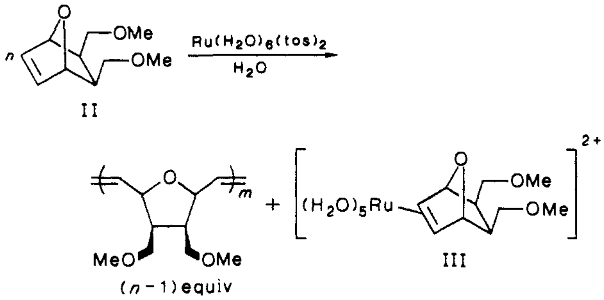
$(H_2O)_6(tos)_2$ in D_2O, $(n - 1)$ equiv of II are polymerized, and conversion of the catalyst to the mono-olefin adduct $Ru(H_2O)_5(II)(tos)_2$, III, (λ_{max} = 294 nm) is observed by NMR (eq 2).[17]



(2)

Aqueous solutions of III are highly active in subsequent polymerizations, displaying the same rapid initiation times (10–12 s) as the limiting initiation times observed for the recycled Ru^{3+} solutions. We therefore attribute the increased activity of the recycled catalyst solutions to the in situ formation of Ru^{2+} olefin complexes.[18] When the polymerization of II is carried out by using Ru^{3+} salts ($RuCl_3$ or K_2RuCl_5) in D_2O to generate the active catalyst solution, resonances identical with the olefin resonances of adduct III are observed.[17] Because Ru^{3+} does not form stable olefin complexes,[19] we therefore conclude that these resonances are due to Ru^{2+} olefin adducts formed from the reduction of Ru^{3+} in the reaction mixture. On the basis of formation of Ru^{4+} (as Ru Red, λ_{max} = 544 nm)[20] and a Ru^{2+} olefin complex[21] when II is polymerized by $Ru(NH_3)_5(H_2O)^{3+}$ (λ_{max} = 325 nm), we propose a mechanism which involves the disproportionation of an equilibrium amount of Ru^{3+}–olefin complex to provide a Ru^{2+}–olefin complex and a Ru^{4+} species which is trapped by additional Ru^{3+}. The olefin complex thus produced initiates the observed polymerization chemistry.

The synthetic utility of these aqueous polymerization systems can be expanded to include monomers that are reluctant to polymerize in aqueous solution by using the preformed olefin complex III to catalyze the polymerization. For example, the K_2RuCl_5 catalyzed aqueous polymerization of 2-norbornene-5-methanol provides at best only low yields of the desired polymer (typically <10%). Under the similar conditions with III as the catalyst, yields greater than 90% are obtained.

Our current work on these aqueous ROMP systems is focusing on both the systematic modifications of these classical coordination complexes to enhance and understand their organometallic chemistry as well as the utilization of these new catalysts in the polymerization of highly functionalized monomers.

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(16) The Ru^{2+} is far more active, with an initiation time of 50–55 s for the first polymerization. The recycled catalyst displays subsequent initiation times of 10–12 s.

(17) Characteristic changes in the spectra of the complexed monomer relative to that of free monomer are upfield shifts of the olefinic proton (6.28 to 5.07 ppm) and carbon (135.2 to 84.6 ppm) signals and downfield shifts of the endo proton (1.77 to 2.54 ppm) and carbon (39.6 to 42.6 ppm) signals. Compound III: ^1H NMR (400 MHz, D_2O); olefinic moiety: 5.08 (s), 4.73 (s), 3.44 (m), 3.26 (s), and 2.54 (m) ppm. Tosylate anion: 7.52, 7.50, 7.19, 7.17, and 2.21 ppm. ^{13}C NMR (D_2O); olefinic moiety: 84.6, 77.2, 71.5, 58.9, and 44.6 ppm. Tosylate anion: 143.3, 140.2, 130.2, 126.1, and 21.25 ppm. The cyclic voltammogram of complex III shows one irreversible Ru^{2+}/Ru^{3+} oxidation couple at 1.05 V versus SSCE. This represents an overall stabilization of the Ru^{2+} state by 1.08 V. For a discussion of the stabilization of low valent Ru complexes by electron acceptor ligands, see: Sullivan, B. P.; Baumann, J. A.; Meyer, T. J.; Salmon, D. J.; Lehmann, H.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7368.

(18) In the cases where specific monomers form no olefin complexes in the reaction mixture, no enhancement of activity is observed upon repeated use of the catalyst solution. An example of this would be multiple polymerizations of norbornene (see footnote 14).

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A New Structural Form of Tin as a Double Cube. A Heptanuclear Tin–Sulfur Cluster

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Recently, we reported new classes of organooxotin compounds in the form of cubes,[1,2] drums,[3–6] and oxygen-capped clusters.[2,6,7] The faces of these clusters consist of either four- or six-membered Sn–O rings. The cube and the drum have the same empirical composition, $[R'Sn(O)O_2PR_2]_n$, n = 4 and 6, respectively, whereas the oxygen-capped cluster, $[(R'Sn(OH)O_2PR_2)_3O][R_2PO_2]$, resembles a cube with one corner missing. ^{119}Sn NMR spectra show that the drum[6] and the cube[2] forms undergo hydrolysis in solution giving oxygen-capped clusters. Heating the latter regenerates the starting drum[6] or cube,[8] thus showing the reaction to be reversible. In all of these compositions, tin is hexacoordinated, and chelating phosphinate or phosphate ligands span adjacent tin atoms.

In our continuing exploration of new oligomeric formulations and their structural interconversions, we now report the first heptanuclear tin–sulfur cluster formed from the reaction of n-butylstannonic acid, diphenyl phosphine oxide, and elemental sulfur.[9]

$$24Ph_2P(OH) + 3S_8 + 28n\text{-}BuSn(O)OH \xrightarrow[\text{reflux}]{\text{toluene}} 4[\{n\text{-}BuSnS(O_2PPh_2)\}_3O]_2Sn + 24H_2O + 4n\text{-}BuH$$

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(9) A mixture of n-butylstannonic acid (0.962 g, 4.62 mmol) and diphenyl phosphine oxide (0.935 g, 4.62 mmol) in toluene (75 mL) was heated under reflux for 1 h under an atmosphere of nitrogen. A blank reaction of $Ph_2P(O)H$ with sulfur in a toluene–chloroform mixture (3:1) at 60 °C showed the formation of $Ph_2P(S)OH$ (δ (P) = 71.36 ppm). Elemental sulfur (0.147 g, 0.574 mmol) was added to the mixture, and the contents were heated at reflux for 2 h with the azeotropic removal of water. The resulting homogeneous solution was concentrated to ca. 15 mL. A solid material was deposited from this solution upon standing for a day (0.3 g, 17% based on stannonic acid). Crystals suitable for X-ray analysis were grown from a solvent mixture of benzene and dichloromethane (95:5). Anal. Calcd for $C_{96}H_{114}O_{14}P_6S_6Sn_7$ (after removal of solvent of crystallization): C, 42.69; H, 4.22. Found: C, 42.37; H, 4.26. ^1H NMR ($CDCl_3$) 0.67 (t, CH_3, J = 7.1 Hz, 18 H), 1.20 (m, CH_2, 12 H), 1.50–2.20 (br, CH_2—CH_2, 24 H), 6.80–7.80 (m, H_{Ar}, 60 H); ^{31}P NMR ($CDCl_3$, H_3PO_4 ref) 27.28 (s with satellites, ^2J (Sn–O–P) = 130.0 Hz); ^{119}Sn NMR ($CDCl_3$, TMT ref) −467.66 (t, ^2J (Sn–O–P) = 132.0 Hz). We were unable to locate the signal due to the unique tin connected to six sulfur atoms.

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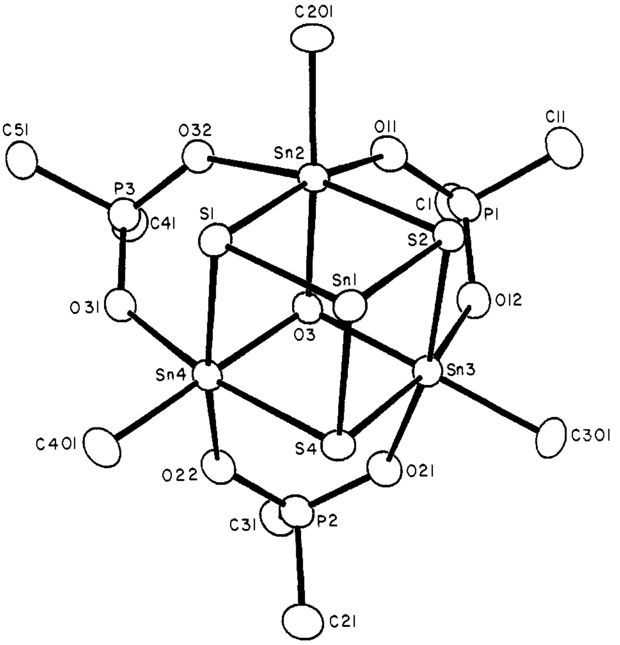

Figure 1. ORTEP plot of the asymmetric unit of the [(nBuSn(S)$O_2PPh_2)_3O]_2$Sn molecule with thermal ellipsoids at the 30% probability level. Atom Sn1 lies on a crystallographic inversion center. Pendant carbon atoms of the six phenyl groups and of the three *n*-butyl groups are omitted for purposes of clarity. Average bond lengths (Å): Sn1–S = 2.561 (1); Sn–S = 2.576 (1); Sn–C = 2.151 (6); Sn–O3 = 2.100 (4); Sn–O = 2.147 (4); P–O = 1.515 (4). Average bond angles (deg): S–Sn1–S = 90 (av value required by symmetry), 180 (required by symmetry); S–Sn–S = 89.41 (4); S–Sn–O3 = 82.2 (1); S–Sn–O = 90.9 (1), 167.1 (1); S–Sn–C = 101.9 (2); O–Sn–O3 = 85.1 (1); O–Sn–O = 86.0 (1); C–Sn–O3 = 174.1 (2); C–Sn–O = 96.3 (2); Sn–O3–Sn = 109.4 (1); Sn–O–P = 132.5 (2); Sn1–S–Sn = 90.18 (4); Sn–S–Sn = 83.38 (4). Sn refers to Sn2–Sn4. O refers to phosphinate oxygen atoms. The unique O3 and Sn1 are so designated.

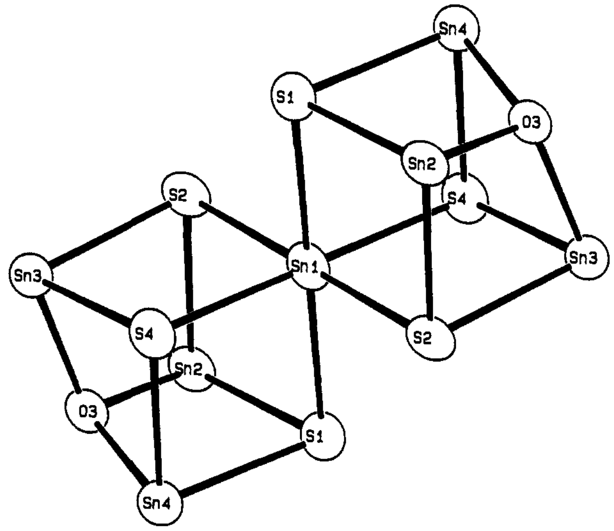

Figure 2. ORTEP plot showing the tin–sulfur–oxygen core of the [(nBuSn(S)$O_2PPh_2)_3O]_2$Sn molecule. Atoms with the same label are related by a crystallographic inversion center (−*x*, −*y*, −*z*).

X-ray analysis[10] reveals a double cube arrangement which we believe is the first such structural entity uncovered for a main group element. An analogous core structure exists for a zinc complex, however, $Zn(OCH_3)_2(C_2H_5ZnOCH_3)_6$.[11] The latter is a polymerization catalyst. Figure 1 shows the chelating phosphinate ligands arranged around the outside of one of the symmetry-related Sn–O cubes. The relation between this geometry and the oxygen-capped formulation may be seen by the formal removal of Sn1 and the introduction of hydrogen atoms on S1, S2, and S4, with S–H bonds replacing S–Sn1 bonds. This results in an SH analogue of the O-capped cluster, [n(BuSn(OH)$O_2PPh_2)_3O]^+$.

The core of the molecule is shown in Figure 2 as a double cube connected at the corners occupied by Sn1. Distortions away from cubic geometry are caused primarily by the geometric requirements of the oxygen atom O3. The four-membered $(Sn–S)_2$ rings are nearly planar (±0.044 Å maximum deviation) with angles that deviate only slightly from 90° (av values from 89.41 (4)° to 90.18 (4)°). The angles at O3, however, are nearly tetrahedral (av 109.4 (1)°), and the four-membered rings containing O3 are not planar. For these, O3 is displaced 0.4 Å out of the plane defined by the remaining three atoms in a direction toward the center of the cube. The angles at Sn and S in these rings average 82.2 (1)° and 83.38 (4)°, respectively.

^{119}Sn and ^{31}P NMR indicate that the double cube structure is retained in solution.[2,9] A single tin signal with triplet character due to phosphorus atom coupling appearing in the hexacoordinated region is assigned to the six equivalent tin atoms. Consistent with the presence of equivalent phosphorus atoms, one phosphorus signal with tin satellites is observed in the ^{31}P NMR spectrum.

It is interesting that an analogy exists between the topology of tin–oxygen or tin–sulfur clusters and iron–sulfur clusters. Some of the latter are relevant to the chemistry of metallobiomolecules. Recent work[12] has shown core conversions among Fe_4S_4, Fe_6S_6, and Fe_7S_6 clusters which resemble the core compositions of the Sn_4O_4 cubes,[1,2] Sn_6O_6 drums,[3–6] and Sn_7S_6 bicube reported here. There is also a structural analogy between the iron–sulfur and tin–oxygen cubes and drums. Although the Fe_7S_6 and Sn_7S_6 cores refer to compounds having different geometries, the former resembles an iron-capped drum,[12] while the latter is a double cube; insight into the existence of additional interesting structural forms may be gained by these comparisons.

Acknowledgment. Support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (CHE 8504737) is gratefully acknowledged.

Supplementary Material Available: Atomic coordinates (Table S1) and thermal parameters (Table S2) for [(n-BuSn(S)$O_2PPh_2)_3O]_2Sn·3C_6H_6$ (8 pages). Ordering information is given on any current masthead page.

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(10) Colorless large plates obtained as the benzene solvate are very unstable when removed from the mother liquor. The crystal used for the X-ray study (cut to dimensions of 0.25 × 0.45 × 0.65 mm) was wedged wet with mother liquor into a glass capillary which was then sealed. Crystal data: [(n-BuSn(S)(O_2PPh_2))$_3O]_2Sn·3C_6H_6$, triclinic space group $P\bar{1}$ (no. 2), a = 13.104 (9) Å, b = 16.154 (5) Å, c = 17.091 (4) Å, α = 65.17 (2)°, β = 81.68 (4)°, γ = 72.26 (4)°, Z = 1, and $\mu_{MoK\bar{\alpha}}$ = 16.1 cm^{-1}. A total of 8140 independent reflections ($+h,\pm k,\pm l$) was measured on an Enraf-Nonius CAD4 diffractometer (23 ± 2 °C, graphite monochromated Mo K$\bar{\alpha}$ radiation, λ = 0.71073 Å, θ–2θ scan mode, $2\theta_{max}$ = 45°). An empirical absorption correction based on ψ scans was applied (from 0.63 to 1.00 on I). The structure was solved by the heavy atom method and was refined by full-matrix least squares (function minimized $\Sigma w(|F_o| - |F_c|)^2$, $w^{1/2} = 2F_oLp/\sigma_I$). Of the 75 independent non-hydrogen atoms, 72 were refined anisotropically (two positions for one of the terminal atoms of an *n*-Bu group in half occupancy). The remaining three non-hydrogen atoms comprising a benzene of solvation about an inversion center were poorly defined and were refined isotropically. Hydrogen atoms were omitted from the refinement. The final agreement factors were R = 0.032 and R_w = 0.054 for the 7169 reflections having $I \geq 3\sigma_I$. The molecule has crystallographic C_i symmetry with atom Sn1 lying on an inversion center. All seven of the tin atoms are hexacoordinated. The geometry at the unique Sn1 is nearly perfectly octahedral. The six Sn1–S bond lengths range from 2.546 (1) Å to 2.570 (1) Å with an average value of 2.561 (1) Å. Angles at Sn1 between trans ligand atoms are required by symmetry to be 180°. Angles between cis ligand atoms range from 89.49 (4)° to 90.51 (4)° with an average value which is required by symmetry to be 90°. The idealized molecular symmetry of the species is C_{3i} (S_6) with Sn1 lying on the intersection of the symmetry elements. The remaining tin atoms are therefore chemically equivalent. The geometry about these tin atoms is distorted octahedral, where average bond angles compared to the idealized value of 90° range from 82.2 (1)° to 101.9 (2)°, while average angles compared to the idealized value of 180° range from 167.1 (1)° to 174.1 (2)°.

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