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Synthesis and structural characterization of the complexes of 2-(menthoxycarbonyl)ethyltin chloride

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Abstract: The complexes of 2-(menthoxycarbonyl)ethyltin chloride, MenOCOCH2CH2SnCl3·L (Men = Menthyl, L = benzyl phenyl sulfoxide (bpSO), 1; 2,2'-bipyridine (bpy), 2; 1,10-phenanthroline (phen), 3) and [MenOCOCH,CH,SnCl,(OCH,)], (4), have been synthesized and characterized by means of elemental analysis, FT-IR, NMR (¹H, ¹³C and ¹¹⁹Sn) spectra. The crystal structures of 1, 3 and 4 have been determined by single crystal X-ray diffraction. The tin atoms in 1-4 are all hexa-coordinated. The tin atom in 1 adopts a distorted [CSnCl₂O₃] octahedral geometry with an oxygen atom of the ligand and an intramolecular coordination of the oxygen atom from the carbonyl group to the tin atom. Complex 3 possesses a distorted [CSnCl₃N₃] octahedral geometry with two nitrogen atoms of a chelating phen ligand. The carbonyl oxygen atom of the ester moiety is not coordinating. Compound 4 is a centrosymmetric dimer with a four-membered Sn₂O₂ ring, and the tin atom has a distorted [CSnCl₂O₂] octahedral geometry with an intramolecular C=O→Sn coordination and intermolecular methoxy bridging.

Keywords: organotin; crystal structure; 2,2'-bipyridine; 1,10-phenanthroline 2-(menthoxycarbonyl)ethyltin

1 Introduction

The Lewis acid strengths of the organotin chlorides $R_n SnCl_{(n,n)}$ (n = 1-3) decrease as n increases. When n = 2 or 1, five- or six-coordinate complexes with Lewis bases, such as N- and O-donor ligands, are usually formed via both inter- and intramolecular interactions (Davies, 2004). 2-Alkoxycarbonylethyltin trichlorides, ROCOCH₂CH₂SnCl₂, are functionally substituted alkyltin chlorides, and are readily available from the reactions of CH₂=CHCOOR with SnCl₃ and HCl (Hutton et al., 1978). These compounds have received considerable attention because of the variety of coordination geometries regarding the tin atom (de Morais et al., 2017; Harrison et al., 1979; Howie and Wardell, 2002; Lima et al., 2009; Tian et al., 2005; Tian et al., 2016). Crystal structure determinations and spectra data (Balasubramanian et al., 1997; Buchanan, et al., 1996; Harrison et al., 1979; Howie and Wardell, 2002; Lima et al., 2009; Liu et al., 2015; Maughan et al., 1981; Tian et al., 2005) have shown that the ROCOCH₂CH₂ unit is a *C*,*O*-chelating ligand by the intramolecular coordination of the carbonyl oxygen atom to the tin atom. However, the coordination can be broken and replaced by the other N and O donors (Balasubramanian et al., 1997; Buchanan, et al., 1996; de Morais et al., 2017; Maughan et al., 1981; Tian et al., 2016). In order to continue to expand the structural chemistry of functional alkyltin chlorides, we recently reported the crystal structure of the complexes of 2-(methoxycarbonyl)ethyltin trichloride with HMPA (hexamethylphosphoryltriamide) and phen (Guo et al., 2017). 2-(Menthoxycarbonyl)ethyltin trichloride containing an optically active menthyl group is a potential Lewis acid chiral catalyst, and the reaction with the Lewis base has been not investigated. Herein, we report the synthesis and characterization of the complexes formed by the reaction of MenOCOCH, CH, SnCl, with bpSO, bipy, phen, or py (pyridine) in the methanol.

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2 Results and discussion

2.1 Synthesis

Complexes 1-4 were prepared by the reactions of 2-(menthoxycarbonyl)ethyltin trichloride with the ligand bpSO, bpy, phen or py in 1:1 molar ratio in methanol.

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Scheme 1: Synthesis of the complexes 1 - 4.

When complex was used, the expected MenOCOCH, CH, SnCl, py was not obtained, and compound 4, a methoxide of 2-(menthoxycarbonyl)ethyltin trichloride, was generated (Scheme 1). The complexes are colorless crystalline, and can be dissolved in common organic solvents such as chloroform, methanol, and acetone.

2.2 Spectroscopic analysis

In the IR of 2-(menthoxycarbonyl)ethyltin trichloride, the stretching vibration absorption of intramolecularly coordinated carbonyl is at 1645 cm⁻¹. In 1-4, this band appears at 1645, 1719, 1730, and 1648 cm⁻¹, respectively, indicating that the C=O→Sn coordination is maintained in 1 and 4 and is broken to accommodate two nitrogen atoms of the chelate ligands in 2 and 3. Considerable changes are observed for the ligand vibrations in 1-3. In 1, the v(S=0) at 1035 cm⁻¹ in the free bpSO is shifted to 955 cm⁻¹, and the decreased value can be attributed to the complex formation with tin (Howie et al., 2012; Maughan et al., 1981). In free bpy molecule, the v(C=N) and v(C=C)(ring stretching vibrations) are observed at 1570 and 1420 cm⁻¹. New bands are observed at 1601 and 1446 cm⁻¹ in 2 as a result of complex formation. The out-of-plane C-H bending vibration at 750 cm⁻¹ in free ligand appears at 778 and 729 cm⁻¹ in 2, indicating the bidentate nature of the ligand (Garad et al., 1981). Similar behavior is observed in phen complex 3.

In CHCl, solution (ca. 0.02 mol/L), IR absorption frequency of carbonyl (C=O) in 1-4 is almost the same as in the solid, and is respectively observed at 1649, 1720,

1724, and 1652 cm⁻¹, indicating that in the solution the intramolecular coordination of carbonyl to tin atom still exists in 1 and 4, and the carbonyl is free in 2 and 3.

The assignment of NMR for 1-4 was achieved by examining their chemical shift values, integration values and multiplicity patterns and also by careful comparison of NMR data with the related compounds reported earlier, such as MenOCOCH₂CH₂SnCl₂ (Tian et al., 2005), CH₂COOMen (Lu et al., 2016), bpSO (Wang et al., 2018), $[Ru(bpy)_{3}(4,4'-bpy(COOH)_{3})](PF_{6})_{3}$ (Wang et al., 1999), and (p-CH₂C₂H₂CH₂)₂SnCl₂·phen (Chandrasekar et al., 2015) (see experimental section). The ¹H and ¹³C NMR data also support the presence of C=O→Sn coordination in 1 and 4. The proton resonance of -OCH- (H-4) in the substrate, 1 and 4 that appeared at ~5.0 ppm shows a downfield shift by ~0.3 ppm compared with that of 2 and **3**, and the δ (13 C) values of C=O (C-3) and -OCH- (C-4) in the substrate, 1 and 4 are deshielded by ~8 ppm (C-3) and ~5 ppm (C-4), respectively, relative to those of 2 and 3. The C=O→Sn coordination in the substrate, 1 and 4 causes the deshielding of the ¹H and ¹³C nuclei of the -CHOC=O moiety. However, when the coordination is broken by an external ligand (bpy and phen), the shielding of -CHOC=O is recovered again. In complex 2, the chemical environment of two pyridine rings from the ligand bpy is different due to the rigid chelate ring formed by bpy coordination to the tin atom, so that the pyridine ring displays two sets of ¹H and ¹³C NMR signals (Tian et al., 2018; Van Koten and Noltes, 1976; Wang et al., 1999). The same behavior is also found in phen complex 3. The formation of the complexes is further confirmed by the changes of chemical shifts of the ligands. For example, the δ (1H) value of H-6' (H-6") at

8.59 ppm in free bpy shifts to 9.24 (H-6') and 9.90 (H-6") ppm in 2, and the δ (¹H) value of H-2a (H-2b) at 9.18 ppm in free phen shifts to 9.61 (H-2a) and 10.22 (H-2b) ppm in 3.

The ¹¹⁹Sn chemical shifts (δ) primarily depend on the coordination number and the nature of the donor atom directly bound to the central tin atom. It has been reported that the δ values from +200 to -60 ppm for fourcoordinated, -90 to -190 ppm for five-coordinated and -210 to -400 ppm for six-coordinated tin atoms in solution (Holecek et al., 1986). The complexes 1-4 exhibit a single ¹¹⁹Sn resonance at -332.6, -278.3, -293.7 and -364.5 ppm, respectively, which fall well within the range proposed for six-coordinate tin centres (Airapetvan et al., 2015; Holecek et al., 1986). Thus, the tin atoms in these complexes have six-coordinate environments in CDCl, solution, and it is suggested that compound 4 is an oxygen-bridged dimer in solution (see below X-ray analysis).

2.3 Crystal structure analysis

The molecular structures of 1, 3, and 4 are shown in Figures 1-4. The selected bond lengths and bond angles are listed in Table 1. Complex 1 crystallizes in chiral space group P2,2,2, and is a discrete molecule with no close intermolecular contacts (Figure 1). The complex contains a five-membered chelate ring formed via intramolecular C=O→Sn coordination. The tin atom is hexa-coordinated

with the coordinating atoms C(1), Cl(1), Cl(2), Cl(3), O(1) and O(2) in a distorted octahedral arrangement. The distortion from ideal octahedral geometry is expressed by C(1)-Sn(1)-Cl(3), O(2)-Sn(1)-Cl(2) and O(1)-Sn(1)-C1(1) angles of 156.89(19), 172.72(11) and 174.43(12)°, respectively, deviating from 180°. The interatomic Sn(1)-O(2) distance of 2.403(4) Å) is similar to 2.397(7) Å reported for MenOCOCH₂CH₂SnCl₂ (Tian et al., 2005). The Sn(1)-O(1) distance of 2.259(4) Å is obviously shorter than Sn(1)-O(2) (2.403(4) Å), indicating a stronger S=O→Sn than C=O→Sn interaction (Maughan et al., 1981). In addition, the Sn(1)-O(1) distance is also in agreement with that observed in other organotin sulfoxide complexes, such as Ph₂SnCl₂[(PhCH₂)₂SO]₂ (Sn-O 2.258(4) Å) (Sousa et al., 2009) and [2-(Me₂NCH₂)C₂H₄]SnCl₂[(CH₂)₂SO] (Sn-O 2.253(2) Å) (Varga et al., 2005). Compared with the S(1)-O(1) (1.501(4) Å) in free bpSO (Fuller et al. 2009), the bond in 1 becomes longer (1.513(4) Å), further confirming the formation of S=0-Sn coordination. The Sn-Cl distance lies in the range of 2.3320(18)-2.4310(19) Å, and the Sn(1)-Cl(1) bond involving the ligand O(l) atom trans to Cl(1) atom is the longest. The features are comparable with those found in CH₃OCOCH₂CH₂SnCl₃·O=P[N(CH₃)₂]₃ (Guo et al., 2017), $H_2NCOCH_2CH_2SnCl_3 \cdot O=S(CH_3)_2$ (Howie et al., 2012).

Complex **3** crystallizes in the monoclinic space group P2,, and the asymmetric unit contains two independent molecules which do not differ from each other significantly (Figure 2). The central Sn atom exists in a

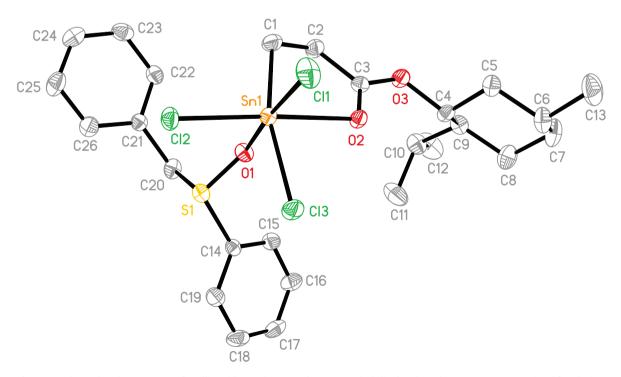


Figure 1: The molecular structure of 1. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

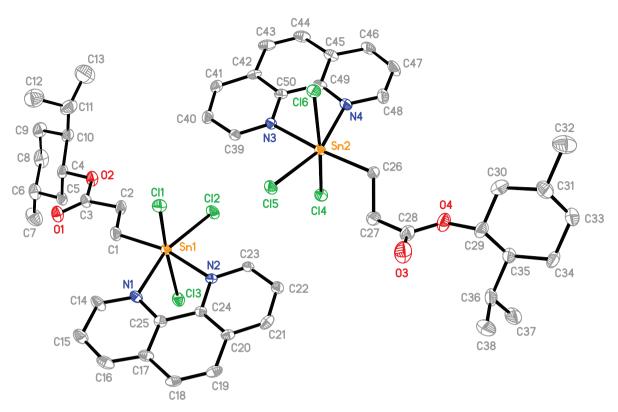


Figure 2: The molecular structure of 3. Ellipsoids are drawn at the 30% probability level. Chloroform and hydrogen atoms are omitted for clarity.

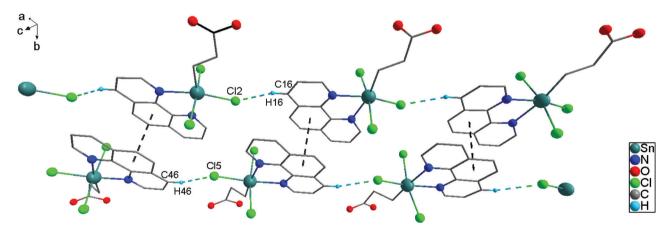


Figure 3: The 1D double-chain supramolecular architecture formed by intermolecular C-H····Cl and π - π stacking interactions. Menthyl and hydrogen atoms except H16 and H46 are omitted for clarity.

distorted octahedral geometry defined by a carbon atom of menthoxycarbonylethyl group, three Cl atoms and the two N atoms from a chelating phen ligand with the axial bond angles of $160.22(17)-173.5(3)^{\circ}$. The distortions from the ideal geometry may be rationalized by the restricted bite angle N(1)-Sn(1)-N(2) (72.5(2)°) and N(3)-Sn(2)-N(4) (73.0(2)°) of the chelate ligand (Guo et al., 2017; Tian et al., 2016,). The five-membered chelate ring formed by the intramolecular C=O \rightarrow Sn coordination in

the substrate $MenOCOCH_2CH_2SnCl_3$ (Tian et al., 2005) has been broken and the carbonyl oxygen atom of the ester moiety is not coordinating $(Sn(1)\cdots O(1)\ 4.905\ \text{Å}$ and $Sn(2)\cdots O(3)\ 5.249(6)\ \text{Å}$). The new five-membered chelate ring consisting of N(1), Sn(1), N(2), C(24) and C(25) or N(3), Sn(2), N(4), C(49) and C(50) is essentially planar, and the maximum deviation from the mean plane is $0.049(3)\ \text{Å}$ for the Sn(1) atom and $0.033(3)\ \text{Å}$ for the Sn(2) atom, respectively. The Sn(1)-N(2) (2.231(6)\ \text{Å}) and Sn(2)-N(3)

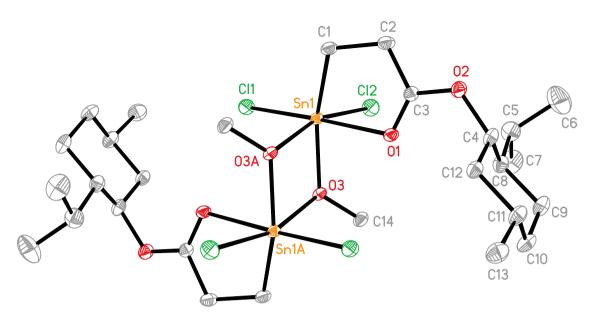


Figure 4: The molecular structure of 4. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. A = -x, -y+1, -z+1.

Table 1: Selected bond lengths (Å) and angles (°) for **1,3** and **4**.

1					
Sn(1)-O(1)	2.259(4)	Sn(1)-C(1)	2.135(7)	Sn(1)-Cl(2)	2.3855(15)
Sn(1)-O(2)	2.403(4)	Sn(1)-Cl(1)	2.4310(19)	Sn(1)-Cl(3)	2.3320(18)
C(1)-Sn(1)-O(1)	82.7(2)	Cl(3)-Sn(1)-Cl(2)	97.26(7)	C(1)-Sn(1)-Cl(1)	96.3(2)
C(1)-Sn(1)-Cl(3)	156.89(19)	C(1)-Sn(1)-O(2)	76.2(2)	O(1)-Sn(1)-Cl(1)	174.43(12)
O(1)-Sn(1)-Cl(3)	86.11(12)	O(1)-Sn(1)-O(2)	83.00(14)	Cl(3)-Sn(1)-Cl(1)	92.80(9)
C(1)-Sn(1)-Cl(2)	102.9(2)	Cl(3)-Sn(1)-O(2)	82.37(11)	Cl(2)-Sn(1)-Cl(1)	95.83(7)
O(1)-Sn(1)-Cl(2)	89.73(11)	Cl(2)-Sn(1)-O(2)	172.72(11)	O(2)-Sn(1)-Cl(1)	91.44(11)
3 · CHCl ₃ Sn(1)-C(1) Sn(1)-N(1) Sn(1)-N(2) Sn(1)-Cl(1) C(1)-Sn(1)-N(2) C(1)-Sn(1)-N(1) N(2)-Sn(1)-N(1) C(1)-Sn(1)-Cl(2) N(2)-Sn(1)-Cl(2) N(1)-Sn(1)-Cl(2) C(1)-Sn(1)-Cl(1) N(2)-Sn(1)-Cl(1) N(1)-Sn(1)-Cl(1)	2.122(8) 2.286(5) 2.231(6) 2.450(2) 165.4(3) 92.9(3) 72.5(2) 104.6(2) 89.99(15) 162.26(18) 95.6(3) 84.64(15) 87.96(16) 93.30(8)	Sn(1)-Cl(2) Sn(1)-Cl(3) Sn(2)-C(26) Sn(2)-N(3) C(1)-Sn(1)-Cl(3) N(2)-Sn(1)-Cl(3) N(1)-Sn(1)-Cl(3) Cl(2)-Sn(1)-Cl(3) Cl(2)-Sn(1)-Cl(3) C(26)-Sn(2)-N(3) C(26)-Sn(2)-N(4) N(3)-Sn(2)-N(4) C(26)-Sn(2)-Cl(5) N(3)-Sn(2)-Cl(5)	2.4111(19) 2.467(2) 2.157(7) 2.256(6) 94.0(3) 84.51(15) 85.35(16) 90.29(8) 168.56(8) 173.5(3) 100.5(3) 73.0(2) 98.4(2) 88.12(15)	Sn(2)-N(4) Sn(2)-Cl(5) Sn(2)-Cl(4) Sn(2)-Cl(6) N(4)-Sn(2)-Cl(5) C(26)-Sn(2)-Cl(4) N(3)-Sn(2)-Cl(4) Cl(5)-Sn(2)-Cl(4) Cl(5)-Sn(2)-Cl(6) N(3)-Sn(2)-Cl(6) N(4)-Sn(2)-Cl(6) Cl(5)-Sn(2)-Cl(6) Cl(5)-Sn(2)-Cl(6) Cl(5)-Sn(2)-Cl(6) Cl(4)-Sn(2)-Cl(6)	2.291(6) 2.4195(17) 2.4493(19) 2.466(2) 160.22(17) 95.5(2) 83.76(16) 89.31(17) 94.71(7) 94.2(2) 85.75(16) 81.77(17) 91.04(8) 167.86(7)
Cl(2)-Sn(1)-Cl(1) 4	93.30(6)	N(3)-311(2)-C1(3)	00.12(13)	Ci(4)-3ii(2)-Ci(0)	107.00(7)
_	2.2(7(2)	C~(1) O(2)#1	2 404(2)	Cn(1) Cl(2)	2 27/2/44)
Sn(1)-O(1) Sn(1)-O(3)	2.367(3) 2.048(3)	Sn(1)-O(3 ^{)#1} Sn(1)-C(1)	2.181(3) 2.147(4)	Sn(1)-Cl(2) Sn(1)-Cl(3)	2.3742(11) 2.4013(12)
` ' ' '	` '	` ' ' ' '		., .,	
0(3)-Sn(1)-C(1)	152.16(15)	$O(3)^{\#1}-Sn(1)-O(1)$	88.84(10)	O(3)-Sn(1)-Cl(2)	92.74(8)
O(3)-Sn(1)-O(3) ^{#1} C(1)-Sn(1)-O(3) ^{#1}	70.59(11) 94.35(15)	O(3)-Sn(1)-Cl(1) C(1)-Sn(1)-Cl(1)	97.47(8)	C(1)-Sn(1)-Cl(2) O(3) ^{#1} -Sn(1)-Cl(2)	99.54(14)
0(3)-Sn(1)-0(1)	80.27(10)	O(3) ^{#1} -Sn(1)-Cl(1)	106.10(12) 90.20(8)	0(3)**-Sn(1)-Cl(2) 0(1)-Sn(1)-Cl(2)	163.04(8) 85.16(8)
C(1)-Sn(1)-O(1)	76.02(13)	0(1)-Sn(1)-Cl(1)	90.20(8) 177.73(7)	Cl(1)-Sn(1)-Cl(2)	95.20(5)

Symmetry code #1: -x, -y+1, -z+1.

(2.256(6) Å) interatomic distances involving the N atom trans to C atom are shorter than the Sn(1)-N(1) (2.286(5) Å) and Sn(2)-N(4) bonds (2.291(6) Å) involving the N atom trans to Cl atom. The distances of six bonds around the tin atom are similar to those found in a closely related complex, CH₃OCOCH₂CH₂SnCl₃ · phen (Guo et al., 2017). An arrangement of the Cl₂N₂C donor atoms in complex 3 is not different from another analogue C, H, CH, SnCl, phen (Hall and Tiekink, 1996). The tin-bound organic group is trans to a nitrogen atom in 3, while it is trans to a chlorine atom in C.H.CH.SnCl. phen. Complex 3 is linked into a onedimensional double-chain supramolecular structure by intermolecular C-H $\cdot \cdot \cdot$ Cl hydrogen bonds (C(16) $\cdot \cdot \cdot$ Cl(2)#1 3.61(1) Å, C(16)-H(16) · · · Cl(2)*1 157.3° and C(46) · · · Cl(5)*2 3.65(2) Å, C(46)-H(46)···Cl(5)** 154.4°, symmetry code #1: x+1, y, z+1; #2: x-1, y, z-1) and $\pi-\pi$ stacking interactions between phenyl rings (dihedral angle = 1.14°) from phen ligand with the centroid-centroid separations of 3.540(2) Å (Glowka et al., 1999) (Figure 3).

Compound 4 exists as a centrosymmetric hexacoordinated dimer with bridging methoxy groups (Figure 4). Each tin atom is coordinated by two chlorine atoms occupying mutually cis-positions, a carbon atom and a carbonyl oxygen atom from the chelating COCH₂CH₃ moiety. The remaining positions in the distorted octahedral coordination geometry about each tin atom are occupied by two μ_{a} -methoxy groups. The major distortions in the tin atom geometries may be traced to the acute angles induced by the Sn,O, ring (O(3)-Sn(1)-O(3A) 70.59(11)°) and five-membered chelate CSnO ring (C(1)-Sn(1)-O(1) 76.02(13)°). The Sn-O distances within the Sn₂O₂ fourmembered ring are not symmetrical, with the bond trans to a carbon atom being shorter (Sn(1)-O(3) 2.048(3) Å) than that *trans* to a chlorine atom (Sn(1A)-O(3) 2.181(3) Å, symmetry code A: -x, -y+1, -z+1), which is comparable with that found in [H₂NCOCH₂CH₂SnCl₂(OCH₂)], (Howie et al., 2011). The Sn(1)-O(1) distance in the five-membered chelate ring is 2.367(3) Å, which is shorter than that (2.403(4) Å) of the hexa-coordinated 1, indicating that the central tin atom in 4 has a stronger Lewis acidity.

3 Conclusion

Four new complexes of 2-(menthoxycarbonyl) ethyltin chloride, MenOCOCH, CH, SnCl, ·L (1-3) and [MenOCOCH₂CH₂SnCl₂(OCH₂)], (4), have been synthesized by the reaction of 2-(menthoxycarbonyl)ethyltin trichloride with pbSO, bpy, phen or py in methanol solution and characterized by NMR spectra and single crystal X-ray diffraction analysis. The tin atoms of the complexes are hexa-coordinated and adopt a distorted octrahedron geometry with [CSnCl₂O₃], [CSnCl₂N₃], and [CSnCl₂O₃], respectively. Compounds 1-3 are molecular addition complexes, and 4 is a centrosymmetric dimer with a four-membered Sn₂O₂ ring. The intramolecular C=O→Sn coordination still exists in 1 and 4, and has been replaced by the chelating bpy and phen ligands, respectively, leaving the carbonyl moieties non-coordinating in 2 and 3.

Experimental

Materials and physical measurements

2-(Menthoxycarbonyl)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 obtained using a Perkin Elmer 2400 Series II elemental analyzer (Perkin Elmer, Waltham, Massachusetts, 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, Wisconsin, USA). ¹H and ¹³C NMR spectral data were collected using a Bruker Avance HD 500 NMR spectrometer (Bruker BioSpin, Switzerland) with CDCl as solvent and TMS as internal standard. 119Sn NMR spectra were recorded in CDCl₂ on a Varian Mercury Vx300 spectrometer using Me Sn external reference (Varian Corporation, USA).

Synthesis of the complexes

A solution of 2-(menthoxycarbonyl)ethyltin trichloride (0.872 g, 2 mmol) in methanol (30 mL) was added to the solutions of the ligand (2 mmol) (for bpSO, 0.432 g; for bpy, 0.312 g; for phen, 0.360 g; for py, 0.158 g) in methanol (30 mL) under stirring. The mixture was heated at reflux for 1 h, and then the solution was concentrated under reduced pressure by a rotary evaporator. The residual solution was cooled to room temperature and filtered. The obtained solid was washed with cold methanol and dried in a vacuum dryer for 12 h. The characterization data of the products are shown below (see Scheme 2):

MenOCOCH, CH, SnCl, · bpSO (1)

Yield 1.069 g (82%), m.p. 106-108°C. Anal. Found: C, 47.23; H, 5.19. Calc. for C₂H₂Cl₂O₂SSn: C, 47.84; H, 5.41%. IR (KBr,

Scheme 2: The numbering scheme in 1-4 for the NMR assignment.

ν, cm⁻¹): 1645 (C=O), 955 (S=O). ¹H NMR (CDCl₂, d, ppm): 0.71 (d, J = 7.0 Hz, 3H, H-13), 0.84 (d, J = 7.0 Hz, 3H, H-12), 0.862.07 (m, 14H, H-1+H-5~H-11), 2.86 (t, J = 7.5 Hz, $J(^{119/117}Sn^{-1}H)$ = 208/198 Hz, 2H, H-2), 4.15 (AB system, d, J = 12.5 Hz, 1H, H-a), 4.31 (AB system, d, J = 12.5 Hz, 1H, H-b), 4.97 (dt, J = 4.5, 11.0 Hz, 1H, H-4), 6.94 (d, J = 7.0 Hz, 2H, o-H), 7.23 (t, J = 7.5 Hz, 2H, m-H), 7.28-7.33 (m, 3H, p-H + o'-H), 7.43 (t, J = 7.5 Hz, 2H, m'-H), 7.50 (t, J = 7.5 Hz, 1H, p'-H). ¹³C NMR (CDCl₃, d, ppm): 30.11 (C-1), 28.73 ($J(^{119/117}Sn^{-13}C) = 78$ Hz, C-2), 181.66 (C-3), 80.25 (C-4), 46.99 (C-5), 23.24 (C-6), 33.86 (C-7), 31.29 (C-8), 40.41 (C-9), 20.60 (C-10), 26.41 (C-11), 21.89 (C-12), 16.28 (C-13); 130.80 (i-C), 128.89 (o-C), 128.55 (m-C), 127.18 (p-C), 137.72 (i'-C), 125.39 (o'-C), 129.23 (m'-C), 132.32 (p'-C), 61.57 (α-C). ¹¹⁹Sn NMR (CDCl₂, d, ppm): -332.6.

MenOCOCH, CH, SnCl, · bpy (2)

Yield 1.055 g (89%), m.p. 194-1195°C. Anal. Found: C, 46.65; H, 5.17, N, 4.69. Calc. for C₂₃H₂₁Cl₃N₂O₂Sn: C, 46.62; H, 5.27; N, 4.73%. IR (KBr, ν, cm⁻¹): 1719 (C=O), 1601, 1446 (C=N+C=C). ¹H NMR $(CDCl_2, d, ppm)$: 0.74 (d, J = 7.0 Hz, d)3H, H-13), 0.83-2.02 (m, 15H, H-5 \sim H-12), 2.43 (t, J = 7.5 Hz, J (119/117Sn-1H) = 104/99 Hz, 2H, H-1), 3.02 (t, J = 7.5 Hz, J $(^{119/117}Sn^{-1}H) = 194/186 Hz$, 2H, H-2), 4.70 (dt, J = 4.5, 11.0 Hz, 1H, H-4), 7.80 (t, J = 6.5 Hz, 1H, H-5'), 7.88 (t, J = 6.5 Hz, 1H, H-5"), 8.23 (t, J = 7.5 Hz, 1H, H-4'), 8.30 (t, J = 7.5 Hz, 1H, H-4''), 8.42 (d, J = 8.0 Hz, 1H, H-3'), 8.46 (d, J = 8.0 Hz, 1H, H-3"), 9.24 (d, J = 5.0 Hz, 1H, H-6"), 9.90 (d, J = 5.0 Hz, 1H, H-6"). ¹³C NMR (CDCl₃, d, ppm): 31.31 (C-1), 30.63 (J(^{119/117}Sn-¹³C) = 46 Hz, C-2), 174.03 (C-3), 74.48 (C-4), 47.01 (C-5), 23.38 (C-6), 34.25 (C-7), 31.43 (C-8), 40.90 (C-9), 20.84 (C-10),

26.06 (C-11), 22.06 (C-12), 16.36 (C-13); 145.34 (C-2'), 145. 98 (C-2"), 127.92 (C-3', C-3"), 142.43 (C-4"), 142.50 (C-4"), 123.02 (C-5'), 123.17 (C-5"), 142.76 (C-6'), 143.25 (C-6"). 119Sn NMR (CDCl₂, d, ppm): -278.3.

MenOCOCH, CH, SnCl, · phen (3)

Yield 1.048 g (85%), m.p. 189-190°C. Anal. Found: C, 48.79; H, 4.96, N, 4.49. Calc. for C₂H₂₁Cl₂N₂O₂Sn: C, 48.70; H, 5.07; N, 4.54%. IR (KBr, ν, cm⁻¹): 1730 (C=O), 1523, 1429 (C=N+C=C). ¹H NMR (CDCl₂, d, ppm): 0.73 (d, J=7.0 Hz, 3H, H-13), 0.83-2.04 (m, 15H, H-5 \sim H-12), 2.54 (t, J = 7.5 Hz, $J(^{119/117}\text{Sn}^{-1}\text{H}) = 108/102 \text{ Hz}, 2\text{H}, \text{H}^{-1}), 3.09 \text{ (t, } J = 7.5 \text{ Hz},$ $J(^{119/117}\text{Sn}^{-1}\text{H}) = 196/185 \text{ Hz}, 2\text{H}, \text{H}^{-2}), 4.72 \text{ (dt, } J = 4.5, 11.0 \text{ Hz},$ 1H, H-4), 8.10 (dd, J = 5.0, 8.0 Hz, 1H, H-3a), 8.15 (dd, J =5.0, 8.0 Hz, 1H, H-3b), 8.16 (s, 2H, H-5a+H-5b), 8.73 (d, J =8.0 Hz, 1H, H-4a), 8.75 (d, J = 8.0 Hz, 1H, H-4b), 9.61(d, J = 5.0 Hz, 1H, H-2a), 10.22 (d, J = 5.0 Hz, 1H, H-2b). ¹³C NMR $(CDCl_{2}, d, ppm)$: 31.17 (C-1), 30.60 $(J(^{119}Sn^{-13}C) = 46 Hz, C-2)$, 174.12 (C-3), 74.46 (C-4), 47.02 (C-5), 23.37 (C-6), 34.26 (C-7), 31.43 (C-8), 40.90 (C-9), 20.83 (C-10), 26.05 (C-11), 22.05 (C-12), 16.35 (C-13); 145.83 (C-2a), 146.30 (C-2b), 126.04 (C-3a, C-3b), 134.18 (C-4a), 135.32 (C-4b), 127.56 (C-5a), 127.79 (C-5b), 129.81 (C-6a, C-6b), 140.92 (C-7a), 141.14 (C-7b). 119Sn NMR (CDCl₂, d, ppm): -293.7.

[(CH₂O)Cl₂SnCH₂CH₂COOMen]₂ (4)

Yield 0.518 g (60%), m.p. 98-99°C. Anal. Found: C, 38.74; H, 5.89. Calc. for $C_{10}H_{26}Cl_2O_3Sn$: C, 38.93; H, 6.07%. IR (KBr,

Table 2: Crystallographic and refinement data of 1,3 and 4.

Compound	1	3 · CHCl ₃	4
Empirical formula	C ₂₆ H ₃₅ Cl ₃ O ₃ SSn	C ₂₆ H ₃₂ Cl ₆ N ₂ O ₂ Sn	C ₂₈ H ₅₂ Cl ₄ O ₆ Sn ₂
Formula weight	652.64	735.93	863.88
Crystal system	Orthorhombic	monoclinic	triclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁	P-1
a /Å	8.0424(6)	8.2101(13)	8.8045(10)
b/Å	10.3818(7)	42.742(7)	10.3430(12)
c/Å	35.337(3)	9.4003(15)	11.6693(14)
α /(°)	90	90	66.019(2)
β /(°)	90	105.545(2)	83.732(2)
γ /(°)	90	90	72.472(2)
Volume /ų	2950.4(4)	3178.0(9)	925.75(19)
Z	4	4	1
$D_{c} / (g \cdot cm^{-3})$	1.469	1.538	1.550
μ / mm ⁻¹	1.233	1.334	1.672
F(000)	1328	1480	436
Crystal size / mm	$0.32\times0.20\times0.02$	$0.35 \times 0.30 \times 0.25$	$0.38 \times 0.22 \times 0.04$
θ range /(°)	2.04 to 26.00	1.91 to 26.00	2.25 to 26.00
Tot. reflections	19018	24106	5848
Uniq. Reflections, R_{int}	5800, 0.0728	12371, 0.0245	3596, 0.0308
Reflections with I>2σ(I)	4420	11499	3338
GOF on F ²	0.981	1.099	1.122
Flack parameter	-0.03(3)	0.06(2)	-
R indices [/>2σ(/)]	R=0.0479, wR=0.0994	R=0.0530, wR=0.1309	R=0.0346, wR=0.0934
R indices (all data)	R=0.0678, wR=0.1075	<i>R</i> =0.0569, <i>wR</i> =0.1331	R=0.0371, wR=0.0949
Δho_{\min} , $\Delta ho_{\max}/(e\cdot \mathring{A}^{-3})$	-0.323, 0.568	-1.757, 0.875	-0.558, 0.783

v, cm⁻¹): IR (KBr): 1648 (C=O), 1222 (C-O), ¹H NMR (CDCl_a, d, ppm): 0.77-2.04 (m, 40H, H-1+H-5~H-13), 2.83 (t, J = 7.5 Hz, $J(^{119/117}Sn^{-1}H) = 194/188 Hz, 4H, H-2), 3.79 (s, J(^{119/117}Sn^{-1}H) =$ 38 Hz, 6H, OCH₂), 5.07 (dt, J = 4.5, 11.0 Hz, 2H, H-4). ¹³C NMR (CDCl₂, d, ppm): 26.43 (C-1), 28.17 (C-2), 182.14 (C-3), 81.71 (C-4), 46.90 (C-5), 23.34 (C-6), 33.97 (C-7), 31.41 (C-8), 40.41 (C-9), 20.72 (C-10), 26.40 (C-11), 21.92 (C-12), 16.42 (C-13), 52.35 (CH₂O). ¹¹⁹Sn NMR (CDCl₂, d, ppm): -364.5.

Crystal structure determination

The colorless single crystals of the complexes were obtained from chloroform or methanol 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 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 F² using the SHELXL-97 (Sheldrick, 2008). The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at calculated positions. In the complex $\mathbf{4}$, the menthyl (C(4)-C(13)) is disordered over two conformations. The site occupancies were refined to 0.517(4):0.483(4). In 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. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1856984-1856986.

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