

# Synthesis and Structure of Siloxy-Substituted ZnO Aggregates Having $(\text{ZnO})_n$ ( $n = 2, 4$ ) and $\text{Zn}_3\text{O}_4$ Cores

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Convenient syntheses and X-ray crystallographic characterizations of the first bis(trimethylsilyl)amido-, methyl-, and iodozinc triorganosiloxide aggregates **1–5** are described. They are accessible by the simple reaction of  $\text{ZnR}'_2$  [R = Me, N(SiMe<sub>3</sub>)<sub>2</sub>] with the respective silanols R<sub>3</sub>SiOH (R = Me, Et, *i*Pr), which affords the dimeric [(Me<sub>3</sub>Si)<sub>2</sub>NZnOSiR<sub>3</sub>]<sub>2</sub> (**1a**: R = *i*Pr; **1b**: R = Et), trinuclear [(MeZn)<sub>2</sub>Zn(OSiPr<sub>3</sub>)<sub>4</sub>] (**2a**), {[(Me<sub>3</sub>Si)<sub>2</sub>NZn]<sub>2</sub>Zn(OSiR<sub>3</sub>)<sub>4</sub>} (**2b**: R = Et; **2c**: R = Me), and tetranuclear heterocubanes [MeZnOSiR<sub>3</sub>]<sub>4</sub> (**3a**: R = Me; **3b**: R = Et), respectively. The latter were oxidized with four equivalents of elemental iodine to form the tetraiodo derivatives [IZnOSiR<sub>3</sub>]<sub>4</sub> (**4a**: R = Me; **4b**: R = Et) in 82 and 88% yield,

respectively. Due to the higher polarity of the Zn–I vs. Zn–C  $\sigma$ -bond, the Zn–O distances of the almost regular Zn<sub>4</sub>O<sub>4</sub> core in **4a** are 2–6 pm shorter than those observed in the less Lewis-acidic cluster **3b**. However, the Zn–O distances in **3b** and **4a** are ca. 10–15 pm longer than those in **1a**, **2a**, and **2c**, due to different coordination numbers at Zn and the effects of ring strain. Remarkably, the iodo derivatives **4a,b** undergo dissociation in THF to give the respective dimeric THF solvates [IZn(THF)OSiR<sub>3</sub>]<sub>2</sub> (**5a**: R = Me; **5b**: R = Et), whereas the Zn<sub>4</sub>O<sub>4</sub> cores in **3a** and **3b** are retained even in aprotic polar solvents.