

Short Communication

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Synthesis and crystal structure of [2-(menthoxy carbonyl)ethyl]tris(8-quinolinato)tin

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Abstract: In this study, [2-(Menthoxy carbonyl)ethyl]tris(8-quinolinato)tin, $\text{MenOCOCH}_2\text{CH}_2\text{Sn}(\text{Ox})_3$ (Men = Menthyl, HOx = 8-hydroxyquinoline) has been synthesized and characterized by means of elemental analysis, FT-IR, ^1H NMR, and single crystal X-ray diffraction. The tin atom of the monomeric complex is seven-coordinate and possesses $[\text{CN}_3\text{O}_3\text{Sn}]$ pentagonal bipyramidal environment formed by C atom as well as N and O atoms of the chelating Ox ligands. The carbonyl of ester is not coordinated to tin.

Keywords: crystal structure; 8-hydroxyquinoline; 2-(menthoxy carbonyl)ethyltin; organotin.

Introduction

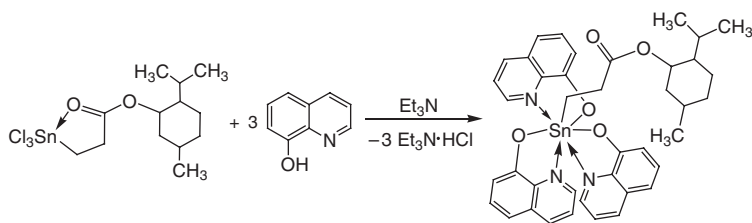
Since their synthesis has been reported 2-alkoxy carbonyl ethyltin trihalides, $\text{ROCOCH}_2\text{CH}_2\text{SnX}_3$ (X = Cl, Br, I) have received considerable attention owing to the variety of coordination geometries of the tin atom (Hutton et al., 1978; Harrison et al., 1979; Howie and Wardell, 2002; Tian et al., 2003, 2005; Lima et al., 2009). Crystal structure determinations and spectra data (Harrison et al., 1979; Maughan et al., 1981; Buchanan et al., 1996; Balasubramanian et al., 1997; Howie and Wardell, 2002; Tian et al., 2003, 2005; Lima et al., 2009; Liu et al., 2015) have shown that the $\text{ROCOCH}_2\text{CH}_2$ unit is a *C,O*-chelating ligand by the intramolecular coordination of carbonyl oxygen to tin atom. However, the coordination can be broken and replaced by the other N and O donors (Maughan et al., 1981; Deb and Ghosh, 1986; Buchanan et al., 1996; Balasubramanian et al., 1997). Meanwhile, 8-Hydroxyquinoline (HOx)

is a *N,O*-chelating ligand and its organotin complexes, $\text{R}_n\text{Sn}(\text{Ox})_{4-n}$ ($n=1-3$), have been widely investigated by X-ray diffraction (XRD) (Ng et al., 1989; Kellö et al., 1995; Schürmann et al., 1999; Szorcsik et al., 2005; Basu Baul et al., 2006, 2008). However, less attention has been paid to mono-organotin complexes $\text{RSn}(\text{Ox})_3$. Thus far, only one X-ray structure of species $\text{RSn}(\text{Ox})_3$ (i.e. $4\text{-ClC}_6\text{H}_4\text{Sn}(\text{Ox})_3$) has been reported in the literature (Schürmann et al., 1999). In order to continue to expand the structural chemistry of $\text{RSn}(\text{Ox})_3$ and compare the coordination strength of $\text{ROCOCH}_2\text{CH}_2$ and Ox to tin atom, we synthesized the complex of 2-(menthoxy carbonyl)ethyltin trichloride with 8-hydroxyquinoline, $\text{MenOCOCH}_2\text{CH}_2\text{Sn}(\text{Ox})_3$, and determined its crystal structure.

In this study, [2-(menthoxy carbonyl)ethyl]tris(8-quinolinato)tin is prepared by the reaction of 2-(menthoxy carbonyl)ethyltin trichloride with 8-hydroxyquinoline in 1 : 3 mole ratio in the presence of triethylamine (Scheme 1). The complex is orange-yellow crystalline, and can be dissolved in common organic solvents, such as benzene, chloroform, methanol, and acetone.

The complex does not show a strong band at around 3200 cm^{-1} assigned to $\nu(\text{OH})$, indicating the deprotonation of the hydroxyl of 8-hydroxyquinoline upon complexation with tin atom (Deb and Ghosh, 1986; Schürmann et al., 1999). This is further confirmed by the appearance of a sharp band at 513 cm^{-1} , which is assigned to the Sn-O stretching vibration and a strong band at 1234 cm^{-1} assigned to C(aryl)-O [Figure 1; C(14)-O(3), C(31)-O(4), and C(9)-O(5)] stretching vibration, which is shifted by 26 cm^{-1} towards high wave-number compared with free 8-hydroxyquinoline ligand (1208 cm^{-1}) (Deb and Ghosh, 1986; Schürmann et al., 1999; Basu Baul et al., 2008). The $\nu(\text{C}=\text{N})$ band (1571 cm^{-1}) of the quinoline ring is shifted towards lower frequencies with respect to the position (1580 cm^{-1}) of the free ligand, confirming the coordination of the aromatic nitrogen to tin atom. Thus, it may be concluded that 8-quinolinato anion chelates to Sn through the coordination by O and N atoms. The carbonyl stretching frequency (1730 cm^{-1}) of [2-(menthoxy carbonyl)ethyl]tris(8-quinolinato)tin appears at a higher wave-number than that (1645 cm^{-1}) in 2-(menthoxy carbonyl)ethyltin

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Scheme 1: Synthesis of the complex.

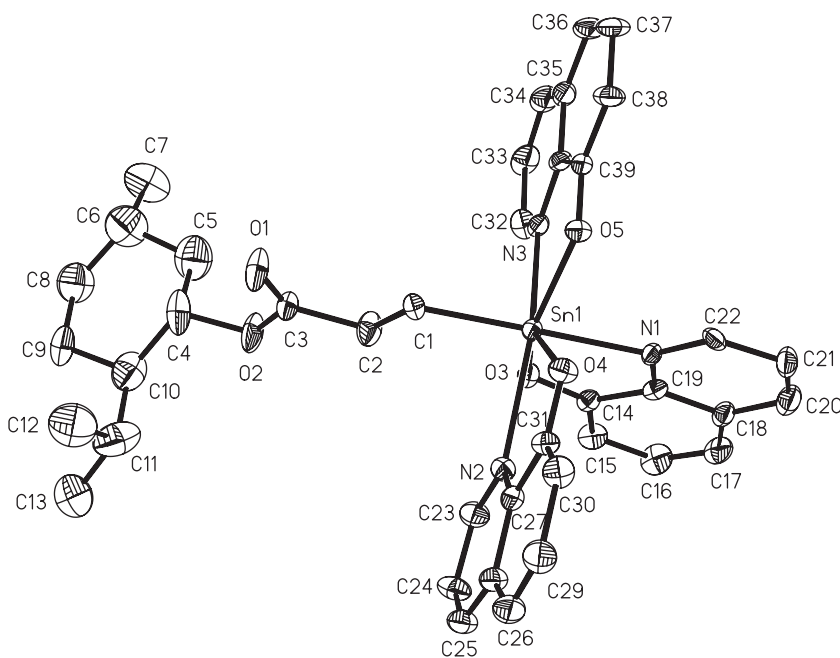


Figure 1: Molecular structure of the MenOCOCH₂CH₂Sn(Ox)₃ complex.

Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

trichloride (Tian et al., 2005), thereby indicating that the intramolecular carbonyl coordination in the parent chloride is cleaved, and that the ester carbonyl is free.

The occurrence of N→Sn in the complex de-shields the protons of the quinoline ring. The protons at the 2- and 4-positions of the quinoline ring are affected most and appear at 9.12 and 8.76 ppm, respectively. The proton resonances of the SnCH₂CH₂COOCH fragment appear at 1.85, 2.77, and 4.62 ppm, respectively, and shift to the higher magnetic field compared with those of 2-(menthoxyacetyl)ethyltin trichloride (2.20, 2.91, and 4.97 ppm, respectively). This indicates that the coordination of carbonyl to tin (CHOC=O→Sn) has been broken and that the shielding of these protons has been recovered.

The complex crystallizes in the $P\bar{1}$ space group, and is a discrete molecule with no close intermolecular contacts (Figure 1). The selected bond lengths and angles are given in Table 1. In the complex, the carbonyl of ester is free and does not involve the coordination to tin atom. The tin atom

is seven-coordinate and possesses the distorted pentagonal bipyramidal geometry. Three Ox ligands are bidentate, and two N and three O atoms yield a pentagonal plane; two Ox ligands lying in the equatorial plane, while the third Ox is perpendicular to the plane with axial N and equatorial O. The axial sites are occupied by the N atom from the third Ox ligand and the C atom of the 2-(menthoxyacetyl)ethyl group. The five bond angles on the pentagonal plane are in the range of 69.8(3)–75.3(3)°, and the bond angle C(1)-Sn(1)-N(1) at the axial position is 172.8(3)°. The Sn(1)-C(1) bond length is 2.104(9) Å, which is slightly shorter than that (2.136(4) Å) of 4-ClC₆H₄Sn(Ox)₃ (Schürmann et al., 1999). The three Sn-O distances are near (from 2.099(7) to 2.128(6) Å), whereas the axial Sn(1)-N(1) bond (2.209(7) Å) is clearly shorter than the equatorial Sn(1)-N(2) (2.486(8) Å) and Sn(1)-N(3) (2.448(8) Å) bonds. The structural feature is similar to that reported in 4-ClC₆H₄Sn(Ox)₃.

In summary, [2-(menthoxyacetyl)ethyl]tris(8-quinolinato)tin has been synthesized and structurally

Table 1: Selected bond lengths (Å) and angles (°).

Bond (Å)			
Sn(1)-C(1)	2.104(9)	Sn(1)-N(1)	2.209(7)
Sn(1)-O(3)	2.128(6)	Sn(1)-N(2)	2.486(8)
Sn(1)-O(4)	2.099(7)	Sn(1)-N(3)	2.448(8)
Sn(1)-O(5)	2.117(6)		
Angles (°)			
O(4)-Sn(1)-C(1)	101.8(3)	C(1)-Sn(1)-N(3)	87.9(3)
O(4)-Sn(1)-O(5)	73.9(2)	O(5)-Sn(1)-N(3)	71.0(3)
C(1)-Sn(1)-O(5)	99.2(3)	O(3)-Sn(1)-N(3)	74.2(3)
O(4)-Sn(1)-O(3)	136.2(3)	N(1)-Sn(1)-N(3)	88.0(2)
C(1)-Sn(1)-O(3)	97.9(3)	O(4)-Sn(1)-N(2)	69.8(3)
O(5)-Sn(1)-O(3)	140.3(2)	C(1)-Sn(1)-N(2)	88.8(3)
O(4)-Sn(1)-N(1)	85.0(3)	O(5)-Sn(1)-N(2)	143.8(3)
C(1)-Sn(1)-N(1)	172.8(3)	O(3)-Sn(1)-N(2)	71.9(3)
O(5)-Sn(1)-N(1)	85.0(3)	N(1)-Sn(1)-N(2)	91.3(3)
O(3)-Sn(1)-N(1)	75.3(3)	N(3)-Sn(1)-N(2)	145.0(3)
O(4)-Sn(1)-N(3)	144.7(3)		

characterized. The intramolecular carbonyl coordination in the substrate has been broken and replaced by the chelating 8-quinolinato ligands. The complex is the second example of mono-organotin tris(8-quinolinates), $R\text{Sn}(\text{Ox})_3$, by X-ray structural characterization, and the first X-ray structure of functionally substituted alkyltin tris(8-quinolinates).

Experimental details

Materials and physical measurements

In this study, 2-(menthoxy carbonyl)ethyltin trichloride was prepared according to the reported method (Tian et al., 2005). The other chemicals (Sinopharm Chemical Reagent Company Limited, Shanghai, China) were of reagent grade and were used without further purification. Carbon, hydrogen, and nitrogen analyses were performed using a Perkin Elmer 2400 Series II elemental analyzer (Perkin Elmer, Waltham, MA, USA). IR spectra were recorded on a Nicolet 470 FT-IR spectrophotometer using KBr discs in the range 4000–400 cm^{-1} (Thermo Nicolet Corporation, Madison, WI, USA). ^1H NMR spectral data were collected using a Bruker Avance 300 FT-NMR spectrometer (Bruker Corporation, Switzerland) with CDCl_3 as solvent and TMS as internal standard.

Synthesis of [2-(menthoxy carbonyl)ethyl]tris(8-quinolinato)tin

A solution of 2-(menthoxy carbonyl)ethyltin trichloride (0.872 g, 2 mmol) in chloroform (30 mL) was added to the solutions of 8-hydroxyquinoline (0.870 g, 6 mmol) and triethylamine (0.606 g, 6 mmol) in chloroform (30 mL) under stirring. The yellow mixture was refluxed for 3 h, after which it was cooled to room temperature and filtered.

The filtrate was evaporated under reduced pressure by a rotary evaporator. The leaving yellow solid was washed with $\text{MeOH-H}_2\text{O}$ (1:1, V/V) and re-crystallized from the chloroform-methanol (1:1, V/V). Yield 1.126 g (73.8%), m.p. 186–187°C. Anal. Found: C, 63.13; H, 5.24; N, 5.54. Calc. for $\text{C}_{40}\text{H}_{41}\text{N}_3\text{O}_5\text{Sn}$: C, 63.01; H, 5.42; N, 5.51%. IR (KBr, ν , cm^{-1}): 1730 (C=O), 1571 (C=N), 1234 (Ar-O), 1191 (C(O)-O), 513 (Sn-O). ^1H NMR (CDCl_3 , δ , ppm): 0.67 (d, $J=7.0$ Hz, 3H, CH_3), 0.78–1.76 (m, 15H, Men), 1.85 (t, $J=7.5$ Hz, 2H, CH_2Sn), 2.77 (t, $J=7.5$ Hz, 2H, COCH_2), 4.62 (dt, $J_{\text{aa}}=11.0$ Hz, $J_{\text{ae}}=4.5$ Hz, 1H, HCO), 7.10–7.52 (m, 4H, Ar-H), 8.76 (d, $J=8.2$ Hz, 1H, H-4), 9.12 (d, $J=4.4$ Hz, 1H, H-2).

Crystal structure determination

The orange single crystal of the complex was obtained from chloroform-hexane (1:1, v/v) by slow evaporation at room temperature. The intensity data were measured at 295(2) K on a Bruker Smart Apex area-detector fitted with graphite monochromatized $\text{Mo-K}\alpha$ radiation (0.71073 Å) using the φ and ω scan technique. The structure was solved by direct method and refined by a full-matrix least squares procedure based on F^2 using the SHELXL-97 (Sheldrick, 2008). The non-hydrogen atoms were refined anisotropically, after which hydrogen atoms were placed at calculated positions. In the complex, the menthyl (C(4)-C(13)) is disordered over two conformations. The site occupancies were refined to 0.75(3):0.25(3). In the refinements, the C-C bonds and 1,3-distances of the disorderly menthyl were restrained to 1.52(1) and 2.50(2) Å, respectively. The crystallographic parameters and refinements are summarized in Table 2. The crystallographic

Table 2: Crystallographic data and structure refinements.

	1
Empirical formula	$\text{C}_{40}\text{H}_{41}\text{N}_3\text{O}_5\text{Sn}$
Formula weight	762.45
Temperature/K	295(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a /(Å)	9.639(3)
b /(Å)	9.821(3)
c /(Å)	20.488(6)
α /(°)	82.298(4)
β /(°)	77.133(4)
γ /(°)	70.307(3)
Volume/Å ³	1776.5(9)
Z	2
D_c /($\text{g}\cdot\text{cm}^{-3}$)	1.425
μ /mm ⁻¹	0.767
$F(000)$	784
θ range (°)	1.02–25.07
Crystal size (mm)	0.21 × 0.13 × 0.04
Tot. reflections	12423
Uniq. Reflections, R_{int}	6195, 0.0695
Reflections with $I > 2\sigma(I)$	3855
Ref. parameters	524
GOF on F^2	1.052
R_1 , wR_2 [$I > 2\sigma(I)$]	0.0789, 0.1791
R_1 , wR_2 (all data)	0.1253, 0.2056
$\Delta\rho_{\text{min}}^*$, $\Delta\rho_{\text{max}}^*/(\text{e}\cdot\text{Å}^{-3})$	–1.328, 1.114

data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1489652.

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