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有机锡 5-甲基/氨基-1*H*-四唑乙酸酯的合成、结构与抗肿瘤活性

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摘要:通过 5-甲基/氨基-1*H*-四唑乙酸与$(R_3Sn)_2O$(R 为苯基或正丁基)及三环已基氢氧化锡的反应,合成了 5 个三有机锡 5-甲基/氨基-1*H*-四唑乙酸酯。通过核磁,红外及 X 射线单晶衍射分析,对这些化合物进行了详细的结构表征。结果表明,这些化合物往往通过分子间的 Sn…N 作用形成配位高分子。初步的生物活性测试表明,这些配合物对 Hela 和 A549 细胞具有明显的体外细胞毒性。

关键词:含氮配体;有机锡羧酸酯;晶体结构;抗肿瘤活性
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Syntheses, Structures and Antitumor Activities of Organotin 5-Methyl/amino-1*H*-tetrazolyl-1-acetates

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Abstract: Five triorganotin 5-methyl-1*H*-tetrazolyl-1-acetates and 5-amino-1*H*-tetrazolyl-1-acetates have been synthesized by the reaction of $(R_3Sn)_2O$ (R=Ph or *n*-Bu) or Cy_3SnOH (Cy=cyclohexyl) with 5-methyl-1*H*-tetrazolyl-1-acetic acid or 5-amino-1*H*-tetrazolyl-1-acetic acid. All the complexes were characterized by elemental analysis, IR and multinuclear NMR (^1H, ^{13}C and ^{119}Sn). Their structures have been confirmed by the X-ray single crystal diffraction analysis, suggesting that they form linkage coordination polymers through the intermolecular Sn…N interactions. The cytotoxic activity of the complexes for Hela and A549 cells was tested, showing that most of them displayed good cytotoxicities for these two cells *in vitro*. CCDC: 1854152, **2**; 1854153, **4**; 1854154, **5**.

Keywords: nitrogen-containing ligand; organotin carboxylate; X-ray crystal structure; antitumor activity

The chemistry of organotin carboxylates has flourished for decades, owing to their remarkable structural diversity[1] and significant biological activity[2-3], for example as antibacterial and antitumor agents, as well as other potential applications in catalysis[4-5]. Recently, carboxylic acids with additional donor atoms have proved their values in the capability of affecting the coordination modes of tin atom as well as decent bioactivities, and therefore attracted a great deal of attention. Lots of organotin carboxylates derived from S- or N-functionalized carboxylic acids have been synthesized and characterized in recent years, which displayed fascinating structural features[6-11] and excellent biological activities[12-15]. On the other hand,

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tetrazole has been extensively exploited as ligand in coordination chemistry because of its variable coordination modes, and its derivatives have prominent versatile biological activities[16-17]. Our previous work showed that organotin derivatives of tetrazolyl-1-acetic acid exhibited considerable structural diversity and good antifungal activity[12,18]. As an extension of our investigations on biologically active organotin derivatives, we herein report the syntheses, structures and antitumor activities *in vitro* of organotin 5-substituted 1*H*-tetrazolyl-1-acetates.

1 Experimental

NMR spectra were obtained with a Bruker 400 spectrometer, and the chemical shifts were reported with respect to reference standards (internal $SiMe_4$ for ^1H and ^{13}C NMR spectra, external $SnMe_4$ for ^{119}Sn NMR). IR spectra were obtained from a Tensor 27 spectrometer as KBr discs. Elemental analyses were carried out on an Elementar Vario EL analyzer. Melting points were measured with an X-4 digital micro melting-point apparatus and were uncorrected. 5-Methyl-1*H*-tetrazolyl-1-acetic acid (L^1) and 5-amino-1*H*-tetrazolyl-1-acetic acid (L^2)[19] were prepared according to the published methods. Organotin oxide and organotin hydroxide are commercially available and used as received without further purification.

1.1 Synthesis of 1

The mixture of 5-methyl-1*H*-tetrazolyl-1-acetic acid (0.28 g, 2 mmol) and $(Ph_3Sn)_2O$ (0.72 g, 1 mmol) in anhydrous benzene (40 mL) was stirred and heated at reflux for 8 h. The reaction mixture was filtered off while hot, and the filtrate was concentrated to give the crude product, which was recrystallized from benzene/hexane to afford colorless crystals of **1**. Yield: 80% (0.79 g), m.p. 96~98 ℃. ^1H NMR ($CDCl_3$): δ 2.34 (s, 3H, CH_3), 5.08 (s, 2H, CH_2), 7.45~7.55 (m, 9H, C_6H_5), 7.60~7.74 (m, 6H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 8.8 (CH_3), 48.5 (CH_2), 128.5, 129.0 ($^3J(^{13}C\text{-}^{119/117}Sn)$=64.3 Hz), 130.9, 136.9 ($^2J(^{13}C\text{-}^{119/117}Sn)$=48.9 Hz) ($C_6H_5$), 152.6 ($CN_4$), 169.9 (COO). ^{119}Sn NMR ($CDCl_3$): δ −82.7. IR (cm^{-1}): ν_{as}(COO) 1 674, ν_s(COO) 1 393. Anal. Calcd. for $C_{22}H_{20}N_4O_2Sn$ (%): C 53.80, H 4.10, N 11.41; Found(%): C 53.99, H 4.31, N 11.07.

1.2 Synthesis of 2

This complex was obtained similarly using tricyclohexyltin hydroxide instead of $(Ph_3Sn)_2O$ as described above for **1**, but in a 1∶1 molar ratio. Yield: 68%, m.p. 133~135 ℃. ^1H NMR ($CDCl_3$): δ 1.24~1.42 (m, 9H), 1.60~1.73 (m, 15H), 1.81~1.98 (m, 9H) (C_6H_{11}), 2.55 (s, 3H, CH_3), 5.06 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 8.9 (CH_3), 26.8, 28.8 ($^3J(^{13}C\text{-}^{119/117}Sn)$=63.8 Hz), 30.9 ($^2J(^{13}C\text{-}^{119/117}Sn)$=14.6 Hz), 34.5, 48.7 ($CH_2$), 152.3 ($CN_4$), 168.8 (COO). ^1H NMR (acetone-d_6): δ 1.11~1.20 (m, 9H), 1.46~1.58 (m, 16H), 1.73~1.80 (m, 8H) (C_6H_{11}), 2.41 (s, 3H, CH_3), 5.10 (s, 2H, CH_2). ^{13}C NMR (acetone-d_6): δ 7.3 (CH_3), 47.8 (CH_2), 26.0 ($^4J(^{13}C\text{-}^{119/117}Sn)$=7 Hz), 28.1, 30.1 ($^2J(^{13}C\text{-}^{119/117}Sn)$=18 Hz), 34.4 ($^1J(^{13}C\text{-}^{119/117}Sn)$=359, 343 Hz) ($C_6H_{11}$), 151.9 ($CN_4$), 168.7 (COO). ^{119}Sn NMR (acetone-d_6): δ 17.7. IR (cm^{-1}): ν_{as}(COO) 1 663, ν_s(COO) 1 351. Anal. Calcd. for $C_{22}H_{38}N_4O_2Sn$ (%): C 51.88, H 7.52, N 11.00; Found(%): C 51.60, H 7.55, N 10.78.

1.3 Synthesis of 3

The mixture of 5-amino-1*H*-tetrazolyl-1-acetic acid (0.29 g, 2 mmol) and $(Ph_3Sn)_2O$ (0.72 g, 1 mmol) in anhydrous benzene (40 mL) was stirred and heated at reflux for 8 h. After cooling to room temperature, the solid was filtered off and recrystallized from acetone/benzene to afford white crystals of **3**. Yield: 66% (0.65 g), m.p. 165~166℃. ^1H NMR (DMSO-d_6): δ 4.79 (s, 2H, CH_2), 6.59 (s, 2H, NH_2), 7.39~7.48 (m, 9H), 7.70~7.92 (m, 6H) (C_6H_5). ^{13}C NMR (DMSO-d_6): δ 47.4 (CH_2), 128.3 ($^3J(^{13}C\text{-}^{119/117}Sn)$=70 Hz), 129.0, 136.2 ($^2J(^{13}C\text{-}^{119/117}Sn)$=47 Hz), 142.5 ($C_6H_5$), 155.8 ($CN_4$), 168.8 (COO). ^{119}Sn NMR (DMSO-d_6): δ −262.2. IR (cm^{-1}): $\nu(NH_2)$ 3 403 and 3 192, ν_{as}(COO) 1 624, ν_s(COO) 1 384. Anal. Calcd. for $C_{21}H_{19}N_5O_2Sn$(%): C 51.25, H 3.89, N 14.23; Found(%): C 51.13, H 4.14, N 14.18.

1.4 Synthesis of 4

This complex was obtained similarly using 5-amino-1*H*-tetrazolyl-1-acetic acid and $(^nBu_3Sn)_2O$ instead of 5-methyl-1*H*-tetrazolyl-1-acetic acid and $(Ph_3Sn)_2O$ as described above for **1**. Yield: 69%, m.p. 113~116 ℃. ^1H NMR (acetone-d_6): δ 0.74 (t, *J*=7.3 Hz, 9H, CH_3), 1.09~1.23 (m, 12H, $CH_2CH_2CH_2CH_3$), 1.40~

1.56 (m, 6H, $SnCH_2$), 4.78 (s, 2H, CH_2), 5.98 (s, 2H, NH_2). ^{13}C NMR (acetone-d_6): δ 13.1 (CH_3), 17.5 ($^1J(^{13}C\text{-}^{119/117}Sn)$=412,394 Hz) ($SnCH_2$), 26.7 ($^3J(^{13}C\text{-}^{119/117}Sn)$=72 Hz) ($CH_2CH_3$), 27.7 ($^2J(^{13}C\text{-}^{119/117}Sn)$=26 Hz) ($SnCH_2CH_2$), 47.4($CH_2$), 156.0($CN_4$), 169.7(COO). ^{119}Sn NMR (acetone-d_6): δ 69.9. IR (cm^{-1}): $\nu(NH_2)$ 3 372 and 3 202, ν_{as}(COO) 1 647, ν_s(COO) 1 376. Anal. Calcd. for $C_{15}H_{31}N_5O_2Sn$ (%): C 41.69, H 7.23, N 16.21; Found(%): C 41.37, H 6.81, N 16.70.

1.5 Synthesis of 5

This complex was obtained similarly using 5-amino-1*H*-tetrazolyl-1-acetic acid and tricyclohexyltin hydroxide instead of 5-methyl-1*H*-tetrazolyl-1-acetic acid and $(Ph_3Sn)_2O$ as described above for **1**, but in a 1:1 molar ratio. Yield: 72%, m.p. 164~166 ℃. ^1H NMR (acetone-d_6): δ 1.11~1.22 (m, 9H), 1.46~1.61 (m, 16H), 1.72~1.82 (m, 8H) (C_6H_{11}), 4.86 (s, 2H, CH_2), 5.91 (s, 2H, NH_2). ^{13}C NMR (acetone-d_6): δ 27.6, 29.9, 31.6 ($^2J(^{13}C\text{-}^{119/117}Sn)$=17 Hz), 35.7 ($^1J(^{13}C\text{-}^{119/117}Sn)$=357, 341 Hz) ($C_6H_{11}$), 48.0 ($CH_2$), 156.9 ($CN_4$), 171.0 (COO). ^{119}Sn NMR (DMSO-d_6): δ −89.9. IR (cm^{-1}): $\nu(NH_2)$ 3 390 and 3 202, ν_{as}(COO) 1 644, ν_s(COO) 1 367. Anal. Calcd. for $C_{21}H_{37}N_5O_2Sn$ (%): C 49.43, H 7.31, N 13.73; Found(%): C 49.27, H 7.37, N 14.15.

1.6 Crystal structure determination

Crystals of **2**, **4** and **5** suitable for X-ray analysis were obtained by slowly cooling their hot acetone/hexane solutions. All intensity data were collected with a Rigaku Saturn diffractometer using Mo $K\alpha$ radiation (λ=0.071 073 nm). The structures were solved by direct methods and difference Fourier map using SHELXS of the SHELXTL package and refined with SHELXL[20] by full-matrix least-squares on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added geometrically and refined with riding model position parameters. The partial cyclohexyl carbons in **2** were disordered, and their occupancy factors were refined to 0.457 for C(18), C(19), C(21) and C(22) as well as 0.543 for C(18)′, C(19)′, C(21)′ and C(22)′. The butyl carbons of C(4)-C(15) in **4** were also disordered, satisfactory results were obtained when they were given occupancy factor of 0.5. A summary of the fundamental crystal data for these three complexes is listed in Table 1.

CCDC: 1854152, **2**; 1854153, **4**; 1854154, **5**

Table 1　Crystallographic data and refinement parameters for complexes 2, 4 and 5

Complex	2	4	5
Formula	$C_{22}H_{38}N_4O_2Sn$	$C_{15}H_{31}N_5O_2Sn$	$C_{21}H_{37}N_5O_2Sn$
Formula weight	509.25	432.14	510.27
Crystal size / mm	0.20×0.20×0.20	0.20×0.18×0.06	0.20×0.20×0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a / nm	1.653 7(1)	1.663 4(3)	1.639 7(2)
b / nm	1.626 0(1)	1.451 4(3)	1.623 7(2)
c / nm	1.967 0(2)	1.835 5(4)	1.950 1(2)
β / (°)	113.223(1)	114.72(3)	114.665(7)
T / K	293(2)	113(2)	293(2)
V / nm^3	4.860 6(7)	4.025 4(2)	4.718 4(9)
Z	8	8	8
D_c / ($g\cdot cm^{-3}$)	1.392	1.426	1.437
θ range / (°)	1.835~25.005	1.945~25.02	3.37~25.01
F(000)	2 112	1 776	2 112
μ / mm^{-1}	1.075	1.285	1.108
Measured reflection	12 647	14 425	17 242
Unique reflection (R_{int})	4 292 (0.070 1)	3 550 (0.091 9)	4 156 (0.068 0)
Observed reflection with [$I\geqslant 2\sigma(I)$]	3 420	2 429	3 119

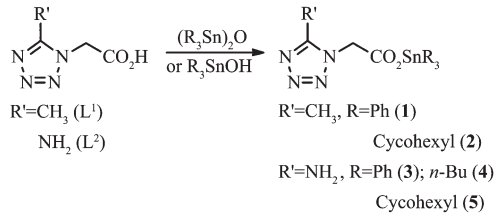
Continued Table 1

Parameter	276	318	270
GOF	1.005	1.073	1.024
Residuals R_1, wR_2	0.035 7, 0.089 1	0.077 4, 0.221 4	0.048 9, 0.097 9

2 Results and discussion

2.1 Syntheses of complexes 1~5

Triorganotin 5-substituted 1*H*-tetrazolyl-1-acetates (**1~5**) were easily obtained by the reaction of organotin oxide or organotin hydroxide with 5-methyl-1*H*-tetrazolyl-1-acetic acid or 5-amino-1*H*-tetrazolyl-1-acetic acid in anhydrous benzene (Scheme 1). The complexes showed significantly different solubility in organic solvents. Complexes **1** and **2** were moderate soluble in chlorinated solvents, while complexes **3~5** were slightly soluble in these solvents. All complexes were soluble in acetone, and very soluble in strong polar solvents such as DMF and DMSO. The complexes have been characterized by IR and NMR (^{1}H, ^{13}C and ^{119}Sn) spectra as well as elemental analyses.



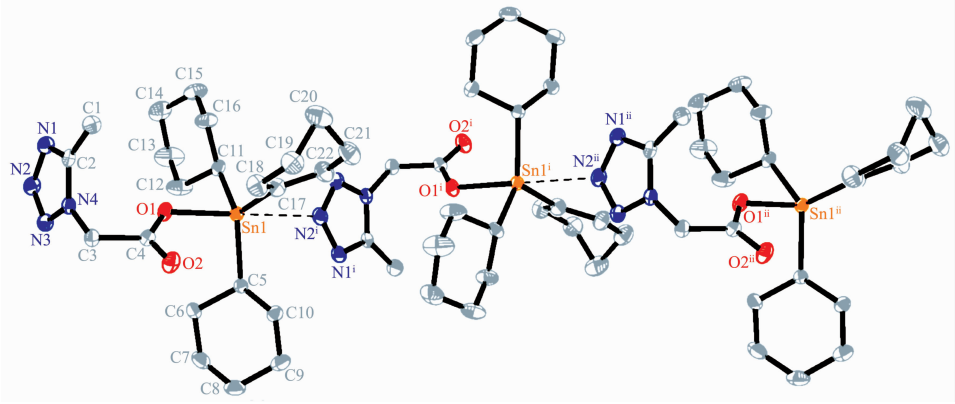
Scheme 1 Syntheses of complexes **1~5**

The IR spectra of complexes **1~5** showed the absence of the strong and broad band ascribed to the carboxyl group as well as the low carbonyl stretching frequencies, which indicated the removal of the carboxyl proton and the formation of the Sn-O bonds[21]. The values of $\Delta\nu(\nu_{as}(COO)-\nu_s(COO))$ for **1~5** were observed in the region of 240~312 cm^{-1}, larger than those detected in the corresponding sodium salts of acids L^1 (216 cm^{-1}) and L^2 (226 cm^{-1}), in which the asymmetric and symmetric stretching vibrations of the carboxylate groups appeared at 1 624 and 1 408 cm^{-1} for L^1, as well as 1 632 and 1 406 cm^{-1} for L^2, respectively, implying the monodentate manner of the carboxylate groups in the complexes to the tin atom[22-23]. The ^{1}H NMR spectroscopic data are also consistent with the suggested structures, exhibiting the expected integral values and chemical shifts. The ^{13}C NMR spectra of **1~5** clearly showed the carbonyl carbon resonances at δ 168.8~171.1. The ^{119}Sn NMR chemical shift of triphenyltin complex **1** (δ −82.7) in $CDCl_3$ solution was in the range of those values for four-coordinated triphenyltin carboxylates[1], suggesting that this complex should be monomeric four-coordinated structure in non-coordinating solvent. Due to the relatively low solubility of other complexes, their satisfactory ^{119}Sn and ^{13}C NMR signals in $CDCl_3$ solution could not be observed. However, the ^{119}Sn NMR values of tricyclohexyltin complex **2** (δ 17.7) and tributyltin complex **4** (δ 69.9) in the weakly coordinating solvent acetone-d_6 were also compared to those values reported in the corresponding four-coordinated tricyclohexyltin and tributyltin carboxylates[1]. These results show that the polymeric structures in solid as shown in Fig.1~3 break down to monomeric structures in solution possibly owing to the weak Sn…N interactions.

2.2 Crystal structures of complexes 2, 4 and 5

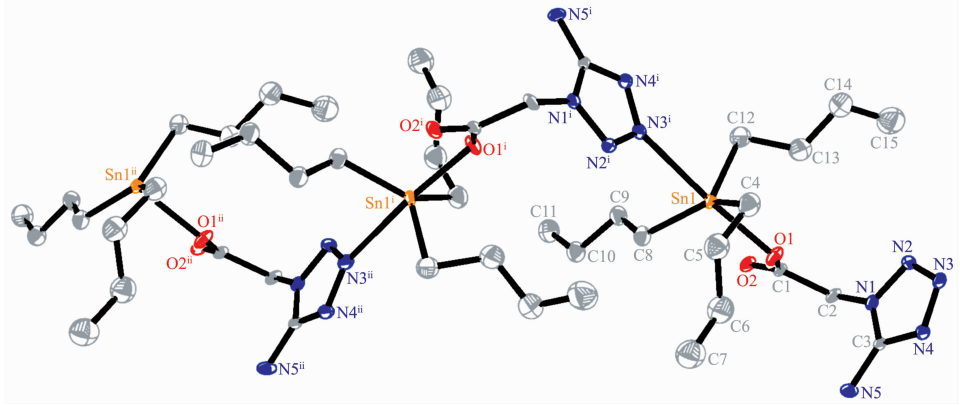
The molecular structures of **2**, **4** and **5** have been confirmed by X-ray crystallography, and presented in Fig.1~3, respectively. The selected bond distances and angles are listed in Table 2. Fig.1~3 show that the carboxylate group exhibits a monodentate coordination mode in the complexes, as above-mentioned by their IR spectra. Furthermore, the complexes form a similar linkage structure through the intermolecular Sn … N interactions. The Sn…N distance is markedly different in these three complexes. The Sn-N distance is 0.257 2(7) nm in **4**, slightly shorter than those in triorganotin derivatives of tetrazolylacetic acid, such as triphenyltin 1*H*-tetrazolyl-1-acetate (0.260 9(6) nm)[12]. The Sn…N distances in **2** (0.281 4(4) nm) and **5** (0.298 9(6) nm) are markedly longer than that in **4**, but similar to that in tricyclohexyltin 1*H*-tetrazolyl-1-acetate (0.292 4(9) nm)[12], indicating that the Sn … N

interactions are very weak in **2** and **5**. The non-bond Sn···O distances are in the range of 0.333 9~0.338 4 nm, markedly longer than the covalent Sn-O bond distances (0.212 7~0.218 5 nm) in these three complexes, but still shorter than the sum of the van der Waals radii for the Sn and O atoms of 0.357 nm[24], suggesting that some weak interactions possibly exist between these two atoms. It is worth pointing out that complexes **4** and **5** form 3D supramolecular architectures through intermolecular N–H···N, N–H···O or C–H···O hydrogen bonds (Supporting Information) owing to the presence of amino group.



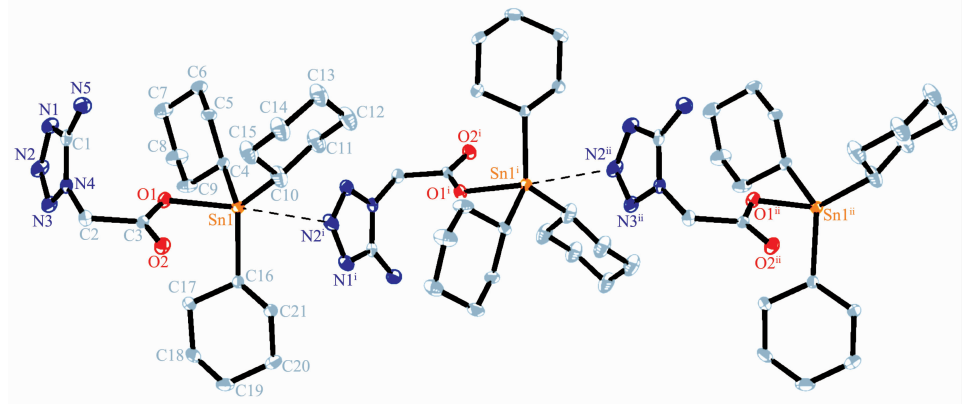
H atoms are omitted for clarity; Symmetry codes: ⁱ 0.5–*x*, 0.5+*y*, 0.5–*z*; ⁱⁱ *x*, 1+*y*, *z*

Fig.1　Molecular structure of **2** with 30% probability displacement ellipsoids



H atoms are omitted for clarity; Symmetry codes: ⁱ 0.5–*x*, 0.5+*y*, 0.5–*z*; ⁱⁱ 0.5+*x*, 1+*y*, *z*

Fig.2　Molecular structure of **4** with 30% probability displacement ellipsoids



H atoms are omitted for clarity; Symmetry codes: ⁱ 0.5–*x*, 0.5+*y*, 0.5–*z*; ⁱⁱ *x*, 1+*y*, *z*

Fig.3　Molecular structure of **5** with 30% probability displacement ellipsoids

Table 2 Selected bond distances (nm) and angles (°) for complexes 2, 4 and 5

Complex **2**					
Sn1-C5	0.214 4(3)	Sn1-O1	0.214 6(2)	Sn1…O2	0.333 9(2)
Sn1…N2^{i}	0.281 4(4)	C4-O1	0.128 8(4)	C4-O2	0.121 9(4)
O1-Sn1-N2^{i}	170.6(2)	C5-Sn1-C11	116.7(1)	C5-Sn1-O1	99.6(1)
C11-Sn1-O1	90.0(1)	O1-C4-O2	126.7(3)	C4-C3-N4	114.0(3)
Complex **4**					
Sn1-C4	0.191(3)	Sn1-O1	0.218 5(6)	Sn1…O2	0.335 0(7)
Sn1-N3^{i}	0.257 2(7)	C1-O1	0.126 9(10)	C1-O2	0.122 4(9)
O1-Sn1-N3^{i}	174.3(2)	C4-Sn1-C8	133.9(9)	C4-Sn1-O1	83.1(9)
C8-Sn1-O1	103.4(8)	O1-C1-O2	127.1(8)	C1-C2-N1	114.0(7)
Complex **5**					
Sn1-C4	0.215 0(5)	Sn1-O1	0.212 7(4)	Sn1…O2	0.338 4(4)
Sn1…N2^{i}	0.298 9(6)	C3-O1	0.128 2(6)	C3-O2	0.121 3(6)
O1-Sn1-N2^{i}	172.2(1)	C4-Sn1-C16	114.9(2)	C4-Sn1-O1	90.3(2)
C10-Sn1-O1	102.3(2)	O1-C3-O2	127.5(5)	C3-C2-N4	114.9(4)

Symmetry codes: ^{i} 0.5−x, 0.5+y, 0.5−z for **2**, **4** and **5**.

2.3 Cytostatic activity evaluation

The cytotoxic activity of complexes **1**~**5** and the free acids (L^1 and L^2) for Hela and A549 cells *in vitro* was assayed by the MTT method[25], and the data of IC_{50} are summarized in Table 3. From these results, it is observed that the free acids have scarcely any activity against Hela and A549 cells, but all complexes except **4** display good activity to these two cells. It is also found that the complexes exhibit higher activity against A549 cells than Hela cells. Moreover, complex **3** exhibits promising result. This complex is even more active against A549 cells than cisplatin supported by its smaller IC_{50} value compared to that of cisplatin.

Table 3 IC_{50} values of complexes 1~5 for HeLa and A549 cells

μmol·L^{-1}

Compound	HeLa	A549
1	12.39±0.38	5.38±0.05
2	12.60±0.20	6.67±0.14
3	10.50±0.40	2.46±0.02
4	84.60±3.77	49.72±1.23
5	20.47±0.73	6.16±0.18
L^1	>200	>200
L^2	>200	>200
Cisplatin	6.86±0.18	4.66±0.07

3 Conclusions

In conclusion, five triorganotin 5-methyl-1*H*-tetrazolyl-1-acetates and 5-amino-1*H*-tetrazolyl-1-acetates have been synthesized and characterized. The crystal structural analyses of three of them reveal that the carboxylate group acts as a monodentate ligand in the complexes, and the complexes form linkage coordination polymers through the intermolecular Sn…N interactions in solid state. Most of the complexes display good cytotoxicities for Hela and A549 cells *in vitro*, especially complex **3** exhibits excellent cytotoxicity for A549 cells.

Supporting information is available at http://www.wjhxxb.cn

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