

## Unusual Kinetically Stable Dialkyltin(IV) Oxides; X-Ray Structures of $[\{\text{SnR}_2(\mu\text{-O})\}_2]$ and $[\{\text{SnR}_2(\text{OH})\}_2(\mu\text{-O})]$ [ $\text{R} = \text{CH}(\text{SiMe}_3)_2$ ]<sup>†</sup>

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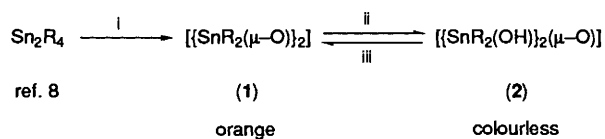
Treatment of  $\text{Sn}_2\text{R}_4$  [ $\text{R} = \text{CH}(\text{SiMe}_3)_2$ ] with  $\text{Me}_3\text{NO}$  in  $n\text{-C}_6\text{H}_{14}$  affords orange  $[\{\text{SnR}_2(\mu\text{-O})\}_2]$  (**1**), which with  $\text{H}_2\text{O}$  in tetrahydrofuran instantly yields colourless  $[\{\text{SnR}_2(\text{OH})\}_2(\mu\text{-O})]$  (**2**) which under reflux in PhMe readily reverts to (**1**); the average Sn–O( $\mu$ ) bond lengths are 1.96(2) for (**1**) and 1.956(4) for (**2**), Sn–OH is 2.032(7) Å for (**2**), and the Sn–O( $\mu$ )–Sn' angles are 97.5(6) for (**1**) and 125.0(5)° for (**2**).

Stannoxanes  $[\{\text{SnR}'_2(\mu\text{-O})\}_n]$  are often insoluble polymers. If R' is a bulky hydrocarbyl group, cyclic, crystalline, lipophilic trimers are established. These, like the unsymmetrical cyclo-stannoxane  $[\{\text{Sn}(\text{MeR}'')(\mu\text{-O})\}_2\{\text{Sn}(\text{MeR})(\mu\text{-O})\}]$  (**I**),<sup>1</sup> have a planar [ $\text{R}' = \text{Bu}^t$ , (**II**);<sup>2,3</sup> *t*-pentyl, (**III**);<sup>3</sup> or  $\text{C}_6\text{H}_3\text{Et}_2$ -2,6, (**IV**)<sup>4</sup>] or a flattened boat-shaped [ $\text{R}' = \text{C}_6\text{H}_2\text{Me}_3$ -2,4,6, (**V**)<sup>5</sup>] ( $\text{SnO}$ )<sub>3</sub> ring [ $\text{R} = \text{CH}(\text{SiMe}_3)_2$ ,  $\text{R}'' = \text{C}(\text{SiMe}_3)_3$ ]. By contrast, four-membered, planar ring structures are found for the colourless, crystalline (i) heavier chalcogen analogues  $[\{\text{SnBu}^t_2(\mu\text{-E})\}_2]$  (E = S, Se, or Te),<sup>6</sup> and (ii) a mixed *O*-, *S*-compound  $[\{\text{SnR}'_2(\mu\text{-O})(\mu\text{-S})\}]$  [ $\text{R}' = \text{C}_6\text{H}_2\text{Pr}_3$ -2,4,6, (**VI**)];<sup>7</sup> but  $[\{\text{SnMe}_2(\mu\text{-Te})\}_3]$  has a puckered ( $\text{SnTe}$ )<sub>3</sub> skeleton.<sup>8</sup> Each compound was prepared from an appropriate  $\text{Sn}^{\text{IV}}$  precursor:  $\text{SnR}'_2\text{X}_2$  (X = Cl or Br),<sup>2–6</sup>  $\text{SnMe}(\text{R}'')\text{Cl}_2$ ,<sup>1</sup> or  $(\text{SnR}'_2\text{Br})_2$ .<sup>7</sup>

We now report the first cyclodistannoxane,  $[\{\text{SnR}_2(\mu\text{-O})\}_2]$  (**1**), an orange, crystalline compound. It was obtained by a novel, mild, oxidative route from a  $\text{Sn}^{\text{II}}$  precursor, Scheme 1. Such oxidation using  $\text{Me}_3\text{NO}$  may have some generality for preparing complexes of type  $[\{\text{ML}_m(\mu\text{-O})\}_n]$  having M in the oxidation state *x* from an  $\text{M}^{(x-2)}$  precursor (*e.g.*,  $\text{M}^x = \text{Tl}^{\text{III}}$ ,  $\text{Ge}^{\text{IV}}$ ,  $\text{Pb}^{\text{IV}}$ , or  $\text{Zr}^{\text{IV}}$ ). We further find that (i) controlled hydrolysis of (**1**) yields colourless  $[\{\text{SnR}_2(\text{OH})\}_2(\mu\text{-O})]$  (**2**),<sup>‡</sup> the first member of a new class of organotin(IV) hydroxide;

<sup>‡</sup> NMR chemical shifts ( $\delta$ ) [ $\delta$  in ppm,  $\text{C}_6\text{D}_6\text{CD}_3$ , 305 K, for  $^1\text{H}$  at 80.13 MHz, for  $^{13}\text{C}$  at 90.66 MHz, and for  $^{119}\text{Sn}$  at 134.29 MHz rel. to  $\text{SnMe}_4$ ]. For  $^1\text{H}$ : (**1**): 0.21 (s, 36H) and 1.46 (s, 4H); (**2**): 0.37 (s, 18H), 0.43 (s, 18H), and 1.48 (s, 4H). For  $^{13}\text{C}$ : (**1**) 3.61 (Me) and 15.82 (CH); (**2**): 4.03 and 4.35 (Me), 16.32 (CH) [ $^1J(^{13}\text{C}\text{--}^{119}\text{Sn})$  132 Hz,  $^1J(^{13}\text{C}\text{--}^{117}\text{Sn})$  138.5 Hz]. For  $^{119}\text{Sn}$ : (**1**) not observed; (**2**) 17.45 [ $^2J(^{119}\text{Sn}\text{--}^{117}\text{Sn})$  524 Hz]. The magnetically inequivalent  $\text{SiMe}_3$  groups in (**2**) are a consequence of the prochirality at Sn.

<sup>†</sup> No reprints available.



**Scheme 1.** Synthesis of the cyclodistannoxane (1) and the bis-[dialkyl(hydroxo)tin(IV)] oxide (2). *Abbreviation:* R = CH(SiMe<sub>3</sub>)<sub>2</sub>. *Reagents and conditions:* i, 2Me<sub>3</sub>NO, n-C<sub>6</sub>H<sub>14</sub>, 0 °C, 2 h; ii, 1H<sub>2</sub>O, thf, 20 °C; iii, PhMe, reflux, 5 min. *Isolation:* (1), 67% (reaction i), by crystallisation from C<sub>6</sub>H<sub>14</sub> at 25 °C; (2), 82%, by crystallisation from PhMe at -30 °C.

**Table 1.** Selected X-ray data on cyclostannoxanes.

| Compound <sup>a</sup> | <Sn-O> (Å) | <Sn-O-Sn> (°) | Ref.      |
|-----------------------|------------|---------------|-----------|
| (I)                   | 1.96(1)    | 133(1)        | 1         |
| (II)                  | 1.96(1)    | 133(1)        | 3         |
| (III)                 | 1.96(1)    | 134(1)        | 3         |
| (IV)                  | 1.95(2)    | 136(1)        | 4         |
| (V)                   | 1.97(1)    | 121(1)        | 5         |
| (VI)                  | 2.03(1)    | 101.7(4)      | 7         |
| (1)                   | 1.96(2)    | 97.5(6)       | This work |

<sup>a</sup> See text for structures.

and (ii) dehydration of (2) regenerates (1), Scheme 1. Compound (1), unlike (2), surprisingly, was only sparingly soluble in hydrocarbons, Et<sub>2</sub>O, or tetrahydrofuran (thf).

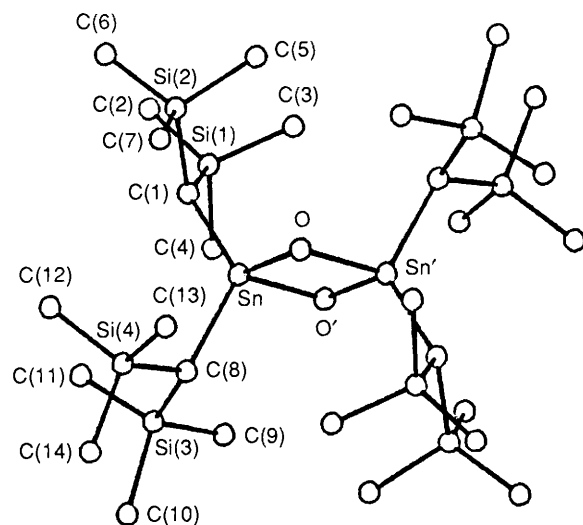
The X-ray structure<sup>§</sup> of the unusual cyclodistannoxane (1) is illustrated in Figure 1. It warrants juxtaposition with that of the recently reported colourless, crystalline, lipophilic cyclodisiloxane [Si(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)<sub>2</sub>(μ-O)]<sub>2</sub> (VII), for which SiSi bonding was discussed.<sup>9</sup> Important bond lengths (Å) and angles (°) are given in structures (1a) and (VIIa). Relevant also are (i) the interatomic distances for the tetrahedral Group 14 elements: 2.35 Å (Si) and 2.81 Å (Sn); and (ii) twice the sum of the van der Waals radii for Si (4.20 Å), Sn (4.40 Å), and O (2.80 Å). Further comparative data on Sn<sup>IV</sup>O cyclic systems are in Table 1. The preference for the four-membered ring in (1) cannot be attributed solely to a steric effect as the more hindered crystalline [(Sn{CH(Bu<sup>t</sup>)SiMe<sub>3</sub>})<sub>2</sub>(μ-O)]<sub>3</sub> has been reported to have a configuration similar to that of (V).<sup>10</sup>

<sup>§</sup> *Crystal data:* (a) [(SnR<sub>2</sub>(μ-O))<sub>2</sub>] (1): C<sub>28</sub>H<sub>76</sub>O<sub>2</sub>Si<sub>8</sub>Sn<sub>2</sub>, *M* = 907.0, triclinic, space group *P* $\bar{1}$ , *a* = 9.572(6), *b* = 11.712(9), *c* = 12.326(13) Å,  $\alpha$  = 77.33(7),  $\beta$  = 68.27(7),  $\gamma$  = 67.19(6)°, *U* = 1178 Å<sup>3</sup>, *Z* = 1, *D*<sub>c</sub> = 1.28 g cm<sup>-3</sup>, *F*(000) = 472,  $\mu$ (Mo-K $\alpha$ ) = 12.8 cm<sup>-1</sup>,  $\lambda$ (Mo-K $\alpha$ ) = 0.71069 Å. Data were collected on an Enraf-Nonius CAD4 diffractometer at room temperature in the range 2 <  $\theta$  < 20°. Of the 2189 unique reflections measured, 1343 with *I* >  $\sigma$ (*I*) were used in the refinement, giving *R* = 0.082, *R*<sub>w</sub> = 0.089. The molecule lies on a crystallographic inversion centre.

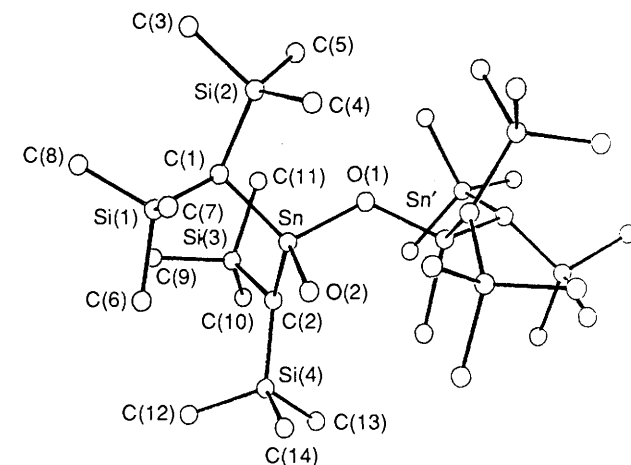
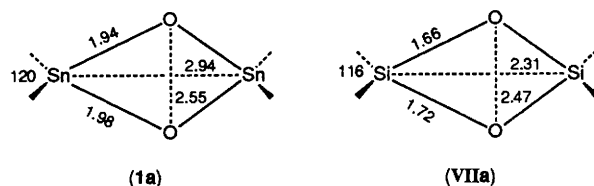
(b) [(SnR<sub>2</sub>(OH))<sub>2</sub>(μ-O)] (2): C<sub>28</sub>H<sub>78</sub>O<sub>3</sub>Si<sub>8</sub>Sn<sub>2</sub>, *M* = 925.0, orthorhombic, space group *Pbcn*, *a* = 15.524(4), *b* = 16.468(6), *c* = 19.258(6) Å, *U* = 4923 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.25 g cm<sup>-3</sup>, *F*(000) = 1928,  $\mu$ (Mo-K $\alpha$ ) = 12.3 cm<sup>-1</sup>. Of the 4812 unique reflections measured (for 2 <  $\theta$  < 25°), 1886 with *I* > 3 $\sigma$ (*I*) were used in the refinement, giving *R* = 0.054, *R*<sub>w</sub> = 0.056. The molecule lies on a crystallographic twofold rotation axis.

For both structures an empirical absorption correction was applied. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at fixed calculated positions, but in (2) the hydroxy hydrogen atoms were omitted.

Atomic co-ordinates bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Figure 1.** The molecular structure of [(SnR<sub>2</sub>(μ-O))<sub>2</sub>] (1). Selected bond lengths and angles are: Sn-O 1.94(2), Sn-O' 1.98(1), Sn-C(1) 1.97(3), Sn-C(8) 2.10(2) Å; O-Sn-O' 82.5(6), O-Sn-C(1) 113.3(7), O-Sn-C(8) 110.4(9), O'-Sn-C(1) 116.2(7), O'-Sn-C(8) 108.5(6), C(1)-Sn-C(8) 119.9(9)°.



**Figure 2.** The molecular structure of [(SnR<sub>2</sub>(OH))<sub>2</sub>(μ-O)] (2). Selected bond lengths and angles are: Sn-O(1) 1.956(4), Sn-O(2) 2.032(7), Sn-C(1) 2.108(10), Sn-C(2) 2.146(10) Å, O(1)-Sn-O(2) 100.7(3), O(1)-Sn-C(1) 111.9(3), O(1)-Sn-C(2) 103.9(3), O(2)-Sn-C(1) 103.5(3), O(2)-Sn-C(2) 115.1(3), C(1)-Sn-C(2) 120.2(4), Sn-O(1)-Sn' 125.0(5)°.

The colour of (1) must be due to an unusually small HOMO-LUMO separation. The low hydrocarbon-solubility cannot be due to close intermolecular contacts: there are none less than 6 Å to Sn.

The X-ray structure of [(SnR<sub>2</sub>(OH))<sub>2</sub>(μ-O)] (2) is illustrated in Figure 2. Because (i) the Sn-O(μ) bond length is similar to that in cyclostannoxanes (Table 1), (ii) the Sn-O(μ)-Sn' angle is similar to that in cyclotristannoxanes

(Table 1), and (iii) the Sn–O(H) bond is significantly longer than Sn–O( $\mu$ ), it is likely that there is significant Sn–O( $\mu$ )  $\pi$ -bonding, or O–O-nonbonded interactions.<sup>11</sup> The relative disposition of the two hydroxy oxygen atoms, one pointing away from and the other into the Sn–O( $\mu$ )–Sn' plane, makes it unlikely that there is hydrogen bonding. Organotin hydroxides generally have a bridging –OH, as in [Sn( $\mu$ -OH)Ph<sub>3</sub>]<sub>∞</sub>, Sn–O 2.197(5) Å.<sup>12</sup> A rare case of a compound having a terminal –OH is tris(tropolonato)tin hydroxide, Sn–O(H) 1.974(6) Å.<sup>13</sup>

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