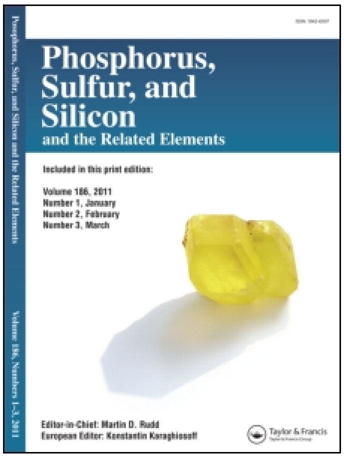

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OXYGEN- AND SULFUR-CAPPED ORGANOTIN CLUSTERS

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Abstract The synthesis and structural features of the oxygen-capped cluster, $[(\underline{n}\text{-BuSn(OH)O}_2\text{P(OBu}^t)_2)_3\text{O}][\text{O}_2\text{P(OBu}^t)_2]$ ($\underline{1}$), are compared to that of the analogous formulations containing framework sulfur atoms in place of oxygens, $[(\underline{n}\text{-BuSn(S)(OH)OP(OBu}^t)_2)_3\text{S}][\text{O}_2\text{P(OBu}^t)_2]\cdot 2\text{H}_2\text{S}\cdot \text{H}_2\text{O}$ ($\underline{2}$) and $[(\underline{n}\text{-BuSn})_3\text{(S)(O)(O}_2\text{CPh)}_5]$ ($\underline{3}$). Solution NMR, ^{119}Sn and ^{31}P, indicate that the solid state structures determined by X-ray analysis are retained in solution.

INTRODUCTION

We have synthesized and structurally characterized monoorganooxotin(IV) clusters having a variety of tin-oxygen framework geometries.[2] These include drums,[3-6] ladders[4,5] (open-drums), cubes,[7,8] crowns,[9] oxygen-capped[7,9,10] and butterfly formations,[7] and extended tetranuclear clusters.[9] It is of interest to search for the existence of other possible types of organotin geometries in an effort to develop the structural principles governing the formation of clusters of increasing nuclearity.

As one means to accomplish this goal, we initiated a study to prepare analogous tin-sulfur systems for comparison with the stannoxane clusters. The present report describes our initial effort.

SYNTHESES

The oxygen-capped cluster $[(\underline{n}\text{-BuSn(OH)O}_2\text{P(OBu}^t)_2)_3\text{O}][\text{O}_2\text{P(OBu}^t)_2]$ ($\underline{1}$) was prepared by condensation of $\underline{n}$-butylstannonic acid with di-

tert-butyl phosphoric acid at room temperature in benzene solution.

$$3\ \underline{n}\text{-BuSn(O)OH} + 4\ (\text{Bu}^t\text{O})_2\text{PO}_2\text{H} \longrightarrow$$

$$[(\underline{n}\text{-BuSn(OH)O}_2\text{P(OBu}^t)_2)_3\text{O}][\text{O}_2\text{P(OBu}^t)_2] + 2\ \text{H}_2\text{O}$$

The sulfur-capped cluster $[(\underline{n}\text{-BuSn(S)OP(OH)(OBu}^t)_2)_3\text{S}][\text{O}_2\text{P(OBu}^t)_2]\cdot 2\text{H}_2\text{S}\cdot\text{H}_2\text{O}$ (2) was prepared by passing hydrogen sulfide through a benzene solution of $\underline{n}\text{-BuSn[O}_2\text{P(OBu}^t)_2]_3$ at room temperature.

$$3\ \underline{n}\text{-BuSn[O}_2\text{P(OBu}^t)_2]_3 + 4\ \text{H}_2\text{S} \longrightarrow$$

$$[(\underline{n}\text{-BuSn(S)OP(OH)(OBu}^t)_2)_3\text{S}][\text{O}_2\text{P(OBu}^t)_2] + 5(\text{Bu}^t\text{O})_2\text{PO}_2\text{H}$$

For the preparation of $[(\underline{n}\text{-BuSn})_3\text{(S)(O)(O}_2\text{CPh)}_5]$ (3), hydrogen sulfide was passed through a CCl_4 solution of *n*-butyltin tribenzoate at room temperature in the presence of atmospheric moisture.

$$3\ \underline{n}\text{-BuSn(O}_2\text{CPh)}_3 + \text{H}_2\text{S} + \text{H}_2\text{O} \longrightarrow$$

$$\underset{\underline{3}}{[(\underline{n}\text{-BuSn})_3\text{(S)(O)(O}_2\text{CPh)}_5]} + 4\ \text{PhCO}_2\text{H}$$

STRUCTURES

The single crystal X-ray analysis of 1 reveals the cation portion containing a trinuclear oxygen-capped cluster. This cation also contains bridging hydroxide and phosphate ligands between the tin atoms. The anion consists of a phosphate unit that is hydrogen bonded to the hydroxides. This molecule is structurally similar to other O-capped derivatives previously reported.[7,10]

A ^{119}Sn NMR spectrum shows a triplet centered at -507.7 ppm (ref. TMT). The chemical shift is consistent with the presence of a hexacoordinated tin atom. Two-bond tin-phosphorus coupling was measured to be 189 Hz. The ^{31}P NMR spectrum shows a singlet

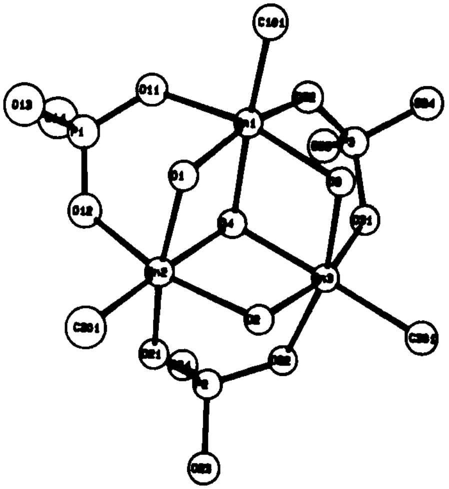

FIGURE 1 ORTEP plot of the cation of 1 with pendant atoms removed for clarity.

with tin satellites at -12.8 ppm (ref. H_3PO_4) due to the bridging phosphate ligands and another singlet at -5.7 ppm assigned to the phosphate anion.

An X-ray diffraction study of 2 revealed the molecular

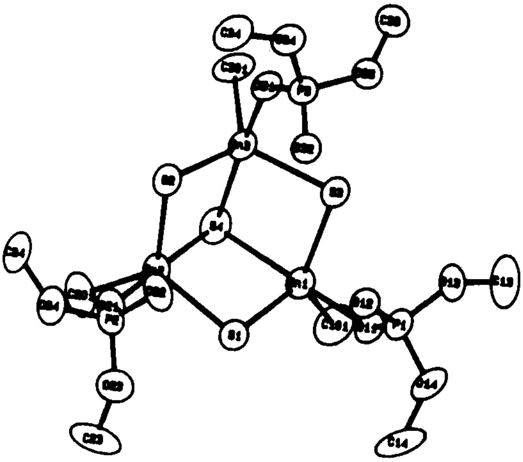

FIGURE 2 An ORTEP drawing of the cation of 2 with pendant atoms removed for clarity.

formula, $[(\underline{n}\text{-BuSn(S)OP(OH)(OBu}^t)_2)_3\text{S}][\text{O}_2\text{P(OBu}^t)_2]\cdot 2\text{H}_2\text{S}\cdot\text{H}_2\text{O}$, corresponding to a trinuclear sulfur-capped organotin cluster containing sulfide bridges and monodentate di-tert-butylphosphate ligands.

Several structural features differentiate this sulfur-capped molecule from the oxygen-capped species (1). First, the tin atoms are pentacoordinate. This is borne out in solution as well. The ^{119}Sn NMR spectrum reveals a broad resonance at −205 ppm with no observable tin-phosphorus coupling. The ^{31}P NMR spectrum shows only a single broad resonance, centered at −12.0 ppm. This might imply a rapid exchange of the coordinated phosphate ligands with the capping phosphate anion. Only a slight broadening of the signal is observed upon lowering the temperature to −90°C. Second, the ligands are monodentate. They reach out above the face of the cage instead of angling back towards the capping atom as in the O-capped analog. This leaves little space for a close interaction between the sulfur atoms of the cation and the solvate molecules. Instead, there arises an involved network of hydrogen bonding between the dangling P-O-H moieties of the coordinated phosphates,

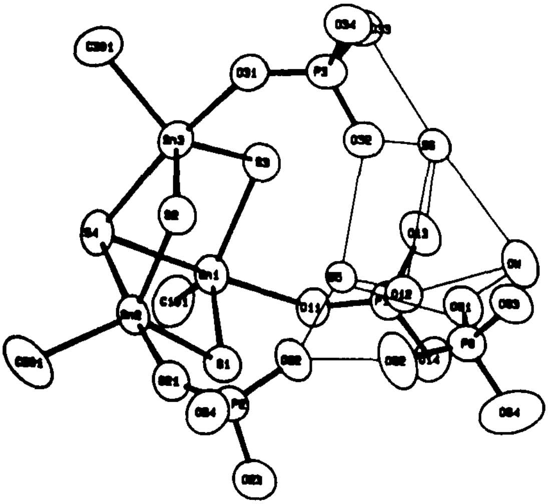

FIGURE 3 ORTEP illustrating the hydrogen bonding network in 2.

the two H_2S solvates, the H_2O solvate, and the anionic capping phosphate. This is evidenced by a large number of close O-O and O-S contacts shown as narrow solid lines in Figure 3.

X-ray analysis of 3 revealed a trinuclear cluster with a tricoordinate oxygen atom joining the three tin centers. Five carboxylate groups span the tin atoms with one Sn-S-Sn linkage present to form a mixed Sn-S-Sn-O ring system.

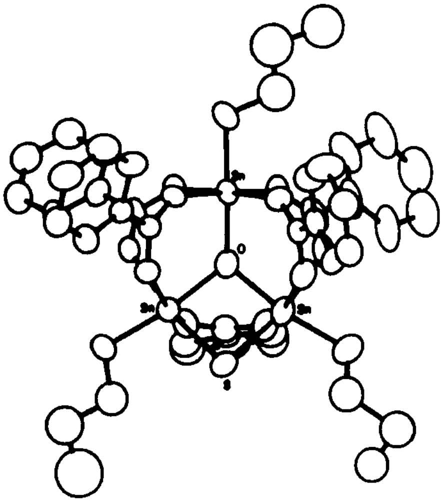

FIGURE 4 An ORTEP drawing of 3.

The ^{119}Sn NMR spectrum shows two kinds of tin centers present in a 2:1 ratio. One resonance appears at -414.1 ppm and contains two sets of tin-tin satellites, $^{2}J_{(^{119}Sn-^{117}Sn)}$ = 178 Hz and $^{2}J_{(^{119}Sn-^{119}Sn)}$ = 222 Hz. A second resonance, one half the intensity of the first, occurs at -593.4 ppm. It has a single set of tin satellites, $^{2}J_{(^{119}Sn-^{119}Sn)}$ = 222 Hz, which are twice as intense as the corresponding satellites of the first signal. An inverse gated decoupled ^{13}C NMR spectrum shows three different carboxylate carbons in a 2:2:1 ratio.

CONCLUSION

It is apparent that sulfur insertion into organotin-capped clusters causes structural differences compared to oxygen-capped analogs. This is noted particularly in the sulfur-capped, Sn-S-Sn bridged cluster (2) showing both five-coordinated tin atoms and monocoordinated phosphate ligands. A rearrangement of hydrogen bonding effects in 2 compared to that in the O-capped cluster (1) appears partly responsible for these differences.

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