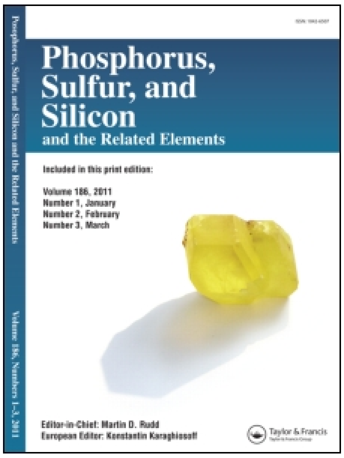

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Novel Trinuclear Spirostannoxane Tin(IV) Compound

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The reaction of $nBuSnCl_3$ and sodium salt of 2-mercaptoethanol gave the compound $Sn(n\text{Bu})(Cl)\{(OCH_2CH_2S)_2Sn(n\text{Bu})\}_2$ (**1**). The compound **2**, $[(n\text{Bu})Sn(SCH_2CH_2O)SCH_2CH_2OH]$, was initially isolated from the reaction of **1**, but was also synthesized from another route. Both compounds were characterized by IR, ^{119}Sn, ^{13}C and ^{1}H NMR, FAB mass spectroscopy and elemental analyses and X-ray diffraction of single crystal. **1** is a tri-metallic Tin(IV) compound in which the central atom is in six-fold coordination while the two remaining tin atoms show five-fold coordination. The pentacoordinated tin atoms are bonded to two $[OCH_2CH_2S]^{-2}$ ligands forming two stannolanes, which are fused with the hexacoordinated tin atom forming a distannoxane system. This arrangement is quite different from previous staircase structures. NMR data point the same structure in solution. **2** consists of $[(n\text{Bu})Sn(SCH_2CH_2O)(SCH_2CH_2OH)]$ units, which are associated via intermolecular SnO interactions. The tin atom forms two 'stannolane' units by interaction with $[OCH_2CH_2S]^{-2}$ and $[HOCH_2CH_2S]^{-}$ ligands.

Keywords: Spirostannolane; stannolane; distannoxane; trinuclear; tin(IV); 2-mercaptoethanol

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INTRODUCTION

Holmes and his co-workers have studied extensively the chemistry of spirocyclic tin compounds containing oxygen, sulfur and mixed oxygen-sulfur ligands (See [1-2] and references there) and a list of parameters have been cited as factors in the geometry and formation of stannolane structures.

In the course of our studies on the chemistry of heavy main group metalolanes, we obtained an unexpected tri-nuclear tin(IV) compound, $Sn(nBu)(Cl)\{(OCH_2CH_2S)_2Sn(nBu)\}_2$ (**1**). In addition, we also identified the spirostannolane $(nBu)Sn(SCH_2CH_2O)SCH_2CH_2OH$ (**2**). Both compounds were characterized by IR, ^{119}Sn, ^{13}C and ^{1}H NMR, mass spectroscopy and elemental analyses. The molecular structure of **1** and **2** were determined using single-crystal X-ray diffraction.

RESULTS AND DISCUSSION

^{1}H- and ^{13}C-NMR data for compound **1** and **2** are listed in reference [4]. The ^{1}H-NMR spectrum of **1** points to maintenance of the solid state structure in solution.

All three butyl groups attached to the tin atoms are equivalent on the ^{1}H NMR time scale, but not on the ^{13}C NMR time scale. The proton resonance shows that all the methylene , to the tin nucleus are magnetically equivalents, meanwhile ^{13}C NMR spectrum shows two ,-carbon atoms magnetically equivalent from the two five-coordinate tin atoms and the remaining ,-carbon resonance from six-coordinate tin atom. The three .-carbon atoms are non-equivalent.

The ^{1}H- and ^{13}C-NMR resonance associated with the butyl and the SCH_2CH_2O– units for **2** exhibit a similar pattern to those of **1**. The proton signal from the $-SCH_2CH_2OH$ fragment occurs as a broad peak at 5.55 ppm, which disappears on addition of D_2O. Carbon atoms bonded to the oxygen atom in the $-SCH_2CH_2OH$ and the cycle $-SCH_2CH_2O-$ fragments are distinguishable.

The ^{119}Sn NMR spectra are straightforward [4]. For compound **1**, the signal at highest field is associated with the six-coordinated tin center, which carries the chorine atom. Only one signal at 28.7 ppm is observed in the ^{119}Sn NMR spectrum of **2**, which is within the range for the four-coordinated tin nucleus [3]. Therefore, the structure in solution is different from that observed in the solid state.

Description of Structures

The structure of compound **1** is illustrated in Figure 1, consists of discrete tri-nuclear $[Sn(nBu)(Cl)\{(OCH_2CH_2S)_2Sn(nBu)\}_2]$ units, in which two of the tin centers are five-coordinated and the other is six-coordinated. Both pentacoordinated tin atoms (Sn(2) and Sn(3)) are bonded to a butyl group and two $[OCH_2CH_2S]^{-2}$ ligands forming two stannolanes, which are fused with the central six-coordinated tin atom [Sn(1)] throw oxygen atoms forming a spirostannoxane unit $Sn(2)O_2Sn(1)O_2Sn(3)$. The SnO bond in stannolane units are longer than those in distannoxanes (av. SnO = 2.128 Å).

The five coordinated tin atoms exhibit very distorted square pyramidal geometry with the butyl group in the apical position. This distortion may be a consequence of the constraints imposed by the fused five- and four-membered systems. The five membered rings adopt an envelope conformation with the carbon atoms (C(3) and C(7)) attached to the sulfur atom at the lap.

The six-coordinate Sn(1) atom exhibits octahedral geometry highly distorted from constraints imposed by the two four-membered distannoxane ring system. Since in this compound the two distannoxane rings form a spirostannoxane system, the present structure represents a totally different type from the common ladder or staircase structures observed previously for tri-nuclear distannoxanes, for examples see [2] and references there.

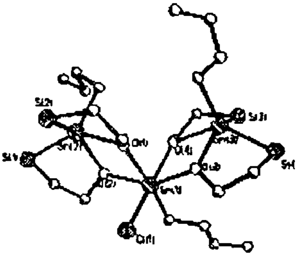

FIGURE 1 ORTEP plot of $[Sn(nBu)(Cl)\{(OCH_2CH_2S)_2Sn(nBu)\}_2]$, 1.

The structure of compound **2** is illustrated in Figure 2, consists of $[(n\mathrm{Bu})\mathrm{Sn}(\mathrm{SCH_2CH_2O})(\mathrm{SCH_2CH_2OH})]$ units, associated into dimers via intermolecular SnO interactions that produces a distannoxane unit. Crystal packing of **2** consists of dimeric $[(\mathrm{nBu})\mathrm{Sn}(\mathrm{SCH_2CH_2O})(\mathrm{SCH_2CH_2OH})]_2$ units, interconnected by S2H1bO2b hydrogen bridges of 2.31(8) Å between the alcohol group and a symmetry related sulfur atoms.

It is clear that many factors are involved in determining the formation and the structure of stannolane systems and the behavior of the new compounds (**1** and **2**) reported here well exemplify some of those points. Clearly the presence of oxygen donor atoms promoted higher tin coordination numbers, leading both to stabilization of the tri-nuclear compound **1** in the solution and solid state and to dimer formation for **2** in the solid state. However, the most remarkable feature is that the arrangement of **1** is quite different from previous ladder or staircase analogous structures.

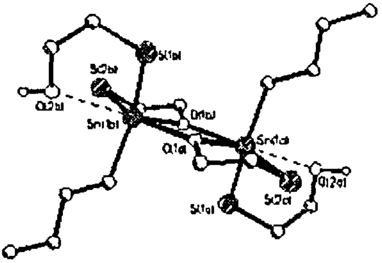

FIGURE 2 ORTEP plot of [(nBu)Sn(SCH2CH2O)(SCH2CH2OH)], 2.

EXPERIMENTAL SECTION

For full information about synthesis and spectroscopy results see reference [4].

Acknowledgments
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