¹⁹Sn NMR δ -490.45. IR (KBr): ν_{as}(OCO), 1661 cm⁻¹; ν_s(OCO), 1327 cm⁻¹; ν(Sn-C), 545 cm⁻¹; ν(Sn-N), 486 cm⁻¹; ν(Sn-O), 462 cm⁻¹.

2.2.5. [(4-F-C₆H₄CH₂)₂SnCl₂(2-quin)]⁻(HNEt₃)⁺ (5)

0.50 g, yield 74%, m.p. 214–215 °C. Anal. Calc. for C₃₀H₃₄Cl₂F₂N₂O₂Sn: C, 52.82; H, 5.02; N, 4.11; Sn, 17.40. Found: C, 52.70; H, 4.87; N, 4.20; Sn, 17.25%. ¹H NMR (CDCl₃): δ 11.11 (s, 1H, HNEt₃), 8.77 (1H, d, *J* = 8 Hz, H-3), 8.50 (1H, d, *J* = 7 Hz, H-4), 8.37 (1H, d, *J* = 7 Hz, H-9), 8.00 (1H, d, *J* = 6 Hz, H-6), 7.95 (1H, dd, *J* = 7, 4 Hz, H-8), 7.84 (1H, dd, *J* = 8, 4 Hz, H-7), 6.32–7.43 (8H, m, Ar-H), 2.94 (4H, d, *J*_{Sn-H} = 86 Hz, SnCH₂), 2.74 (6H, q, *J* = 7 Hz, CH₂), 1.20 (9H, t, *J* = 7 Hz, CH₃). ¹³C NMR (CDCl₃): δ 175.31 (COO), 155.89, 146.25, 132.77, 130.62, 129.61, 128.04, 126.65, 126.11, 125.27, 124.32, 123.78, 122.63, 118.10 (Ar-C), 32.89 (CH₂Ar), 53.28 (NCH₂), 7.47 (CH₃). ¹¹⁹Sn NMR δ -497.52. IR (KBr): ν_{as}(OCO), 1657 cm⁻¹; ν_s(OCO), 1320 cm⁻¹; ν(Sn-C), 554 cm⁻¹; ν(Sn-N), 487 cm⁻¹; ν(Sn-O), 445 cm⁻¹.

2.2.6. [(4-CN-C₆H₄CH₂)₂SnCl₂(2-quin)]⁻(HNEt₃)⁺ (6)

0.47 g, yield 68%, m.p. 214–215 °C. Anal. Calc. for C₃₂H₃₄Cl₂N₄O₂Sn: C, 55.20; H, 4.92; N, 8.05; Sn, 17.05. Found: C, 55.46; H, 5.05; N, 8.16; Sn, 17.13%. ¹H NMR (CDCl₃): δ 11.04 (s, 1H, HNEt₃), 8.70 (1H, d, *J* = 8 Hz, H-3), 8.38 (1H, d, *J* = 8 Hz, H-4), 8.25 (1H, d, *J* = 8 Hz, H-9), 8.12 (1H, d, *J* = 7 Hz, H-6), 8.03 (1H, dd, *J* = 8, 3 Hz, H-8), 7.87 (1H, dd, *J* = 8, 4 Hz, H-7), 6.28–7.30 (8H, m, Ar-H), 2.93 (4H, d, *J*_{Sn-H} = 88 Hz, SnCH₂), 2.77 (6H, q, *J* = 7 Hz, CH₂),

1.23 (9H, t, $J = 7$ Hz, CH₃). ¹³C NMR (CDCl₃): δ 171.84 (COO), 152.26, 137.40, 131.35, 130.68, 129.04, 128.57, 126.74, 126.48, 125.43, 124.65, 123.15, 122.64, 118.45 (Ar–C), 115.87 (CN), 32.67 (CH₂Ar), 53.54 (NCH₂), 7.42 (CH₃). ¹¹⁹Sn NMR δ –492.43. IR (KBr): ν (CN), 2215, $\nu_{\text{as}}(\text{OCO})$, 1642 cm⁻¹; $\nu_{\text{s}}(\text{OCO})$, 1333 cm⁻¹; $\nu(\text{Sn–C})$, 544 cm⁻¹; $\nu(\text{Sn–N})$, 490 cm⁻¹; $\nu(\text{Sn–O})$, 459 cm⁻¹.

2.2.7. [Ph₂SnCl₂(2-quin)]⁻(HNEt₃)⁺ (7)

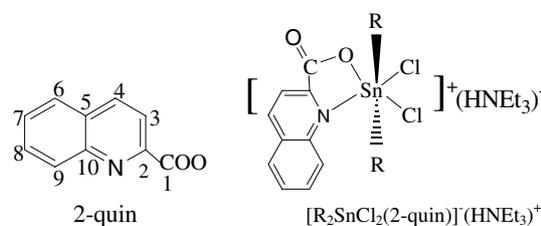
0.48 g, yield 78%, m.p. 185–187 °C. Anal. Calc. for C₂₈H₃₀Cl₂N₂O₂Sn: C, 54.58; H, 4.91; N, 4.55; Sn, 19.26. Found: C, 54.83; H, 5.09; N, 4.48; Sn, 19.19%. ¹H NMR (CDCl₃): δ 11.00 (s, 1H, HNEt₃), 8.84 (1H, d, $J = 7$ Hz, H-3), 8.65 (1H, d, $J = 8$ Hz, H-4), 8.47 (1H, d, $J = 7$ Hz, H-9), 8.31 (1H, d, $J = 6$ Hz, H-6), 8.13 (1H, dd, $J = 7, 4$ Hz, H-8), 8.08 (1H, dd, $J = 7, 4$ Hz, H-7), 6.75–7.65 (10H, m, Ph–H), 2.77 (6H, q, $J = 7$ Hz, CH₂), 1.23 (9H, t, $J = 7$ Hz, CH₃). ¹³C NMR (CDCl₃): δ 172.58 (COO), 149.22, 147.47, 136.21, 131.75, 130.43, 128.76, 126.44, 125.08, 124.74, 123.58, 122.64, 121.33, 118.32 (Ar–C), 54.25 (NCH₂), 7.56 (CH₃). ¹¹⁹Sn NMR δ –498.76. IR (KBr): $\nu_{\text{as}}(\text{OCO})$, 1654 cm⁻¹; $\nu_{\text{s}}(\text{OCO})$, 1348 cm⁻¹; $\nu(\text{Sn–C})$, 491 cm⁻¹; $\nu(\text{Sn–N})$, 457 cm⁻¹; $\nu(\text{Sn–O})$, 435 cm⁻¹.

2.2.8. [(2,4-Cl₂-C₆H₃CH₂)₂SnCl₂(2-quin)]⁻(HNEt₃)⁺ (8)

0.53 g, yield 68%, m.p. 165–166 °C. Anal. Calc. for C₃₀H₃₂Cl₆N₂O₂Sn: C, 45.96; H, 4.11; N, 3.57; Sn, 15.14. Found: C, 45.91; H, 4.27; N, 3.49; Sn, 15.22%. ¹H NMR (CDCl₃): δ 11.21 (s, 1H, HNEt₃), 8.80 (1H, d, $J = 8$ Hz, H-3), 8.63 (1H, d, $J = 7$ Hz, H-4), 8.42 (1H, d, $J = 7$ Hz, H-9), 8.20 (1H, d, $J = 6$ Hz, H-6), 8.04 (1H, dd, $J = 8, 5$ Hz, H-8), 7.97 (1H, dd, $J = 8, 4$ Hz, H-7), 6.55–7.65 (8H, m, Ph–H), 2.98 (4H, d, $J_{\text{Sn–H}} = 89$ Hz, SnCH₂), 2.75 (6H, q, $J = 7$ Hz, CH₂), 1.25 (9H, t, $J = 7$ Hz, CH₃). ¹³C NMR (CDCl₃): δ 174.04 (COO), 152.56, 148.43, 137.02, 133.32, 132.45, 129.34, 128.74, 127.32, 125.98, 126.43, 124.76, 123.45, 120.56, 121.23, 118.80 (Ar–C), 34.49 (CH₂Ar), 54.21 (NCH₂), 7.58 (CH₃). ¹¹⁹Sn NMR δ –491.32. IR (KBr): $\nu_{\text{as}}(\text{OCO})$, 1666 cm⁻¹; $\nu_{\text{s}}(\text{OCO})$, 1339 cm⁻¹; $\nu(\text{Sn–C})$, 568 cm⁻¹; $\nu(\text{Sn–N})$, 488 cm⁻¹; $\nu(\text{Sn–O})$, 457 cm⁻¹ (see Scheme 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 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 K α ($\lambda = 0.71073$ Å) radiation and



Scheme 1.

Table 1
Crystallographic data of compound **8**

Empirical formula	C ₃₀ H ₃₂ Cl ₆ N ₂ O ₂ Sn
Formula weight	783.97
Temperature (K)	273(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	12.358(6)
<i>b</i> (Å)	16.765(7)
<i>c</i> (Å)	16.966(8)
β (°)	110.315(6)
Volume (Å ³)	3297(3)
$\rho_{\text{max}}/\rho_{\text{min}}$ (e Å ⁻³)	0.923/–0.457
<i>Z</i>	4
Calculated density (Mg/m ³)	1.580
<i>F</i> (000)	1576
Crystal size (mm)	0.48 × 0.43 × 0.39
Scan range θ (°)	1.76–25.03
Limiting indices <i>h, k, l</i>	–14 to 13, –19 to 19, –14 to 20
Total/unique/ <i>R</i> _{int}	16,810/5821/0.0285
Goodness-of-fit on F^2	1.001
<i>R</i> ₁ / <i>wR</i> ₂	0.0366/0.1024
μ (mm ⁻¹)	1.785

the $\varphi - \omega$ scan technique. All non-hydrogen atoms were included in the model at their calculated positions. The positions of hydrogen atoms were calculated, and their contributions in structure factor calculations were included.

3. Results and discussions

3.1. Physical properties

Physical data for compounds **1–8** are shown above. All the compounds are colorless crystals. They are soluble in many organic solvents as CCl₄, CHCl₃, C₆H₆, (CH₃)₂CO and C₂H₅OH, but insoluble in hexane, petroleum ether and slightly soluble in water.

3.2. IR data

The infrared spectra of diorganotin(IV) compounds have been recorded and some important assignments are shown above. The $\Delta\nu(\nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2))$ value is used to determine the nature of bonding of carboxylate

to tin(IV) compounds according to the previous report [12]. It is generally believed that the difference in $\Delta\nu$ between asymmetric ($\nu_{as}(\text{CO}_2)$) and symmetric ($\nu_s(\text{CO}_2)$) absorption frequencies below 200 cm^{-1} for the bidentate carboxylate moiety, but greater than 200 cm^{-1} for the unidentate carboxylate moiety [13]. Study shows that the values of $\Delta\nu$ of the complex **1–8** are between 303 and 327 cm^{-1} and this strongly indicate that these eight title compounds adopt unidentate carboxylate structure [14]. Compared with the free ligand the new occurrence of the bands in the region of $482\text{--}491\text{ cm}^{-1}$ for all the eight compounds were assigned to the Sn–N vibrations, and the bands in the region of $435\text{--}462\text{ cm}^{-1}$ were assigned to the Sn–O vibrations according to the literature [15,16].

3.3. ^1H , ^{13}C and ^{119}Sn NMR Spectra

The ^1H NMR of compounds **1–6**, and **8** show that the chemical shifts of the protons of methylene on the benzyl groups exhibit signals at the region $2.91\text{--}3.02\text{ ppm}$ as doublet which are caused by tin (^{119}Sn) hydrogen coupling. And the spin–spin coupling constant $J_{\text{Sn–H}}$ is equal $84\text{--}90\text{ Hz}$. The signals at $7.72\text{--}8.85$ as multiplicity for all the eight compounds are assigned to the protons of 2-quin ligand, which are shifting slightly to the low field compared with the free ligand $7.68\text{--}9.02$.

The ^{13}C NMR spectral of all the compounds shows significant downfield shifts of all carbon resonances compared with the free ligand. The shift may be the consequence of an electron density transfer from the ligand to the acceptor.

The ^{119}Sn chemical shift values in eight compounds are found to be in the range of -490.45 to -498.76 ppm . The appearance of chemical shift values in this region indicates six-coordination environment [17] around the central tin atoms in these complexes.

3.4. X-ray studies of $[(2,4\text{-Cl}_2\text{-C}_6\text{H}_3\text{CH}_2)_2\text{SnCl}_2\text{(2-quin)}_2]^- (\text{HNEt}_3)^+$ (**8**)

The molecular structure of compound **8** is shown in Fig. 1. All hydrogen atoms have been omitted for the purpose of clarity. Table 2 lists selected bond lengths and angles for compound **8**.

Compound **8** consists of $[(2,4\text{-Cl}_2\text{-C}_6\text{H}_3\text{CH}_2)_2\text{SnCl}_2\text{(2-quin)}_2]^-$ anion and the $(\text{HNEt}_3)^+$ cation. The $(\text{HNEt}_3)^+$ cation in general position balances the charge. The tin atom is six-coordinate in a distorted octahedral configuration in $[(2,4\text{-Cl}_2\text{-C}_6\text{H}_3\text{CH}_2)_2\text{SnCl}_2\text{(2-quin)}_2]^-$ anion. The central tin atom is surrounded equatorial by one oxygen and one nitrogen atom from 2-quin ligand and two chlorine atoms and axially by two carbon atoms of the tin-bound 2,4-dichlorobenzyl groups.

In compound **8**, the Sn–O bond length of $2.196(3)\text{ \AA}$ is a little shorter than that in $\{[{}^n\text{Bu}_2\text{Sn}(2\text{-pic})]_2\text{O}\}_2$ [18]

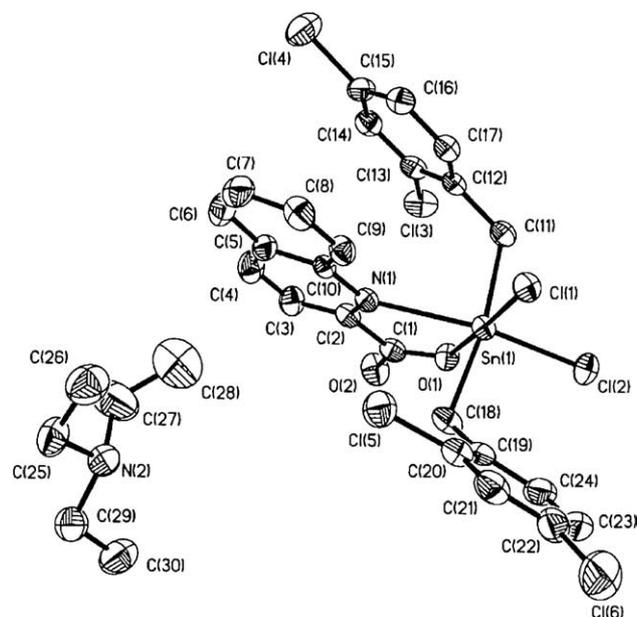


Fig. 1. Molecular structure of compound **8**.

(2.0544 and 2.110 \AA), but a little longer than that of the corresponding distances found in $[(\text{PhCH}_2)_3\text{Sn}(\text{O}_2\text{CC}_5\text{H}_4\text{N}) \cdot (\text{H}_2\text{O})]_n$ [19] ($2.188(4)\text{ \AA}$). The Sn–N bond distance, $2.539(4)\text{ \AA}$, is longer than the sum of the covalent radii of Sn and N (2.15 \AA), but considerably shorter than the sum of the van der Waals radii (3.75 \AA) and should be considered as a bonding interaction, which is similar to other crystal structures of organotin compounds containing the 2-pyridine and 2-quin carboxylate ligands. In the polymer $[\text{Me}_2\text{SnCl}(2\text{-pic})]_n$ [20] the two unique Sn–N bond distances are $2.50(3)$ and $2.47(2)\text{ \AA}$, in the polymer $[\text{Me}_2\text{Sn}(2\text{-pic})_2]_n$ [21] the two Sn–N bond distances are $2.507(4)$ and $2.477(4)\text{ \AA}$ and in $\{[{}^n\text{Bu}_2\text{Sn}(2\text{-pic})]_2\text{O}\}_2$ and $\text{Me}_2\text{Sn}(2\text{-quin})_2$ [18,22] the Sn–N bond distances are $2.550(5)$, $3.150(5)$, $2.594(3)$ and $2.473(4)\text{ \AA}$, respectively. The Sn–Cl bond lengths are $2.5611(14)\text{ \AA}$ for Sn(1)–Cl(1) and $2.4535(16)\text{ \AA}$ for Sn(1)–Cl(2) lying in the range of the normal covalent radii $2.37\text{--}2.60\text{ \AA}$ [23].

In the $(2,4\text{-Cl}_2\text{-C}_6\text{H}_3\text{CH}_2)_2\text{SnCl}_2\text{(2-quin)}_2]^-$ anion, the 2-quin ligand coordinates to the tin atom in bidentate fashion by one carboxyl group oxygen atom and quinoline ring nitrogen atom, which made the angle of oxygen atom and nitrogen atom occupy equatorial place obviously deviating from the standard octahedron angle. For example: the angles of one oxygen atom, one nitrogen atom and two chlorine atoms around Sn(1) atom are O(1)–Sn(1)–N(1) $69.62(11)^\circ$, N(1)–Sn(1)–Cl(1) $108.15(9)^\circ$, Cl(2)–Sn(1)–Cl(1) $95.66(4)^\circ$, O(1)–Sn(1)–Cl(2) $86.56(9)^\circ$. All angles deviate from 90° , but the sum of these angles is 360.02° , which shows that these atoms are in the same plane. Furthermore, the bond angles $177.72(9)^\circ$ for O(1)–Sn(1)–Cl(1), $170.73(19)^\circ$ for C(11)–Sn(1)–C(18) and $156.17(9)^\circ$ for

Table 2
Selected bond distances (Å) and angles (°) for compound **8**

Sn(1)–C(11)	2.169(5)	Sn(1)–C(18)	2.172(5)
Sn(1)–O(1)	2.196(3)	Sn(1)–N(1)	2.539(4)
Sn(1)–Cl(1)	2.5611(14)	Sn(1)–Cl(2)	2.4535(16)
Cl(3)–C(13)	1.744(5)	Cl(4)–C(15)	1.732(55)
Cl(5)–C(20)	1.731(6)	Cl(6)–C(22)	1.728(6)
N(1)–C(2)	1.323(5)	N(1)–C(10)	1.379(6)
N(2)–C(29)	1.484(7)	N(2)–C(25)	1.503(7)
N(2)–C(27)	1.540(9)	O(1)–C(1)	1.270(5)
O(2)–C(1)	1.238(5)	C(1)–C(2)	1.516(6)
C(2)–C(3)	1.386(6)	C(3)–C(4)	1.365(8)
C(11)–Sn(1)–C(18)	170.73(19)	C(11)–Sn(1)–O(1)	90.85(15)
C(18)–Sn(1)–O(1)	86.70(16)	C(11)–Sn(1)–Cl(2)	92.53(14)
C(18)–Sn(1)–Cl(2)	96.24(16)	O(1)–Sn(1)–Cl(2)	86.56(9)
C(11)–Sn(1)–N(1)	87.18(5)	C(18)–Sn(1)–N(1)	83.58(17)
O(1)–Sn(1)–N(1)	69.62(11)	Cl(2)–Sn(1)–N(1)	156.17(9)
C(11)–Sn(1)–Cl(1)	88.57(13)	C(18)–Sn(1)–Cl(1)	93.56(13)
O(1)–Sn(1)–Cl(1)	177.72(9)	Cl(2)–Sn(1)–Cl(1)	95.66(4)
N(1)–Sn(1)–Cl(1)	108.15(9)	C(2)–N(1)–Sn(1)	111.0(3)
C(10)–N(1)–Sn(1)	130.4(3)	C(1)–O(1)–Sn(1)	123.9(3)
C(12)–C(11)–Sn(1)	117.9(3)	C(19)–C(18)–Sn(1)	118.2(3)
O(2)–C(1)–O(1)	123.0(4)	N(1)–C(2)–C(3)	124.6(4)
N(2)–C(29)–C(30)	114.3(5)	C(26)–C(25)–N(2)	115.1(5)

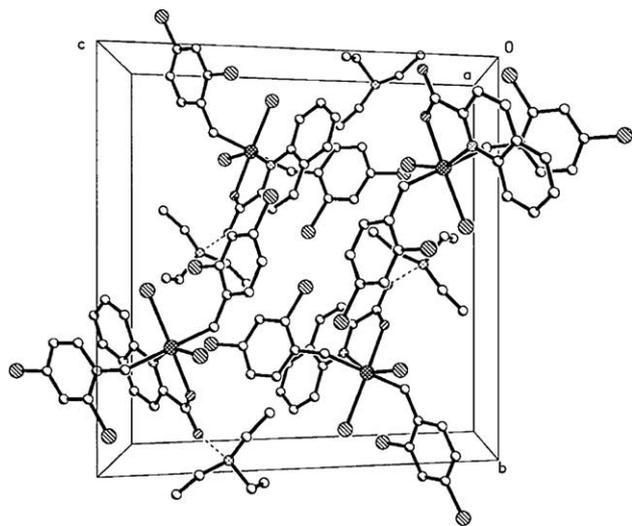


Fig. 2. Projection of compound **8**.

Cl(2)–Sn(1)–N(1) deviate from linear angle 180°, for which the coordination at the tin atom is in a distorted octahedral configuration.

Moreover, the H-bonding exists between the (HNEt₃)⁺ cation and free oxygen atom of carboxyl group as verified by the N(2)–H(2)⋯O(2ⁱ) (*i*: –*x* + 1, *y* + 1/2, –*z* + 1/2) distance of 2.822(6) Å (seen Fig. 2).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 241414 for compound **8**. Cop-

ies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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