A New Structural Form of Tin in an Oxygen-Capped Cluster

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Recently we have shown that oligomeric organotin oxy-carboxylates based on the compositions $[R'Sn(O)O_2CR]_6$ and $[(R'Sn(O)O_2CR)_2R'Sn(O_2CR)_3]_2$ have "drum"[1-3] and "ladder"[2,3] structures, respectively. Reaction of *n*-butylstannoic acid with diphenylphosphoric acid instead of a carboxylic acid results in the formation of an analogous drum composition, $[n\text{-BuSn-}(O)O_2P(OPh)_2]_6$.[4] However, when diphenylphosphinic acid is reacted with *n*-butylstannoic acid under reflux in toluene, a new structural form of tin is obtained. This report concerns the synthesis and structural characterization of this novel substance.

The reaction proceeds according to eq 1 giving the stable oxide composition in 90% yield, mp 198–208 °C dec.[5] Colorless,

$$3n\text{-BuSn(O)OH} + 4Ph_2PO_2H \rightarrow$$
$$[(n\text{-BuSn(OH)O}_2PPh_2)_3O][Ph_2PO_2] + 2H_2O \quad (1)$$
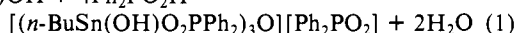
brick-shaped crystals for X-ray diffraction analysis were grown from hot ether. Anal. Calcd for $C_{60}H_{70}O_{12}P_4Sn_3$: C, 49.25; H, 4.82. Found: C, 49.01; H, 4.97.

Crystal data for $[(n\text{-BuSn(OH)O}_2PPh_2)_3O][Ph_2PO_2]$, crystal dimensions 0.30 mm × 0.30 mm × 0.33 mm, triclinic space group $P\bar{1}$ (C_i^1, No. 2),[6] $a = 11.260$ (2) Å, $b = 12.672$ (2) Å, $c = 22.804$ (2) Å, $\alpha = 96.98$ (1)°, $\beta = 99.36$ (1)°, $\gamma = 98.64$ (1)°, $Z = 2$, μ(Mo Kα) = 1.353 mm^{-1}. Independent reflections (7044) were measured at 23 ± 2 °C on an Enraf-Nonius CAD4 automated diffractometer, using graphite monochromated Mo Kα radiation and the θ–2θ scan mode to a maximum $2\theta_{\text{Mo K}\alpha}$ of 43°. The structure was solved by using Patterson and difference Fourier techniques. Full-matrix least-squares refinement[7] (anisotropic refinement of 76 non-hydrogen atoms, isotropic refinement of three *n*-Bu carbon atoms, hydrogen atoms omitted) led to a conventional unweighted residual $R = \sum ||F_o| - |F_c||/\sum |F_o|$ of 0.051 for the 6038 reflections having $I \geq 2\sigma_I$.

X-ray analysis shows tin(IV) present in an oxygen-capped cluster molecule. The basic framework consists of a tristannoxane ring in a cyclohexane chair arrangement. Hydroxyl groups comprise the oxygen components of the ring system. A tricoordinated oxygen atom caps one side of this framework while three additional diphenylphosphinate groups bridge adjacent hexacoordinated tin atoms.

It is noted that three distannoxane ring units form as a consequence of the presence of the unique capping oxygen atom.

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(4) Chandrasekhar, V.; Holmes, J. M.; Day, R. O.; Holmes, R. R., unpublished work.

(5) A suspension of *n*-butylstannoic acid (1.05 g, 5.03 mmol), Koriyama Kasei Co., Ltd., Japan, and diphenylphosphinic acid (1.10 g, 5.04 mmol), Aldrich, was heated in toluene (125 mL) at reflux for 4 h. A Dean-Stark apparatus was used to azeotropically remove water. Removal of solvent yielded a semisolid. Diethyl ether (30 mL) was added, and the mixture heated, and then filtered. Needlelike crystals formed from the filtrate.

(6) *International Tables for X-ray Crystallography;* Kynoch: Birmingham, England, 1969; Vol. I, p 75.

(7) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean atomic scattering factors were taken from ref 6, 1974; Vol. IV, pp 72–98. Real and imaginary dispersion corrections for Sn, O, and P were taken from the same source, pp 149–150.
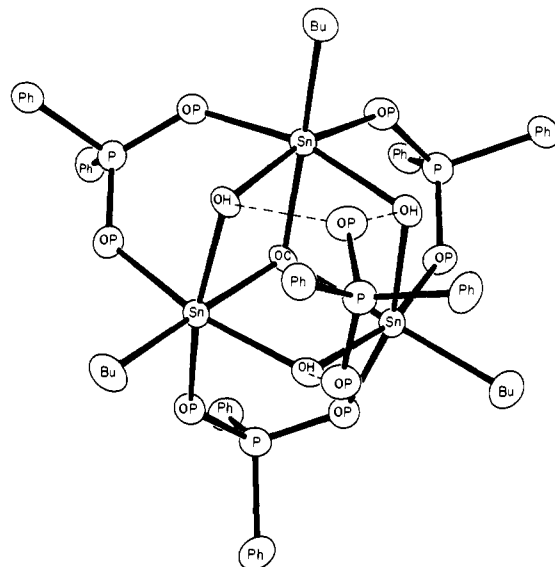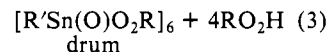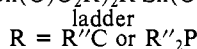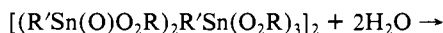

Figure 1. ORTEP plot of $[(n\text{-BuSn(OH)O}_2PPh_2)_3O][Ph_2PO_2]$ with thermal ellipsoids shown at the 30% probability level. Pendant atoms of the three *n*-Bu groups and of the eight Ph groups are omitted for purposes of clarity. Hydrogen-bonding interactions are shown as dashed lines. Average bond lengths (Å): Sn–OC = 2.075 (5); Sn–OH = 2.128 (6); Sn–OP = 2.122 (6); Sn–Bu = 2.15 (1). Average bond angles (deg): OC–Sn–OH = 77.2 (2); OC–Sn–OP = 85.3 (2); OC–Sn–Bu = 178.4 (3); OH–Sn–OH = 91.3 (2); OH–Sn–OP = 162.7 (2), 86.8 (2); OH–Sn–Bu = 102.1 (3); OP–Sn–OP = 90.1 (2); OP–Sn–Bu = 95.0 (3); Sn–OC–Sn = 103.6 (2); Sn–OH–Sn = 100.1 (2).

These three four-membered rings contain the latter atom and form a portion of a cube. The presence of four- and six-membered rings also is a primary structural feature of the drum structure.[1,2] The ladder framework, however, only possesses four-membered rings.[2]

The oxygen-capped cluster can be viewed as a hydrolysis product of the drum just as the drum is viewed as a hydrolysis product of the ladder,[2] i.e., eq 2 and 3, respectively. The drum

$$[R'Sn(O)O_2R]_6 + 2RO_2H + 2H_2O \rightarrow$$
$$\text{drum}$$
$$2[(R'Sn(OH)O_2R)_3O][RO_2] \quad (2)$$
$$\text{cluster}$$

$$[(R'Sn(O)O_2R)_2R'Sn(O_2R)_3]_2 + 2H_2O \rightarrow$$
$$\text{ladder}$$
$$R = R''C \text{ or } R''_2P$$
$$[R'Sn(O)O_2R]_6 + 4RO_2H \quad (3)$$
$$\text{drum}$$
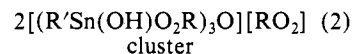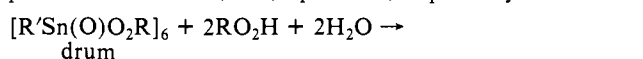
to ladder conversion has been followed by ^{119}Sn NMR and shown to be reversible.[2b] The ^{119}Sn NMR spectrum for the oxygen-capped cluster exhibits a single resonance with triplet character centered at -498.5 ppm ($^2J^{119}\text{Sn–O–}^{31}\text{P}) = 132.0$ Hz). This observation is consistent with the presence of three equivalent tin atoms provided by a cluster unit which has the hydrogen-bonded anionic phosphinate undergoing fast exchange among the three hydroxyl groups of the tristannoxane ring.

The schematic for a drum indicates how it is related to two cluster molecules. Formally, two bridging phosphinates rearrange,
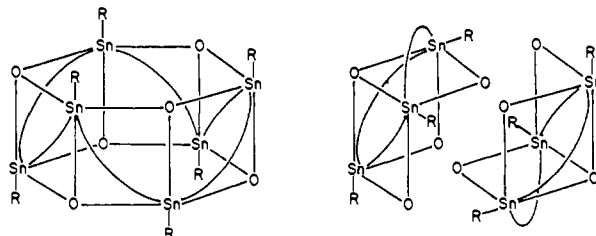
two oxygen atoms are added, four Sn–O bonds are cleaved, the six Sn–O–Sn linkages become Sn(OH)Sn units, and two phosphinates are added to hydrogen bond to the hydroxyls.

The discovery of these three novel types of stannoxane structural entities, the drum,[1-3] the ladder,[2,3] and the oxygen-capped cluster, suggests that additional cluster arrangements remain to be discovered possessing interesting properties.

Supplementary Material Available: Atomic coordinates (Table S1) and isotropic thermal parameters (Table S2) (5 pages). Ordering information is given on any current masthead page.

Preparation of the First Molecular η²-Acetylene Complex of a 4f Transition Metal, (Me₅C₅)₂Yb(η²-MeC≡CMe)

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Most d-block transition metals form well-defined complexes with acetylenes.[1] Even Cu(I) and its congeners yield isolable complexes.[2] No η²-acetylene complexes of the f-block transition metals have been described, though lanthanide metal atoms react with acetylenes,[3a,b] and a black substance of unknown structure whose composition is [(Me₅C₅)₂Sm]₂[PhC≡CPh] has been isolated.[3c] Monosubstituted acetylenes such as PhC≡CH react with (Me₅C₅)₂Yb(OEt₂) to give the mixed-valence phenylacetylide (Me₅C₅)₄Yb₃(μ-C≡CPh)₄ presumably by way of prior acetylene coordination.[3d] The bonding in metal–acetylene complexes is similar to that in olefin complexes, viz., the filled orbitals of σ-symmetry act as donors and the empty π-symmetry orbitals on the acetylene act as acceptor orbitals.[4a-c] (η⁶-Me₆C₆)Sm(AlCl₄)₃ has been isolated recently.[4d] Because lanthanide metallocenes can act as Lewis acids, though not as π-donors since the filled energy levels are too low in energy,[5] a reasonable strategy for synthesis of acetylene complexes is to use donor rather than acceptor substituents on the acetylene. The first vertical ionization energy of MeC≡CMe and tetrahydrofuran are 9.59[6a] and 9.57 eV,[6b] respectively, so it is, perhaps, not unexpected that MeC≡CMe will yield an isolable complex since the THF complex is known.[7]

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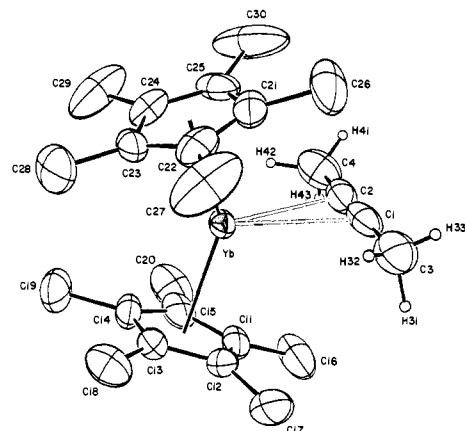

Figure 1, ORTEP diagram of (Me₅C₅)₂Yb(η²-MeC≡CMe). Thermal ellipsoids represent 50% probability surfaces except those of the hydrogen atoms which are arbitrary.

Addition of 2-butyne to base-free (Me₅C₅)₂Yb[5] in pentane results in a color change from orange to red from which dark purple-red needles, mp 170–173 °C, may be isolated in quantitative yield on cooling to –70 °C. The infrared spectrum of the complex as a Nujol mull shows no absorptions which may be attributed to ν(C≡C).[8] The ¹H NMR spectrum in C₆D₆ at 30 °C shows that the complex is diamagnetic and that the Me₅C₅ resonance in the complex is slightly deshielded relative to the base-free compound, δ 1.92 vs. 1.99, under identical conditions. The ¹³[¹H] NMR chemical shifts of the Me₅C₅ rings in the complex are also slightly perturbed relative to the base-free complex; the ring carbons are unchanged at δ 113.4 and the methyl carbons are deshielded in the complex, δ 10.6 vs. 10.9. The greatest effect is on the resonances of the 2-butyne ligand. The free ligand at 30 °C in C₆D₆ shows a resonance in the ¹H NMR spectrum at δ 1.52 which shifts to δ 1.27 on coordination. In the ¹³C[¹H] NMR spectrum the methyne and methyl carbons are deshielded on coordination, δ 74.6 to 76.9 and δ 3.08 to 3.76, respectively. The complexed 2-butyne is undergoing chemical exchange at 30 and –75 °C (200 MHz) since at 30 °C the ¹H NMR resonance of the acetylene in methylcyclohexane-d₁₄ with a 10-fold molar excess of acetylene occurs as a sharp singlet at δ 1.63 (relative to the most intense resonance due to residual protons of the solvent at δ 0.82); free 2-butyne resonates at δ 1.64 in C₇D₁₄. Cooling to –75 °C changes the averaged chemical shift to δ 1.73 with no discernible change in line shape. Both the vibrational spectrum of the solid and solution NMR spectra show that MeC≡CMe is only weakly perturbed on coordination to the lanthanide center. This contention is supported by the crystal structure at –80 °C.

An ORTEP diagram is shown in Figure 1. The geometry of the Me₅C₅ portion of the complex is not greatly perturbed from that of (Me₅C₅)₂Yb(thf).[7] The averaged Yb–C and Yb–Me₅C₅ ring centroid distances and the Me₅C₅ ring centroid–Yb–Me₅C₅ ring centroid angle in the acetylene complex are 2.659 ± 0.009 Å, 2.38

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(8) We have isolated the unsymmetrical acetylene complexes (Me₅C₅)₂Yb(L), L = PhC≡CMe or Me₃CC≡CMe, though the ν(C≡C) is not observable in the infrared. As yet, we have not been able to observe the Raman spectrum of the MeC≡CMe complex in the solid state nor in a methylcyclohexane solution.

(9) The compound crystallizes in the monoclinic crystal system in space group P2₁/n with cell dimensions a = 15.738 (2) Å, b = 15.299 (2) Å, and c = 9.724 (1) Å, β = 103.90 (1)°, V = 2272.6 (8) Å³ with Z = 4, and d(calcd) = 1.45 g cm⁻³. The data were collected on a Nonius CAD4 automated diffractometer with Mo Kα X-rays (λ = 0.71073 Å) at –80 °C. The structure was solved from Patterson and electron density maps and refined by full-matrix least squares to a conventional R factor of 0.022 (R_W = 0.029 and GOF = 1.505) by using 2449 absorption corrected data, where F_o² > 3σ(F_o²) against 251 variables. The R value for all 2971 unique data was 0.044. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the 2-butyne ligand were located in a difference map and they were refined with isotropic thermal parameters. All other hydrogen atoms were located in a difference Fourier map and then placed in calculated positions included in the structure factor calculations, but were not refined.