Synthesis and crystal structures of four ladder distannoxane dimers

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Abstract. Four distannoxane dimers [ClR2SnOSnR2X]2 (X=Cl, R=PhCH2 1, 2-FC6H4CH2 2, 2-ClC6H4CH2 3, X=OH, R=2,4-Cl2C6H3CH2 4) have been synthesized by the hydrolytic reaction of (PhCH2)2SnCl2 with sodium alkoxides. And all these four complexes were characterized by elemental analysis, IR, 1H NMR spectroscopies and X-ray diffraction. All compounds were assigned tetranuclear distannoxane structures in solid state, which contain so-called ladder arrangement with a central planar Sn2O2 four-membered ring. The endo- and exo-cyclic Sn atoms are both five-coordinate, and have distorted trigonal bipyramidal geometries.

1. Introduction

Tetraorganodistannoxanes of the type [R2(X)SnOSn(X)R2]2 and [R2OSnOSn(X)R2]2 (R=alkyl, Ar; X=halide, OR, OAc, NCS) are a kind of interesting organotin oxo clusters (Figure 1) and have received considerable attention in view of their application as catalysts in industry and as biocides [1-4]. A characteristic feature of this kind of complexes in the solid state is their dimerization that results in the so-called ladder or staircase arrangement which contains a central planar Sn2O2 four-membered ring. They are usually prepared by the controlled hydrolysis of diorganotin dihalides or from reaction of equimolar amount of diorganotin oxide with diorganotin dihalides. Here the tin atoms are pentacoordinated. In order to investigate this type of ladder structure as well as the hydrolysis course further, we performed hydrolysis of Bz2SnCl2 under basic condition giving four distannoxane dimers [ClR2SnOSnR2X]2 (X=Cl, R=PhCH2 1, 2-FC6H4CH2 2, 2-ClC6H4CH2 3, X=OH, R=2,4-Cl2C6H3CH2 4). And all these four complexes were characterized by IR, 1H NMR spectroscopy and X-ray diffraction analysis. The reaction sequences are as follows:

(Bz2)2SnCl2+H2O+EtONa→(Bz2)2(Cl)SnOH+NaCl+EtOH
Bz2(Cl)SnOH+EtONa→Bz2SnO+NaCl+EtOH
2(Bz2)2SnO+2(PhCH2)2SnCl2→[(Bz2)2(Cl)SnOSnCl]( Bz2)2]
[(Bz2)(Cl)SnOSn(Cl)( Bz2)2]+2EtONa+2H2O→[(Bz2)2O3SnSn(Cl)( Bz2)2]2+2NaCl+2EtOH
2. Experimental section

2.1. General procedure

All the reaction is carried out under nitrogen atmosphere using standard Schlenk technique. The (ArCH2)2SnCl2 were prepared by the reported methods [5]. The melting points were obtained with kofler micro-melting points apparatus and were uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr as discs. NMR spectra were obtained with Mercury Plus-400 NMR spectrometer and the chemical shifts are given in ppm relative to Me4Si and Me4Sn in CDCl3. Elemental analyses were performed on PE-2400-II elemental analyzer. Tin was estimated as SnO2. X-ray measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo-Kα (0.71073 Å) radiation.

2.2. Synthesis of diorganotin complexes

Syntheses of [(C6H5CH2)2ClSnOSnCl(C6H5CH2)2]: 1

The (C6H5CH2)2SnCl2 (744 mg, 2.0 mmol) was added to the solution of sodium hydroxide (136 mg, 2.0 mmol) in ethanol (30ml, 95%). Then the mixture was heated under reflux with stirring for 5-7 h and the solvent was removed by evaporation in vacuo. The crude adduct was recrystallized from ether-dichloromethane. Colorless crystal compound 1 was formed. Yield 89%, mp (174-176) °C; 1H NMR (CDCl3, 400MHz) δ: 7.15-7.65 (40H, PhH), 2.71 (s, 8H, JSn-H=71 Hz, PhCH2Sn), 2.80 (s, 8H, JSn-H=73 Hz, PhCH2Ph); IR (KBr) v: 3021 (w, Ph-H), 2923 (m, C-H), 1631, 1597, 1491, 1451 (m, Ph), 561 (m, Sn-C), 671 (s, Sn-O-Sn), 337 (m, Sn-Cl) cm-1. Anal. calcd for C56H56Cl4O2Sn4: C 48.82, H 4.10; found C 48.78, H 4.07.

Syntheses of [(2-FC6H4CH2)2ClSnOSnCl(2-FC6H4CH2)2]: 2

Compound 2 is prepared in the similar way as that of compound 1, Add (2-FC6H4CH2)2SnCl2 (816 mg, 2.0 mmol) to the solution of sodium hydroxide (136 mg, 2.0 mmol) in ethanol (30ml, 95%). Then the mixture was heated under reflux with stirring for 5-7 h and the solvent was removed by evaporation in vacuo. The crude adduct was recrystallized from ether-dichloromethane. Colorless crystal compound 2 was formed. Yield 75%, mp (210-211) °C; 1H NMR (CDCl3, 400MHz) δ: 6.98-7.40 (m, 32H, ArH), 2.78 (s, 8H, JSn-H=75 Hz, ArCH2Sn), 3.12 (s, 8H, JSn-H=77 Hz, ArCH2Ph); IR (KBr) v: 3065 (w, Ar-H), 2910 (m, C-H), 1631, 1597, 1491, 1451 (m, Ph), 561 (m, Sn-C), 675 (s, Sn-O-Sn), 335 (m, Sn-Cl) cm-1. Anal. calcd for C56H52Cl14F8O4Sn4: C 43.145, H 3.34; found C 43.13, H 3.35.

Syntheses of [(2-ClC6H4CH2)2ClSnOSnCl(2-ClC6H4CH2)2]: 3

Compound 3 is prepared in the similar way as that of compound 1, Add (2-ClC6H4CH2)2SnCl2 (882 mg, 2.0 mmol) to the solution of sodium hydroxide (136 mg, 2.0 mmol) in ethanol (30ml, 95%). Colorless
crystal compound 3 was formed. Compound 3: Yield 76%, mp (239-240) °C; 1H NMR (CDCl3, 400MHz) δ: 7.10-7.27 (32H, ArH), 3.10 (s, 8H, JSn-H=72 Hz, ArCH2Sn), 3.25 (s, 8H, JSn-H=74 Hz, ArCH2Ph); IR (KBr) v: 3070 (w, Ar-H), 2880 (m, C-H), 1630, 1589, 1473, 1439 (m, Ph), 565 (m, Sn-C), 680 (s, Sn-O-Sn), 338 (m, Sn-Cl) cm⁻¹. Anal. calcd for C₅₆H₄₈Cl₁₂O₂Sn₄: C 40.65, H 2.91; found C 40.58, H 2.96.

Syntheses of [(2, 4-Cl₂C₆H₃CH₂)₂OSnOSnCl(2, 4-Cl₂C₆H₃CH₂)₂]₂ 4

Compound 4 is prepared in the similar way as that of compound 1, Add (2, 4-Cl₂C₆H₃CH₂)₂SnCl₂ (1019 mg, 2.0 mmol) to the solution of sodium hydroxide (136mg, 2.0 mmol) in ethanl (30ml, 95%). Colorless crystal compound 4 was formed. Yield 79%, mp (245-246) °C; 1H NMR (CDCl₃, 400MHz) δ: 6.92-7.42 (24H, ArH), 5.31(s, 2H, HOSn), 2.73 (s, 8H, JSn-H=72 Hz, ArCH2Sn), 2.90 (s, 8H, JSn-H=74 Hz, ArCH2Ph); IR (KBr) v: 3080 (w, Ar-H), 2931 (m, C-H), 1636, 1558, 1469 (m, Ph), 566 (m, Sn-C), 677 (s, Sn-O-Sn) cm⁻¹, 523 (m, Sn-O), 334 (m, Sn-Cl) cm⁻¹. Anal. calcd for C₅₆H₄₆Cl₁₈O₆Sn₄: C 34.86, H 2.39; found C 34.88, H 2.41.

2.3. Crystal structure

X-ray crystallographic data for these compounds were collected on a Bruker smart-1000 CCD diffractometer using Mo-Kα radiations (0.71073Å). The structure was solved by direct method and difference Fourier map using SHELXL-97 program, and refined by full-matrix least-squares on F². All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically [6-10].

The crystal data and refinement details are given in Table 1. The selected bond distances and angles are listed in Table 2.

| Compound | 1 | 2 | 3 | 4 |
|----------|---|---|---|---|
| Chemical formula | C₅₆H₅₆Cl₄O₂Sn₄ | C₅₆H₅₂Cl₁₄F₈O₄Sn₄ | C₅₆H₄₈Cl₁₂O₂Sn₄ | C₅₆H₄₆Cl₁₈O₆Sn₄ |
| Crystal system | Monoclinic | Monoclinic | Orthorhobic | Monoclinic |
| Space group | C2/c | P-1 | Pbc a | P-1 |
| a (Å) | 25.08(3) | 10.6243(17) | 18.839(3) | 11.435(2) |
| b (Å) | 10.428(12) | 10.8750(18) | 15.767(2) | 11.912(3) |
| c (Å) | 21.44(2) | 14.157(2) | 20.353(3) | 14.217(3) |
| α(°) | 90 | 104.983(2) | 90 | 79.734(3) |
| β(°) | 93.253(15) | 107.084(2) | 90 | 85.212(3) |
| γ(°) | 90 | 91.115(2) | 90 | 69.988(3) |
| V (Å³) | 5596(11) | 5596(11) | 6045.6(14) | 7107.3 |
| Z | 4 | 4 | 4 | 1 |
| F(000) | 2704 | 760 | 3216 | 936 |
| Crystal size (nm) | 0.48×0.43×0.35 | 0.41×0.37×0.32 | 0.42×0.35×0.19 | 0.45×0.41×0.27 |
| θ tange(°) | 2.12 to 25.03 | 2.14 to 25.02 | 1.96 to 25.02 | 2.40 to 25.03 |
| μ(mm⁻¹) | 1.994 | 1.889 | 2.204 | 2.109 |
| Total/unique/Rint | 10735/4550/0.1854 | 7857/5182/0.0135 | 29459/5200/0.0507 | 9095/6102/0.0211 |
| Goodness-of-fit | 1.076 | 0.994 | 1.068 | 1.000 |
| R1/wR2 | 0.081/0.1585 | 0.0273/0.0716 | 0.0485/0.1024 | 0.0448/0.1151 |
| ρmax/ρmin (e Å⁻³) | 1.348 and -1.430 | 0.673 and -0.394 | 1.834 and -0.870 | 1.450 and -0.489 |
| Compound  | Bond Distance (nm) | Bond Angle (°) |
|-----------|--------------------|---------------|
| Sn(1)---O(1A) | 0.2508(8)         |               |
| Sn(1)---C(8)  | 0.2137(15)         |               |
| Sn(1)---C(1)  | 0.2157(15)         |               |
| Sn(1)---O(1)  | 0.2197(7)          |               |
| Sn(1)---Cl(1) | 0.2676(4)          |               |
| Sn(2)---O(1)  | 0.2026(7)          |               |
| Sn(2)---Cl(2) | 0.2134(4)          |               |
| Sn(2)---C(15) | 0.2157(15)         |               |
| Sn(1)---O(1A) | 0.2024(2)          |               |
| Sn(1)---O(8)  | 0.2135(5)          |               |
| Sn(1)---C(1)  | 0.2147(5)          |               |
| Sn(1)---Cl(1) | 0.24074(12)        |               |
| Sn(2)---O(1)  | 0.2049(3)          |               |
| Sn(2)---C(20) | 0.2148(4)          |               |
| Sn(2)---O(1)  | 0.2161(2)          |               |
| Sn(2)---Cl(1) | 0.25720(11)        |               |
| Sn(1)---O(1)  | 0.2046(5)          |               |
| Sn(1)---C(8)  | 0.2143(9)          |               |
| Sn(1)---C(1)  | 0.2147(8)          |               |
| Sn(1)---O(1A) | 0.2187(5)          |               |
| Sn(1)---Cl(1) | 0.25362(2)         |               |
| Sn(2)---O(1)  | 0.2020(5)          |               |
| Sn(2)---C(22) | 0.21489(8)         |               |
| Sn(2)---C(15) | 0.21589(9)         |               |
| Sn(2)---Cl(2) | 0.2406(3)          |               |
| Sn(2)---Cl(1) | 0.2843(3)          |               |
| Sn(1)---O(1)  | 0.2018(4)          |               |
| Sn(1)---C(8)  | 0.2142(8)          |               |
| Sn(1)---C(1)  | 0.2148(8)          |               |
| Sn(1)---O(2)  | 0.2243(5)          |               |
| Sn(1)---Cl(1) | 0.2455(2)          |               |
| Sn(2)---O(1)  | 0.2043(4)          |               |
| Sn(2)---C(15) | 0.2130(7)          |               |
| Sn(2)---O(1A) | 0.2134(4)          |               |
| Sn(2)---C(22) | 0.2144(8)          |               |
| Sn(2)---O(2)  | 0.2162(5)          |               |
3. Results and Discussion

The molecular structures of compounds 1, 2, 3, and 4 are illustrated in Figs. 1-4.

Figure 2. Molecular structure of the compound 1.

Figure 3. Molecular structure of the compound 2.

Figure 4. Molecular structure of the compound 3.

Figure 5. Molecular structure of the compound 4.

3.1. IR spectra

The (ArCH2)2SnCl2 were prepared by the reported methods [5]. The infrared spectra of compounds 1-4 have been recorded and some important assignments are shown above. The band in 334-338 cm⁻¹ are assigned to the stretching mode of the Sn-Cl linkage. The strong bands in the 671-680 cm⁻¹ are attributed to ν(Sn-O-Sn) indicating a Sn-O-Sn link in compounds 1-4 [11].

3.2. H-NMR spectra

The ¹H NMR assignments for the compounds 1-4 are shown above. It is shown that the chemical shifts of the protons on the benzyl groups of the compounds 1-4 exhibit two signals about 6.92-7.65 ppm as multiplet and 2.71-3.15 ppm as a singlet with 119/117-Sn satellites, the coupling constant J(Sn-H) = 71 - 77 Hz.

3.3. Crystal structures

All these four distannoxane dimers [ClR2SnOSnR2X]2 (X=Cl, R=PhCH2 1, 2-FC6H4CH2 2, 2-CIC6H5CH2 3, X=OH, R=2,4-Cl2C6H3CH2 4) adopt the common structural type found for compounds of the general formula [R2(Cl)SnOSn(X)R2]2 (X=Cl or OH) and exist as ladder structure that contain two endo- and two exo-cyclo tin atoms. They can be viewed as centrosymmetric ladder distannoxane dimer, which is an essentially planar. Of the center SnO2, the bridgeoxo atom function as tridendate and the internal angles (74.5° and 105.5° for 1; 73.86° and 106.14° for 2; 74.6° and 105.4° for 3; 73.3° and 106.7°...
for 4) are consistent with those in other distannoxane systems, such as 74.9°, 105.1° of [ClMe2SnOSnMe2Cl][12], 75.3º, 104.7° of [Cl(nBu)2SnOSn(nBu)2Cl][10,13], 74.2°, 106.0° of [ClPh2SnOSnPh2OH][2] and 76.2°, 105.5° of [ClPh2SnOSnPh2Cl][10,13].

The distance of μ3-Ο to Sn atoms are extremely similar in the four compounds: O(1)-Sn(1) 0.2197(7)nm O(1)-Sn(1A) 0.2058(8)nm for 1; O(1)-Sn(2) 0.2160(2)nm O(1)-Sn(1A) 0.2049(3)nm for 2; O(1)-Sn(1A) 0.2187(5)nm O(1)-Sn(1) 0.2046(5)nm for 3; O(1)-Sn(2A) 0.2134(4)nm O(1)-Sn(2) 0.2043(4)nm for 4, respectively, reflecting the strong coordination of bridges in those compounds, linking the crystallographic asymmetric unit and the inversion center, for 1, 2 and 3, which are chloro-bridges (0.2676(4) nm and 0.2730(4) nm; 0.2520(11) nm and 0.28153(11) nm; 0.2536(2) nm and 0.2834(3) nm, respectively); while for 4, are oxo-bridges(0.2243(5) nm and 0.2162(5) nm). It seems that with more substitute halogen, the bond distance become shorter.

The ladder structures of 1, 2, 3 and 4 are different from the staircase structure of [Me4Sn2(OSiMe3)2O][18] (three four member rings are not coplanar), as evidenced by the near coplanarity of the atoms comprising the fused ring system. For 1, the eight atoms Sn(1), Sn(2), O(1), Cl(1), Sn(1A), Sn(2A), O(1A) and O(2A) are coplanar (within ±0.0065 nm), for 2, the eight atoms are coplanar (within ±0.0052nm), for 3, the eight atoms are coplanar (within ±0.00438nm), for 4, the eight atoms are also coplanar (within ±0.00190nm). And the distance between Cl connect with the exo-cycle tin and the endo-cycle tin is 3.548 nm(compound 1), 3.628 nm(compound 2), 3.655 nm (compound 3), 3.725 nm (compound 4), respectively. They are too long to occur function [13-15].

4. Conclusion
In summary, four distannoxane dimers have been synthesized by the hydrolytic reaction of (ArCH2)2SnCl2 with soditma alkoxides. All compounds were assigned tetranuclear distannoxane structures in solid state, which contain so-called ladder arrangement with a central planar Sn2O2 four-membered ring. The endo- and exo-cyclic Sn atoms are both five-coordinate, and have distorted trigonal bipyramidal geometries. The successful synthesis of these compounds confirms that it is crucial to choose an appropriate ligand for the formation of tetranuclear distannoxane structures. The continuous research in this field is currently going on in our group.

Acknowledgments
We acknowledged the Talent Team Culturing Plan for Leading Disciplines of University in Shandong Province.

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