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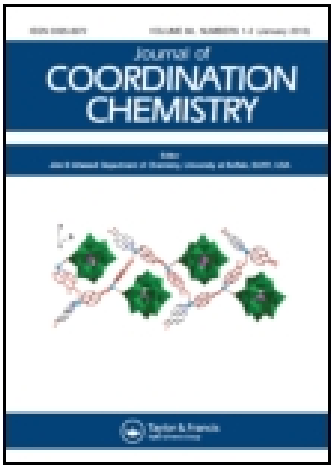

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

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Accepted author version posted online: 21 Feb 2014.Published online: 24 Mar 2014.

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To cite this article: Ru-Fen Zhang, Pei-Zhen Yan, Qian-Li Li & Chun-Lin Ma (2014) Novel μ_2-oxo-bridged dinuclear aryltelluronic triorganotin(IV) esters: syntheses, structural characterizations, and in vitro cytotoxicity, Journal of Coordination Chemistry, 67:4, 649-659, DOI: 10.1080/00958972.2014.897337

To link to this article: http://dx.doi.org/10.1080/00958972.2014.897337

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Journal of Coordination Chemistry, 2014
Vol. 67, No. 4, 649–659, http://dx.doi.org/10.1080/00958972.2014.897337

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Novel μ_2-oxo-bridged dinuclear aryltelluronic triorganotin (IV) esters: syntheses, structural characterizations, and *in vitro* cytotoxicity

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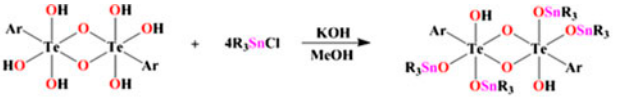
(*Received 4 November 2013; accepted 31 January 2014*)



Ar = 4-n-propyl-Ph, R = Me, **1**; Ar = 4-n-propyl-Ph, R = Ph, **2**;
Ar = 4-i-propyl-Ph, R = Me, **3**; Ar = 4-i-propyl-Ph, R = Ph, **4**.

Four new μ_2-oxo-bridged dinuclear aryltelluronic triorganotin esters $[ArTe(\mu\text{-}O)(OH)(OSnR_3)_2]_2$ (Ar = *n*-propyl-Ph, *R* = Me: **1**, *R* = Ph: **2**; Ar = *i*-propyl-Ph, *R* = Me: **3**, *R* = Ph: **4**) were synthesized by reaction of μ_2-oxo-bridged dinuclear aryltelluronic acids and the corresponding R_3SnCl (*R* = Me, Ph) with potassium hydroxide in methanol. The complexes were characterized by X-ray crystallography, elemental analysis, FT-IR, and NMR (^1H, ^{13}C, ^{119}Sn) spectroscopy. The structural analysis indicates that these complexes are isostructural and crystallized as Sn_4Te_2 molecules, in which the asymmetric four-membered $Te_2(\mu_2\text{-}O)_2$ units are situated in the center. The geometry of tellurium is described as a distorted octahedron and each tin is described as a distorted tetrahedron. Complex **2** has a 2-D network structure connected by intermolecular C–H···π interactions. Complexes **1–4** were tested for *in vitro* cytotoxicity against human lung cancer cells (A549) and human hepatocellular carcinoma cells (HepG2).

Keywords: Organotin(IV); Aryltelluronic acids; X-ray crystallography; Structural characterization; Cytotoxic activity

1. Introduction

Organotin derivatives have attracted attention for structural diversity, various coordination modes, and tumor-inhibiting activities [1–3]. Since antitumor activities of organotin complexes were discovered by Gielen [4], a series of traditional organotin derivatives including organotin carboxylate, organotin phosphonate, organotin sulfonate, and organotin selenate

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have been investigated for their biochemical activities [5–8]. However, only a few complexes of organotin tellurate are involved. According to reports [9], the bioactive properties of tellurium have attracted a lot of interest, since the biochemical mechanisms of tellurium cytotoxicity are beginning to emerge. Some organic tellurium compounds have good effects on the body just as antilipid peroxidation [10], anticarcinoma activity [11], and leukemia cell proliferation inhibition [12]. With these in mind, we turn our attention to incorporate bioactive Te into the structures of organotin complexes to obtain organotin tellurate as a strategy of preparation of new drug candidates in which the metal and the aryltelluronic ligands could act synergistically. Herein, μ_2-oxo-bridged dinuclear aryltelluronic acids were synthesized [13, 14], followed by treatment with triorganotin chloride in a 1 : 4 ratio which successfully afforded dinuclear aryltelluronic triorganotin esters $[ArTe(\mu\text{-}O)(OH)(OSnR_3)_2]_2$ (Ar = *n*-propyl-Ph, *R* = Me: **1**, *R* = Ph: **2**; Ar = *i*-propyl-Ph, *R* = Me: **3**, *R* = Ph: **4**). The complexes were characterized by X-ray crystallography, elemental analysis, FT-IR and NMR (^{1}H, ^{13}C, ^{119}Sn) spectroscopy, and were tested for *in vitro* cytotoxicity against human lung cancer cells (A549) and human hepatocellular carcinoma cells (HepG2).

2. Experimental details

2.1. *Materials and measurements*

Trimethyltin chloride and triphenyltin chloride were commercially available and used without purification. μ_2-oxo-bridged dinuclear aryltelluronic acids were prepared by a standard method [13, 14]. The melting points were obtained with a Kofler micro-melting point apparatus and are uncorrected. Elemental analyses were performed with a PE-2400II apparatus. Infrared spectra were recorded with a Nicolet-5700 spectrometer using KBr disks. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded with a Varian Mercury Plus 400 spectrometer operating at 400, 100.6, and 149.2 MHz, respectively. The spectra were acquired at room temperature (298 K), unless otherwise specified. ^{13}C NMR spectra are broadband-proton-decoupled. The chemical shifts are reported in ppm with respect to the references and are stated relative to external tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR and to tetramethyltin for ^{119}Sn NMR.

2.2. *Syntheses of 1–4*

2.2.1. $[n\text{-}C_3H_7C_6H_5Te(\mu\text{-}O)(OH)(OSnMe_3)_2]_2$ (1). The reaction was carried out under nitrogen by use of standard Schlenk techniques. The μ_2-oxo-bridged dinuclear 4-*n*-propylbenzenetelluronic acid (0.599 g, 1.0 mM) was added to solution of methanol (30 mL) with potassium hydroxide (0.336 g, 4.0 mM), and the mixture was stirred for 0.5 h. After addition of trimethyltin chloride (1.194 g, 4.0 mM), the mixture was stirred at 50 °C for 12 h and then filtered. The solvent was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was then recrystallized from diethyl ether and colorless crystals of **1** were recovered. Yield: 62%. m.p. 181–183 °C. Anal. Calcd for $C_{30}H_{60}O_8Sn_4Te_2$: C, 28.18; H, 4.73%. Found: C, 28.07; H, 4.71%. IR (KBr, cm^{-1}): ν(–OH), 3420; ν(Sn–C), 546; ν(Sn–O), 451; ν(Te–O–Te), 411; ν(Te–O), 697. ^{1}H NMR ($CDCl_3$, ppm): δ 7.85–7.99 (m, 8H, -Ph), 2.95–3.15 (m, 4H, PhCH_2CH$_2$CH$_3$), 1.93–2.21

(m, 4H, $PhCH_2CH_2CH_3$), 0.93 (brs, 6H, $PhCH_2CH_2CH_3$), 0.37 (s, $^2J_{SnH} = 29.20$, 36H, $Sn(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 126.82–131.05 (Ph-C), 34.4 ($PhCH_2CH_2CH_3$), 30.7 ($PhCH_2CH_2CH_3$), 14.3 ($PhCH_2CH_2CH_3$), −5.5 ($^1J_{SnC} = 351.6$ Hz, Sn-CH_3). ^{119}Sn NMR ($CDCl_3$, ppm): δ 115.9, 128.4.

2.2.2. [*n*-$C_3H_7C_6H_5Te(\mu$-O)(OH)$(OSnPh_3)_2]_2$ (2). Complex **2** was prepared in the same method as **1**; triphenyltin chloride (2.313 g, 4.0 mM) was added to 4-*n*-propylbenzenetelluronic acid (0.599 g, 1.0 mM) and potassium hydroxide (0.336 g, 4.0 mM). The reaction mixture was stirred at 50 °C for 12 h and then filtered. The solvent was gradually removed by evaporation under vacuum until the solid product was obtained. Yield: 78%. m.p. 185–187 °C. Anal. Calcd for $C_{90}H_{84}O_8Sn_4Te_2$: C, 53.42; H, 4.18%. Found: C, 53.23; H, 4.20%. IR (KBr, cm^{-1}): ν(–OH), 3430; ν(Sn–C), 546; ν(Sn–O), 450; ν(Te–O–Te), 404; ν(Te–O), 697. ^1H NMR ($CDCl_3$, ppm): δ 6.99–7.67 (m, 68H, -Ph and -Ar), 3.47(t, $J = 6.8$ Hz, 4H, $PhCH_2CH_2CH_3$), 2.17 (brs, 4H, Ph $CH_2CH_2CH_3$), 1.22 (t, 6H, $J = 6.8$ Hz, $PhCH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 128.1–140.9 (Ph-C), 31.1 ($PhCH_2CH_2CH_3$), 29.9 ($PhCH_2CH_2CH_3$), 15.5 ($PhCH_2CH_2CH_3$). ^{119}Sn NMR ($CDCl_3$, ppm): δ −108.2, −114.5.

2.2.3. [*i*-$C_3H_7C_6H_5Te(\mu$-O)(OH)$(OSnMe_3)_2]_2$ (3). Complex **3** was prepared in the same method as **1**. Yield: 57%. m.p. 181–183 °C. Anal. Calcd for $C_{30}H_{60}O_8Sn_4Te_2$: C, 28.18; H, 4.73%. Found: C, 28.07; H, 4.74%. IR (KBr, cm^{-1}): ν(–OH), 3423; ν(Sn–C), 539; ν(Sn–O), 458; ν(Te–O–Te); 408; ν(Te–O), 696. ^1H NMR ($CDCl_3$, ppm): δ 7.79–7.91 (m, 8H, Ph), 2.84–2.94 (m, 2H, $PhCH(CH_3)_2$), 1.19–1.25 (m, 12H, $PhCH(CH_3)_2$), 0.43 (s, $^2J_{SnH} = 18.80$ Hz 36H, $Sn(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 127.13–150.91 (Ph-C), 34.3 ($PhCH(CH_3)_2$), 24.1($PhCH(CH_3)_2$), –6.9 ($^1J_{SnC} = 365.3$ Hz, Sn-CH_3). ^{119}Sn NMR ($CDCl_3$, ppm): δ 115.5, 128.6.

2.2.4. [*i*-$C_3H_7C_6H_5Te(\mu$-O)(OH)$(OSnPh_3)_2]_2$ (4). Complex **4** was prepared in the same method as **2**. Yield: 75%. m.p. 186–188 °C. Anal. Calcd for $C_{90}H_{84}O_8Sn_4$: C, 53.42; H, 4.18%. Found: C, 53.22; H, 4.19%. IR (KBr, cm^{-1}): ν(–OH), 3420; ν(Sn–C), 546; ν(Sn–O), 451; ν(Te–O–Te), 406; ν(Te–O), 697. ^1H NMR ($CDCl_3$, ppm): δ 6.85–7.68 (m, 68H, -Ph and -Ar), 2.81–2.97 (m, 2H, $PhCH(CH_3)_2$), 1.20–1.32 (m, 12H, $PhCH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm): δ 128.2–140.8 (Ph-C), 34.3 ($PhCH(CH_3)_2$), 24.2 ($PhCH(CH_3)_2$), ^{119}Sn NMR ($CDCl_3$, ppm): δ −108.9, −114.8.

2.3. *X-ray crystallographic studies*

Diffraction data were collected with a Smart CCD area detector with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A semiempirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against F^2 by full-matrix least-squares using SHELXL-97 [15]. Hydrogens were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in table 1.

2.4. In vitro *cytotoxicity*

Two tumor cell lines (HepG2 and A549) were used to assay the cytotoxicity of the complexes. Cells were inoculated into 96 well plates, with 1×10^4 cells per well. RPMI-1640

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Table 1. Crystallographic data and structure refinement parameters for **1–4**.

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{30}H_{60}O_8\ Sn_4Te_2$	$C_{90}H_{84}O_8Sn_4Te_2$	$C_{30}H_{60}O_8\ Sn_4Te_2$	$C_{90}H_{84}O_8Sn_4Te_2$
M	1278.74	2023.53	1278.74	2023.53
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P-1*	*C2/c*	*C2/c*	*P-1*
a [Å]	12.5852(12)	27.747(2)	23.453(2)	12.9633(11)
b [Å]	13.1006(11)	17.1201(14)	10.5543(7)	13.2105(12)
c [Å]	15.3229(13)	20.2166(17)	21.3711(19)	14.4040(14)
α [°]	70.4380(10)	90	90	108.972(2)
β [°]	87.396(2)	112.979(2)	113.488(2)	104.4310(10)
γ [°]	73.1190(10)	90	90	96.2190(10)
V [Å^3]	2274.2(3)	8841.4(13)	4851.7(7)	2210.3(3)
Z	2	4	4	1
D_{Calcd} (Mg/m^3)	1.867	1.520	1.751	1.520
μ [mm^{-1}]	3.465	1.815	3.249	1.815
F (0 0 0)	1216	3968	2432	992
Crystal size (mm)	0.64 × 0.38 × 0.32	0.37 × 0.28 × 0.28	0.43 × 0.39 × 0.28	0.42 × 0.35 × 0.26
Reflections collected	14,532	21,961	11,756	10,949
Independent reflections	8023	7805	4277	7600
R_{int}	0.0856	0.0460	0.0549	0.0374
Goodness-of-fit on F^2	1.005	0.801	1.105	1.069
$R_1[I>2\sigma(I)]$, R_1 (all data)	0.0883, 0.1716	0.0462, 0.1088	0.0623, 0.1726	0.0563, 0.1565
$wR_2[I>2\sigma(I)]$, wR_2 (all data)	0.2062, 0.2869	0.0880, 0.1361	0.0912, 0.2039	0.1081, 0.1923

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Sn(1)–O(1)	2.010(14)	Sn(1)–C(14)	2.09(3)
Sn(1)–C(13)	2.09(2)	Sn(1)–C(15)	2.15(2)
Sn(2)–O(3)	2.007(12)	Sn(2)–C(10)	2.12(2)
Sn(2)–C(11)	2.13(2)	Sn(2)–C(12)	2.15(2)
Te(1)–O(3)	1.894(12)	Te(1)–O(1)	1.914(12)
Te(1)–O(4)	1.964(12)	Te(1)–O(2)	1.966(11)
Te(1)–O(2)#1	1.967(10)	Te(1)–C(7)	2.131(17)
O(2)–Te(1)#1	1.967(10)	Te(1)–O(3)–Sn(2)	126.7(7)
O(3)–Te(1)–O(1)	89.4(6)	O(3)–Te(1)–O(4)	89.0(5)
O(1)–Te(1)–O(4)	176.4(6)	O(3)–Te(1)–O(2)	92.0(5)
O(1)–Te(1)–O(2)	90.2(5)	O(4)–Te(1)–O(2)	86.6(5)
O(3)–Te(1)–O(2)#1	171.3(5)	O(1)–Te(1)–O(2)#1	90.3(5)
O(4)–Te(1)–O(2)#1	90.7(5)	O(2)–Te(1)–O(2)#1	79.3(5)
O(3)–Te(1)–C(7)	96.7(6)	O(1)–Te(1)–C(7)	91.2(6)
O(4)–Te(1)–C(7)	92.2(7)	O(2)–Te(1)–C(7)	171.2(6)
O(2)#1–Te(1)–C(7)	92.1(6)	O(3)–Te(1)–Te(1)#1	131.6(4)
O(1)–Te(1)–Te(1)#1	90.3(4)	O(4)–Te(1)–Te(1)#1	88.3(4)
O(2)–Te(1)–Te(1)#1	39.6(3)	O(2)#1–Te(1)–Te(1)#1	39.6(3)
O(1)–Sn(1)–C(14)	97.1(10)	O(1)–Sn(1)–C(13)	108.2(9)
C(14)–Sn(1)–C(13)	114.4(11)	O(1)–Sn(1)–C(15)	108.3(8)
C(14)–Sn(1)–C(15)	114.2(12)	C(13)–Sn(1)–C(15)	113.0(10)
O(3)–Sn(2)–C(10)	105.3(7)	O(3)–Sn(2)–C(11)	100.2(8)
C(10)–Sn(2)–C(11)	109.0(11)	O(3)–Sn(2)–C(12)	110.6(7)
C(10)–Sn(2)–C(12)	118.1(12)	C(11)–Sn(2)–C(12)	112.0(13)
Te(1)–O(1)–Sn(1)	122.6(6)	Te(1)–O(2)–Te(1)#1	100.7(5)

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+2, -z+2$; #2 $-x+1, -y+2, -z+1$.

containing antibiotics (100 μg mL^{-1} streptomycin and 100 U penicillin) and 10% fetal bovine serum were used as the culture medium. After 4 h preincubation of the cells in a

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Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Sn(1)–O(1)	1.994(5)	Sn(1)–C(28)	2.145(9)
Sn(1)–C(34)	2.121(9)	Sn(1)–C(40)	2.156(8)
Sn(2)–O(2)	2.011(5)	Sn(2)–C(22)	2.121(9)
Sn(2)–C(16)	2.130(10)	Sn(2)–C(10)	2.138(8)
Te(1)–O(2)	1.907(5)	Te(1)–O(1)	1.920(5)
Te(1)–O(4)#1	1.956(5)	Te(1)–O(3)	1.962(5)
Te(1)–O(4)	1.972(5)	Te(1)–C(7)	2.118(8)
O(4)–Te(1)#1	1.956(5)	Te(1)–O(2)–Sn(2)	120.9(2)
O(2)–Te(1)–O(1)	89.9(2)	O(2)–Te(1)–O(4)#1	92.8(2)
O(1)–Te(1)–O(4)#1	89.6(2)	O(2)–Te(1)–O(3)	86.4(2)
O(1)–Te(1)–O(3)	175.1(2)	O(4)#1–Te(1)–O(3)	87.4(2)
O(2)–Te(1)–O(4)	171.5(2)	O(1)–Te(1)–O(4)	91.6(2)
O(4)#1–Te(1)–O(4)	78.8(2)	O(3)–Te(1)–O(4)	91.6(2)
O(2)–Te(1)–C(7)	99.8(3)	O(1)–Te(1)–C(7)	92.6(3)
O(4)#1–Te(1)–C(7)	167.3(3)	O(3)–Te(1)–C(7)	91.2(3)
O(4)–Te(1)–C(7)	88.6(3)	O(1)–Sn(1)–C(34)	118.1(3)
O(1)–Sn(1)–C(28)	97.9(3)	C(34)–Sn(1)–C(28)	109.0(4)
O(1)–Sn(1)–C(40)	105.1(3)	C(34)–Sn(1)–C(40)	115.0(4)
C(28)–Sn(1)–C(40)	110.4(4)	O(2)–Sn(2)–C(22)	114.9(3)
O(2)–Sn(2)–C(16)	94.8(4)	C(22)–Sn(2)–C(16)	108.8(4)
O(2)–Sn(2)–C(10)	114.6(3)	C(22)–Sn(2)–C(10)	113.4(3)
C(16)–Sn(2)–C(10)	108.4(4)	Te(1)–O(1)–Sn(1)	126.6(3)

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2, -y+3/2, -z+1$.

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

Sn(1)–O(2)	2.062(9)	Sn(1)–C(14)	2.093(17)
Sn(1)–C(15)	2.109(13)	Sn(1)–C(13)	2.176(17)
Sn(2)–O(3)	2.008(8)	Sn(2)–C(10)	2.109(19)
Sn(2)–C(11)	2.129(19)	Sn(2)–C(12)	2.134(18)
Te(1)–O(2)	1.881(8)	Te(1)–O(3)	1.915(8)
Te(1)–O(4)#1	1.965(8)	Te(1)–O(4)	1.969(8)
Te(1)–O(1)	1.980(8)	Te(1)–C(7)	2.101(13)
O(4)–Te(1)#1	1.965(8)	Te(1)#1–O(4)–Te(1)	101.3(3)
O(2)–Te(1)–O(3)	90.5(4)	O(2)–Te(1)–O(4)#1	92.8(3)
O(3)–Te(1)–O(4)#1	90.1(4)	O(2)–Te(1)–O(4)	171.4(4)
O(3)–Te(1)–O(4)	88.7(3)	O(4)#1–Te(1)–O(4)	78.7(3)
O(2)–Te(1)–O(1)	90.8(4)	O(3)–Te(1)–O(1)	176.8(4)
O(4)#1–Te(1)–O(1)	86.9(3)	O(4)–Te(1)–O(1)	89.7(4)
O(2)–Te(1)–C(7)	96.0(4)	O(3)–Te(1)–C(7)	93.6(4)
O(4)#1–Te(1)–C(7)	170.4(4)	O(4)–Te(1)–C(7)	92.5(4)
O(2)–Sn(1)–C(14)	101.1(6)	O(2)–Sn(1)–C(15)	98.9(5)
C(14)–Sn(1)–C(15)	127.7(7)	O(2)–Sn(1)–C(13)	95.8(6)
C(14)–Sn(1)–C(13)	113.0(8)	C(15)–Sn(1)–C(13)	112.4(7)
O(3)–Sn(2)–C(10)	109.9(6)	O(3)–Sn(2)–C(11)	96.5(6)
C(10)–Sn(2)–C(11)	111.2(9)	O(3)–Sn(2)–C(12)	109.0(6)
C(10)–Sn(2)–C(12)	116.8(10)	C(11)–Sn(2)–C(12)	111.6(8)
Te(1)–O(2)–Sn(1)	128.0(5)	Te(1)–O(3)–Sn(2)	122.1(4)

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+2, -z$.

humidified 5% CO_2 incubator at 37 °C, the complexes were added with final concentration of 1–200 μg mL^{-1}, followed by further incubation for 24 h. Five mg mL^{-1} MTT solution dissolved in PBS was added to each well by administering 10 μL per well. The cells were cultured for another 4 h, then the culture medium was discarded. Finally, 100 μL DMSO was added to each well, mixed, and measured at 570 nm.

Table 5. Selected bond lengths (Å) and angles (°) for **4**.

Te(1)–O(2)	1.895(7)	Te(1)–O(1)	1.899(6)
Te(1)–O(3)#1	1.958(7)	Te(1)–O(4)	1.959(6)
Te(1)–O(3)	1.975(6)	Te(1)–C(1)	2.095(10)
Sn(1)–O(1)	2.000(6)	O(3)–Te(1)#1	1.958(7)
Sn(1)–C(22)	2.120(11)	Sn(1)–C(10)	2.135(10)
Sn(1)–C(16)	2.154(11)	Sn(2)–O(2)	2.021(7)
Sn(2)–C(34)	2.115(11)	Sn(2)–C(40)	2.149(11)
Sn(2)–C(28)	2.156(11)	Te(1)#1–O(3)–Te(1)	101.2(3)
O(2)–Te(1)–O(1)	89.5(3)	O(2)–Te(1)–O(3)#1	171.3(3)
O(1)–Te(1)–O(3)#1	90.4(3)	O(2)–Te(1)–O(4)	87.0(3)
O(1)–Te(1)–O(4)	175.4(3)	O(3)#1–Te(1)–O(4)	92.6(3)
O(2)–Te(1)–O(3)	92.5(3)	O(1)–Te(1)–O(3)	89.4(3)
O(3)#1–Te(1)–O(3)	78.8(3)	O(4)–Te(1)–O(3)	87.8(3)
O(2)–Te(1)–C(1)	98.9(4)	O(1)–Te(1)–C(1)	92.5(4)
O(3)#1–Te(1)–C(1)	89.8(3)	O(4)–Te(1)–C(1)	91.0(4)
O(3)–Te(1)–C(1)	168.5(4)	O(1)–Sn(1)–C(22)	116.9(4)
O(1)–Sn(1)–C(10)	104.4(4)	C(22)–Sn(1)–C(10)	117.0(5)
O(1)–Sn(1)–C(16)	97.3(4)	C(22)–Sn(1)–C(16)	105.8(5)
C(10)–Sn(1)–C(16)	114.1(4)	O(2)–Sn(2)–C(34)	113.9(4)
O(2)–Sn(2)–C(40)	114.8(3)	C(34)–Sn(2)–C(40)	111.0(4)
O(2)–Sn(2)–C(28)	96.1(4)	C(34)–Sn(2)–C(28)	111.7(4)
C(40)–Sn(2)–C(28)	108.3(5)	Te(1)–O(1)–Sn(1)	125.7(3)
Te(1)–O(2)–Sn(2)	123.6(4)		

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+2, -z+1$.

3. Results and discussion

3.1. *Syntheses*

The syntheses of **1–4** are given in scheme 1.

3.2. *General aspects*

The synthesis of μ_2-oxo-bridged dinuclear aryltelluronic acids $[ArTe(O)(OH)_3]_2$ were carried out according to previously reported methods [13, 14]. Complexes **1–4** have been synthesized by corresponding telluronic acid, potassium hydroxide, and triorganotin chloride R_3SnCl in 1 : 6 : 4, 1 : 6 : 6, and 1 : 6 : 8 ratios in methanol, but only four $OSnR_3$ were coordinated. Maybe the space stereo-hindrance effect results in this product. Complexes **1–4** are stable in air and in solution. Crystals suitable for X-ray analysis were obtained by slow evaporation of diethyl ether for **1** and **3**. Crystals of **2** and **4** were obtained by slow evaporation of petroleum ether solution.

3.3. *IR spectra*

IR spectra of **1–4** were recorded 4000–400 cm^{-1}. The stretching frequencies of interest are those associated with the –OH, Sn–C, Sn–O, Te–O, and Te–O–Te groups. The strong absorption at 450–483 cm^{-1}, which is absent in the spectrum of the free ligands, is assigned to Sn–O stretch. Absorptions that appear at 404–412 cm^{-1} are assigned to Te–O–Te vibrations, while the absorption bands that appear at 691–697 cm^{-1} are assigned to Te–O vibrations [16, 17]. The strong absorptions at 3406–3430 cm^{-1} in these spectra are assigned to the vibrations of unreacted OH [16]. All these values are consistent with those detected in a number of organotin(IV)-oxygen derivatives [18, 19].

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3.4. *NMR spectra*

The ^{1}H NMR spectra show signals of the –OH in the spectrum of the ligands are weakened and some are even too weak to be detected in these complexes, revealing removal of some –OH protons, consistent with the IR data. The ^{13}C NMR spectra of the complexes show a significant downfield shift of all carbon resonances compared with the free ligands because of electron-density transfer from the ligands to metal. These data are consistent with the structures of **1–4**.

The ^{119}Sn NMR spectra of complexes can be divided into two groups. One group is between 115.5 and 128.6 ppm (**1** and **3**). As reported [20], δ values for ^{119}Sn NMR spectra from −40 to 200 ppm have been associated with four-coordinate alkyltin centers. Thus, we conclude that **1** and **3** are four coordinate. The other group is between −108.2 and −114.8 ppm (**2** and **4**). According to literature [21], δ for ^{119}Sn NMR spectra in the −60 to −120 ppm range are associated with four-coordinate aryltin centers. Therefore, **2** and **4** are also typically four coordinate.

3.5. *Description of crystal structures of 1–4*

The solid-state structures of **1–4** are depicted in figures 1–4, while selected bond lengths and angles of **1–4** are summarized in tables 2–5, respectively. As can be seen from figures 1–2 and 3–4, the structures of **1–4** are similar, with only small differences in angles and bond lengths. Therefore, we choose **1** as an example to describe the structures of these complexes. The molecular structure of **1** (figure 1) displays an almost planar four-membered Te_2O_2 core. The spatial arrangement of Te(1) is distorted octahedral, the equatorial plane

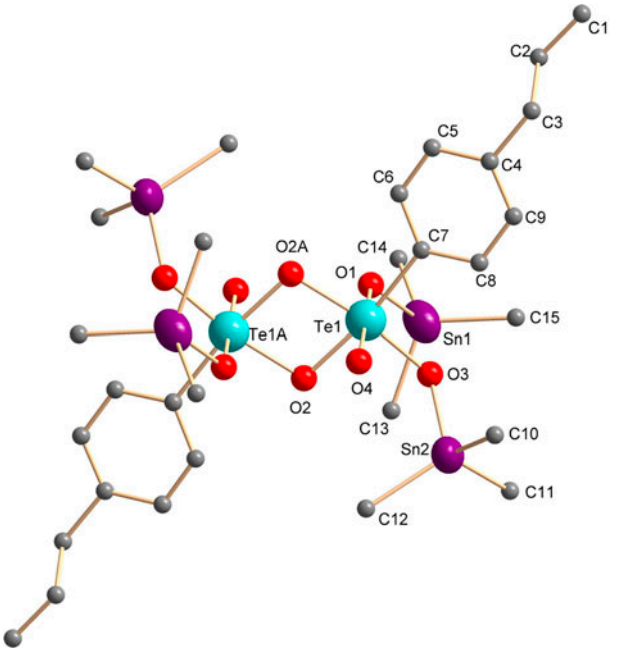

Figure 1. Molecular structure of **1**.

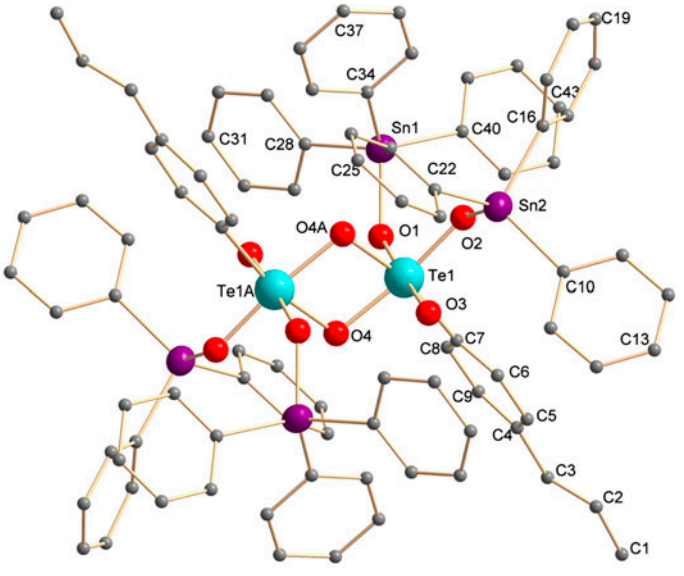

Figure 2. Molecular structure of **2**.

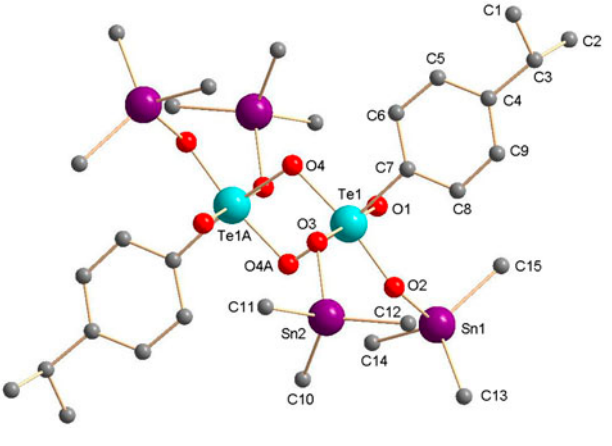

Figure 3. Molecular structure of **3**.

defined by one C from aryl, one O(3) from $OSnR_3$, and two O from Te_2O_2, while the axial positions are occupied by another O(1) from $OSnR_3$ and one O from OH. The sum of the angles subtended at Te(1) (360.1°) in the equatorial plane is typical; the axial-Te(1)-axial angle (176.4(6)°) slightly deviates from the normal angle of 180°, suggesting some distortion from an ideal octahedron. Each tin in **1** forms four primary bonds, three from the methyl carbons and one from bridging O. The bond angles around Sn(1) and Sn(3) range from 97.1(10)° to 118.1(12)°, suggesting distortion from an ideal tetrahedron. Both Sn–O distances [Sn(1)–O(1) 2.010(14) Å, Sn(2)–O(3) 2.007(12) Å] are shorter than the sum of the covalent radii of Sn and O (2.13 Å) [22], and much shorter than the sum of the van der

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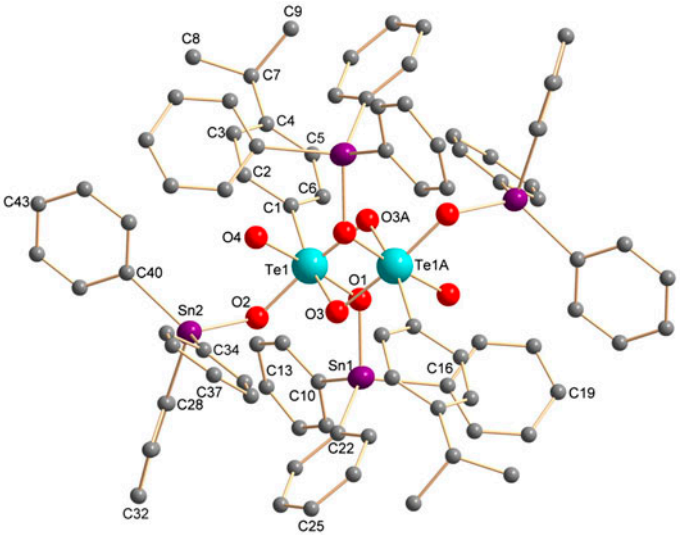

Figure 4. Molecular structure of **4**.

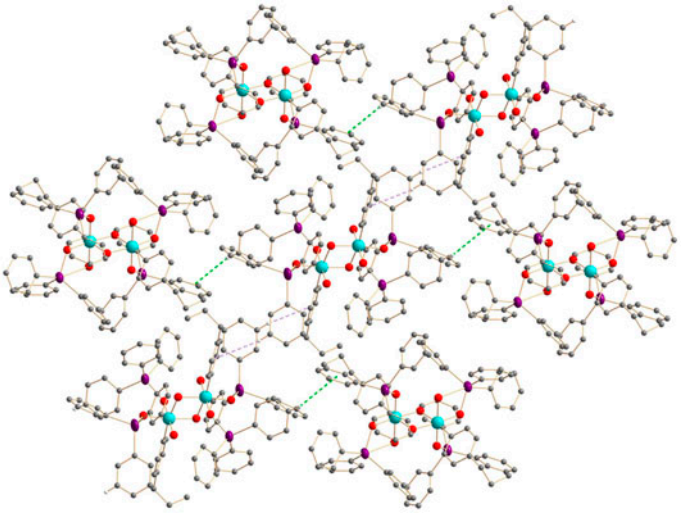

Figure 5. 2-D network structures of **2** with intermolecular C–H···π interactions.

Waals radii 3.69 Å [23], which proves that oxygens are coordinated to Sn by strong chemical bonds. The Sn–C bond lengths [2.09(2)–2.15(2) Å] are consistent with those reported in other triorganotin complexes [24].

As for the four-membered Te_2O_2 core of **1–4**, data are comparable with those reported in the dinuclear m-terphenyltellurinic acid $[2,6\text{-}Mes_2C_6H_3Te(\mu\text{-}O)(OH)]_2$ and the dinuclear m-terphenyltelluronic acid $[2,6\text{-}Mes_2C_6H_3Te(\mu\text{-}O)(OH)_3]_2$ [14], in which the typical Te-(μ-O) single bond lengths of **1–4** (1.956(5)–1.975(6) Å), Te-(μ-O)-Te internal angles

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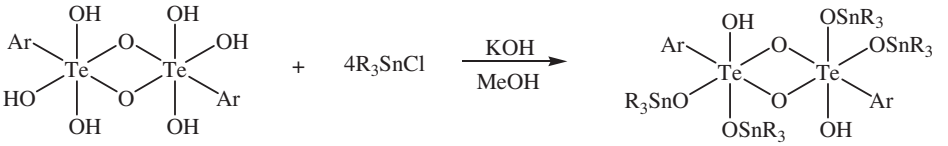

Ar = 4-n-propyl-Ph, R = Me, **1**; Ar = 4-n-propyl-Ph, R = Ph, **2**;
Ar = 4-i-propyl-Ph, R = Me, **3**; Ar = 4-i-propyl-Ph, R = Ph, **4**.

Scheme 1.

between 100.7(2) and 101.3(17)°, and (μ-O)-Te-(μ-O)internal angles between 78.7(3) and 79.3(5)°. The average Te-(μ-O) distance in the four-membered Te_2O_2 ring is 1.966 Å, whereas the terminal Te–O bonds (O from OH) are about 0.003 Å longer, which are significantly shorter than the average 'standard Te–O single bonds' of $[(4\text{-}MeOC_6H_4)_2TeO]_n$ (2.063(2) Å) [25].

In the case of **2**, intramolecular C–H···π interactions lead to a 2-D polymeric assembly, which is shown in figure 5.

3.6. *Cytotoxic activities*

The cytotoxicity *in vitro* of **1–4** and cisplatin against two different cell lines, human lung carcinoma cell line (A549), and human hepatocellular carcinoma cell line (HepG2), have been evaluated by MTT-based assays. The IC_{50} values, calculated from the dose survival curves obtained after 12 h of drug exposure (MTT test), are shown in table 6. As can be seen from table 6, those complexes with R = Ph (**2** and **4**) exhibit strong activity against A549 or HepG2. The IC_{50} values for **2** against A549 and HepG2 are 1.4 and 1.2 μg mL^{-1}, respectively, 7 and 18 times more active than that of cisplatin; **4** against A549 and HepG2 are 8 and 15 times stronger than that of cisplatin, respectively. However, those complexes with R = Me (**1** and **3**) display a little more activity against HepG2 (IC_{50} 15.8, 14.7 μg mL^{-1}) than cisplatin, while exhibiting weaker activity towards A549 than cisplatin. On the basis of the data analysis, the cytotoxic activities of triorganotin(IV) complexes (R = Ph, Me) decrease in the order Ph > Me, which is comparable with the result of the recently reported triorganotin carboxylates [26, 27]. The higher cytotoxic activity of **2** and **4** are presumably due to the presence of phenyls which show high lipophilic character and facilitate binding to biological molecules by $\pi\cdots\pi$ interactions [28, 29]. As the experimental results are preliminary, further study on the cytotoxic activity of these complexes is highly recommended.

Table 6. Half maximal inhibitory concentration (μg mL^{-1}) of **1–4** against tumor cell lines.

	IC_{50} (μg mL^{-1})	
Complex	A549	HepG2
1	65 ± 1	15.8 ± 0.4
2	1.4 ± 0.03	1.2 ± 0.03
3	64 ± 2	14.7 ± 0.4
4	1.2 ± 0.02	1.4 ± 0.03
CPT	10.1 ± 0.5	22 ± 1

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Supplementary material

CCDC 969640 (**1**), 969641 (**2**), 969642 (**3**), and 969643 (**4**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Funding

We thank the National Natural Science Foundation of China [grant number 21371087]; and Natural Science Foundation of Shandong Province [grant numbers ZR2012BM019 and J12LD13] for financial support.

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