Synthesis and Characterization of $[Sn_8(2,6\text{-}Mes_2C_6H_3)_4]$ (Mes = 2,4,6-$Me_3C_6H_2$): A Main Group Metal Cluster with a Unique Structure**

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Most polyhedral compounds with heavier Group 14 element frameworks fall into one of two broad categories; the Zintl anions E_n^{m-},[1] and the substituted species of the formula E_nR_n,[2] which are accessible through the use of sterically demanding organic (R) groups. Several structural types are known for the latter category[2] which extend from the simplest tetrahedrane cluster E_4R_4, through trigonal-prismatic, cubic, and pentagonal-prismatic clusters E_6R_6, E_8R_8, and $E_{10}R_{10}$, respectively. A range[2] of alkyl, aryl, and silyl[3] ligands has been used to stabilize these frameworks. Recently, it has been shown that sterically crowding terphenyl ligands can limit the degree of aggregation in these clusters to $n = 2$ or 3 as in the dimeric alkynelead analogue $[Pb_2(2,6\text{-}Trip_2C_6H_3)_2]$[4a] (Trip = 2,4,6-*i*$Pr_3C_6H_2$) or the trimeric germanium radical species $[Ge_3(2,6\text{-}Mes_2C_6H_3)_3]$[4b] (Mes = 2,4,6-$Me_3C_6H_2$). The different degrees of aggregation in these two molecules can be rationalized on the basis of the different sizes of germanium and lead as well as the different steric requirements of their terphenyl substituents. These data also suggested that the use of the smaller 2,6-$Mes_2C_6H_3$ aryl ligand in conjunction with tin might result in the isolation of the elusive tetrahedrane cluster Sn_4R_4. Herein we show that the attempted preparation of such a species by a coupling reaction of the aryltin halide $[\{Sn(\mu\text{-}Cl)(2,6\text{-}Mes_2C_6H_3)\}_2]$ with potassium led not to the expected tetrameric product but to the species $[Sn_8(C_6H_3\text{-}2,6\text{-}Mes_2)_4]$ (**1**), featuring a novel main group element cluster framework which may represent a real structure along the decomposition pathway of Sn_nR_n clusters toward metallic tin.

Compound **1** was synthesized as purple crystals in 38% yield by reduction of $[\{Sn(\mu\text{-}Cl)(2,6\text{-}Mes_2C_6H_3)\}_2]$[5] with a slight excess of potassium in THF. It was characterized by ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy, UV/Vis spectroscopy, and by X-ray crystallography.[6] A thermal ellipsoid drawing (Figure 1) illustrates the crowded environment provided by the ligands. Figure 2 shows that the eight tin atoms of the Sn_8 core are arranged as a distorted rhombic prism with approximate D_{2h} symmetry. The Sn_8 array may also be thought of as a grossly distorted cubane structure if the long (3.107(2) Å) Sn(2)–Sn(3) and Sn(2A)–Sn(3A) bonds are uncoupled. It can be seen that only four of the tin atoms carry organic substituents. A similar ratio or organic groups to metal atoms was observed in the cubane cluster $[In_8\{2,6\text{-}Mes_2C_6H_3\}_4]$,[7] but in that compound the four organic groups are attached to alternating corners of an In_8 distorted cubane array with D_{2d} point symmetry rather than to adjacent metal atoms as in **1**. It seems that four 2,6-$Mes_2C_6H_2$ groups provide the appropriate amount of surface coverage to stabilize the eight metal core in both cases. The Sn–Sn distances fall in the range 2.853(2) – 3.107(2) Å which is comparable to the range observed in Sn_nR_n clusters[2, 9] and Zintl anions such as Sn_9^{4-}.[10] For example, average Sn–Sn distances of 2.89(2) and 2.86(2) Å have been reported for the species $[\{(thf)_2Na\}_2Sn_8\{Si(tBu)_3\}_6]$[11] and $[Sn_5(2,6\text{-}Et_2C_6H_3)_6]$,[12] respectively. The tin–carbon distances of 2.22(2) and 2.28(2) Å are within the normal range.[13] The distortions in the structure are apparent from the selection of angles given in the legend to Figure 2.

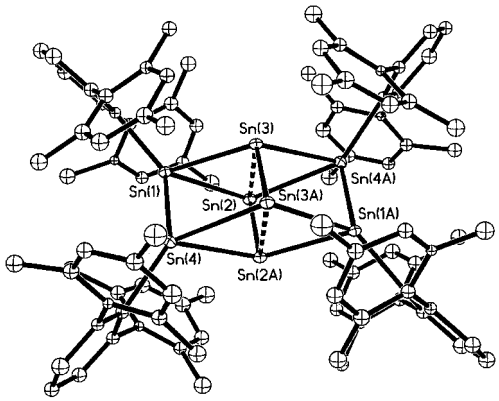

Figure 1. Structure of **1** (thermal ellipsoid (30%) plot without H atoms) illustrating the crowding nature of the 2,6-$Mes_2C_6H_3$ substituents.

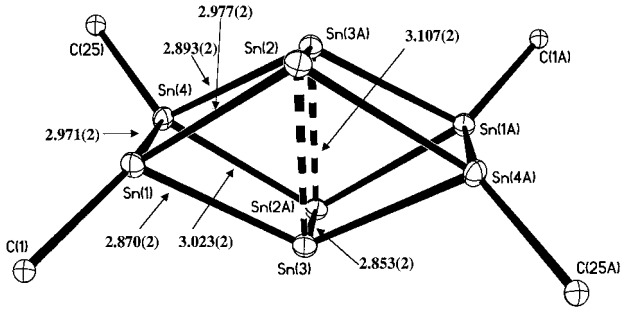

Figure 2. Structure of the core tin and *ipso*-carbon atoms of **1** (thermal ellipsoid (30%) plot) showing the tin–tin distances [Å]. Important angles [°]: C(1)-Sn(1)-Sn(3) 112.4(4), C(1)-Sn(1)-Sn(4) 127.9(4), Sn(3)-Sn(1)-Sn(4) 79.70(4), C(1)-Sn(1)-Sn(2) 131.9(4), Sn(3)-Sn(1)-Sn(2) 64.16(4), Sn(4)-Sn(1)-Sn(2) 99.62(5), Sn(3A)-Sn(2)-Sn(1) 77.94(4), Sn(3A)-Sn(2)-Sn(4A) 79.10(4), Sn(1)-Sn(2)-Sn(4A) 112.38(5), Sn(3A)-Sn(2)-Sn(3) 65.32(4), Sn(1)-Sn(2)-Sn(3) 56.24(4), Sn(4A)-Sn(2)-Sn(3) 56.30(4), Sn(2A)-Sn(3)-Sn(1) 103.61(5), Sn(1)-Sn(3)-Sn(4A) 119.80(6), Sn(2A)-Sn(3)-Sn(2) 114.68(4), Sn(1)-Sn(3)-Sn(2) 59.60(4), Sn(4A)-Sn(3)-Sn(2) 60.39(4), Sn(3A)-Sn(4)-Sn(1) 77.42(4), Sn(3A)-Sn(4)-Sn(2A) 63.31(4), Sn(1)-Sn(4)-Sn(2A) 97.23(4).

The bonding in **1** may be considered in a number of ways. One possibility is that it consists of a central unit of four Sn atoms (Sn(2), Sn(3), Sn(2A), Sn(3A)) which is complexed by two R-Sn(1)-Sn(4)-R and R-Sn(1A)-Sn(4A)-R fragments. In this model, the planar, rhombic Sn_4 core (Sn(2)-Sn(3)-Sn(2A) 114.68(4)°, Sn(3)-Sn(2)-Sn(3A) 65.32(4)°) involves single bonding between four divalent tin atoms (each with a lone pair), which are bound on each side of the Sn_4 plane by the RSnSnR units. The latter moieties bear little resemblance to a "distannyne" suggested by the alkyne-like formula; however,

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the Sn–Sn distance of 2.971(2) Å is longer than the normal tin–tin single bond of 2.80 Å found in gray tin.[14] Moreover, the torsion angle for the C(1)-Sn(1)-Sn(4)-C(25) unit is 85.0°. The average Sn–Sn bond length (including the diagonal Sn(2)–Sn(3) and Sn(2A)–Sn(3A) distances) is very similar at about 2.96(7) Å and suggests that the formal Sn–Sn bond order in the cluster is less than one. The lower bond order is consistent with electron counting for the metal framework bonding. Thus, each of the four unsubstituted tin atoms, if they bear a lone pair of electons, supplies two electrons, and the four RSn moieties each supply three electrons for a total of twenty electrons available for framework bonding or an average bond order of about 0.7 if fourteen Sn–Sn bonds are assumed. It is also possible to consider the Sn_8 core as a very distorted cube by uncoupling the relatively long Sn(2)–Sn(3) and Sn(2A)–Sn(3A) bonds. However, the acute angles (ca. 64°) at Sn(1), Sn(4), Sn(1A), Sn(4A) opposite these bonds seem to favor the existence of Sn(2)–Sn(3) and Sn(2A)–Sn(3A) interactions (as indicated by the dashed lines in Figure 2).

The ^1H and ^{13}C NMR spectra of **1** display peaks typical for a 2,6-$Mes_2C_6H_3$-substituted species with the expected low-field shift ($\delta = 174.04$) for the *ipso*-carbon atom of the central ring of the terphenyl group. The ^{119}Sn $\{^1H\}$ NMR spectrum of **1** features two signals at $\delta = 751.7$ and 483.1 that are attributable to two different types of tin center. The lowest field signal at $\delta = 751.7$ displays two sets of $^{117}Sn/^{119}Sn$ satellites due to coupling ($^1J_{Sn,Sn} = 5.005$ and 2.625 Hz) to two distinct tin centers. Moreover, the satellites display a 1:2 intensity ratio suggesting that this signal can be assigned to the tin atoms that carry organic groups since these tin centers are bound to one substituted and two equivalent unsubstituted tin centers. The more upfield peak at $\delta = 483.1$ also displays two sets of satellite peaks ($^1J_{Sn,Sn} = 5.005$ and 4.098 Hz) that have equal intensities which can be assigned to the unsubstituted tin atoms since these tin centers are bound to two substituted and two unsubstituted tin centers. In addition, ^{119}Sn NMR spectroscopy of the reaction mixture used to synthesize **1** showed other, less intense, peaks (e.g., at $\delta = 126.9, 8.5, -335, -390.5$) indicating that at least one other tin cluster is present in the crude reaction mixture.[15] Attempts to structurally characterize these and other Group 14 clusters are in progress.

Experimental Section

Under anaerobic and anhydrous conditions THF (40 mL) was added to a flask charged with potassium (0.33 g, 8.4 mmol) and $[\{Sn(\mu\text{-}Cl)(2,6\text{-}Mes_2C_6H_3)\}_2]$[5] (3.27 g, 3.50 mmol). The yellow solution was heated until the potassium became molten at which point the solution rapidly turned red. The reaction mixture was allowed to cool to room temperature and upon stirring for 14 h it had assumed a purple color. The solvent was then removed under reduced pressure and the purple residue was extracted with benzene (30 mL). The solution was filtered and the volume was reduced to about 20 mL. Storing the flask at ca. 6 °C overnight afforded the product **1** as purple crystals. Yield: 0.77 g, 0.33 mmol, 38%; m.p. 215–218 °C; elemental analysis calcd for $Sn_2C_{24}H_{25}$ (%): C 53.33, H 4.57; found: C 53.76, H 4.23; UV/Vis (hexanes): λ_{max} [nm] (ε) [$M^{-1}cm^{-1}$]: 307 (11 000), 522 (1460); ^1H NMR (C_6D_6, 399.77 MHz, 25 °C): $\delta = 1.91$ (br s, 6H; *o*-CH_3), 2.00 (br s, 6H; *o*-CH_3), 2.30 (br s, 6H; *p*-CH_3), 6.75 (br s, 4H; *m*-Mes), 6.87 (d, 2H, $^3J = 7.4$ Hz; *m*-C_6H_3), 7.08 (t, 1H, $^3J = 7.4$ Hz; *m*-C_6H_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.53 MHz, 25 °C): $\delta = 21.57$ (*o*-CH_3), 21.64 (*o*-CH_3), 22.79 (*p*-CH_3), 127.29 (*m*-Mes), 128.53 (*m*-Mes), 128.68 (*p*-C_6H_3), 129.39 (*m*-C_6H_3), 135.94 (*o*-Mes), 136.07 (*o*-Mes), 136.83 (*p*-Mes), 141.16 (*ipso*-Mes), 147.66 (*o*-C_6H_3), 174.04 (*ipso*-C_6H_3); $^{119}Sn\{^1H\}$ NMR (C_6D_6, 149.16 MHz, 25 °C): $\delta = 751.7$ and 483.1.

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[15] Preliminary analytical data indicate that one of these clusters has the formula $[Sn_9(2,6\text{-}Mes_2C_6H_3)_4]$.

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