

Synthesis and Structure of Mixed Distannoxane Dimers [ClR₂SnOSnR'₂Cl]₂

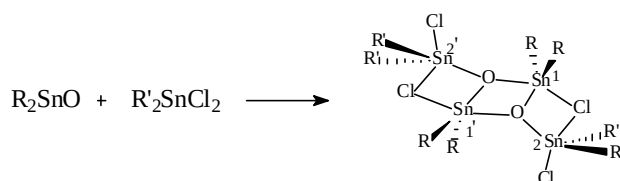
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Abstract: Mixed distannoxane dimers [ClR₂SnOSnR'₂Cl]₂ were synthesized by the reaction of R₂SnO (R = Bu, Pr) and R₂SnCl₂ (R = Me, Ph, Cy, Oct). The crystal structures of compound **1** and **5** show they are ladder-type dimers that contain a central planar Sn₂O₂ four-membered ring. Both endo- and exo-Sn atoms are five-coordinate.

Keywords: Asymmetric tetraorganodistannoxane, synthesis, crystal structure.

1,1,3,3-Tetraorganodistannoxanes [XR₂SnOSnR'₂X]₂ (R = alkyl, Ph; X = halogen, NCS, OAc, OR) are a kind of organotin oxo clusters. They have received considerable attention because they are useful catalysts for many reactions¹⁻⁵. And recently S. W. Ng reported that [XR₂SnOSnR'₂X]₂ (R = Bu, X = OOCCH₂SC(O)N(CH₂CH₂)₂O) had more active antitumor activity than *cis*-platin *in vitro*⁶. A characteristic feature of symmetric tetraorganodistannoxanes in the solid state is their dimerization that results in the so-called ladder-type arrangement that contains a central planar Sn₂O₂ four-membered ring. But tetraorganodistannoxanes with different R groups have not been fully studied yet. There is only one report of mixed distannoxane dimers [Cl(*t*-Bu)₂SnOSnR₂Cl]₂ (R = Me, *n*-Bu)⁷. In this paper, we reported the synthesis and structure of some asymmetric distannoxanes in which R and R' groups provide the asymmetry. The reaction equations were as follows:



R = *n*-Bu, R' = Ph (**1**), Me (**2**), Cy (**3**), Oct (**4**); R = *n*-Pr, R' = Ph (**5**), Me (**6**)

Experimental

R₂SnO (R = Bu, Pr) and R₂SnCl₂ (R = Me, Ph, Cy, Oct) were prepared according to literature procedures⁸. Reaction mixture of equimolar amounts of R₂SnO (R = *n*-Bu, Pr)

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with $R'_2\text{SnCl}_2$ ($R' = \text{Ph, Me, Cy, Oct}$) in acetone or chloroform was refluxed until the solutions became clear. The dimeric products $[\text{ClR}_2\text{SnOSnR}'_2\text{Cl}]_2$ were crystallized from the filtrate. The corresponding analytical and physical data were listed in **Table 1**.

Table 1 The physical and analytical data of **1**~**6**

Entry	MP (°C)	Yield (%)	Elemental Analysis	
			C (calcd.)	H (calcd.)
1	148~149	96.6	40.54 (40.52)	4.28 (4.76)
2	84~86	90.2	25.31 (25.61)	4.77 (5.16)
3	>340	72.2	40.12 (39.70)	6.65 (6.67)
4	70~73	74.4	44.06 (43.35)	7.35 (7.88)
5	160~162	70.4	38.07 (38.29)	4.24 (4.28)
6	103~105	66.4	21.92 (21.81)	3.89 (4.58)

Crystal structure determination of **1** and **5**

The single crystal structures of **1** and **5** were determined on a BRUKER SMART 1000 diffract meter with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods using SHELXL-97 program and refinement on F^2 was performed using SHELXL-97 program by Full-Matrix least squares with anisotropic parameters for all non-hydrogen atoms. All hydrogen atoms positions were located in calculation positions and isotropically refined. Absorption correction was made using SADABS. Molecular graphics were drawn with the program packages SHELXL-97. C (2) and C (4) atoms in butyl were disorder to some degree. The crystal data were as follows: compound **1**: $\text{C}_{40}\text{H}_{56}\text{Cl}_4\text{O}_2\text{Sn}_4$, Triclinic, space group $P\bar{1}$, $a = 8.8454 (11) \text{ \AA}$, $b = 12.2500 (15) \text{ \AA}$, $c = 12.6032 (15) \text{ \AA}$, $\alpha = 64.815 (2)^\circ$, $\beta = 77.194 (2)^\circ$, $\gamma = 73.614 (2)^\circ$, $V = 1177.5 (2) \text{ \AA}^3$, $Z = 1$, $R1 = 0.0404$. compound **5**: $\text{C}_{36}\text{H}_{48}\text{Cl}_4\text{O}_2\text{Sn}_4$, Triclinic, space group $P\bar{1}$, $a = 9.564 (3) \text{ \AA}$, $b = 10.193 (3) \text{ \AA}$, $c = 11.570 (3) \text{ \AA}$, $\alpha = 79.951 (5)^\circ$, $\beta = 77.011 (5)^\circ$, $\gamma = 78.510 (5)^\circ$, $V = 1470.8 (9) \text{ \AA}^3$, $Z = 1$, $R1 = 0.0452$.

The molecular structures of **1** and **5** are shown in **Figure 1** and **Figure 2**.

Compounds **1** and **5** exist as ladder-type dimers that are analogous to the traditional structure of symmetric distannoxanes. The larger bulk Ph groups link exo-Sn atoms while the smaller groups (Bu, Pr) connect with endo-Sn atoms dimer. In an asymmetric unit, both Ph_2SnCl and SnR_2 ($R = n\text{-Bu}$ for **1**, Pr for **5**) groups are connected by a Cl and an O atom to form $\text{Ph}_2\text{Sn}(\text{Cl})(\mu_2\text{-Cl})(\mu\text{-O})\text{SnR}_2$ fragment. The bridging-oxo atom functions as tridentate and the internal angles $(105.69 (17), 74.31 (17)^\circ$ for **1** and $105.7 (2), 74.3 (2)^\circ$ for **5** of the center Sn_2O_2 are consistent with those in other distannoxane systems, such as $104.6 (2)^\circ$ of $[\text{Cl}(t\text{-Bu})_2\text{SnOSnMe}_2\text{Cl}]_2$ and $104.8 (2)^\circ$ of $[\text{Cl}(t\text{-Bu})_2\text{SnOSnPh}_2\text{Cl}]_2$.⁷ The distances of $\mu_3\text{-O}$ to tin atoms are similar (Sn (2)-O (1A), $2.015 (4) \text{ \AA}$, Sn (1)-O (1), $2.128 (4) \text{ \AA}$, Sn (1)-O (1A), $2.054 (4) \text{ \AA}$ for **1** and Sn (2)-O (1), $2.028 (5) \text{ \AA}$, Sn (1)-O (1), $2.066 (4) \text{ \AA}$, Sn (1A)-O (1), $2.114 (4) \text{ \AA}$ for **5**, respectively), reflecting the bridge-oxo strong coordination with tin atoms in the dimer. All four Sn atoms, four-Cl atoms and two O atoms comprise a fused ring system that is coplanar with mean deviation of $\pm 0.0379 \text{ \AA}$ for **1** and $\pm 0.0152 \text{ \AA}$ for **5**.

Figure 1 Molecular structure of **1** $[\text{Cl}(n\text{-Bu})_2\text{SnOSnPh}_2\text{Cl}]_2$

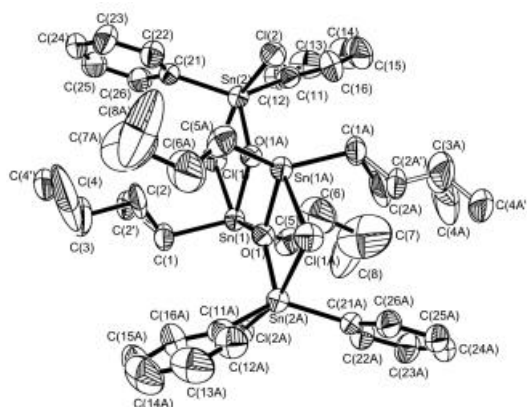
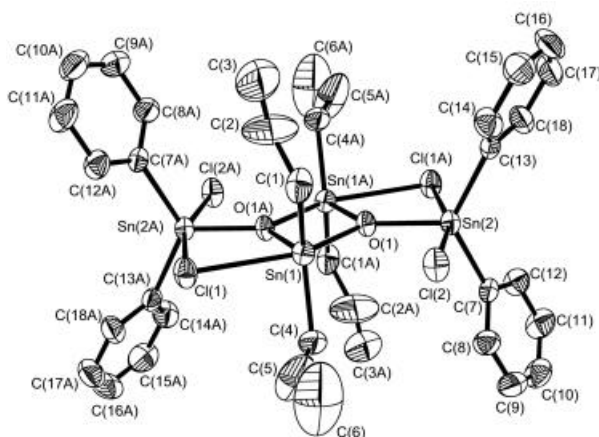
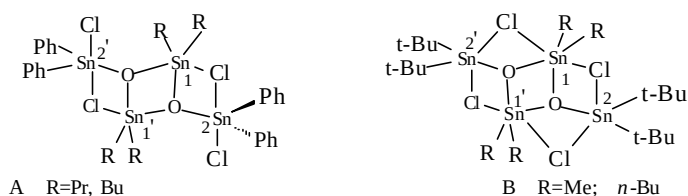


Figure 2 Molecular structure of **5** $[\text{Cl}(n\text{-Pr})_2\text{SnOSnPh}_2\text{Cl}]_2$



The geometry about the Sn atoms in **1** and **5** can be described as distorted trigonal bipyramid. With regard to Sn (2) atom, one O and two C atoms of phenyl groups are in equatorial positions. The axial angle Cl-Sn-Cl is 163.10 (6)° for **1** and 162.06 (7)° for **5**, which deviate from the ideal value of 180°. This deviation may be due to the interaction of the Cl atoms with the endocyclic Sn atoms.

Figure 3 The contrastive structure of two kinds of asymmetric distannoxanes



The structures of **1** and **5** as **Figure 3A** are not the same as Dakternieks had reported as **Figure 3B**⁷. Compounds **1** and **5** contain two pentacoordinated tin atoms in compounds **A**. With regard to Sn (1), there is a weak bonding interaction with Cl (2'), The Sn (1)—Cl (2') distance is 3.324 Å for **1** and 3.232 Å for **5**, compared to the Van Der Waals' sum of 4.0 Å. The approach of Cl (2') to Sn (1) might account for the extruding effect of Ph groups. But in **B** both Cl atoms interact with the endocyclic Sn atom to make Sn (1) atom six-coordinate (the bond lengths of Sn (1)—Cl and Sn (2)—Cl are 2.802 (2) Å, 2.907 (2) Å (R = Me) and 2.675 (2) Å, 2.598 (2) Å (R = *n*-Bu) respectively). The reason may be attribute to the fact that Sn (2) atom connect with the more larger bulk of *t*-Bu groups while Sn (1) atom connect with smaller groups in dimmer (II).

The asymmetric distannoxanes reported in this paper have shown good activities as catalysts in acetalization of crotonic aldehyde and esterification of acetic acid and butyl alcohol. Further investigations of their antitumor activities are under way.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 29972025).

References and note

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Received 25 May, 2001