DOI: 10.1002/ejic.200600546

New Coordination Modes of Substituted Benzohydroxamic Acid with Dialkyltin(IV): Structural Diversity through Ligand Isomerization

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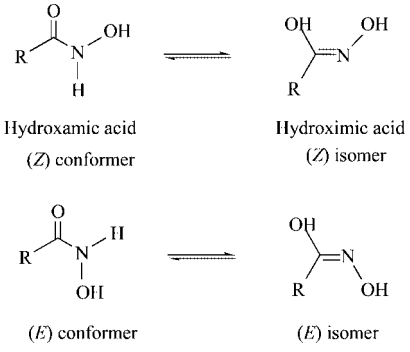
Keywords: Coordination modes / Organotin / Hydroxamic / Hydroximic / Isomerization

When R_2SnCl_2 (R = Me, *n*Bu) reacted with substituted benzohydroxamic acid (substituent = 4-F; 2,4-Cl_2; 2,5-F_2) and potassium hydroxide in aqueous methanol solution, two types of condensation products could be obtained, depending on the molar ratio R_2SnCl_2/RCONHOH/KOH. When a 1:1:2 molar ratio was used, 1:1 alkyltin hydroxamates $\{(n\text{-}C_4H_9)_2Sn[4\text{-}FC_6H_4C(O)NO]\}_n$ (**1**) and $\{(CH_3)_2Sn[2,5\text{-}F_2C_6H_3C(O)NO]\}_n$ (**2**) were formed. When a 1:2:2 ratio was used, another two unexpected 2:3 alkyltin hydroxamates, $\{(CH_3)_4Sn_2[(2,4\text{-}Cl_2C_6H_3C(O)NHO)_2][2,4\text{-}Cl_2C_6H_3C(O)NO]\}_n$ (**3**) and $\{(n\text{-}C_4H_9)_4Sn_2[(4\text{-}FC_6H_4C(O)NHO)_2][4\text{-}FC_6H_4C(O)NO]\}_n$ (**4**), were obtained. All these complexes were characterized by elemental analysis, IR, ^1H, ^{13}C, ^{119}Sn NMR spectra and X-ray diffraction analysis. The results indicated overall (*Z*)-iminol coordination mode in the hydroximic tautomeric form for **1** and **2**, and keto-iminol mixed-coordination mode including both in (*Z*)-hydroxamic and -hydroximic tautomeric forms for **3** and **4**.

Introduction

Hydroxamic acids (HAs) have attracted considerable attention recently as supporting ligands in organometallic chemistry and biology because of their tautomerization,[1] and potential as therapeutics agents.[2] The biological importance and different conformation of HAs may make their organometallic derivatives exert a subtle influence on their medicinal applications. In principle, each of the two oxygen atoms of the hydroxamato ligand is capable of acting as a coordination site, and the bonding modes are flexible. Moreover, tautomers of HAs assume different conformations or configurations, as indicated in Scheme 1. The HAs preferentially adopt the (*Z*) configurations when binding with metal ions to form a complex, either through the hydroxamic acid form or the hydroximic acid form. In addition, it is well documented by both theoretical[3] and experimental studies that the hydroxamic form is the dominant one in free acids[4] or metal hydroxamates.[5]

Despite these attractive features, studies on the coordination modes of the complexes possessing hydroxamic ligands are still relatively scarce. According to the literature,[6] the complexes of hydroxamic derivatives with metal formed O,O five-membered chelate rings in most cases, and the ligands were usually in the hydroxamic form rather than hydroximic form. To the best of our knowledge, the complexes in which ligands are only in the hydroximic form are rarely observed, and indeed, a case with the ligands coordinated to the metal center both in the hydroxamic and hydroximic forms in the same complex has not yet been reported.



Scheme 1. Isomers of hydroxamic acids.

On the other hand, in contrast to the extensive chemistry of transition-metal hydroxamato complexes,[7,8] little is known about the hydroxamato organotin(IV) complexes,[9] especially their coordination modes. The synthesis and structure of 1:2 diorganotin(IV)/hydroxamato complexes have been previously reported by our group,[10,11] which provides a novel coordination mode for hydroxamato diorganotin(IV) complexes. To obtain a deeper insight into the influence of the ligand and to further explore structural diversity, in this work, an extension of the work on the 1:2 diorganotin(IV)/hydroxamato complexes was carried out, and four unusual complexes containing the (*Z*) isomer hydroximic ligand were obtained, presenting novel 1:1 and 2:3 organotin(IV)/hydroxamato complexes with hydroximic ligands. Furthermore, the reaction of substituted benzohydroxamic acid with dialkyltin(IV) compounds, leading to

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the formation of these special organotin(IV) complexes with hydroximato ligands, is also discussed.

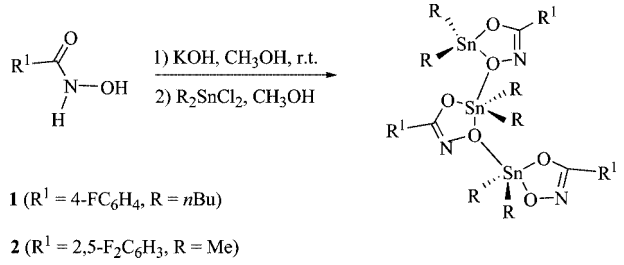
Results and Discussion

Reaction of Dialkyltin Dichloride with Substituted Benzohydroxamic Acid

To obtain a deeper insight into the coordination of hydroxamic acid to the tin center, the reaction of dialkyltin dichloride with substituted benzohydroxamic acid was studied. It was found that the reaction of dialkyltin dichloride (Bu_2SnCl_2 and Me_2SnCl_2) with substituted benzohydroxamic acid and potassium hydroxide at a 1:1:2 ratio in methanol/water gave 1:1 dialkyltin hydroxamates $\{(n\text{-}C_4H_9)_2Sn[4\text{-}FC_6H_4(O)C{=}NO]\}_n$ (**1**) and $\{(CH_3)_2Sn[2,5\text{-}2F\text{-}C_6H_3C(O)NO]\}_n$ (**2**). When a 1:2:2 ratio was used, another two unexpected 2:3 alkyltin hydroxamates, $\{(CH_3)_4Sn_2[(2,4\text{-}Cl_2C_6H_3C(O)NHO)_2][2,4\text{-}Cl_2C_6H_3C(O)NO]\}_n$ (**3**) and $\{(n\text{-}C_4H_9)_4Sn_2[(4\text{-}FC_6H_4C(O)NHO)_2][4\text{-}FC_6H_4C(O)NO]\}_n$ (**4**), were obtained. All of these complexes contain chelating hydroximic acid ligands [(*Z*) isomer], which is obviously different from well-known dialkyltin hydroxamates. Although the reactions of metal ions with hydroxamic acid have been studied extensively, most of them form 1:2 complexes containing hydroxamic acid ligands [(*Z*) conformer], and very little is reported on complexes containing hydroximic acid ligands [(*Z*) isomer]. Presumably, complexes **1**, **2**, **3**, and **4** could result from the tautomerism of the hydroxamic acid ligand, as shown in Scheme 1. The present observation might be attributed to three favorable factors: (1) the alkaline reaction conditions might make the equilibrium (as shown in Scheme 1) move from hydroxamic acid [(*Z*) conformer] toward hydroximic acid [(*Z*) isomer] easily, and thus, the hydrogen atom linked to the nitrogen atom could migrate to the oxygen atom of the carbonyl group; then the ratio of hydroximic acid in the keto-iminol tautomerism equilibrium would be raised in this way, resulting in these complexes with new coordinated modes; (2) the strong electron-withdrawing nature of F or Cl may enhance the 1,3-migratory aptitude of the hydrogen atom in the hydroxamic acid ligands; (3) it is also conceivable that a hydroxamic acid in the (*E*) conformation could also give the observed products, as any energy requirement for isomerism to the (*Z*) form would be compensated for by the favorable energetics associated with the formation of a stable five-membered chelate ring (i.e. chelate effect).

Syntheses and Characterizations of 1 and 2

When dialkyltin dichloride (Bu_2SnCl_2; Me_2SnCl_2) reacts with substituted benzohydroxamic acid (substituent = 4-F; 2,5-F_2) and potassium hydroxide, 1:1 condensation products **1** and **2** can be obtained (Scheme 2). In the IR spectra for the two complexes, a remarkable difference is the complete disappearance of the stretching vibration bands of N–H in contrast to their free ligands. This unambiguously confirms that these ligands are coordinated to the tin atoms through the hydroximic form. The characteristic absorptions at both 1661–1610 cm^{-1} in the spectra of **1** and **2** indicate the presence of a C=N group.[12–15] For **1**, the Bu–Sn–Bu angle of 129° calculated from the equation of Holeček and Lyčka[16] is very close to the value of 130.1(4)° found by X-ray analysis (Table 1). The Me–Sn–Me angle for **2** in solution calculated from the equation of Lockhart and Manders[17] is 128°, also close to the 131.45(19)° observed in the solid state (Table 2). The ^{119}Sn NMR spectroscopic data show only one signal at $\delta \approx -124.8$ ppm for **1** and $\delta \approx -129.9$ ppm for **2**, indicating a typical five-coordinate species,[16] which was further confirmed by single-crystal X-ray analysis.

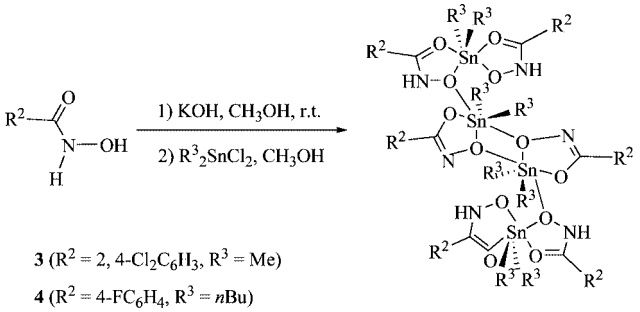


1 (R^1 = 4-FC_6H_4, R = *n*Bu)

2 (R^1 = 2,5-$F_2C_6H_3$, R = Me)

Scheme 2.

Reaction of dialkyltin dichloride (Me_2SnCl_2; Bu_2SnCl_2) with substituted benzohydroxamic acid (substituent = 2,4-Cl_2; 4-F) in 1:2 stoichiometry yields 2:3 condensation products **3** and **4** (Scheme 3). In their free ligands, a strong band near 3207 cm^{-1} is observed, assigned to be the ν(NH) absorption, which is shifted to higher frequency (near 3290 cm^{-1}) in the two complexes. This shows that the NH group is retained in the two complexes. In the ^1H NMR spectra of complex **3**, two single resonances for the proton in the –NH–O– group are observed at δ = 9.21 and 10.56 ppm, indicating that the proton of the –NH–O– group exists in complex **3**, and confirming the ligand coordinates to the tin atom in the keto (hydroxamato) form.



3 (R^2 = 2, 4-$Cl_2C_6H_3$, R^3 = Me)

4 (R^2 = 4-FC_6H_4, R^3 = *n*Bu)

Scheme 3.

The ^{119}Sn NMR spectroscopic data show two signals at $\delta \approx -222.6$ and –221.0 ppm for **3** ($\delta \approx -217.4$, –216.6 ppm for **4**), indicating the presence of two different tin sites in solution, which has been confirmed in the solid state for **3** and **4**. The $\delta(^{119}Sn)$ values of compounds **3** and **4** belong in the range of six-coordinate compounds.[16,18] In complexes

3 and **4**, the ligands are also coordinated to the tin atom in the iminol (hydroximato) form, which was verified by X-ray crystal diffraction technique and is discussed below.

Crystal Structures of Complexes 1 and 2

Selected bond lengths and angles of complexes **1** and **2** are listed in Tables 1 and 2, respectively. The molecular structures of the two complexes are shown in Figures 1 and 2 for a single chain based on the one-dimensional oxygen-bridged dialkyltin(IV) complex. The substituted benzohydroximic ligands are found to be chelated to the Sn atom through the carbonyl O atom and the hydroxy O atom, and Sn–O bond lengths are 2.065(6) and 2.191(5) Å for **1**, and 2.064(2) and 2.155(2) Å for **2**. The Sn^{IV} atoms are bonded to two alkyl groups, and the C(8)–Sn1–C(12) linkage for **1** [C(8)–Sn1–C(9) for **2**] is not linear, having an angle of 130.1(4)° for **1** [131.45(19)° for **2**]. All these Sn–C and Sn–O bond lengths and also all bond angles around the Sn center are typical values compared with other diorganotin(IV) complexes.[19,20]

However, the endocyclic C–N and C–O bond lengths are special in contrast with those of well-known 1:2 diorganotin hydroxamates. The bond length C(7)–N(1) in complex **1** is 1.237(9) Å, and is significantly shorter than the values in the known 1:2 complexes [the average C–N distance of 1.32 Å is comparable to the corresponding distance in diorganotin(IV) hydroxamates]. Moreover, no hydrogen atom is at the N1 position, suggesting that the C–N bond in complex **1** is a typical double bond.[21] Meanwhile, the bond length C(7)–O(1) in complex **1** is 1.378(9) Å, and is significantly longer than the typical value of C=O [the average C=O distance of 1.25 Å is comparable to the corresponding distance in diorganotin(IV) hydroxamates],[22] which shows the C–O bond in the complex should be a typical single bond. The bonding mode is in good agreement with hydroximic acid [(*Z*) isomer]. From the above analysis it could be concluded that the ligand is coordinated to the tin(IV) atom in the hydroximic acid form, and complex **1** is a hydroximate rather than a hydroxamate.

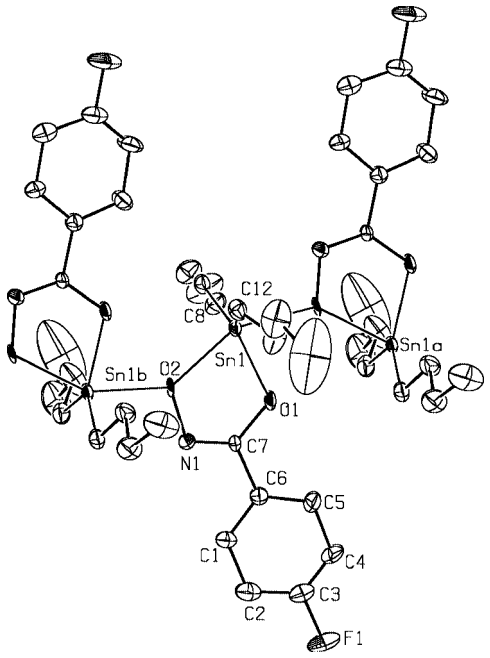


Figure 1. Diagram of a section of polymeric **1**. Hydrogen atoms are omitted for clarity.

For complex **2**, the overall structure (Figure 2, Table 2) is similar to that of complex **1**. The Sn^{4+} ion is bonded with two CH_3 groups and one substituted benzohydroximic ligand. The coordination number of the Sn atom is 5. The complex has no unusual distances or angles in the Me_2Sn unit.

Like complex **1**, the bond length C(7)–N(1) in complex **2** is 1.286(5) Å, and is significantly shorter than those values in the known 1:2 complexes.[11] Consistently, the average C(7)–O(2) distance [1.318(4) Å] of complex **2** is significantly

Table 1. Selected bond lengths [Å] and angles [°] for **1**. Symmetry operators: #1: $-x + 2, y + 1/2, -z + 1/2$; #2: $-x + 2, y - 1/2, -z + 1/2$.

O(1)–Sn(1)	2.065(6)	C(7)–N(1)	1.237(9)
O(2)–Sn(1)	2.191(5)	C(7)–O(1)	1.378(9)
O(2)–Sn(1)#1	2.134(4)	N(1)–O(2)	1.428(8)
Sn(1)–O(2)#2	1.512(14)	C(8)–Sn(1)	2.085(10)
C(8)–Sn(1)–C(12)	130.1(4)	O(1)–Sn(1)–C(12)	114.2(4)
O(1)–Sn(1)–C(8)	115.7(3)	O(1)–Sn(1)–O(2)#2	76.4(2)
C(8)–Sn(1)–O(2)#2	96.3(3)	C(12)–Sn(1)–O(2)#2	95.3(3)
O(1)–Sn(1)–O(2)	75.0(2)	C(8)–Sn(1)–O(2)	96.0(3)
C(12)–Sn(1)–O(2)	96.3(3)	O(2)#2–Sn(1)–O(2)	151.45(9)

Table 2. Selected bond lengths [Å] and angles [°] for **2**. Symmetry operators: #1: $-x + 1, y - 1/2, z + 1/2$; #2: $-x + 1, y + 1/2, -z + 1/2$.

Sn(1)–O(1)	2.155(2)	C(7)–N(1)	1.286(5)
Sn(1)–O(2)	2.064(2)	C(7)–O(2)	1.318(4)
Sn(1)–O(1)#1	2.151(2)	N(1)–O(1)	1.430(4)
O(1)–Sn(1)#2	2.151(2)	Sn(1)–C(8)	2.097(4)
C(8)–Sn(1)–C(9)	131.45(19)	C(9)–Sn(1)–O(1)#1	95.40(15)
O(2)–Sn(1)–C(8)	111.39(16)	O(2)–Sn(1)–O(1)	74.03(9)
O(2)–Sn(1)–C(9)	117.15(15)	C(8)–Sn(1)–O(1)	98.71(14)
O(2)–Sn(1)–O(1)#1	76.97(9)	C(9)–Sn(1)–O(1)	94.63(15)
C(8)–Sn(1)–O(1)#1	95.00(13)	O(1)#1–Sn(1)–O(1)	150.78(5)

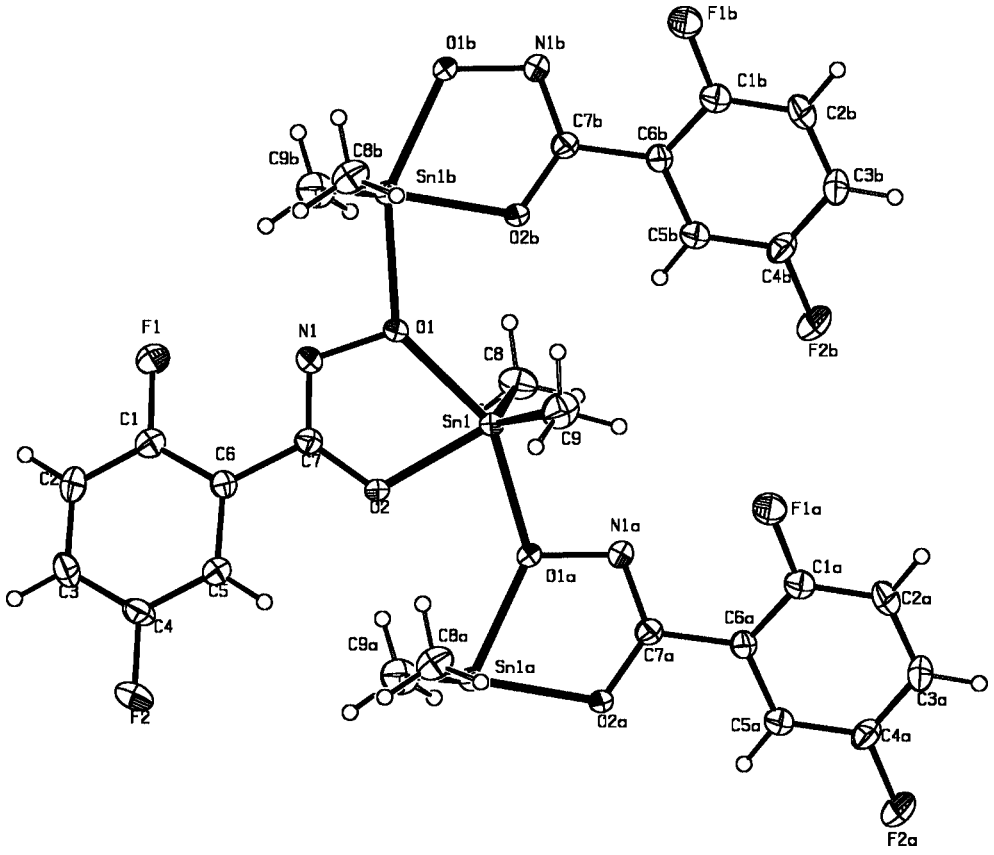


Figure 2. ORTEP drawing of a section of polymeric **2** with atomic numbering scheme.

longer than the corresponding distance of C=O, indicating the C–O bond in complex **2** should be a typical single bond. These data show that the ligand is coordinated to the tin(IV) atom in the hydroximic acid form and the coordination mode of complex **2** is similar to that of complex **1**.

Crystal Structures of Complexes 3 and 4

The molecular structures of **3** and **4** are shown in Figures 3 and 4, respectively. Selected bond lengths and angles for complexes **3** and **4** are listed in Tables 3 and 4, respec-

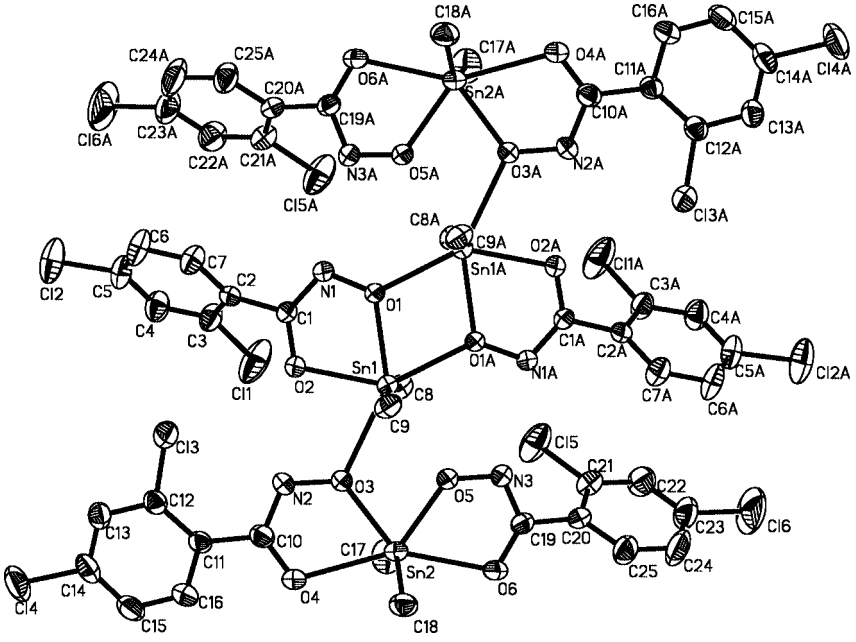


Figure 3. Diagram of the dimeric repeating units in polymeric **3**. Hydrogen atoms are omitted for clarity.

tively. The crystal structure of the two compounds consists of one-dimensional linear chains in which $Me_4Sn_2[(2,4\text{-}Cl_2C_6H_3C(O)NHO)_2][2,4\text{-}Cl_2C_6H_3C(O)NO]$ or $(n\text{-}C_4H_9)_4Sn_2\{[4\text{-}FC_6H_4C(O)NHO]_2\}[4\text{-}FC_6H_4C(O)NO]$ units are sequentially bridged by the oxygen atom of the N–O bond in the ligands and contain a central planar Sn_2O_2 four-membered ring. The ligands in the two complexes have been combined with dialkyltin(IV), forming many five-membered heterometallacycles. However, the number and configuration of the ligand bonded to a different Sn atom are obviously not consistent with each other. Only one ligand is coordinated to Sn1 through the hydroximic form, while the other two ligands are coordinated to Sn2 through the hydroxamic form. In contrast to the behavior observed for the 1:2 or 1:1 diorganotin hydroxamate complexes, both **3** and **4** are 2:3 condensation products with an unusual coordinating mode.

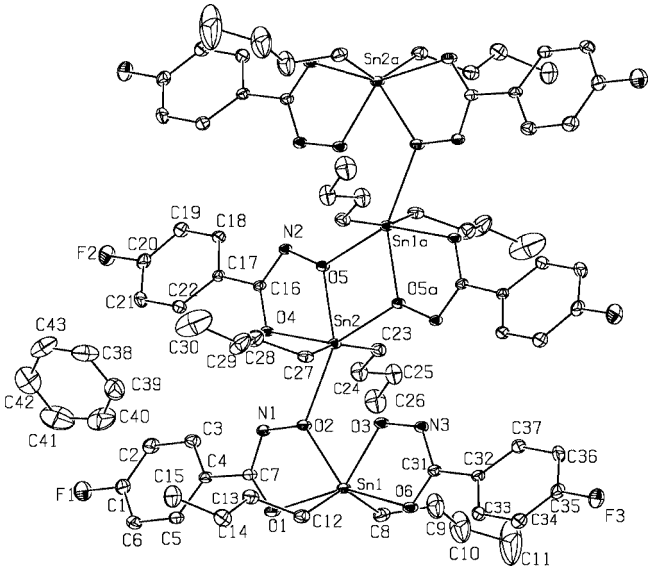


Figure 4. Diagram of the dimeric repeating units in polymeric **4**. Hydrogen atoms are omitted for clarity.

In complex **3**, the bond lengths N(2)–C(10) and N(3)–C(19) are 1.314(6) and 1.314(5) Å respectively. The distances are in the range of a typical single bond, and nearly equivalent N(2)–C(10) and N(3)–C(19) bond lengths suggest two similar hydroxamate ligands attached to the same Sn2 atom. Bond lengths C(10)–O(4) and C(19)–O(6) are 1.247(6) and 1.255(5) Å, respectively, which are in the expected range for C=O bond interaction with obvious double and donor-bond character. The bonding mode of the ligand is well in agreement with the (*Z*) conformer of hydroxamic acid, indicating that ligands are coordinated to Sn2 through the hydroxamic ligand [(*Z*) conformer] form.

Complex **4** is similar to complex **3** in molecular structure. The bond lengths N(1)–C(7) and N(3)–C(31) are 1.323(5) and 1.311(5) Å, respectively, indicating the distances are in the range of a typical single bond in diorganotin(IV) hydroxamates. The slight difference in the bond lengths N(1)–C(7) and N(3)–C(31) may be a result of the existence of solvent molecules (benzene). Bond lengths C(7)–O(1) and C(31)–O(6) are 1.241(5) and 1.255(5) Å, respectively, which are in the expected range for the C=O bond. The bonding mode of the ligand is in good agreement with the (*Z*) conformer of hydroxamic acid, indicating that the ligands are coordinated to Sn1 through the hydroxamic ligand [(*Z*) conformer] form.

Characteristically, the distance between the central carbon atom and the coordinated oxygen atom, C(1)–O(2), is 1.305(5) Å in complex **3** {the C(16)–O(4) distance [1.307(4) Å] in complex **4**}, significantly longer than that of the expected C=O double bond in typical diorganotin(IV) hydroxamates, indicating a typical single bond. Concurrently, the relatively short N(1)–C(1) [1.280(5) Å] bond in complex **3** and N(2)–C(16) [1.302(5) Å] bond in complex **4** exist in the same ligand and no hydrogen atom is at the nitrogen atom, indicating a C=N double bond. The ligand-bonding mode is consistent with hydroximic acid [(*Z*) isomer], indicating the ligand is coordinated to Sn1 in complex **3** (Sn2 in complex **4**) in the hydroximic ligand [(*Z*) isomer] form.

Table 3. Selected bond lengths [Å] and angles [°] for **3**. Symmetry operator: #1: $-x, y, -z + 1/2$.

Sn(1)–C(9)	2.097(5)	N(1)–C(1)	1.280(5)
Sn(1)–C(8)	2.100(5)	N(1)–O(1)	1.422(4)
Sn(1)–O(1)	2.167(3)	N(2)–C(10)	1.314(6)
Sn(1)–O(2)	2.190(3)	N(2)–O(3)	1.381(5)
Sn(1)–O(1)#1	2.274(3)	N(3)–C(19)	1.314(5)
Sn(1)–O(3)	2.450(3)	N(3)–O(5)	1.381(4)
Sn(2)–C(18)	2.095(5)	O(2)–C(1)	1.305(5)
Sn(2)–C(17)	2.105(5)	O(4)–C(10)	1.247(6)
Sn(2)–O(3)	2.109(3)	O(6)–C(19)	1.255(5)
C(9)–Sn(1)–C(8)	163.48(19)	C(18)–Sn(2)–O(3)	108.87(18)
C(9)–Sn(1)–O(1)	95.54(16)	C(17)–Sn(2)–O(3)	101.7(2)
C(8)–Sn(1)–O(1)	99.78(15)	C(18)–Sn(2)–O(5)	101.99(17)
C(9)–Sn(1)–O(2)	98.94(17)	C(17)–Sn(2)–O(5)	110.8(2)
O(1)–Sn(1)–O(2)	71.72(11)	C(18)–Sn(2)–O(6)	89.25(17)
C(9)–Sn(1)–O(1)#1	88.95(17)	C(17)–Sn(2)–O(6)	82.62(19)
C(8)–Sn(1)–O(1)#1	90.24(16)	O(3)–Sn(2)–O(6)	139.41(11)
O(2)–Sn(1)–O(1)#1	142.31(11)	C(18)–Sn(2)–O(4)	85.51(17)
C(8)–Sn(1)–O(3)	88.23(16)	O(3)–Sn(2)–O(4)	68.37(12)
O(2)–Sn(1)–O(3)	75.54(11)	O(6)–Sn(2)–O(4)	151.28(11)

Table 4. Selected bond lengths [Å] and angles [°] for **4**. Symmetry operator: #1: $-x + 1, -y + 2, -z + 1$.

Sn(1)–C(12)	2.109(5)	N(1)–C(7)	1.323(5)
Sn(1)–C(8)	2.111(5)	N(1)–O(2)	1.379(4)
Sn(1)–O(1)	2.492(3)	N(2)–C(16)	1.302(5)
Sn(1)–O(2)	2.130(3)	N(2)–O(5)	1.434(4)
Sn(1)–O(3)	2.137(3)	N(3)–C(31)	1.311(5)
Sn(1)–O(6)	2.353(3)	N(3)–O(3)	1.363(4)
Sn(2)–C(27)	2.110(4)	O(1)–C(7)	1.241(5)
Sn(2)–C(23)	2.112(5)	O(4)–C(16)	1.307(4)
Sn(2)–O(4)	2.167(3)	C(31)–O(6)	1.255(5)
C(12)–Sn(1)–C(8)	138.4(2)	C(27)–Sn(2)–C(23)	161.25(18)
C(12)–Sn(1)–O(2)	103.17(16)	C(27)–Sn(2)–O(5)	97.45(14)
C(8)–Sn(1)–O(2)	107.81(17)	C(23)–Sn(2)–O(5)	98.38(15)
C(12)–Sn(1)–O(3)	112.64(17)	O(5)–Sn(2)–O(4)	72.66(9)
O(2)–Sn(1)–O(3)	68.75(10)	O(4)–Sn(2)–O(5)#1	141.74(9)
C(12)–Sn(1)–O(6)	84.36(15)	C(27)–Sn(2)–O(2)	85.07(14)
C(8)–Sn(1)–O(6)	90.49(17)	C(23)–Sn(2)–O(2)	86.91(15)
O(2)–Sn(1)–O(6)	138.10(10)	O(5)–Sn(2)–O(2)	147.69(9)

Based on the above studies, it could be concluded that a keto-iminol mixed-coordination mode including both hydroxamic and hydroximic tautomeric forms existed for complexes **3** and **4**.

Conclusion

Under alkaline condition, dialkyltin dichloride (Bu_2SnCl_2; Me_2SnCl_2) and substituted benzohydroxamic acid (substituent = 4-F; 2,4-Cl_2; 2,5-F_2) in aqueous methanol solution form two types of condensation products: 1:1 dialkyltin hydroxamate complexes (**1** and **2**) and unexpected 2:3 alkyltin hydroxamate complexes (**3** and **4**). All of them have been verified by spectral methods and X-ray single-crystal diffraction analysis. The present results demonstrate that all of these alkyltin hydroxamates contain hydroximic ligands [(*Z*) isomer], presenting two kinds of new coordination modes. Concurrently, dialkyltin hydroxamate complexes exhibit structural diversity through the isomerism of hydroxamic ligand, which develops the coordination chemistry of diorganotin hydroxamic complexes. So far, the result proves that diorganotin complexes containing substituted hydroxamate ligands could take on three different coordination modes. Namely, ligands of the diorganotin complexes are only in hydroxamic form [(*Z*) conformer], or only in hydroximate form [(*Z*) isomer] or in both hydroxamate form and hydroximate form [(*Z*) conformer and (*Z*) isomer], forming diversiform hydroxamate complexes.

Experimental Section

Materials and Methods: Dibutyltin(IV) dichloride, ethyl 4-fluorobenzoate, ethyl 2,5-difluorobenzoate, and 2,4-dichlorobenzoic acid were purchased from Aldrich and used as received. The other reagents were of analytical grade. 4-Fluorobenzohydroxamic acid, 2,5-difluorobenzohydroxamic acid, and 2,4-dichlorobenzohydroxamic acid were prepared according to reported methods.[23] Elemental analyses were performed with a PE-2400-II elemental analyzer. IR spectra in the range 4000–400 cm^{-1} were recorded with a Perkin–Elmer FTIR spectrophotometer as KBr discs. ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded with a Varian INOVA 600 spectrometer (600.0 MHz for ^1H, 150.8 MHz for ^{13}C, 223.6 MHz for ^{119}Sn) at ambient temperature [δ values in ppm relative to Me_4Si (^1H, ^{13}C) or Me_4Sn (^{119}Sn)].

Synthesis of $\{(n\text{-}C_4H_9)_2Sn[4\text{-}FC_6H_4(O)C{=}NO]\}_n$ (1): Dibutyltin dichloride (0.304 g, 1.0 mmol) in methanol (10 mL) was added dropwise to an aqueous methanol solution (water/methanol, 1:3, v/v, 30 mL) of 4-fluorobenzohydroxamic acid (0.150 g, 1.0 mmol) and KOH (0.112 g, 2.0 mmol). The solution was stirred under N_2 at room temperature overnight. Water (30 mL) was added to form a white precipitate, which was separated by filtration. The white solid was then recrystallized from methanol/water. Colorless sheet-shaped crystals of **1** were slowly formed at room temperature. Yield: 0.12 g, 32%. M.p. 176–178 °C. $C_{15}H_{22}FNO_2Sn$ (385.69): calcd. C 46.67, H 5.74, N 3.63; found C 46.48, H 5.85, N 3.56. IR (KBr): $\tilde{\nu}$ = 1661 s, 1601 s (CO/NC), 913 s (N–O), 587 w (Sn–C), 531 s (Sn–O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.12–7.70 (m, 4 H, C_6H_4), 1.64 [m, ^2J(Sn,H) = 76 Hz, 4 H, 2 CH^1_2], 1.52 (m, 4 H, 2 CH^2_2), 1.37 (m, 4 H, 2 C^3H_2), 0.79 (t, J = 7.2 Hz, 6 H, 2 C^4H_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 164.2 (CO), 161.4, 131.4, 127.6, 115.4 and 114.9 (C_{arom}), 27.3 [^1J(^{119}Sn,^{13}C) = 537 Hz, CH_2–Sn], 23.7 [^2J(^{119}Sn,^{13}C) = 40 Hz, CH_2CH_2Sn], 26.1 [^3J(^{119}Sn,^{13}C) = 138 Hz, $CH_2CH_2CH_2Sn$], 14.0 (R–Sn) ppm. ^{119}Sn NMR ($CDCl_3$): δ = –124.8 ppm.

Synthesis of $\{(CH_3)_2Sn[2,5\text{-}F_2C_6H_3(O)C{=}NO]\}_n$ (2): Dimethyltin dichloride (0.220 g, 1.0 mmol) in methanol (10 mL) was added dropwise to an aqueous methanol solution (water/methanol, 1:3, v/v, 30 mL) of 2,5-difluorobenzohydroxamic acid (0.173 g, 1.0 mmol) and KOH (0.112 g, 2.0 mmol). The solution was stirred under N_2 at room temperature overnight. Water (30 mL) was added to form a white precipitate, which was separated by filtration. The white solid was then recrystallized from methanol/water. Colorless sheet-shaped crystals of **2** were slowly formed at room temperature. Yield: 0.10 g, 28.2%. M.p. 262 °C dec. $C_9H_9F_2NO_2Sn$ (319.86): calcd. C 33.79, H 2.84, N 4.38; found C 33.52, H 2.96, N 4.29. IR (KBr): $\tilde{\nu}$ = 1665 s, 1616 s (CO/NC), 926 s (N–O), 586 w (Sn–C), 528 s (Sn–O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.70–7.16 (m, 3 H, C_6H_3), 0.89 [s, ^2J(Sn,H) = 79 Hz, 6 H, 2 CH_3, R–Sn] ppm. ^{13}C NMR ($CDCl_3$): δ = 165.0 (CO), 163.4, 162.6, 132.3, 127.4 and 115.7 (C_{arom}), 6.6 [^1J(^{119}Sn,^{13}C) = 584 Hz, CH_3, R–Sn] ppm. ^{119}Sn NMR ($CDCl_3$): δ = –129.9 ppm.

Synthesis of $\{(CH_3)_4Sn_2[(2,4\text{-}Cl_2C_6H_3C(O)NHO)_2][2,4\text{-}Cl_2C_6H_3(O)C{=}NO]\}_n$ (3): Dimethyltin dichloride (0.220 g, 1.0 mmol) was

Table 5. Crystal and data collection parameters of complexes **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{15}H_{22}FNO_2Sn$	$C_9H_9F_2NO_2Sn$	$C_{50}H_{54}Cl_{12}N_6O_{12}Sn_4$	$C_{86}H_{112}F_6N_6O_{12}Sn_4$
Formula mass	385.69	319.86	1829.83	2010.58
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic
Space group	*P*2(1)/c	*P*2(1)2(1)2(1)	*C*2/c	$P\bar{1}$
a [Å]	10.3740(17)	6.7490(8)	22.5882(18)	13.6579(12)
b [Å]	7.8608(13)	7.7636(9)	19.8408(16)	14.1315(13)
c [Å]	22.078(4)	20.754(2)	16.2922(13)	14.3894(13)
α [°]	90	90	90	110.0320(10)
β [°]	102.119(3)	90	115.1810(10)	94.206(2)
γ [°]	90	90	90	114.0800(10)
Volume [Å^3]	1760.3(5)	1079.0(2)	6607.8(9)	2307.5(4)
Z	4	4	4	1
$D_{calcd.}$ [Mg/m^3]	1.457	1.969	1.833	1.447
Absorption coefficient [mm^{-1}]	1.462	2.375	2.039	1.140
F(000)	776	616	3552	1020
Crystal size [mm]	0.20 × 0.10 × 0.06	0.12 × 0.06 × 0.01	0.20 × 0.20 × 0.20	0.20 × 0.10 × 0.10
Total no. of reflections measured	16283	12746	34228	26012
No. of unique reflections	3113	2580	6506	9990
R(int)	0.1624	0.0755	0.0832	0.0853
Max./min. transmission	0.9174/0.7587	0.9766/0.7637	0.6859/0.6859	0.8945/0.8040
No. of data/restraints/parameters	3113/2/184	2580/0/138	6506/0/383	9990/2/518
Goodness-of-fit on F^2	0.953	1.029	0.956	0.945
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0664 wR_2 = 0.1248	R_1 = 0.0295 wR_2 = 0.0557	R_1 = 0.0436 wR_2 = 0.0985	R_1 = 0.0461 wR_2 = 0.0976
R indices (all data)	R_1 = 0.1196 wR_2 = 0.1390	R_1 = 0.0313 wR_2 = 0.0561	R_1 = 0.0572 wR_2 = 0.1023	R_1 = 0.0737 wR_2 = 0.1133
Largest diff. peak/hole [e/Å^3]	0.860/–0.686	0.637/–0.670	0.942/–0.582	1.599/–0.606

added dropwise to an aqueous methanol solution (water/methanol, 1:4, v/v, 30 mL) of 2,4-dichlorobenzohydroxamic acid (0.412 g, 2.0 mmol) and KOH (0.112 g, 2.0 mmol). The solution was stirred under N_2 at room temperature overnight. Water (30 mL) was added to form a white precipitate, which was separated by filtration. The white solid was then recrystallized from methanol/benzene. Colorless block-shaped crystals of **3** were slowly formed at room temperature. Yield: 0.12 g, 26.3%. M.p. 188 °C (dec). $C_{50}H_{54}Cl_{12}N_6O_{12}Sn_4$ (1829.83): calcd. C 32.79, H 2.97, N 4.59; found C 32.62, H 3.01, N 4.55. IR (KBr): $\tilde{\nu}$ = 3290 s (N–H), 1591 s, 1569 s (CO/NC), 918 s (N–O), 575 s, 477 m (Sn–C), 541 s (Sn–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 10.56 (s, H, N–H), 9.21 (s, H, N–H), 7.81–7.27 (m, 6 H, 2 C_6H_3), 1.25 [s, ^2J(Sn,^{1}H) = 91 Hz, 2 CH_3, R–Sn], 0.94 [d, ^2J(Sn,H) = 77 Hz, 4 CH_3, R–Sn] ppm. ^{13}C NMR ($CDCl_3$): δ = 164.2, 162.7 (CO), 158.4, 157.2, 131.1, 113.3, 111.1 and 103.3 (C_{arom}), 5.3 [^1J(^{119}Sn,^{13}C) = 717 Hz, CH_3, R–Sn] and 6.9 [^1J(^{119}Sn,^{13}C) = 845 Hz, CH_3, R–Sn] ppm. ^{119}Sn NMR ($CDCl_3$): δ = –222.6, –221.0 ppm.

Synthesis of {$(C_4H_9)_4Sn_2$[(4-$FC_6H_4C(O)NHO)_2$][4-FC_6H_4(O)-C=NO]}$_n$ (4): Dibutyltin dichloride (0.304 g, 1.0 mmol) in methanol (10 mL) was added dropwise to an aqueous methanol solution (30 mL) of 4-fluorobenzohydroxamic acid (0.310 g, 2.0 mmol) and KOH (0.112 g, 2.0 mmol). The solution was stirred under N_2 at room temperature overnight. Water (30 mL) was added to form a white precipitate, which was separated by filtration. The white solid was then recrystallized from methanol/benzene. Colorless block-shaped crystals of **4** were slowly formed at room temperature. Yield: 0.26 g, 56%. M.p. 160–161 °C. $C_{86}H_{112}F_6N_6O_{12}Sn_4$ (2010.58): calcd. C 51.33, H 5.57, N 4.18; found C 51.20, H 5.71, N 4.03. IR (KBr): $\tilde{\nu}$ = 3287 s (N–H), 2956 (Bu), 1617 s, 1559 s (CO/NC), 904 s (N–O), 579 s, 471 m (Sn–C), 579 s (Sn–O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.68–6.94 (m, 16 H, 4 C_6H_4), 1.67–1.62 (m, 8 H, 4 $CH^2{}_2CH^1{}_2$), 1.35–1.34 (m, 8 H, 4 C^3H_2), 0.92–0.84 (t, *J* = 7.2 Hz, 12 H, 4 C^4H_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 165.5, 164.1 (CO), 163.9, 161.9, 133.9, 130.7, 128.8, 126.1, 120.4, 115.7 and 114.9 (C_{arom}), 28.5 [^1J(^{119}Sn,^{13}C) = 701 Hz, $CH^1{}_2$, R–Sn] and 27.4 [^1J(^{119}Sn,^{13}C) = 830 Hz, $CH^1{}_2$, R–Sn], 26.6, 23.2, 13.9–13.7 (R–Sn) ppm. ^{119}Sn NMR ($CDCl_3$): δ = –217.4, –216.6 ppm.

X-ray Data Collection, Structure Determination, and Refinement: Suitable single crystals of the four complexes were mounted in glass capillaries for X-ray structural analysis. Diffraction data were collected with a Bruker SMART CCD diffractometer with Mo-K_α (λ = 0.71073 Å) radiation at room temperature. During the intensity data collection, no significant decay was observed. The intensities were collected for Lorentz-polarization effects and empirical absorption with the SADABS program. The structures were solved by direct methods using the SHELXL-97 program. All non-hydrogen atoms were found from difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker Smart program.[24] A summary of the crystallographic data and selected experimental information are given in Table 5. CCDC-610570, -610571, -610572, and -610573 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Financial support from the Program for New Century Excellent Talents at the University of China (No. NCET-04-0258), from the Science and Technology Commission of Shanxi Province of China (No. 051105-2), and from the Education Commission of Shanxi Province of China (No. 200413) is gratefully acknowledged.

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Received: June 13, 2006
Published Online: August 21, 2006

