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Structural diversity of organotin(IV) complexes self-assembled from hydroxamic acid and mono- or dialkyltin salts

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ABSTRACT

Three hydroxamic acid ligands (HL_1 = acetohydroxamic acid; HL_2 = benzohydroxamic acid; HL_3 = N−phenylbenzohydroxamic acid), have been used to synthesize series of mono- or dialkyltin(IV) complexes, which include (i) the carboxyl acid hybrid five-coordinated dialkyltin complexes $(C_4H_9)_2SnL_1L_4$ (**1**), $[(CH_3)_2SnL_2L_5]\cdot 0.5C_6H_6$ (**2**), (HL_4 = acetic acid; HL_5 = benzoic acid); (ii) the six-coordinated mono-*n*-butyltin complexes $(C_4H_9)SnL_1\cdot Cl_2\cdot H_2O$ (**3**), $(C_4H_9)SnL_2\cdot Cl_2\cdot H_2O$ (**4**), $[(C_4H_9)SnL_3\cdot Cl_2\cdot H_2O]\cdot H_2O$ (**5**), $[(C_4H_9Sn)_2(L_3)_2\cdot Cl_2\cdot (OCH_3)_2]$ (**6**); and (iii) the alkali metal-mingled seven-coordinated mono-*n*-butyltin complexes $[(C_4H_9Sn)_3L_2Na]^+\cdot Cl^-\cdot (CH_3CH_2)_2O$ (**7**), $[(C_4H_9Sn)_3L_2K]^+\cdot Cl^-\cdot CH_2Cl_2$ (**8**). All complexes were characterized by elemental analyses, IR, ^1H, ^{13}C, ^{119}Sn NMR and X-ray single crystal diffraction. In these complexes, hydroxamic acids present bidentate coordination modes with the carbonyl O atom and the hydroxyl O atom binding to tin center. In complexes **1**–**6**, each tin atom is coordinated by one hydroxamic acid ligand. However, in complexes **7** and **8**, tin atom is surrounded by three hydroxamic acid ligands, and all hydroxyl O atoms of the ligands also bind to the alkali metal center (Na or K). This kind of organotin(IV) framework containing one alkali metal is found for the first time. Furthermore, the supramolecular structures of **1**, **3**, **4** and **6** have been found to consist of 1D linear molecular chains formed by intermolecular N–H···X or C–H···X (X = O, N or Cl) hydrogen bonds. For complex **2**, an interesting macrocyclic tetramer has been built by the intermolecular N–H···O hydrogen bonds. Fascinatingly, two unique symmetric dimeric structures are recognized in complexes **7** and **8**, which is individually bridged by intermolecular N–H···Cl and N–H···O hydrogen bonds. In addition, for **8**, the dimeric cycles have been further connected into a 1D supramolecular chain.

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1. Introduction

The studies of organotin(IV) complexes are of current interest owing to their biomedical and commercial application [1–4]. Recently, there have been a mass of reports on the synthesis, antitumor activities and structural elucidations of various organotin(IV) derivatives of carboxylic acid [5–11]. Hydroxamic acids are usually used as supporting ligands in organometallic chemistry and biology because of their tautomerization and potential as therapeutics agents [12–19]. In the last decades, organotin(IV) derivatives of hydroxamic acids are attracting more and more attention due to their biological properties such as antifungicidal and the promising antitumor activity [20,21].

However, from the viewpoint of coordination architecture, their investigation is still very limited, and only a few simple organotin complexes with hydroxamato ligands have been studied. For example, Li and coworkers have reported a series of diorganotin(IV) complexes with substituted benzohydroxamic acids and studied their antitumor activity [12,20–22]. It is well-known that the biochemical activity of organotin(IV) complexes is influenced greatly by the structure of the molecule, the coordination number of the tin atoms and the type of alkyl groups attached to the tin atom. The structural characterization of such organotin(IV) complexes may provide important clues to the structure–activity relationship of the ligand and alkyl species and provide an invaluable insight to the reaction mechanism that may, in turn, allow synthetic chemists to further optimize reaction conditions. Thus it is required to construct a variety of types of organotins through new rational strategies.

As an extension of this field, herein we choose three different hydroxamic acids as building blocks to construct various organotin complexes, particularly systematic investigations on the topology about the effect of alkyltin salts.

We began to treat carboxylic acid and hydroxamic acid reacting with dialkyltin salts with the hope of obtaining interesting

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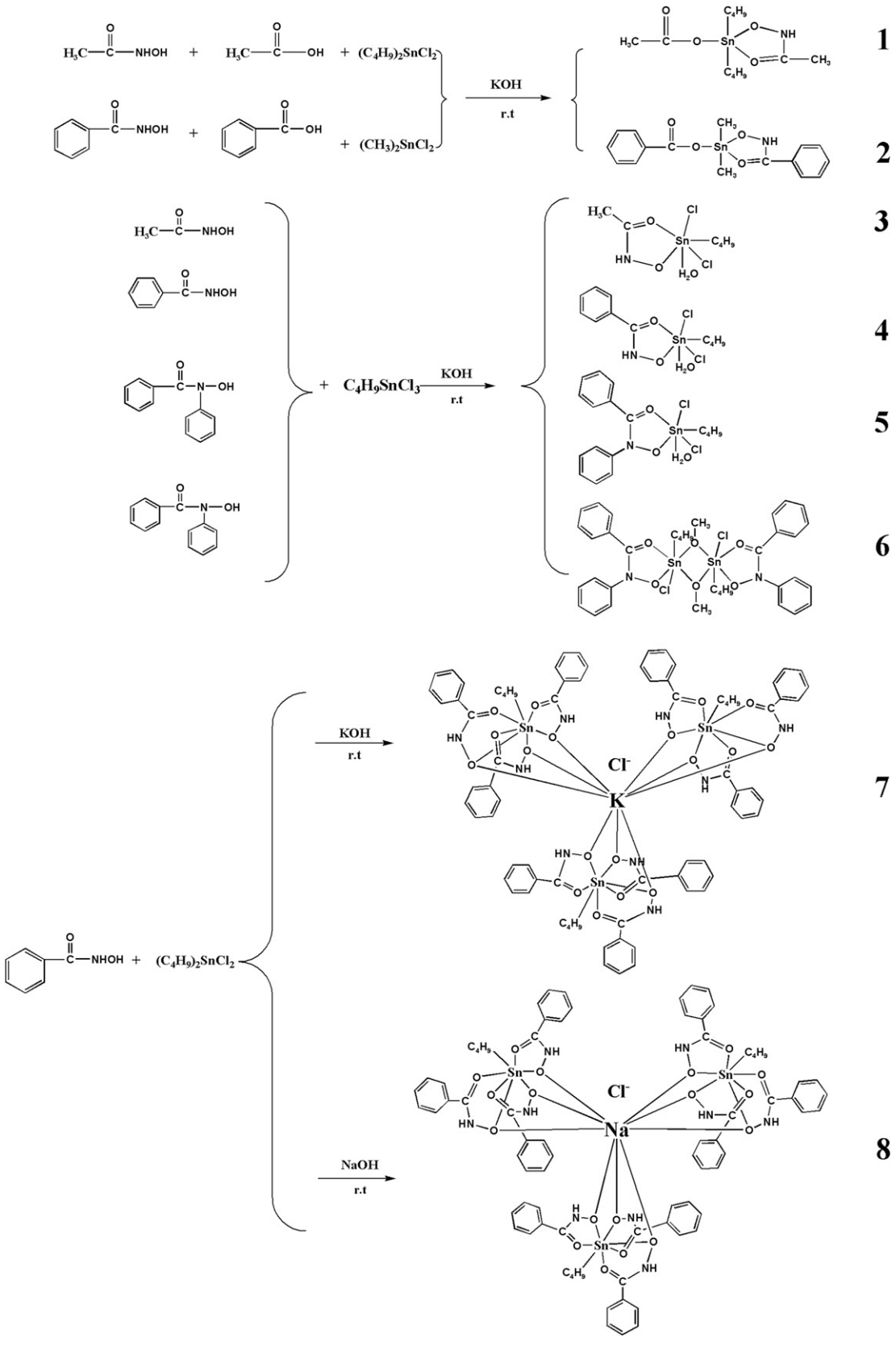

Scheme 1. The syntheses procedures of complexes **1**–**8**.

coordination structures. As a result, complexes **1** and **2** were obtained, in which both monodentate carboxyl group and bidentate *O*-donors hydroxamic acid coordinate to tin center as supporting ligands and both tin atoms are in the five-coordinated trigonal-bipyramid environment. As part of our continuing interest of organotin(IV) complexes with hydroxamato ligands, we have synthesized and characterized four monoorganotin(IV) complexes **3**–**6** by the reaction of hydroxamic acid with mono-*n*-butyltin chlorides. In these four complexes, **3**–**5** are simple monomer, but **6** presents as a methoxy-bridged dimmer. To the best of our knowledge, there are no monoorganotin complexes with hydroxamic acid ligand being reported until now. Unprecedentedly, we have also obtained two novel alkali metal-mingled three tin nuclei monoorganotin(IV) complexes **7** and **8**, which consist of three $C_4H_9SnL_3$ moieties and one half KCl or NaCl, and the alkali metal cation lies in the center of the complex presenting an crown ether-like coordination geometry with nine hydroxyl O atoms from the hydroxamato.

2. Results and discussion

2.1. Syntheses

The syntheses procedures of complexes **1**–**8** are given in Scheme 1.

2.2. IR spectra

By comparing the IR spectra of the free ligands with those of the complexes, a remarkable difference is the complete disappearance of the stretching vibration bands of O–H. The peak appearing at 400–555 cm^{-1} can be assigned to the stretching mode of the Sn–O linkage. The absorption about 3200 cm^{-1} region for the complexes **1**–**4** and **7**–**8** can be assigned to the N–H stretching mode of the vibration. Therefore, the IR spectra suggest the coordination of carbonyl and hydroxyl O atoms to the organotin(IV) ions. For complexes **1** and **2**, it is worthy to note that there are more than one Sn–O bands, which is more obvious for the mixed-ligand complexes. Above these are also confirmed by X-ray structure analyses.

2.3. NMR spectra

The ^1H NMR spectrum of the complex shows that the signal for the –OH proton in the spectrum of the ligand is absent, thus indicating the removal of the –OH proton and the formation of Sn–O bonds in all the complexes. This is consistent with the IR data. The ^{13}C NMR spectral pattern is consistent with the formulation of the complexes. In the ^{13}C NMR spectra in $CDCl_3$ for complex **6**, the data of 50.81 ppm gives evidence for the existence of methanol molecule. The single resonances at 160–166 ppm are attributed to the CON groups in complexes **1**–**8**. Especially, there are two signal

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

Complex **1**			
Sn(1)–O(1)	2.086(5)	O(1)-Sn(1)-O(3)	78.60(18)
Sn(1)–C(5)	2.107(7)	C(5)-Sn(1)-O(3)	94.5(2)
Sn(1)–C(9)	2.109(8)	C(9)-Sn(1)-O(3)	96.0(3)
Sn(1)–O(3)	2.200(5)	O(1)-Sn(1)-O(2)	74.63(18)
Sn(1)–O(2)	2.269(5)	C(5)-Sn(1)-O(2)	91.5(3)
O(1)–Sn(1)–C(5)	104.9(2)	C(9)-Sn(1)-O(2)	91.5(3)
O(1)–Sn(1)–C(9)	104.4(3)	O(3)-Sn(1)-O(2)	153.21(17)
C(5)–Sn(1)–C(9)	150.3(3)		
Complex **2**			
Sn(1)–O(1)	2.102(17)	O(1)-Sn(1)-O(3)	76.2(7)
Sn(1)–C(16)	2.11(3)	C(16)-Sn(1)-O(3)	100.6(9)
Sn(1)–C(15)	2.13(3)	C(15)-Sn(1)-O(3)	99.3(10)
Sn(1)–O(3)	2.178(18)	O(1)-Sn(1)-O(2)	73.2(7)
Sn(1)–O(2)	2.284(17)	C(16)-Sn(1)-O(2)	91.7(9)
O(1)–Sn(1)–C(16)	110.3(10)	C(15)-Sn(1)-O(2)	89.3(10)
O(1)–Sn(1)–C(15)	109.5(10)	O(3)-Sn(1)-O(2)	149.4(8)
C(16)–Sn(1)–C(15)	138.6(12)		

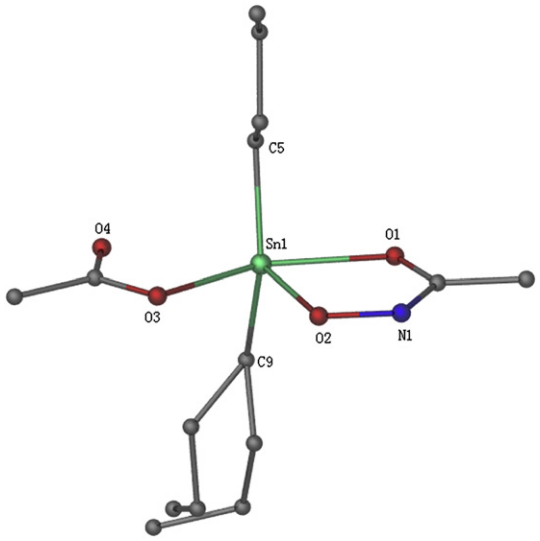

Fig. 1. The molecular structure of complex 1 (Butyl atoms is somewhat disordered).

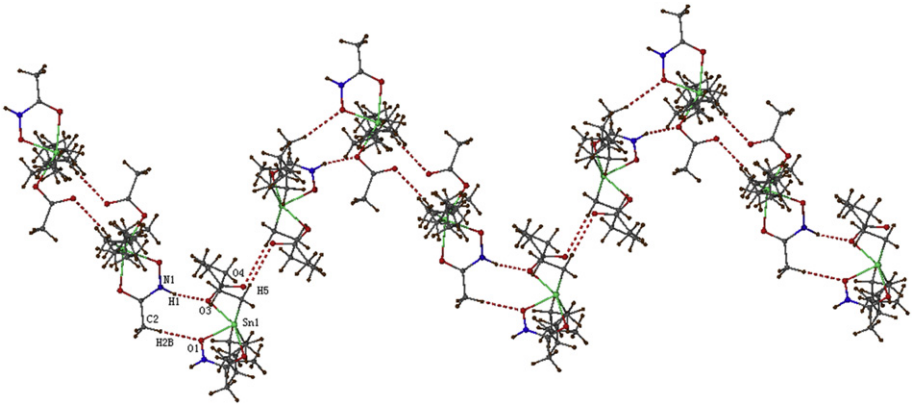

Fig. 2. One-dimension zigzag chain of complex 1, formed by intermolecular C–H···O and N–H···O hydrogen-bonding interactions.

Table 2
Hydrogen-bonding geometries for complexes **1**-**8**.

D-H A	H···A	D···A	D-H···A
Complex **1**			
C(2)–H(2B)…O(1)#1	2.66	3.511(9)	148.3
C(5)–H(5B)…O(4)#2	2.60	3.499(10)	154.5
N(1)–H(1)…O(3)#1	1.96	2.796(7)	163.0
Complex **2**			
N(1)–H(1)…O(1)#3	2.01	2.82(3)	158.2
Complex **3**			
C(1)–H(1A)…O(6)#1	2.71	3.659(7)	168.7
N(1)–H(1)…Cl(1)#2	2.32	3.176(4)	171.4
Complex **4**			
C(17)–H(17)…Cl(4)#1	2.92	3.77(2)	153.2
C(5)–H(5)…Cl(2)#2	2.86	3.78(3)	170.4
C(14)–H(14)…Cl(3)#3	2.92	3.78(2)	154.8
N(1)–H(1)…Cl(4)#4	2.49	3.323(17)	164.9
N(2)–H(2)…Cl(1)#4	2.50	3.310(16)	157.2
Complex **6**			
C(10)–H(10)…O(2)#2	2.61	3.402(10)	143.8
Complex **7**			
N(18)–H(18)…O(13)	2.13	2.938(11)	155.5
N(8)–H(8)…Cl(1)	2.34	3.159(10)	160.4
N(1)–H(1)…Cl(1)	2.33	3.157(9)	160.4
N(4)–H(4)…Cl(1)	2.36	3.155(9)	154.6
N(14)–H(14)…Cl(2)	2.36	3.168(8)	157.0
N(17)–H(17)…Cl(2)	2.30	3.119(9)	159.6
N(11)–H(11)…Cl(2)	2.32	3.127(9)	156.2
N(15)–H(15)…O(9)	2.11	2.944(10)	162.5
N(6)–H(6)…O(25)	2.10	2.910(10)	157.7
N(12)–H(12)…O(3)	2.06	2.877(10)	158.5
N(3)–H(3)…O(19)	2.16	2.964(10)	156.4
N(9)–H(9)…O(31)	2.13	2.936(10)	156.4
Complex **8**			
C(59)–H(59)…Cl(1)	2.83	3.727(16)	163.2
C(17)–H(17)…Cl(1)	2.78	3.640(13)	154.9
C(38)–H(38)…Cl(1)	2.74	3.563(15)	148.3
C(35)–H(35)…O(1)#1	2.53	3.435(17)	164.6
C(52)–H(52)…O(13)#1	2.61	3.497(18)	160.3
C(52)–H(52)…N(7)#1	2.72	3.621(19)	163.0
C(14)–H(14)…O(7)#1	2.57	3.454(19)	158.9
C(14)–H(14)…N(4)#1	2.69	3.59(2)	162.2
C(35)–H(35)…N(1)#1	2.70	3.610(17)	164.9
N(6)–H(6)…Cl(1)	2.33	3.151(9)	158.9
N(9)–H(9)…Cl(1)	2.29	3.113(10)	159.5
N(3)–H(3)…Cl(1)	2.33	3.132(10)	155.8
N(2)–H(2)…O(7)#1	2.10	2.911(11)	157.6
N(8)–H(8)…O(13)#1	2.16	2.952(12)	154.0
N(5)–H(5)…O(1)#1	2.14	2.961(12)	159.0

Symmetry code: (#1 for **1**) −x+1/2,y−1/2,−z+1/2; (#2 for **1**) −x+1/2,−y+3/2,-z; (#3 for **2**) #3 −y+1,x,−z; (#1 for **3**) −x+1,−y,−z+1; (#2 for **3**) −x+1,−y+1,−z+1; (#1 for **4**) −x+1,−y+1,−z; (#2 for **4**) x,y+1,z; (#3 for **4**) -x+1,−y+2,−z; (#4 for **4**) −x, −y+1,-z; (#3 for **6**) −x+1,y+1/2,−z+1/2; (#1 for **5**) −x, −y, 2−z; (#1 for **6**) 1 + x, y, z; (#1 for **8**) −x+1,y,−z+1/2.

resonances in the region 170–180 ppm, indicating the presence of the COO groups in complexes **1** and **2**.

The ^{119}Sn NMR chemical shifts of organotin(IV) complexes appear to depend not only on the coordination number, but also on the types of donor atoms and alkyl groups bound to the metal ion [23]. Although bonding with different alkyl groups, n-butyl group for **1** and methyl group for **2**, the ^{119}Sn NMR spectroscopy data of compounds **1** and **2** show similar resonance signals at $\delta = -70$ ppm for **1** and -76 ppm for **2**, respectively, which are different from the values (−90 to −190 ppm) reported for the di-*n*-butyltin compounds mentioned in the reference [24]. It may be due to the effect of different ligands. The ^{119}Sn NMR spectroscopy data of

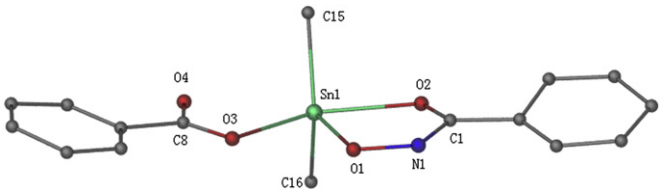

Fig. 3. The molecular structure of complex **2** (For clarity, uncoordinated solvent molecules are omitted).

compound **3**–**6** ($\delta = -380$ ppm for **3**; −377 ppm for **4**; −367 ppm for **5**; −353 ppm for **6**) show signals in the normal range for six-coordinate mono-*n*-butyltin(IV) derivatives, which are similar to that found in the compounds reported previously [25,26]. For compounds **7** and **8**, the ^{119}Sn NMR spectroscopic data show one resonance signal at $\delta = -482$ ppm for **7** and −480 ppm for **8**, respectively, which fall in the range corresponding to a type of seven-coordinated tin compounds [27].

2.4. Description of crystal structures

2.4.1. X-ray crystallography of complexes *1* and *2*

Selected bond lengths and angles of complexes **1** and **2** are listed in Table 1. The molecular structure of complex **1** is shown in Fig. 1. It can be seen that the tin atom has a coordination number of five. Central Sn atom is coordinated by one carboxyl O atom from acetic acid, one carbonyl O atom and one hydroxyl O atom from aceto-hydroxamic acid, and two C atoms of trans *n*-butyl groups. The bond length of Sn(1)–O(1), Sn(1)–O(2) and Sn(1)–O(3) are 2.086 (5) Å, 2.269(5) Å and 2.200(5) Å, which are close to the corresponding bond length in the literature [22]. The angle of C(5)–Sn (1)–C(9), 150.3(3)°, which deviates from the linear angle of 180°. Thus, the coordination geometry of the tin center is best described as distorted trigonal bipyramid. As can be seen in Fig. 2 that molecules of **1** have been connected by intermolecular C–H···O and N–H···O hydrogen-bonding interactions (shown in Table 2)

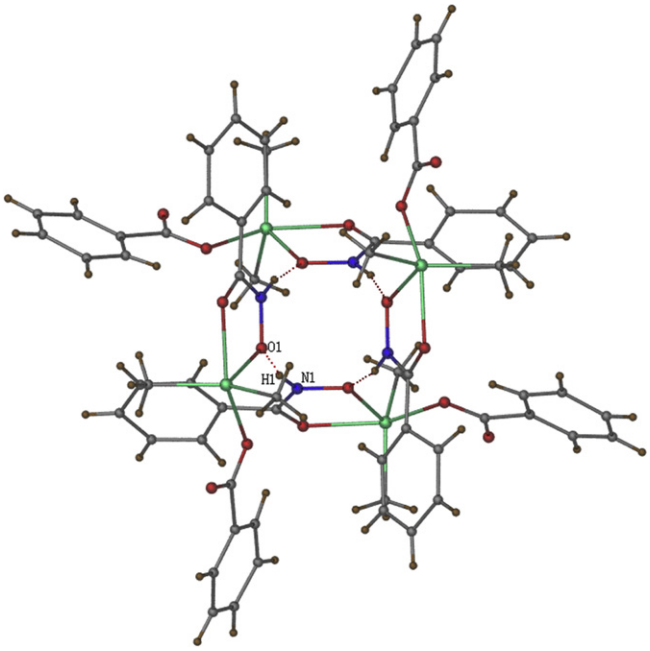

Fig. 4. The macrocyclic polymer structure of complex **2**, formed by intermolecular N–H···O hydrogen-bonding interactions.

Table 3
Selected bond lengths (Å) and angles (°) for complexes **3**–**6**

Complex **3**			
Sn(1)–O(5)	2.087(3)	Sn(1)–O(7)	2.255(4)
Sn(1)–C(6)	2.128(5)	Sn(1)–Cl(2)	2.3783(13)
Sn(1)–O(6)	2.212(3)	Sn(1)–Cl(1)	2.4517(15)
O(5)–Sn(1)–C(6)	165.48(19)	O(6)–Sn(1)–Cl(2)	156.82(9)
O(5)–Sn(1)–O(6)	74.93(12)	O(7)–Sn(1)–Cl(2)	87.91(10)
C(6)–Sn(1)–O(6)	92.44(18)	O(5)–Sn(1)–Cl(1)	88.90(9)
O(5)–Sn(1)–O(7)	83.38(14)	C(6)–Sn(1)–Cl(1)	98.12(17)
C(6)–Sn(1)–O(7)	88.1(2)	O(6)–Sn(1)–Cl(1)	88.79(10)
O(6)–Sn(1)–O(7)	83.19(14)	O(7)–Sn(1)–Cl(1)	170.07(12)
O(5)–Sn(1)–Cl(2)	82.83(9)	Cl(2)–Sn(1)–Cl(1)	97.34(6)
C(6)-Sn(1)–Cl(2)	108.66(16)		
Complex **4**			
Sn(1)–O(1)	2.084(12)	Sn(2)–O(4)	2.094(12)
Sn(1)–C(8)	2.13(2)	Sn(2)–C(19)	2.108(18)
Sn(1)–O(2)	2.155(13)	Sn(2)–O(5)	2.158(13)
Sn(1)–Cl(2)	2.435(5)	Sn(2)–O(6)	2.276(13)
Sn(1)–Cl(1)	2.457(5)	Sn(2)–Cl(3)	2.426(5)
Sn(1)–O(3)	2.260(12)	Sn(2)–Cl(4)	2.448(5)
O(1)–Sn(1)–C(8)	171.0(9)	O(4)–Sn(2)–C(19)	166.6(8)
O(1)–Sn(1)–O(2)	77.2(5)	O(4)–Sn(2)–O(5)	76.8(5)
C(8)–Sn(1)–O(2)	97.9(8)	C(19)–Sn(2)–O(5)	92.5(7)
O(1)–Sn(1)–O(3)	80.1(5)	O(4)–Sn(2)–O(6)	78.3(5)
C(8)–Sn(1)–O(3)	91.9(9)	C(19)–Sn(2)–O(6)	92.6(8)
O(2)–Sn(1)–O(3)	83.0(5)	O(5)–Sn(2)–O(6)	83.9(5)
O(1)–Sn(1)–Cl(2)	83.0(3)	O(4)–Sn(2)–Cl(3)	83.9(3)
C(8)–Sn(1)–Cl(2)	100.9(7)	C(19)–Sn(2)–Cl(3)	105.6(6)
O(2)–Sn(1)–Cl(2)	159.1(4)	O(5)-Sn(2)-Cl(3)	160.0(4)
O(3)–Sn(1)–Cl(2)	87.3(3)	O(6)–Sn(2)–Cl(3)	86.8(4)
O(1)–Sn(1)–Cl(1)	87.4(4)	O(4)–Sn(2)–Cl(4)	88.4(4)
C(8)–Sn(1)–Cl(1)	100.3(9)	C(19)–Sn(2)–Cl(4)	100.3(7)
O(2)–Sn(1)–Cl(1)	90.9(4)	O(5)–Sn(2)–Cl(4)	91.8(4)
O(3)–Sn(1)–Cl(1)	167.0(3)	O(6)–Sn(2)–Cl(4)	166.6(4)
Cl(2)–Sn(1)–Cl(1)	94.76(19)	Cl(3)–Sn(2)–Cl(4)	93.19(19)
Complex **5**			
Sn(1)–O(1)	2.089(3)	Sn(1)–C(14)	2.135(5)
Sn(1)–O(2)	2.172(3)	Sn(1)–O(3)	2.210(3)
Sn(1)–Cl(2)	2.4072(13)	Sn(1)–Cl(1)	2.4505(13)
O(1)–Sn(1)–C(14)	169.89(19)	C(14)–Sn(1)–Cl(2)	103.64(18)
O(1)–Sn(1)–O(2)	74.60(11)	O(2)–Sn(1)–Cl(2)	156.00(10)
C(14)–Sn(1)–O(2)	97.4(2)	O(3)–Sn(1)–Cl(2)	87.46(11)
O(1)–Sn(1)–O(3)	83.49(13)	O(1)–Sn(1)–Cl(1)	85.96(9)
C(14)–Sn(1)–O(3)	89.27(19)	C(14)–Sn(1)–Cl(1)	100.34(17)
O(2)–Sn(1)–O(3)	81.31(14)	O(2)–Sn(1)–Cl(1)	89.71(10)
O(1)–Sn(1)–Cl(2)	83.14(9)	O(3)–Sn(1)–Cl(1)	167.64(11)
Cl(2)–Sn(1)–Cl(1)	97.67(5)		
Complex **6**			
Sn(1)–O(3)#1	2.081(4)	Sn(1)–O(2)	2.127(5)
Sn(1)–C(14)	2.113(7)	Sn(1)–O(3)	2.173(4)
Sn(1)–O(1)	2.114(5)	Sn(1)–Cl(1)	2.428(2)
O(3)#1–Sn(1)–C(14)	105.3(3)	O(1)vSn(1)–O(3)	90.5(2)
O(3)#1–Sn(1)–O(1)	155.26(19)	O(2)–Sn(1)–O(3)	82.96(19)
C(14)–Sn(1)–O(1)	94.4(3)	O(3)#1–Sn(1)–Cl(1)	93.57(14)
O(3)#1–Sn(1)–O(2)	84.57(18)	C(14)–Sn(1)–Cl(1)	97.6(2)
C(14)–Sn(1)–O(2)	169.3(3)	O(1)–Sn(1)–Cl(1)	98.61(17)
O(1)–Sn(1)–O(2)	75.00(18)	O(2)–Sn(1)–Cl(1)	85.80(17)
O(3)#1–Sn(1)–O(3)	73.0(2)	O(3)–Sn(1)–Cl(1)	163.21(13)
C(14)–Sn(1)–O(3)	95.7(3)		

Symmetry code for complex **6**: #1 −x+1, −y, −z+1.

into an interesting 1D zigzag chain structure, and the crystal structure is stabilized by the intramolecular hydrogen bonds.

For complex **2**, the overall structure (Fig. 3) is similar to that of complex **1**. The coordination number of the Sn atom is five. The Sn^{4+} ion is bonded with two CH_3 groups, one benzoic acid and one benzohydroximic ligand. It is worthwhile to note that four molecules of complex **2** form a fascinating macrocyclic tetramer (see Fig. 4), which is linked by intermolecular N–H···O hydrogen-bonding interactions (shown in Table 2).

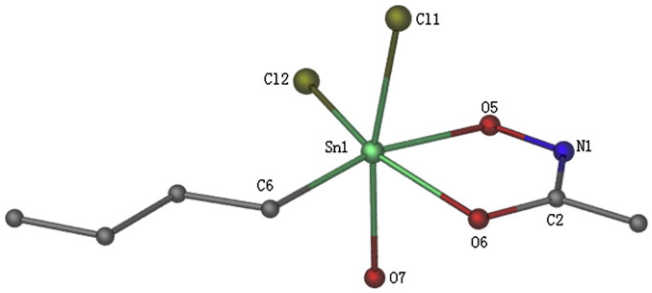

Fig. 5. The molecular structure of complex **3**.

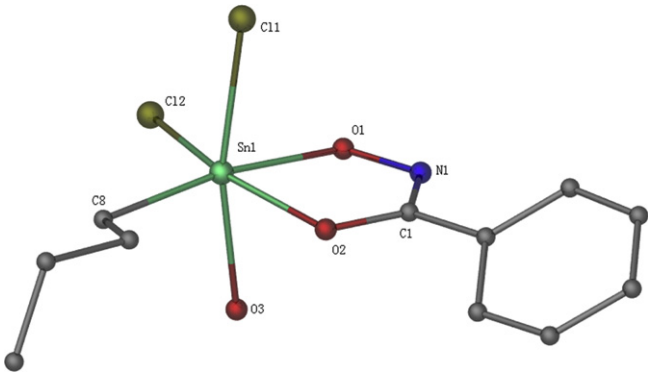

Fig. 6. The molecular structure of complex **4**.

*2.4.2. X-ray crystallography of complexes **3**, **4**, **5** and **6***

Selected bond lengths and angles of complexes **3**–**6** are listed in Table 3. As can be seen from Figs. 5, 6 and 7, complexes **3**–**5** have the similar structure features. The center tin atoms are six-coordinated with one O atom and one Cl atom occupying the axial sites [axial angles: O(7)–Sn(1)–Cl(1) = 170.07°, for complex **3**; O(6)–Sn(2)–Cl(4) = 166.6(4)°, for complex **4**; O(3)–Sn(1)–Cl(1) = 167.64(11)°, for complex 5], and one Cl atom, one C atom and two O atoms define the equatorial plane. All of the center tin atoms have six-coordinate geometry in a distorted octahedral arrangement. The sum of the angles subtended at the tin center in the equatorial plane is 357.9°, 358.9° and 358.78° for complexes **3**, **4** and **5**, respectively. So the central tin atom and the corresponding two oxygen atoms, one chlorine atom and one *n*-butyl carbon atom bonding with tin center are almost coplanar. For complex **6**, to our

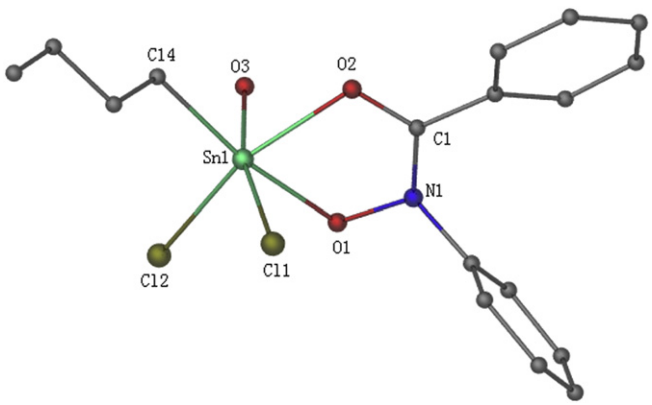

Fig. 7. The molecular structure of complex **5**.

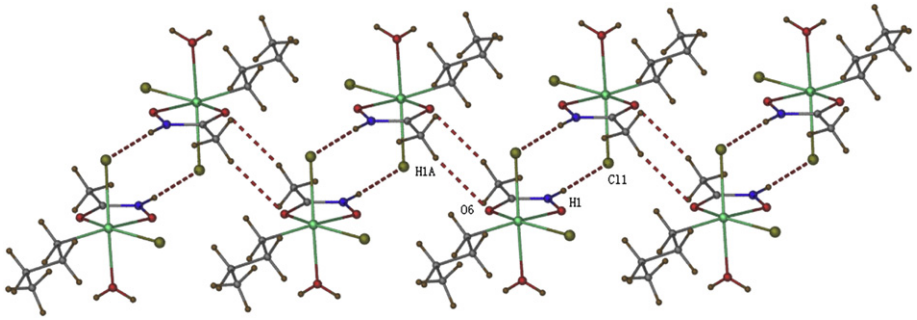

Fig. 8. The 1D chain structure of complex **3**, formed by intermolecular C–H···O and N–H···Cl hydrogen-bonding interactions.

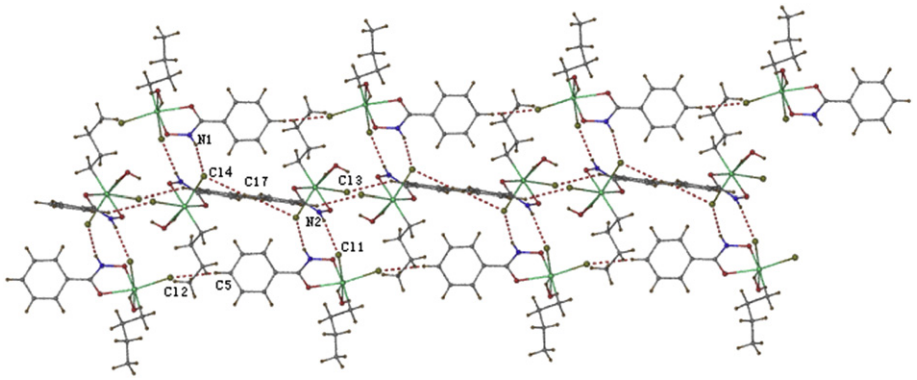

Fig. 9. The 1D chain structure of complex 4, formed by intermolecular C–H···Cl and N–H···Cl hydrogen-bonding interactions.

surprise, the Sn atoms are six-coordinate with a octahedral structure by coordinating two additional methoxy groups [Sn(1)–O(3)#1 (−x+1,−y,−z+1) = 2.081 Å, Sn(1)–O(3) = 2.173 Å]. Each of the tin atoms bounds to one butyl group, two methoxy oxygen atoms, two hydroxamic oxygen atoms and a chlorine atom.

Fascinating supramolecular structures have been found for complexes **3** and **4**, which are built up by intermolecular hydrogen bonds. As can be seen from Fig. 8 that molecules of **3** are connected by intermolecular C–H···O and N–H···Cl hydrogen-bonding interactions forming a 1D extended chain structure (shown in Table 2). For complex **4**, the asymmetric unit contains two monomers, which are different from a crystallographic point of view. The conformations of the two independent molecules are almost the same, with only small differences in bond lengths and bond angles. The molecules are connected by intermolecular C–H···Cl and N–H···Cl hydrogen-bonding interactions (shown in Table 2) forming a 1D supramolcular chain (see Fig. 9). It is worthwhile to note that there were no intermolecular interactions in the complex **5**. As shown in Fig. 10, the complex **6** presents a centrosymmetric dinuclear complex. In the crystal structure, which is shown in Fig. 11, molecules are also connected by intermolecular C–H···O hydrogen-bonding interactions forming a 1D linear chain structure (shown in Table 2).

2.4.3. *X-ray crystallography of complexes **7** and **8***

Selected bond lengths and angles of complexes **7** and **8** are listed in Table 4, and their molecular structures are shown in Figs. 12 and 13, respectively. To obtain a deeper insight into the coordination of hydroxamic acid to the tin center, the reaction of dialkyltin dichloride with benzohydroxamic acid in the different molar ratio was also studied as a part of experimental design. Unexpectedly, we got two novel alkali metal-mingled three tin nuclei monoorganotin (IV) complexes, which are obviously different from the well-known

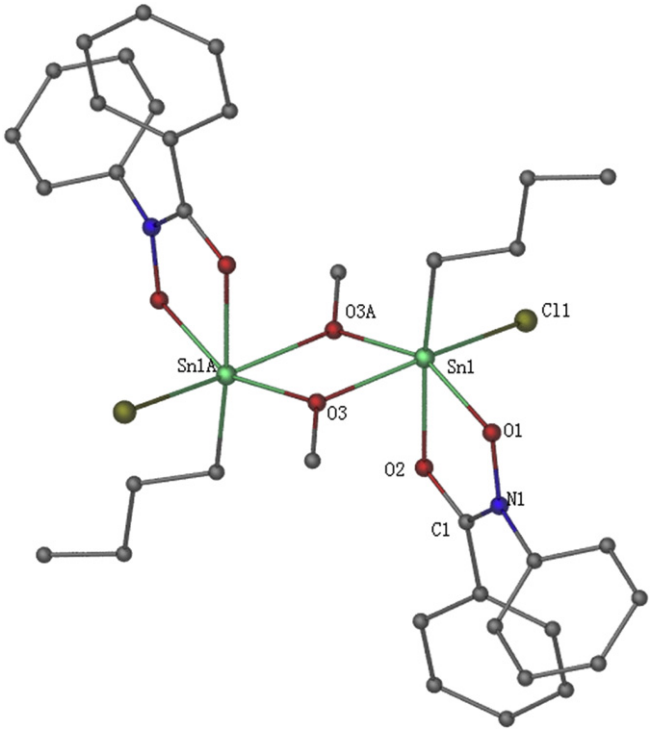

Fig. 10. The molecular structure of complex **6**.

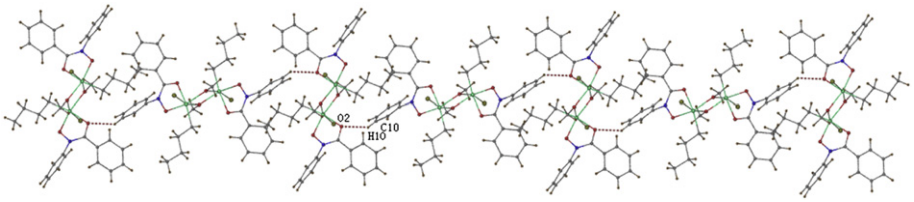

Fig. 11. The 1D chain structure of complex **6**, formed by intermolecular C–H···O hydrogen-bonding interactions.

Table 4
Selected bond lengths (Å) and angles (°) for complexes **7** and **8**

Complex **7**			
Sn(1)–O(1)	2.082(7)	O(1)–Sn(1)–O(2)	74.3(2)
Sn(1)–O(5)	2.158(7)	O(3)–Sn(1)–O(4)	71.6(2)
Sn(1)–O(2)	2.206(6)	O(5)–Sn(1)–O(6)	70.0(2)
Sn(1)–C(127)	2.121(11)	O(2)–Sn(1)–O(4)	73.0(2)
Sn(1)–O(3)	2.189(6)	O(1)–Sn(1)–O(5)	81.4(3)
Sn(1)–O(4)	2.276(7)	O(1)–Sn(1)–O(3)	85.7(3)
Sn(1)–O(6)	2.316(7)	O(5)–Sn(1)–O(3)	69.4(3)
Sn(1)–K(1)	3.863(2)		
Complex **8**			
Sn(1)–O(5)	2.057(7)	O(1)–Sn(1)-O(2)	70.9(3)
Sn(1)–O(3)	2.128(7)	O(3)–Sn(1)-O(4)	69.8(3)
Sn(1)–O(1)	2.169(7)	O(5)–Sn(1)-O(6)	75.4(3)
Sn(1)–O(6)	2.220(7)	O(5)–Sn(1)–O(1)	83.0(3)
Sn(1)–O(2)	2.266(8)	O(6)–Sn(1)-O(2)	74.2(3)
Sn(1)–O(4)	2.326(8)	O(3)–Sn(1)–O(1)	70.6(3)
Sn(1)–C(64)	2.087(12)		

organotin hydroxamates [20–22,28,29]. Figs. 14 and 15 show the dimeric structure of **7** and the 1D supramolecular chain of **8**, which are both formed through intermolecular hydrogen bonds.

As can be seen from Figs. 12 and 13, complexes **7** and **8** have the similar topology architectures, which both consist of three $C_4H_9SnL_3$ moieties and one half KCl or NaCl, and the alkali metal cation lies in the center of the complex presenting a crown ether-like coordination geometry with nine hydroxyl O atoms from the hydroxamato. All the tin atoms possess the same ligand environments, with only minor differences in bond lengths and bond angles. For the coordination environment analysis of tin atoms of

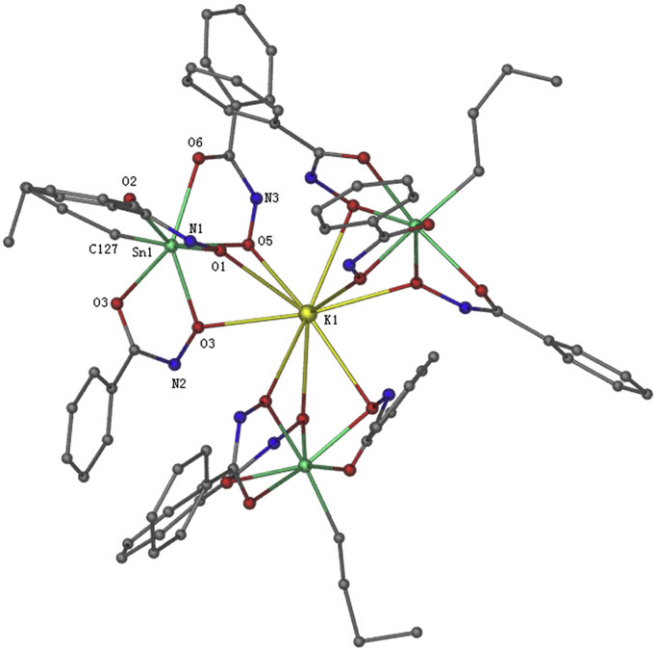

Fig. 12. The molecular structure of complex **7** (For clarity, solvent molecules are omitted).

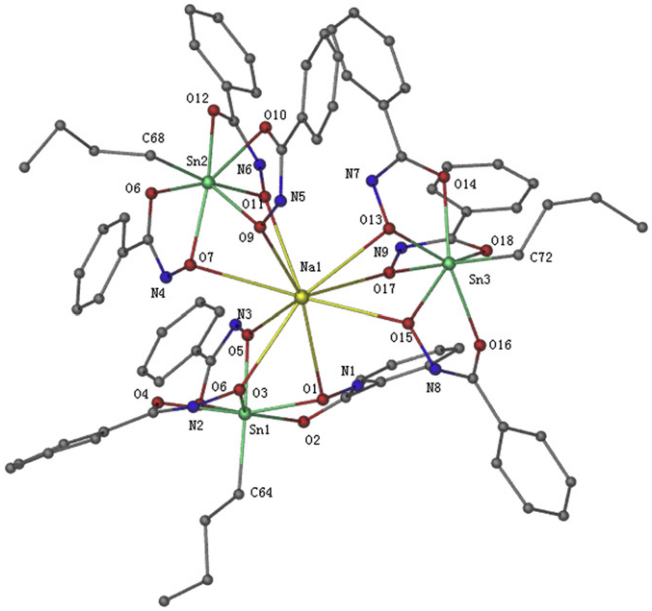

Fig. 13. The molecular structure of complex **8** (For clarity, solvent molecules are omitted).

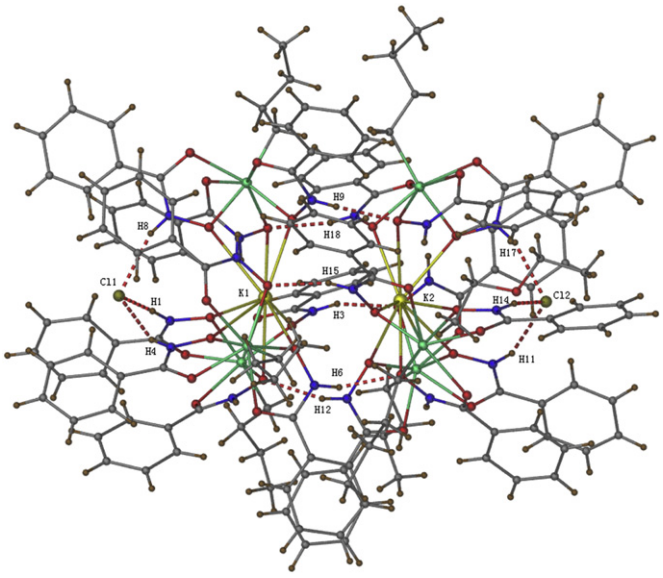

Fig. 14. The symmetric dimeric structure of complex **7**, formed by intramolecular N–H···Cl and N–H···O weak interactions hydrogen-bonding interactions.

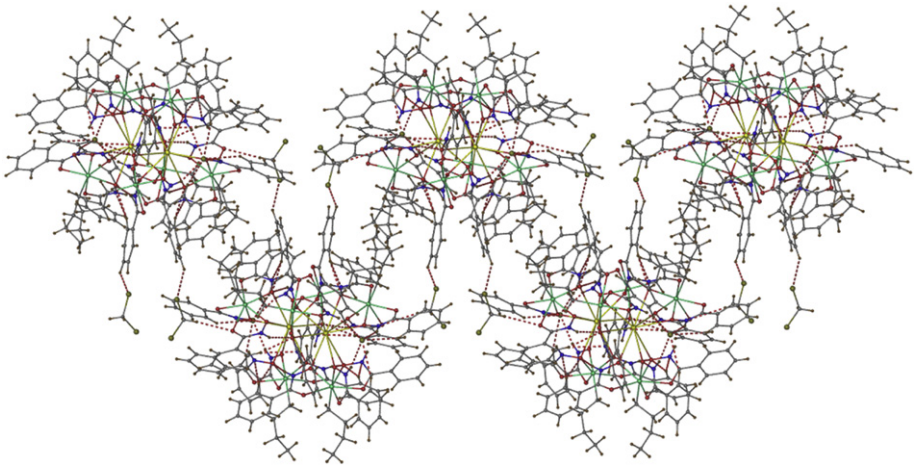

Fig. 15. The 1D chain structure of complex 8, formed by C–H···O, C–H···Cl and C–H···N hydrogen-bonding interactions.

Table 5
Crystal data and structure refinement parameters for complexes **1**–**4**

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{12}H_{25}NO_4Sn$	$C_{19}H_{20}NO_4Sn$	$C_6H_{15}Cl_2NO_3Sn$	$C_{11}H_{17}Cl_2NO_3Sn$
Formula weight	366.02	445.05	338.78	400.85
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	C2/c	P1	P2(1)/n	P-1
a (Å)	25.429(3)	14.1691(15)	12.8174(13)	10.5637(12)
b (Å)	8.9786(11)	14.1691(15)	7.3990(8)	12.9306(13)
c (Å)	17.7388(18)	41.350(4)	14.6512(15)	13.1131(14)
α (°)	90	90	90	63.4760(10)
β (°)	125.543(2)	90	114.273(2)	89.309(2)
γ (°)	90	90	90	84.0920(10)
V (Å^3)	3295.5(6)	8301.6(14)	1266.6(2)	1593.0(3)
Z	8	16	4	4
Dcalc (Mg/m^3)	1.475	1.424	1.777	1.671
μ (mm^{-1})	1.557	1.251	2.419	1.939
F(000)	1488	3568	664	792
Crystal size (mm)	0.21 × 0.17 × 0.16	0.22 × 0.17 × 0.15	0.40 × 0.28 × 0.10	0.48 × 0.37 × 0.36
Reflections collected	8009	18158	6077	8011
Unique reflections [R_{int}]	2894 [R(int) = 0.0485]	3674 [R(int) = 0.2211]	2240 [R(int) = 0.0321]	5432 [R(int) = 0.0294]
Data/restraints/parameters	2894/0/196	3674/0/256	2240/2/128	5432/652/327
Goodness-of-fit on F^2	1.118	1.009	1.066	1.146
Final *R* indices [I > 2σ (I)]	*R*1 = 0.0437 wR2 = 0.0932	*R*1 = 0.1040 wR2 = 0.2830	*R*1 = 0.0328 wR2 = 0.0771	*R*1 = 0.0946 wR2 = 0.2580
R indices (all data)	*R*1 = 0.0854 wR2 = 0.1212	*R*1 = 0.1884 wR2 = 0.3490	*R*1 = 0.0505 wR2 = 0.0918	*R*1 = 0.1166 wR2 = 0.2709

Table 6
Crystal data and structure refinement parameters for complexes **5**–**8**

Complex	**5**	**6**	**7**	**8**
Empirical formula	$C_{17}H_{23}Cl_2NO_4Sn$	$C_{18}H_{22}ClNO_3Sn$	$C_{9.63}H_{10.75}Cl_{0.13}K_{0.13}N_{1.13}O_{2.31}Sn_{0.38}$	$C_{25.33}H_{27.67}ClN_3Na_{0.33}O_6Sn$
Formula weight	494.95	454.51	233.02	631.97
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1	P2(1)/c	Cc	C2/c
a (Å)	8.1542(7)	8.3699(8)	29.957(3)	29.699(3)
b (Å)	10.6201(11)	16.0246(16)	25.681(2)	26.219(2)
c (Å)	14.1153(12)	14.9992(13)	22.521(2)	22.220(2)
α (°)	109.726(2)	90	90	90
β (°)	92.1470(10)	97.9110(10)	101.8590(10)	102.933(2)
γ (°)	110.205(2)	90	90	90
V (Å^3)	1063.28(17)	1992.6(3)	16956(3)	16863(3)
Z	2	4	64	24
Dcalc (Mg/m^3)	1.546	1.515	1.460	1.494
μ (mm^{-1})	1.472	1.430	1.027	1.052
F(000)	496	912	7560	7664
Crystal size (mm)	0.47 × 0.46 × 0.35	0.44 × 0.43 × 0.36	0.19 × 0.18 × 0.13	0.45 × 0.38 × 0.33
Reflections collected	5501	9812	43846	43372
Unique reflections [R_{int}]	3688 [R(int) = 0.0210]	3511 [R(int) = 0.0332]	26087 [R(int) = 0.0423]	14887 [R(int) = 0.0632]
Data/restraints/parameters	3688/0/227	3511/0/219	26087/2/1980	14887/2807/994
Goodness-of-fit on F^2	0.625	1.162	0.936	1.134
Final *R* indices [I > 2σ (I)]	*R*1 = 0.0342 wR2 = 0.0862	*R*1 = 0.0462 wR2 = 0.0946	*R*1 = 0.0514 wR2 = 0.1076	*R*1 = 0.0640 wR2 = 0.1613
R indices (all data)	*R*1 = 0.0450 wR2 = 0.1021	*R*1 = 0.0747 wR2 = 0.1091	*R*1 = 0.1080 wR2 = 0.1305	*R*1 = 0.1757 wR2 = 0.2579

complex **7**, Sn(1) is taken for example, which has a coordination number of seven. The Sn atom is coordinated by three carbonyl O atoms and three hydroxyl O atoms from benzohydroxamic acid, one C atom from *n*-butyl. The bond length of Sn(1)–O(1), Sn(1)–O(2), Sn(1)–O(3), Sn(1)–O(4), Sn(1)–O(5) and Sn(1)–O(6) are 2.082(7) Å, 2.206(6) Å, 2.189(6) Å, 2.276(7) Å, 2.158(7) Å and 2.316(7) Å, which are close to the bond length in the complexes **3**–**6**. The potassium ions in the compound are nine-coordinated, composed of nine hydroxyl oxygens from hydroxamic acid. The K–O bond distances are in the range of [2.761(7) Å-3.025(7) Å]. As can be seen from Fig. 14, the conformations of the two independent molecules are connected by a series of intramolecular N–H···Cl and N–H···O weak interactions forming a symmetric dimer, and the crystal structure is stabilized by the intramolecular hydrogen bonds (shown in Table 2).

The structure of complex **8** is presented in Fig. 13. The tin atoms of complex **8** are seven-coordinated with six oxygens benzohydroxamic acid and one C atom from butyl. The central sodium atom has a coordination number of nine, and is bonded with nine hydroxyl oxygens. The Na–O bond distances are in the range of [2.780(8) Å –3.006(8) Å]. For complex **8**, hydrogen bridged dimmer has also been found. In addition, due to the existing of the uncoordinated dichloromethane solvate molecules, these dimeric structures are connected by intermolecular C–H···O, C–H···Cl and C–H···N hydrogen-bonding interactions (shown in Table 2) forming an interesting 1D extended chain structure, which is shown in Fig. 15.

3. Conclusion

Eight organotin(IV) complexes with hydroxamic acids, the carboxyl acid hybrid five-coordinated dialkyltin complexes, **1** and **2**, the six-coordinated mono-*n*-butyltin complexes, **3**–**6**, and the alkali metal-mingled seven-coordinated mono-*n*-butyltin complexes, **7** and **8**, are reported in this paper. These complexes are obtained by selecting mono- or dialkyltin chlorides and three ligands with different molar ratios. The results demonstrate that the changing of reaction ratio of between the hydroxamic acid ligand and alkyltin salt have a significant influence on the structures from 1 : 1 for complexes **3**–**6** to 2 : 1 for complexes **7** and **8**, and, therefore, the properties of the corresponding organotin complexes. With the aim to finally design and synthesize organotin complexes with desired structures and high anti-tumor activities, more work is required to explore new complexes using hydroxamic acid ligands attached with different tin salts.

4. Experimental details

4.1. Materials and measurements

Dibutyltin dichloride, dimethyltin dichloride, butyltin trichloride, acetic acid, Acetohydroxamic acid and benzoic acid were commercially available, and they were used without further purification. Benzohydroxamic acid was prepared by the reported method [23]. The elemental analyses were performed on a PE-2400–II elemental analyzer. IR spectra were recorded on a Nicolet-5700 spectrophotometer using KBr discs. X-ray measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Varian Mercury Plus-400 NMR spectrometer. Chemical shifts were given in ppm relative to Me_4Si and Me_4Sn in $CDCl_3$ or DMSO-d_6 solvent.

4.2. Syntheses of the complexes **1**–**8**

4.2.1. [$(C_4H_9)_2Sn(CH_3CONHO)(CH_3COO)$] (**1**)

The reaction was carried out under nitrogen atmosphere. Acetohydroxamic acid (0.06 g, 0.8 mmol), acetic acid (0.048 g, 0.8 mmol) and KOH (0.0896 g, 1.6 mmol) were added to a stirred solution of methanol (30 ml) in a Schlenk flask and stirred for 0.5 h. Dibutyltin dichloride (0.243 g, 0.8 mmol) was then added to the reactor. The reaction mixture was stirred for 8 h at room temperature and then filtrated. The filtrate was evaporated in vacuo. The obtained solid was recrystallized from ethylether/petroleum (1:1). yield: 75%, m.p. 65–67 °C. Anal. Calc. for $C_{12}H_{25}NO_4Sn$: C, 39.37; H, 6.88; N, 3.83%. Found: C, 39.28; H, 6.96; N, 3.92%. IR (KBr, cm^{-1}): 3180s (N–H), 1621s, 1539m (CO/NC); 918s (N–O); 520s (Sn–C); 448s (Sn–O); 1380s (COO). ^{1}H NMR ($CDCl_3$, ppm): δ = 1.99 (s, 3H, O=C–CH_3); δ = 0.90 (s, 3H, N–C–CH_3); δ = 1.25–1.63 (m,18H,–$CH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ = 178.98 (COO); δ = 165.26 (CON); δ = 13.60, 22.10, 25.24, 26.10 (–$CH_2CH_2CH_2CH_3$,); δ = 27.21, 29.67 ($\underline{C}H_3$–C=O, $\underline{C}H_3$–CONH). ^{119}Sn NMR ($CDCl_3$, ppm): δ = –70.

4.2.2. [$(CH_3)_2Sn(CONHOC_6H_5)(COOC_6H_5)]\cdot 0.5C_6H_6$ (**2**)

Complex **2** was prepared in the same way as **1**. The colourless solid was recrystallized from benzene/hexane (1:1) to give colourless powder, yield: 77%, m.p.127–130 °C. Anal. Calc. for $C_{19}H_{20}NO_4Sn$: C, 51.27; H, 4.53; N, 3.15%. Found: C, 51.18; H, 4.59; N, 3.21%. IR (KBr, cm^{-1}): 3200 w (N–H); 1598w, 1563w (CO/NC); 1380m (COO); 918s (N–O); 434s, 523m (Sn–O); 548 m and 570w (Sn–C). ^{1}H NMR ($CDCl_3$, ppm):δ = 7.40–7.81 (m,13H, Ph–H); δ = 0.10 (s, 6H, –CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ = 172.10 (COO); δ = 164.22 (CON); δ = 126.61, 127.32, 128.21, 128.41, 128.93, 129.26, 130.08, 130.43, 132.80 (Ph–C). ^{119}Sn NMR ($CDCl_3$, ppm): δ = –76.

4.2.3. [$(C_4H_9)Sn(CH_3CONHO)\cdot Cl_2\cdot H_2O$] (**3**)

The reaction was carried out under nitrogen atmosphere. Acetohydroxamic acid (0.06 g, 0.8 mmol) and KOH (0.0449 g, 0.8 mmol) were added to a stirred solution of methanol (30 ml) in a Schlenk flask and stirred for 0.5 h. Butyltin trichloride (0.2256 g, 0.8 mmol) was then added to the reactor. The reaction mixture was stirred for 8 h at room temperature and then filtrated. The filtrate was evaporated in vacuo. The obtained solid was recrystallized from ethylether/petroleum (1:1), yield: 80% , m.p.107–108 °C. Anal. Calc. for $C_6H_{15}Cl_2NO_3Sn$: C, 21.27; H, 4.46; N, 4.13%. Found: C, 21.19; H, 4.51; N, 4.18%. IR (KBr, cm^{-1}): 3154w (N–H); 1613s, 1559m (CO/NC); 920s (N–O); 590s (Sn–C); 434s (Sn–O). ^{1}H NMR ($CDCl_3$, ppm): δ = 11.60 (s, 1H, N–H); δ = 0.94 (t, 3H, –CH_3); δ = 2.20 (s, 3H, N–C–CH_3); δ = 1.20–1.82 (m, 6H, –$CH_2CH_2CH_2$-); δ = 2.06 (s, 2H, H_2O). ^{13}C NMR ($CDCl_3$, ppm): δ = 164.96(CON); δ = 13.32, 17.39, 25.26, 27.40, 29.68 (–$CH_2CH_2CH_2CH_3$, –CH_3). ^{119}Sn NMR ($CDCl_3$, ppm): δ = –380.

4.2.4. [$(C_4H_9)Sn(CONHOC_6H_5)\cdot Cl_2\cdot H_2O$] (**4**)

Complex **4** was prepared in the same way as **3** The colourless solid was recrystallized from ethylether/petroleum (1:1) to give colourless powder, yield: 83%, m.p. 76–78 °C. Anal. Calc. for $C_{11}H_{17}Cl_2NO_3Sn$: C, 32.96; H, 4.27; N, 3.49%. Found: C, 32.91; H, 4.33; N, 3.52%. IR (KBr, cm^{-1}): 3235w (N–H); 1617s, 1600m (CO/NC); 920s (N–O); 439s, 518s (Sn–O); 573s (Sn–C). ^{1}H NMR [$(CD_3)_2SO$, ppm]: δ = 13.90 (s, 1H, N–H); δ = 7.48–7.88 (m, 5H, Ph–H); δ = 3.36 (s, 2H, H_2O); δ = 1.37–1.78 (m, 6H, –$CH_2CH_2CH_2$-); δ = 0.93 (t, 3H, –CH_3). ^{13}C NMR [$(CD_3)_2SO$, ppm]: δ = 161.14 (CON); δ = 13.44, 25.06, 27.07, 34.99, (–$CH_2CH_2CH_2CH_3$); δ = 126.12, 127.60, 128.44, 131.82 (Ph–C). ^{119}Sn NMR [DMSO-d_6, ppm]: δ = –377.

4.2.5. [$(C_4H_9)SnONCO(C_6H_5)_2\cdot Cl_2\cdot H_2O]\cdot H_2O$ (**5**)

Complex **5** was prepared in the same way as **3**. The brown solid was recrystallized from ethylether/petroleum (1:1) to give

colourless powder, yield: 80%, m.p. 96–97 °C. Anal. Calc. for $C_{17}H_{23}Cl_2NO_4Sn$: C, 41.25; H, 4.68; N, 2.83%. Found: C, 41.20; H, 4.72; N, 2.88%. IR (KBr, cm^{-1}): 1614w, 1587w (CO/NC); 923s (N–O); 439s, 518w (Sn–O); 580w, (Sn–C). ^1H NMR ($CDCl_3$, ppm): δ = 7.27–7.44 (m, 10H, Ph–H); δ = 0.93–1.94 (m, 9H, $-CH_2CH_2CH_2CH_3$) δ = 2.19 (s, 4H, H_2O). ^{13}C NMR ($CDCl_3$, ppm): δ = 163.93 (CON); δ = 13.24, 25.48, 26.79, 33.01 ($-CH_2CH_2CH_2CH_3$); δ = 126.44, 128.17, 129.15, 129.22, 129.28, 129.73, 131.75, 138.62 (Ph–C). ^{119}Sn NMR ($CDCl_3$, ppm): δ = −367.

4.2.6. $[(C_4H_9Sn)_2(ONCO(C_6H_5)_2)_2\cdot Cl_2\cdot(OCH_3)_2]$ (**6**)

Complex **6** was prepared in the same way as 3. The brown solid was recrystallized from methanol/petroleum (2:1) to give colourless powder, yield: 63%, m.p. 93–95 °C. Anal. Calc. for $C_{18}H_{22}ClNO_3Sn$: C, 47.56; H, 4.88; N, 3.08%. Found: C, 47.48; H, 4.95; N,3.12%. IR (KBr, cm^{-1}): 1604w, 1538w (CO/NC); 925s (N–O); 481s and 545s (Sn–O); 569w(Sn–C). ^1H NMR ($CDCl_3$, ppm): δ = 7.23–7.40 (m, 10H, Ph–H); δ = 0.93–1.89 (m, 9H, $-CH_2CH_2CH_2CH_3$); δ = 3.47 (s, 3H, $-OCH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ = 164.13 (CON); δ = 13.45, 25.57, 27.07, 33.84 ($-CH_2CH_2CH_2CH_3$); δ = 50.81($-OCH_3$); δ = 126.80, 128.29, 129.03, 129.32, 129.39, 129.80, 131.82, 139.06 (Ph–C). ^{119}Sn NMR ($CDCl_3$, ppm): δ = −353.

4.2.7. $[(C_4H_9Sn)_3(NHOCOC_6H_5)_9K]^+\cdot Cl^-\cdot(CH_3CH_2)_2O$ (**7**)

The reaction was carried out under nitrogen atmosphere. benzohydroxamic acid (0.1097 g, 0.8 mmol) and KOH (0.0449 g, 0.8 mmol) were added to a stirred solution of methanol (30 ml) in a Schlenk flask and stirred for 0.5 h. Dibutyltin dichloride(0.1215 g, 0.4 mmol) was then added to the reactor. The reaction mixture was stirred for 8 h at room temperature and then filtrated. The filtrate was evaporated in vacuo. The obtained solid was recrystallized from ethylether/petroleum (1:1) to give colourless blocks of crystals, yield: 78%, m.p.124–126 °C. Anal. Calc. for $C_{9.63}H_{10.75}Cl_{0.13}K_{0.13}N_{1.13}O_{2.31}Sn_{0.38}$: C, 49.41; H, 4.63; N, 6.76%. Found: C, 49.35; H, 4.69; N, 6.82%. IR (KBr, cm^{-1}): 3191w (N–H); 1600s, 1569s (CO/NC); 917s (N–O); 449m and 509m (Sn–O); 554s, (Sn–C). ^1H NMR($CDCl_3$, ppm): δ = 7.02–7.93 (m, 45H, Ph–H); δ = 4.02 (m, 4H, $-CH_2OCH_2$-); δ = 0.85–1.70 (m, 33H, $-CH_2CH_2CH_2$-, $-CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ = 162.23 (CON); δ = 126.55, 128.24, 130.12, 131.26 (Ph–C); δ = 15.14, 15.77, 18.75, 25.27, 29.65 ($-CH_2CH_2CH_2CH_3$, $-CH_3$). δ = 63.90 ($-CH_2OCH_2$). ^{119}Sn NMR ($CDCl_3$, ppm): δ = −482.

4.2.8. $[(C_4H_9Sn)_3(NHOCOC_6H_5)_9Na]^+\cdot Cl^-\cdot CH_2Cl_2$ (**8**)

The reaction was carried out under nitrogen atmosphere. Benzohydroxamic acid (0.1097 g, 0.8 mmol) and NaOH (0.032 g, 0.8 mmol) were added to a stirred solution of methanol (30 ml) in a Schlenk flask and stirred for 0.5 h. Dibutyltin dichloride(0.1215 g, 0.4 mmol) was then added to the reactor. The reaction mixture was stirred for 8 h at room temperature and then filtrated. The filtrate was evaporated in vacuo. The obtained solid was recrystallized from dichloromethane/petroleum (1:1) to give colourless blocks of crystals, yield: 78%, m.p.122–124 °C. Anal. Calc. for $C_{25.33}H_{27.67}ClN_3Na_{0.33}O_6Sn$: C, 48.15; H, 4.41; N, 6.65%. Found: C, 48.10; H, 4.35; N, 6.71%. IR (KBr cm^{-1}): 3200m (N–H); 1600s, 1569s (CO/NC); 917s (N–O); 449m and 509m (Sn–O); 554s, (Sn–C); ^1H NMR ($CDCl_3$, ppm): δ = 7.06–7.62 (m, 45H, Ph–H); δ = 0.85–1.70 (m, 27H, $-CH_2CH_2CH_2CH_3$). δ = 5.25 (s, 2H, CH_2Cl_2). ^{13}C NMR ($CDCl_3$, ppm): δ = 162.45 (CON); δ = 128.01, 128.23, 129.75, 130.59 (Ph–C); δ = 13.53, 19.19, 26.16, 29.78 ($-CH_2CH_2CH_2CH_3$); δ = 53.33 (CH_2Cl_2). ^{119}Sn NMR ($CDCl_3$, ppm): δ = −480.

4.3. X-ray crystallographic studies

Diffraction data were collected on a Smart CCD area-detector with graphite monochromated Mo Kα radiation (λ = 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. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 5 and Table 6

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Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.02.017.

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