Syntheses, structures and antitumor activity of four new organotin(IV) carboxylates based on 2-thienylselenoacetic acid

Yuan-Yuan Zhang[a], Ru-Fen Zhang[a], Shao-Liang Zhang[a], Shuang Cheng[b], Qian-Li Li[a], Chun-Lin Ma*[a]

[a]School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, 252059, China.Email: macl856@163.com, macl@lcu.edu.cn

[b]School of Agriculture, Liaocheng University, Liaocheng, 252059, China.

Supporting Information

Table of contents

1. Experimental section……..….....**3**

Scheme S1 The syntheses procedures of complexes **S1**, **S3**……**3**

Synthesis of complexes **S1** and **S3**……..4

2. X-ray crystallography……..…..... **5**

Table S1. Selected bond lengths [Å] and angles [°] for complex **1**……..**5**

Table S2. Selected bond lengths [Å] and angles [°] for complex **2**……..**5**

Table S3. Selected bond lengths [Å] and angles [°] for complex **3**……..**6**

Table S4. Selected bond lengths [Å] and angles [°] for complex **4**……..**6**

Table S5. Crystallographic data and structure refinement parameters for complexes **S1, S3**…..**7**

Table S6. Selected bond lengths [Å] and angles [°] for complex **S1**……**7**

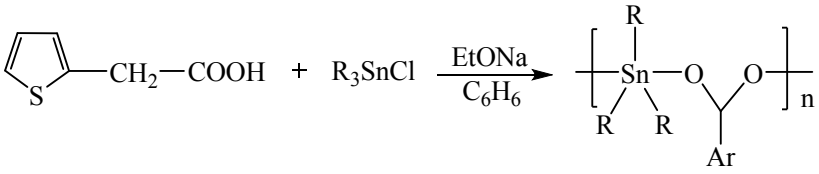
Table S7. Selected bond lengths [Å] and angles [°] for complex **S3**……..…..**8**

3. Figures of crystal structure..……...…….....**9**

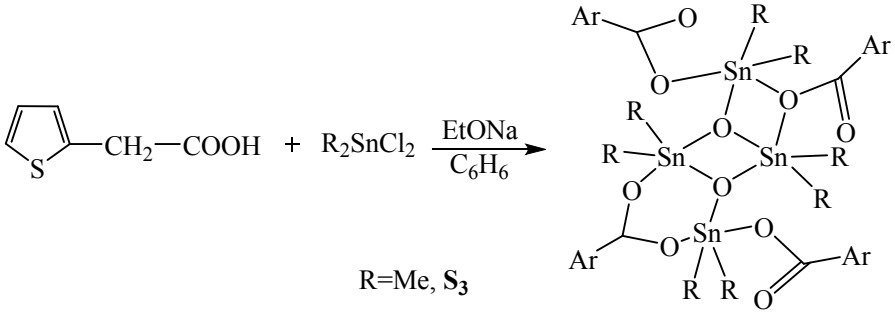
Figure S1. Crystal structure of complex **S1**…….....**9**

Figure S2. Crystal structure of complex **S3**…….....**9**

1. Experimental section



R=Me, **S_1**



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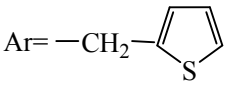

Scheme S1 The syntheses procedures of complexes **S1**, **S3**

Synthesis of complex S1, S3

$[Me_3Sn(O_2CCH_2C_4H_3S\text{-}o)]_n$ **(S1)**: The reaction was carried out under nitrogen atmosphere by use of standard Schlenk techniques. The 2-thiopheneacetic acid (0.142 g, 1.0 mmol) was added to the solution of benzene (30 ml) together with sodium ethoxide (0.068 g, 1.0 mmol), and the mixture was stirred for 0.5 h. Then the trimethyltin chloride (0.199 g,1.0 mmol) was added to the reactor, the mixture was stirred at 50 ℃ for 12 h and then filtered. The solvent was gradually removed by evaporation under reduced pressure until a white powder was obtained. The powder was then recrystallized from ether, and the colorless crystals were recovered. Yield: 60%. M.P. 130-133 ℃. Anal. Calc. for $C_9H_{14}O_2SSn$: C 35.42, H 4.59%; Found: C 35.54, H 4.68%. IR (KBr, cm^{-1}): ν(Sn-O), 478; ν(O-Sn-O), 631; ν(Sn-C), 552; $\nu(COO)_{as}$, 1569; $\nu(COO)_s$, 1372; [$\Delta\nu = \nu(COO)_{as} - \nu(COO)_s$], 197. ^{1}H NMR ($CDCl_3$, ppm): δ 6.96-7.26 (m, 3H, $-C_4H_3S$), 1.55 (s, 2H, $-CH_2$), 0.50 (s, $^2J_{SnH}$ = 70.1 Hz, 9H, $3CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 119.87-132.28 (C_4H_3S), 170.94 (COO), 31.46 (*CH_2*-COO), -1.23 ($^1J_{SnC}$ = 493 Hz, Sn-*CH_3*). ^{119}Sn NMR ($CDCl_3$, ppm): δ -142.4.

$[(Me_2Sn)_4(\mu_3\text{-}O)_2(O_2CCH_2C_4H_3S\text{-}o)_4]$ (**S3**): Complex **S3** was synthesized in a similar way to complex **S1**, by using 2-thiopheneacetic acid (0.142 g, 1.0 mmol), benzene (30 ml), sodium ethoxide (0.068 g, 1.0 mmol), dimethyltin dichloride (0.110 g, 0.5 mmol). The powder was recrystallized from ether, and the colorless crystals of complex **S3** were recovered. Yield: 58%. M.P. 135-138 ℃. Anal. Calc. for $C_{32}H_{44}O_{10}S_4Sn_4$: C 32.22, H 3.69%; Found: C 32.09, H 3.85%. IR (KBr, cm^{-1}): ν(Sn-O), 476; ν(O-Sn-O), 698; ν(Sn-C), 545; $\nu(COO)_{as}$, 1569; $\nu(COO)_s$, 1382; [$\Delta\nu = \nu(COO)_{as} - \nu(COO)_s$], 187. ^{1}H NMR ($CDCl_3$, ppm): δ 6.97-7.26 (m, 12H, $4C_4H_3S$), 1.25 (s, 8H, $4CH_2$), 1.25 (s, $^2J_{SnH}$ = 92.5 Hz, 24H, $8CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 124.80-126.78 (C_4H_3S), 171.23 (COO), 29.71 (*CH_2*-COO), 4.38 ($^1J_{SnC}$ = 824 Hz, Sn-*CH_3*). ^{119}Sn NMR ($CDCl_3$, ppm): δ -175.63, -182.44.

2. X-ray crystallography

Table S1 Selected bond lengths [Å] and angles [°] for complex **1**.

Complex **1**			
Sn(1)-C(7)	2.133(8)	Sn(1)-C(8)	2.114(9)
Sn(1)-C(9)	2.118(8)	Sn(1)-O(1)	2.408(6)
Sn(1)-O(2)#1	2.191(6)	Sn(2)-C(16)	2.120(10)
Sn(2)-C(17)	2.112(8)	Sn(2)-C(18)	2.106(10)
Sn(2)-O(3)	2.384(6)	Sn(2)-O(4)#2	2.174(6)
O(1)-C(6)	1.248(9)	O(2)-C(6)	1.273(10)
O(3)-C(15)	1.236(10)	O(4)-C(15)	1.266(10)
Se(1)-C(4)	1.852(13)	Se(1)-C(5)	1.947(10)
Se(2)-C(13)	1.894(12)	Se(2)-C(14)	1.943(10)
O(2)#1-Sn(1)-O(1)	172.7(2)	C(8)-Sn(1)-C(9)	121.6(4)
C(8)-Sn(1)-C(7)	122.4(4)	C(9)-Sn(1)-C(7)	115.3(4)
O(4)#2-Sn(2)-O(3)	170.7(2)	C(17)-Sn(2)-C(18)	120.9(4)
C(17)-Sn(2)-C(16)	119.4(4)	C(18)-Sn(2)-C(16)	119.2(4)

Symmetry code for complex **1**: #1 -x+1, y-1/2, -z+1/2 #2 -x+2, y+1/2, -z+1/2

Table S2 Selected bond lengths [Å] and angles [°] for complex **2**.

Complex **2**			
Sn(1)-O(1)	2.198(5)	Sn(1)-O(2)	2.388(5)
Sn(1)-C(7)	2.136(6)	Sn(1)-C(13)	2.130(7)
Sn(1)-C(19)	2.145(7)	Se(1)-C(4)	1.905(8)
Se(1)-C(5)	1.973(7)	O(1)-Sn(1)-O(2)	176.16(16)
C(13)-Sn(1)-O(1)	95.0(2)	C(7)-Sn(1)-C(19)	119.4(3)
C(13)-Sn(1)-C(19)	111.3(3)	C(13)-Sn(1)-C(7)	128.6(3)
C(4)-Se(1)-C(5)	99.3(3)	C(6)-C(5)-Se(1)	110.5(5)

Symmetry code for complex **2**: #1 y+1, -x+y+1, -z+2 #2 x-y, x-1, -z+2

Table S3 Selected bond lengths [Å] and angles [°] for complex **3**.

Complex **3**			
Sn(1)-C(9)	2.140(13)	Sn(1)-C(10)	2.140(12)
Sn(1)-O(5)	2.090(6)	Sn(1)-O(5)#1	2.163(6)
Sn(1)-O(2)	2.364(7)	Sn(2)-C(7)	2.149(11)
Sn(2)-C(8)	2.109(10)	Sn(2)-O(5)	2.077(6)
Sn(2)-O(1)	2.326(7)	Sn(2)-O(3)	2.276(8)
Se(1)-C(4)	1.961(12)	Se(1)-C(5)	1.992(11)
Se(2)-C(12)	1.960(13)	Se(2)-C(13)	2.002(15)
C(9)-Sn(1)-C(10)	144.9(6)	O(5)-Sn(1)-C(9)	104.8(4)
O(5)-Sn(1)-O(2)	89.5(3)	O(5)-Sn(1)-O(5)#1	77.5(3)
O(5)#1-Sn(1)-O(2)	166.2(3)	C(8)-Sn(2)-C(7)	153.7(4)
O(5)-Sn(2)-O(3)	77.6(3)	O(5)-Sn(2)-C(8)	105.6(3)
O(5)-Sn(2)-O(1)	93.1(3)	O(3)-Sn(2)-O(1)	170.3(3)
C(8)-Sn(2)-O(3)	93.7(3)	C(4)-Se(1)-C(5)	97.9(5)

Symmetry code for complex **3**: #1 -x+1, -y+2, -z

Table S4 Selected bond lengths [Å] and angles [°] for complex **4**.

Complex **4**			
Sn(1)-O(1)	2.191(6)	Sn(1)-O(4)	2.169(6)
Sn(1)-O(14)	2.083(6)	Sn(1)-O(16)	2.074(6)
Sn(1)-O(18)	2.058(5)	Sn(2)-O(6)	2.143(6)
Sn(2)-O(8)	2.196(6)	Sn(2)-O(15)	2.100(6)
Sn(2)-O(16)	2.112(5)	Sn(2)-O(17)	2.082(5)
Sn(3)-O(10)	2.159(6)	Sn(3)-O(12)	2.165(6)
Sn(3)-O(13)	2.105(6)	Sn(3)-O(17)	2.085(6)
Sn(3)-O(18)	2.120(5)	O(18)-Sn(1)-O(16)	104.3(2)
O(18)-Sn(1)-O(14)	78.3(2)	O(18)-Sn(1)-O(4)	162.0(2)
O(16)-Sn(1)-O(14)	78.5(2)	O(16)-Sn(1)-O(4)	85.3(2)
O(14)-Sn(1)-O(4)	89.0(2)	O(4)-Sn(1)-O(1)	76.9(2)

Table S5 Crystallographic data and structure refinement parameters for complexes **S1**、**S3**

Complex	**S1**	**S3**
Empirical formula	$C_9H_{14}O_2SSn$	$C_{32}H_{44}O_{10}S_4Sn_4$
M	304.95	1191.67
Crystal system	Monoclinic	Triclinic
space group	*P*2(1)/c	*P*-1
a [Å]	9.5306(8)	11.5630(9)
b [Å]	10.1525(9)	13.9921(11)
c [Å]	13.2324(13)	14.0809(12)
α [°]	90	102.954(2)
β [°]	104.104(2)	99.9210(10)
γ [°]	90	95.8710(10)
V [Å^3]	1241.76(19)	2163.3(3)
Z	4	2
Dcalc (Mg/m^3)	1.631	1.829
μ(mm^{-1})	2.197	2.523
F(000)	600	1160
Crystal size(mm)	0.36 x 0.29 x 0.27	0.46 x 0.29 x 0.17
Reflections collected	6078	10976
Unique reflections	2171	7479
R(int)	0.0418	0.0401
Goodness-of-fit on F^2	1.022	1.032
Final R indices [I>2σ(I)]	R_1 = 0.0429	R_1 = 0.0541
	wR_2 = 0.1150	wR_2 = 0.1466
R indices (all data)	R_1 = 0.0562	R_1 = 0.0732
	wR_2 = 0.1247	wR_2 = 0.1614

Table S6 Selected bond lengths [Å] and angles [°] for complex **S1**

Complex **S1**			
Sn(1)-O(1)	2.363(4)	Sn(1)-O(2)#1	2.202(4)
Sn(1)-C(7)	2.105(7)	Sn(1)-C(8)	2.120(6)
Sn(1)-C(9)	2.123(6)	O(1)-Sn(1)-O(2)#1	173.26(14)
C(7)-Sn(1)-O(1)	86.4(2)	C(8)-Sn(1)-O(1)	90.0(2)
C(9)-Sn(1)-O(1)	85.4(2)	C(6)-O(1)-Sn(1)	137.6(4)
C(8)-Sn(1)-C(7)	122.6(3)	C(7)-Sn(1)-C(9)	120.3(3)
C(8)-Sn(1)-C(9)	116.5(3)		

Symmetry code for complex **S1**: #1 -x+1, y-1/2, -z+1/2 #2 -x+1, y+1/2, -z+1/2

Table S7 Selected bond lengths [Å] and angles [°] for complex **S3**

Complex **S3**			
Sn(1)-O(2)	2.200(6)	Sn(1)-O(3)	2.277(6)
Sn(1)-O(5)	2.042(5)	Sn(2)-O(4)	2.248(6)
Sn(2)-O(5)	2.028(5)	Sn(2)-O(6)	2.107(6)
Sn(3)-O(5)	2.181(5)	Sn(3)-O(6)	2.056(6)
Sn(3)-O(8)	2.280(6)	Sn(4)-O(6)	2.026(5)
Sn(4)-O(8)	2.467(7)	Sn(4)-O(9)	2.137(6)
O(5)-Sn(1)-O(2)	79.2(2)	O(5)-Sn(1)-O(3)	89.5(2)
O(2)-Sn(1)-O(3)	168.1(2)	C(25)-Sn(1)-C(26)	149.3(4)
O(5)-Sn(2)-O(6)	75.8(2)	O(5)-Sn(2)-O(4)	87.5(2)
O(6)-Sn(2)-O(4)	162.4(2)	C(29)-Sn(2)-C(30)	131.6(4)
O(6)-Sn(3)-O(5)	73.6(2)	O(6)-Sn(3)-O(8)	72.1(2)
O(5)-Sn(3)-O(8)	145.7(2)	C(27)-Sn(3)-C(28)	141.5(4)
O(6)-Sn(4)-O(8)	68.6(2)	O(9)-Sn(4)-O(8)	149.6(2)
O(6)-Sn(4)-O(9)	81.2(2)	C(32)-Sn(4)-C(31)	139.5(4)

3. Figures of crystal structure

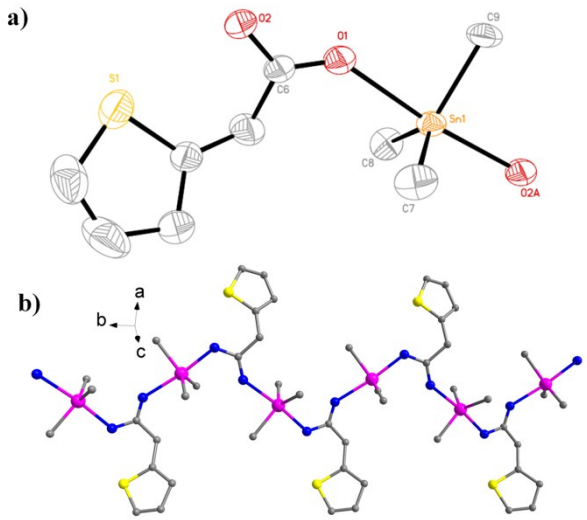

Figure S1 The asymmetry unit (a) and 1D infinite zig-zag chain structure (b) of complex **S1**. Hydrogen atoms are omitted for clarity.

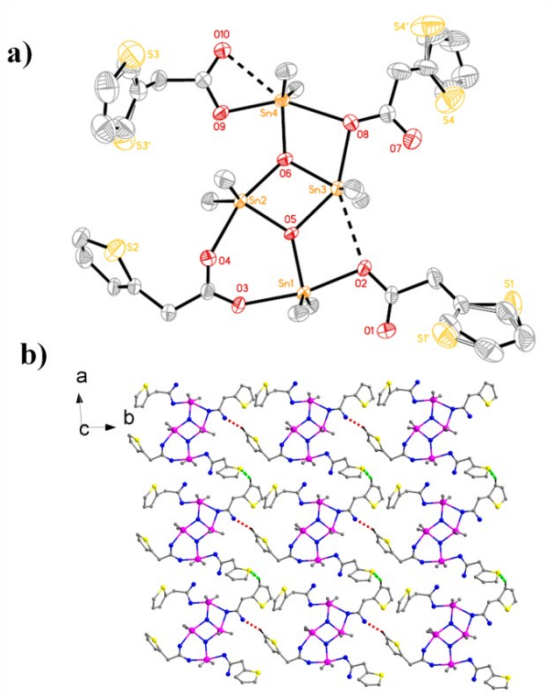

Figure S2 Molecular structure (a) and 1D infinite chain structure connected by C-H···O and C-H···S hydrogen bonding interactions (b) of complex **S3**. Hydrogen atoms are omitted for clarity.