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Organooxotin Cages, $\{[(n\text{-BuSn})_3(\mu_3\text{-O})(\text{OC}_6\text{H}_4\text{-4-X})_3]_2[\text{HPO}_3]_4\}$, X = H, Cl, Br, and I, in Double O-Capped Structures: Halogen-Bonding-Mediated Supramolecular Formation

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The reaction of *n*-BuSn(O)(OH) with H_3PO_3 and HOC_6H_4-4-X (X = H, Cl, Br, and I) afforded the hexanuclear organooxotin cages $\{[(n\text{-BuSn})_3(\mu_3\text{-O})(\text{OC}_6\text{H}_4\text{-4-X})_3]_2[\text{HPO}_3]_4\}$, where X = H (**1**), Cl (**2**), Br (**3**), and I (**4**), in moderate yields. These cages possess *double O-capped* structures. The oxotin cages **1**−**4** contain two tritin motifs that are joined by four tripodal $[HPO_3]^{2-}$ ligands. The three tin atoms in each tritin subunit are held together by a μ_3-capping oxygen atom. In addition three phenolate oxygen atoms act as μ_2-bridging ligands between two tin atoms. The molecular structures of **1**−**4** are intimately related to other organooxotin cages such as the *O-capped cluster*, the *drum*, and the *football* cage. The crystal structures of **2**−**4** reveal intermolecular halogen-bonding-mediated [X- - -O (X = Cl, Br), I- - -I, and I- - -π] supramolecular assemblies.

Introduction

The remarkable structural adaptability of the stannoxane and distannoxane units has been initially demonstrated by the research group of Holmes.[1] Subsequently, a rich structural chemistry of the rings, cages, and clusters containing stannoxane and distannoxane motifs has emerged from our laboratory[2,3] as well as those of other research groups drawn across the world.[4−7] Most of the organooxotin cages are essentially two-component reactions and involve the use of *n*-BuSn(O)(OH) and a protic acid such as carboxylic, phosphinic, phosphonic, or sulfonic acid.[8] In a preliminary communication, we have recently reported the formation of a new structural form of an organooxotin cage, $\{[(n\text{-BuSn})_3(\mu_3\text{-O})(\text{OC}_6\text{H}_5)_3]_2[\text{HPO}_3]_4\}$ (**1**), in a three-component reaction that involves the organotin precursor, a phosphorus-based acid, and a co-ligand, phenol.[2b] Herein, we report the complete details of these investigations. Accordingly, the following account describes the synthesis and structural characterization of the *double O-capped clusters* $\{[(n\text{-BuSn})_3(\mu_3\text{-O})(\text{OC}_6\text{H}_4\text{-4-X})_3]_2[\text{HPO}_3]_4\}$, where X = H (**1**), Cl (**2**), Br (**3**), and I (**4**). We also demonstrate, in the crystal structures of **2**−**4**, the halogen-bonding-mediated [X- - -O (X = Cl, Br), I- - -I, and I- - -π] supramolecular formation of organooxotin compounds.

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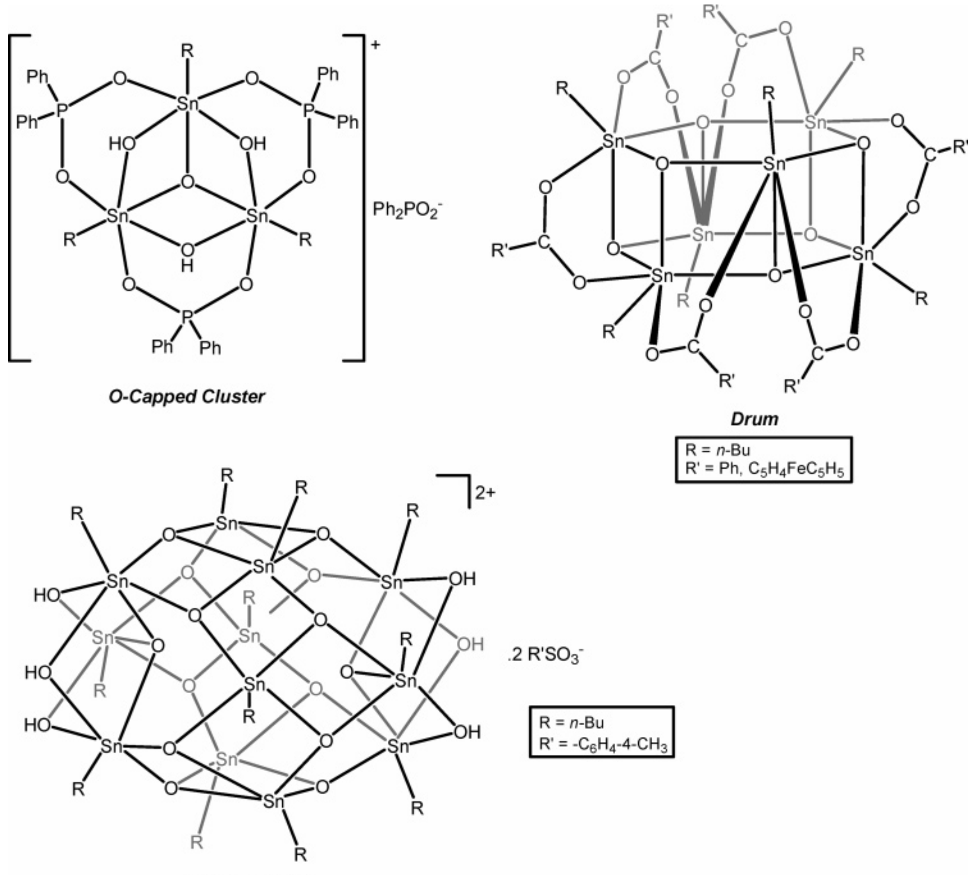
Chart 1. Monoorganooxotin Cages: O-Capped Cluster, Drum, and Football Cage



O-Capped Cluster

Drum

Foot-ball Cage

Results and Discussion

Synthesis. Three related structural forms in organooxotin cages, viz., the *O-capped cluster*, the *drum*, and the *football* cage, are formed in three different reactions involving n-BuSn(O)(OH). Thus, the reaction of n-BuSn(O)(OH) with diphenylphosphinc acid affords the trinuclear O-capped cluster $\{[n\text{-BuSn(OH)}O_2PPh_2]_3O\}^+$-$\{Ph_2PO_2\}^-$ (Chart 1).[1b] On the other hand the reaction of n-BuSn(O)(OH) with many carboxylic acids and also phosphates such as $(PhO)_2P(O)(OH)$ affords the hexameric drums, $[n\text{-BuSn(O)}O_2CR]_6$ or $[n\text{-BuSn(O)}O_2P(OPh)_2]_6$.[1e,f,8] The reactions of many aryl sulfonic acids with n-BuSn(O)(OH) afford the dodecanuclear football cages $[(n\text{-BuSn})_{12}O_{14}(OH)_6]^{2+}[RSO_3^-]_2$ (Chart 1).[9a,b] The latter can also be obtained in alternative hydrolytic reactions involving appropriate organotin precursors.[9c−e] In contrast to these two-component reactions, the reaction of n-BuSn(O)(OH) with H_3PO_3 in the presence of phenols, HOC_6H_4-4-X (X = H, Cl, Br, and I), affords the hexanuclear double O-capped clusters **1**−**4** in moderate yields (vide infra, see Experimental Section) (Scheme 1). As reported earlier by us, **1** can also be synthesized in a reaction between n-BuSn(O)(OH) and $(PhO)_2P(O)H$ which involves the hydrolytic scission of the P−O bond and the in situ generation of the reactants $[HPO_3]^{2-}$ and $[C_6H_5O]^-$.[2b] The cages **1**−**4** are thermally stable solids with high decomposition points (vide infra, see Experimental Section). The $^{31}P\{^1H\}$ NMR spectra of **1**−**4** show a single resonance with nearly the same chemical shift (0.54−0.58 ppm). A strong $^1J(P-H)$ coupling is observed in each case (688−690 Hz). The ^{119}Sn NMR show upfield resonances and are consistent with the coordination environment around the tin atoms (1C, 5O).[8]

Molecular Structures of 2−4. The molecular structures of **1**−**4** are very similar and show spherical cage-like architectures. The structure of **1** has been previously reported by us in a preliminary communication.[2b] The molecular structure of **2** is shown in Figure 1 and is discussed below. The molecular structures of **3** and **4** are given in the Supporting Information.

The structure of **2** reveals that its asymmetric unit contains two molecules (Figure 1). All the tin atoms present in **2** have a coordination number of six (1C, 5O); this coordination is derived from one alkyl group, one μ_3-capping oxygen atom, two μ_2-capping phenolate oxygen atoms, and two phosphonate oxygen atoms. The molecular structure of **2** can be described as a spherical cage that contains two centrosymmetrically related Sn_3O_4 subunits. Each of these subunits contains three mutually perpendicular Sn_2O_2 four-membered rings (Figure 1). One oxygen atom (O4) of this core is μ_3-bridging and is involved in the capping of Sn1, Sn2, and Sn3 atoms; the other three oxygen atoms (O1, O2, and O3) are derived from the phenoxide ligand and bridge only two tin atoms. The Sn−O distances involv-

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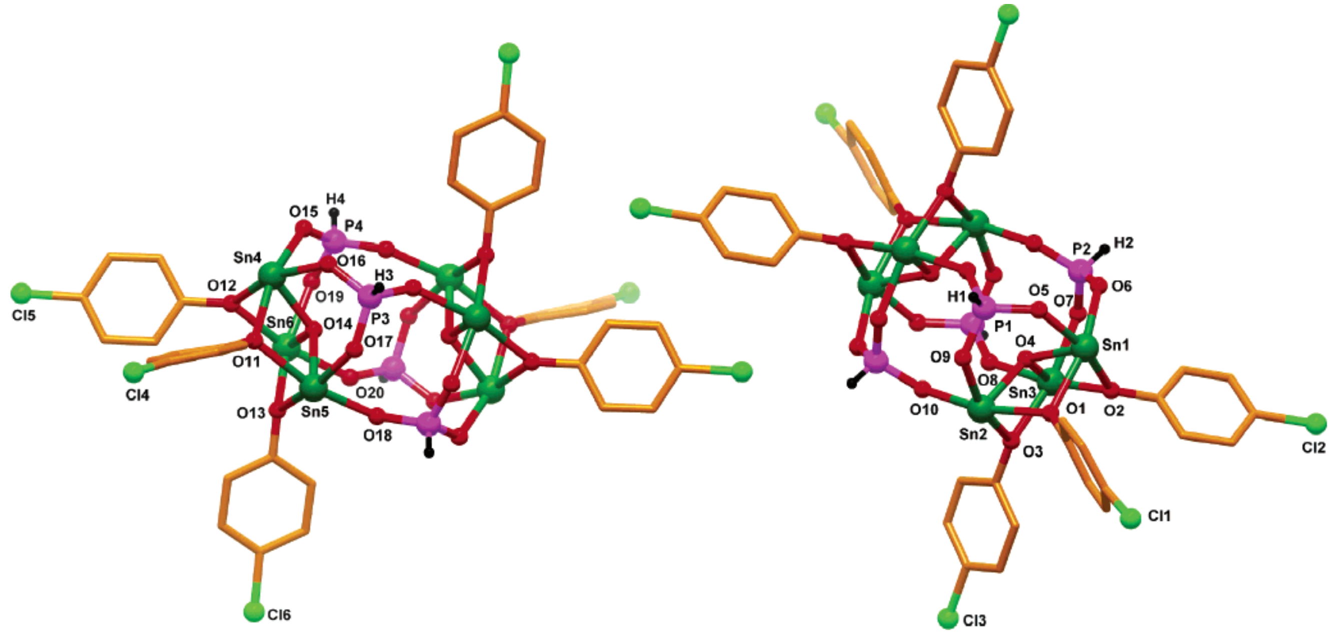
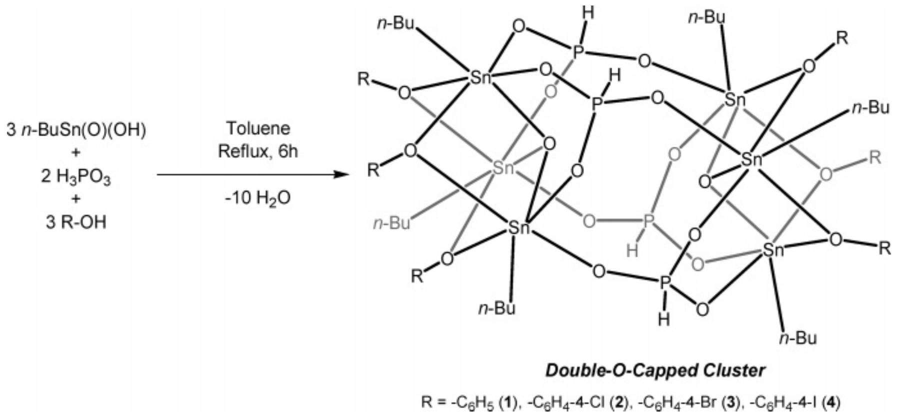


Figure 1. View of the two molecules of **2** present in its asymmetric unit. The unlabeled atoms are symmetry related to the labeled atoms. Selected bond distances (Å) and angles (deg) for one of the molecules: Sn1−O1 2.149(5), Sn1−O2 2.164(6), Sn1−O4 2.044(5), Sn1−O5 2.065(5), Sn1−O6 2.062(5), Sn1−C1 2.113(8), Sn2−O1 2.213(5), Sn2−O3 2.133(6), Sn2−O4 2.044(5), Sn2−O9 2.068(5), Sn2−O10 2.061(6), Sn2−C5 2.102(8), Sn3−O2 2.209(5), Sn3−O3 2.169(5), Sn3−O4 2.026(5), Sn3−O7 2.069(5), Sn3−O8 2.084(5), Sn3−C9 2.113(9), P1−O5 1.523(5), P1−O9 1.517(6), P1−O8* 1.504(6), P2−O6 1.520(6), P2−O7 1.519(6), P2−O10* 1.511(6); Sn1−O4−Sn2 108.5(2), Sn1−O4−Sn3 108.6(2), Sn2−O4−Sn3 111.4(2), O4−Sn1−C1 169.3(3), O4−Sn2−C5 165.1(3), O4−Sn3−C9 164.1(3), Sn1−O1−Sn2 101.1(2), Sn1−O2−Sn3 100.2(2), Sn2−O3−Sn3 102.8(2), Sn1−O5−P1 127.3(3) Sn1−O6−P2 128.5(3), Sn2−O9−P1 128.0(3), Sn2−O10−P2* 142.0(4), Sn3−O7−P2 129.2(3), Sn3−O8−P1* 140.2(3), O5−P1−O8* 111.5(3), O9−P1−O8* 115.4(3), O5−P1−O9 111.5(3), O6−P2−O7 112.5(3), O6−P2−O10* 112.2(3), O7−P2−O10* 113.0(3)°.

Scheme 1. Synthesis of Compounds 1−4



ing the capping μ_3-oxygen are nearly similar, although not equal: Sn1−O4 2.105(6), Sn2−O4 2.044(5), and Sn3−O4 2.026(8) Å. In comparison, Sn−O distances involving the phenoxide oxygen atoms are longer. Each tin atom of the tritin subunit is further bound to two oxygen atoms of the phosphonate ligands. Each of the phosphonate ligands is involved in a tripodal bridging coordination mode. None of the phosphonates act as chelating ligands. The four phosphonates, $[HPO_3]^{2-}$, effectively bridge the two tritin subunits and generate the spherical cage-like architecture. The Sn−O and P−O bond distances in the Sn−O−P structural units are quite similar (av 2.068(10) and 1.516(8) Å respectively).

Comparison of the Molecular Structures of 1−4 with Other Related Organooxotin Cages. It is relevant to compare the molecular structures of **1**−**4** with those of other three very closely related organooxotin cages, viz., the O-capped cluster, the drum, and the football cage (Scheme 2).[2b] It is immediately evident that cages **1**−**4**, as well as the drum and the football cage, are structurally related to the O-capped cluster. The latter itself can be considered as an incomplete cube, with one of the vertexes of the cube remaining unoccupied. The absence of one vertex atom results in a Sn_3O_4 core for the O-capped cluster. Thus, the core structure of the O-capped cluster is *exactly* the same as what is found for **1**−**4**. The bonding parameters in these two types of oxotin structures are also quite comparable (Table 1). The drum compound (Sn_6O_6 core) is a hexameric prism and can be thought of as forming from a face−face condensation of the two incomplete cubes of the O-capped cluster (Scheme 2). Because of such a fusion, the core of the drum does not contain any μ_2-oxygen atoms; all the oxygen atoms of the core of the

Scheme 2. Structural Comparison of the Monoorganooxotin Cages 1−4 with Other Related Systems

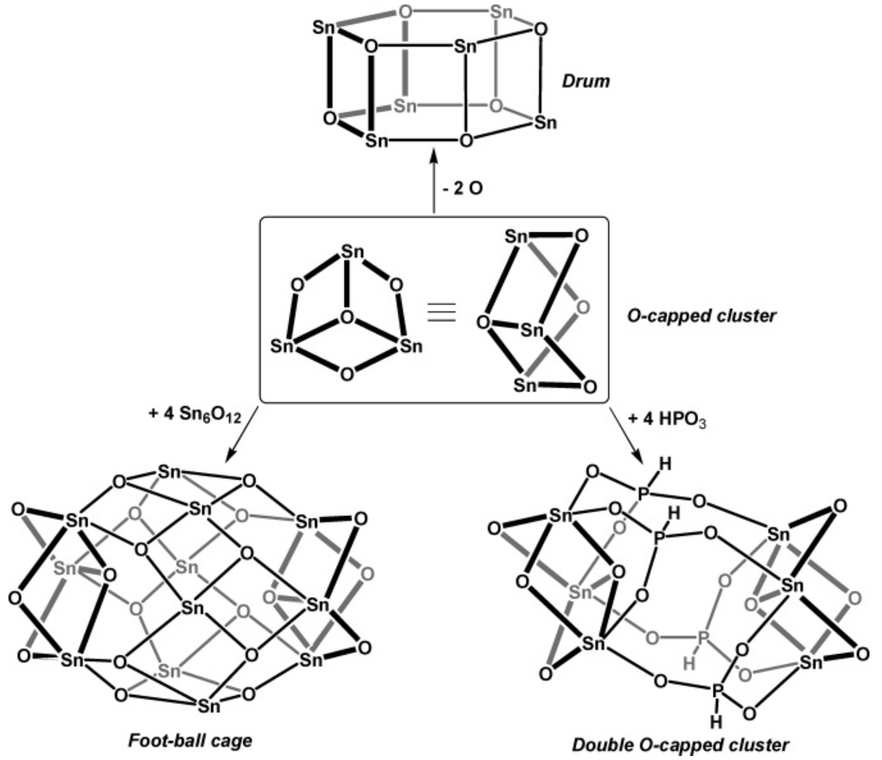


Table 1. Comparison of Bond Distances in the Core Structures of Selected Monoorgano Oxotin Cages

compound	average Sn−O(μ_3) (Å)	average Sn−O(μ_2) (Å)	average Sn−O(P) (Å)	diametrically opposite P−P (Å)	interpole [O(μ_3)-O(μ_3)] (Å)	ref
1	2.065(3)	2.172(2)	2.072(2)	6.337(1)	3.778(4)	2b
2[a]	2.058(5)	2.172(6)	2.068(6)	6.283(2)	3.813(2)	this work
	2.057(5)	2.176(6)	2.064(6)	6.275(3)	3.848(2)	
3[a]	2.063(3)	2.177(4)	2.071(4)	6.294(3)	3.805(5)	this work
	2.064(4)	2.181(4)	2.073(4)	6.294(4)	3.827(6)	
4	2.062(7)	2.172(7)	2.080(7)	6.274(5)	3.825(9)	this work
O-capped cluster	2.075(5)	2.128(6)	2.122(6)			1b
drum	2.101(5)		2.155(5)			1f
football cage	2.091(7)[b] 2.054(8)[c] 2.140(8)[d]	2.096(8)		6.331(6)[e]	3.899(6)	9c

[a] Two crystallographically independent molecules are present. [b] Sn is bonded with μ_3-capped oxygen (O-capped) in the poles. [c] Pole tin atoms bonded with μ_3-oxygens that are part of the equator. [d] Equator tin atoms bonded with μ_3-oxygens that are part of the equator. [e] Average distance between the diametrically opposite tin atoms present in the equator.

drum are μ_3-bridging. The bonding parameters (Sn−O) of the drum are also comparable to that observed for **1**−**4** as well as the O-capped cluster (Table 1). If the two Sn_3O_4 cores of the latter are joined to each other in a back−back manner with the help of additional ligands, one obtains the cages **1**−**4** or the football cage. Thus, the formation of **1**−**4** involves the use of the tripodal phosphonate ligands to join the Sn_3O_4 cores (Scheme 2). On the other hand the football cage is derived by combining two such cores with the help a Sn_6O_{12} unit. The football cage and compounds **1**−**4** are, thus, structurally quite similar. Further evidence for this structural similarity comes from examining some of their bonding parameters. The football cage has been thought of as an ellipsoidal sphere possessing two poles (Sn_3O_4) and a central equator (Sn_6O_{12}). The interpole distance (μ_3O−μ_3O) is 3.899(6) Å in $[(n\text{-BuSn})_{12}O_{14}(OH)_6]^{2+}[OH^-]_2$.[9c] Interestingly, the interpole distance in **1**−**4** ranges from 3.778(4) (for **1**) to 3.825(9) Å (for **4**). The distance between the diametrically opposite phosphorus atoms in **1**−**4** ranges from 6.274(5) to 6.337(1) Å. This is comparable with the distance of the diametrically opposite tin atoms in the football cage (6.331(6) Å, Table 1). Thus, despite the apparent dissimilarities, many of the oxotin cages are structurally quite close.

Halogen Bonding in the Crystal Structures of 2−4. We have shown recently that the hexameric organooxotin drum $[n\text{-BuSn(O)OC(O)CH}_2\text{Fc}]_6$ (Fc = ferrocenyl) and other organooxotin derivatives form interesting noncovalent interaction-mediated (O−H- - -O, C−H- - -O, C−H- - -π, π- - -π, etc.) supramolecular assemblies in their solid state.[2c,3c,d,10] In view of this interest we have examined the crystal structures of **1**−**4** to detect the presence and effect of noncovalent interactions. The crystal structure of **1** does not show any hydrogen bonds (such as C−H- - -O) or other types of noncovalent interactions. On the other hand the crystal

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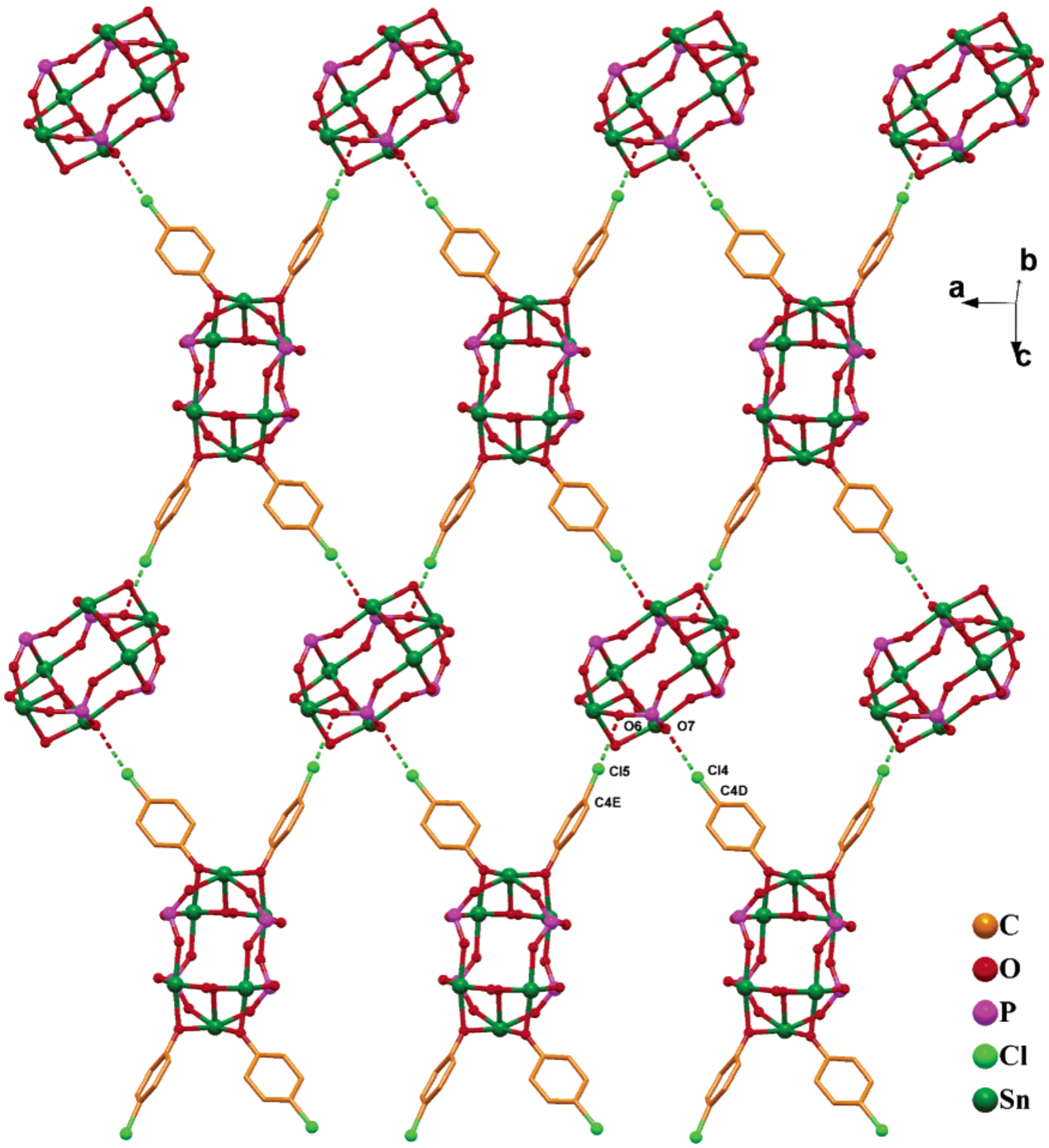

Figure 2. View showing the Cl- - -O-mediated two-dimensional supramolecular network in **2**. The halogen-bonding parameters are Cl5- - -O6 3.303(9) Å, 164.32(2)°.

structures of **2**−**4** reveal robust halogen-bonding interactions that lead to the generation of supramolecular structures. The term halogen bonding (XB), as defined in a recent leading review article,[11] is a noncovalent interaction and encompasses interactions of the type D- - -X−Y (D = donor, a Lewis base; X = halogen, a Lewis acceptor; Y = C, N, or a halogen). Alternatively, the interaction can be viewed as A- - -X−Y (A = halogen acceptor). The XB interaction energy varies over a wide range from 5 to 180 kJ mol^{-1}, with Cl- - -Cl interactions being weak and I^{-}- - -I−I interactions being quite strong.[12] In general it has been shown that XB can prevail over hydrogen bonding in terms of being the *primary glue* that selects and binds the modules in a competitive supramolecular recognition process.[13] Some of these XB interactions such as X- - -O interactions are highly directional multipolar interactions as reviewed recently.[14]

Compounds **2**−**4** crystallize in the triclinic crystal system (space group $P\bar{1}$). Compounds **2** and **3** have two molecules in their asymmetric units. It can be noticed from Figure 1 that the chlorophenoxide moiety present in the pole of one of the molecules (in **2**) protrudes into the core of the other molecule within the same asymmetric unit. A similar situation is found for **3** also.[15] Thus, the molecules are well-positioned for systematic

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Table 2. Crystal Data and Structure Refinement Parameters for Compounds 2−4

	2	3	4
empirical formula	$C_{63.50}H_{86}Cl_6O_{20}P_4Sn_6$	$C_{63.50}H_{86}Br_6O_{20}P_4Sn_6$	$C_{36.50}H_{47}ClI_4O_{11}P_2Sn_3$
fw	2218.04	2484.80	1622.80
temp (K)	223(2)	223(2)	223(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.500(5)	13.5706(7)	13.3902(7)
b (Å)	15.974(5)	16.0101(8)	14.2179(8)
c (Å)	20.487(7)	20.7547(11)	16.9005(10)
α (deg)	109.127(7)	109.512(1)	81.364(1)
β (deg)	90.972(8)	91.172(1)	69.981(1)
γ (deg)	97.352(7)	97.496(1)	62.312(1)
V (Å^3)	4132(2)	4204.1(4)	2676.8(3)
Z	2	2	2
density (calcd, Mg/m^3)	1.783	1.963	2.013
absorp coeff (mm^{-1})	2.120	4.745	3.852
F(000)	2178	2394	1526
cryst size (mm^3)	0.38 × 0.15 × 0.10	0.45 × 0.30 × 0.15	0.63 × 0.45 × 0.38
θ range (deg)	1.42 to 25.00	1.04 to 25.00	1.62 to 25.00
index ranges	$-16 \le h \le 15$, $-18 \le k \le 18$, $-24 \le l \le 22$	$-16 \le h \le 16$, $-19 \le k \le 15$, $-22 \le l \le 24$	$-15 \le h \le 14$, $-16 \le k \le 16$, $-20 \le l \le 9$
no. of reflns collected	23 991	24 524	15 472
no. of indep reflns	14 467 [R(int) = 0.0527]	14 810 [R(int) = 0.0352]	9400 [R(int) = 0.0344]
completeness to θ	99.5%	100.0%	100.0%
absorp corr	SADABS (Sheldrick, 1996)	SADABS (Sheldrick, 1996)	SADABS (Sheldrick, 1996)
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restrains/params	14 467/3/851	14 810/325/873	9400/59/532
goodness-of-fit on F^2	1.018	1.015	1.014
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0491, wR2 = 0.1050	R1 = 0.0353, wR2 = 0.0686	R1 = 0.0628, wR2 = 0.1699
R indices (all data)[a]	R1 = 0.0732, wR2 = 0.1135	R1 = 0.0481, wR2 = 0.0705	R1 = 0.0777, wR2 = 0.1761
largest diff peak and hole (e Å^{-3})	1.262 and −0.929	1.197 and −1.270	2.994 and −3.664

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/[\sum(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

X- - -O interactions. It can be seen that from Figure 2 that the (four) chlorine atoms of one of the molecules of the asymmetric unit of **2** interact with the phosphonate oxygens (halogen acceptors) of the neighboring molecules. This leads to the formation of a regular two-dimensional sheet containing alternate rows of chlorine-donor and chlorine-acceptor clusters. The Cl- - -O distances and the C−Cl- - -O angles involved in these interactions are Cl5- - -O6 3.303(9) Å, 164.32(2)° and Cl4- - -O7 3.269(11) Å, 164.11(3)°. These are consistent with other Cl- - -O interactions known in the literature.[11,16] The 2D grids formed by Cl- - -O interactions are further interconnected by means of C−H- - -O interactions to form a 3D supramolecular network. Compound **3**, which contains 4-bromophenoxide ligands, shows a supramolecular pattern identical with that of **2**. In the crystal structures of **2** and **3** the angle of approach of the halogen toward the nucleophilic center (phosphoryl oxygen) is almost linear and *head on*.[13b] The formation of the supramolecular assembly in **4** is not a consequence of I- - -O interactions, but is due to I- - -I and I- - -π interactions.[15]

Conclusion

In conclusion, we report in this contribution the formation of hexanuclear organooxotin cages, **1**−**4**. Unlike many reactions known for assembling organotin compounds, the synthesis of **1**−**4** is a three-component reaction and involves n-BuSn(O)(OH), H_3PO_3, and 4-substituted phenols. The molecular structures of **1**−**4**, which can be described as double O-capped structures, reveal the presence of two centrosymmetrically related Sn_3O_4 cores that are interconnected by four bridging tripodal phosphonate ligands. The molecular structures of **1**−**4** are intimately related to the other structural forms known for organooxotin cages, viz., the O-capped cluster, the drum, and the football cage. The crystal structures of **2**−**4** show halogen-bonding-mediated supramolecular formation.

Experimental Section

Reagents and General Procedures. All the reactions were performed under a dry nitrogen atmosphere by employing standard Schlenk techniques. Solvents were dried over sodium benzophenone ketyl and were collected from the still at the time of the reaction. The chemicals n-BuSn(O)(OH), HO-C_6H_4-4-X (X = Cl, Br, and I) (all from Aldrich), C_6H_5OH, and H_3PO_3 (from Sd-fine, India) were used as such. Melting points were measured using a JSGW melting point apparatus and are uncorrected. Elemental analyses were carried out using a Thermoquest CE instruments model EA/110 CHNS-O elemental analyzer. ^1H, ^{31}P, and ^{119}Sn NMR spectra were obtained on a JEOL-JNM LAMBDA 400 model spectrometer using $CDCl_3$ solutions in room temperature with the chemical shifts referenced to tetramethylsilane (for ^1H), 85% H_3PO_4 (for ^{31}P), and tetramethyltin (for ^{119}Sn), respectively. ^{31}P and ^{119}Sn NMR were recorded under broad-band decoupled conditions.

Synthesis. Compound **1** was synthesized by two synthetic routes reported by us recently.[2b] The general synthetic proce-

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(14) Paulini, R.; Müller, K.; Diederich, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 1788.

(15) See Supporting Information.

(16) (a) Moorthy, J. N.; Venkatakrishnan, P.; Mal, P.; Dixit, S.; Venugopalan, P. *Cryst. Growth Des.* **2003**, *3*, 581. (b) Thaimattam, R.; Xue, F.; Sarma, J. A. R. P.; Mak, T. C. W.; Desiraju, G. R. *J. Am. Chem. Soc.* **2001**, *123*, 4432, and references therein.

dure for the preparation of the other compounds (**2**−**4**) is as follows. A stoichiometric mixture of the *n*-BuSn(O)(OH), H_3PO_3, and substituted phenols in toluene (60 mL) was heated under reflux for 6 h. The water formed in the reaction was removed by using a Dean−Stark apparatus. The reaction mixture was filtered and reduced to one-tenth of its initial volume in vacuo and kept for crystallization at room temperature. After 3−4 weeks, colorless block-like crystals were formed, which were separated by filtration. The crystals were further purified by quickly washing with CH_2Cl_2 (3 mL). The crystals were crushed and dried in vacuo for further analysis. The stoichiometric ratios of the reactants, the yields of the products **2**−**4**, and the characterization data for these are given below.

2: *n*-BuSn(O)(OH) (1.69 g, 8.09 mmol), HO−C_6H_4-4-Cl (1.04 g, 8.09 mmol), and H_3PO_3 (0.45 g, 5.39 mmol). Yield: 0.40 g (13%).[17] Mp: 305 °C (dec). Anal. Calcd (%) for $C_{60}H_{82}O_{20}Cl_6P_4Sn_6$: C 33.17, H 3.80. Found: C 33.10, H 3.65. ^{1}H NMR (400 MHz, ppm): 0.50−0.78 (m, 18H, CH_3 of *n*-Bu), 0.80−1.50 (m, 36H, CH_2 of *n*-Bu), 6.65−7.30 (m, 24H, phenyl), 7.14 (d, 4H, ^1J(H−P) = 690 Hz). ^{31}P NMR (162 MHz, ppm): 0.58 (d, ^1J(P−H) = 688 Hz). ^{119}Sn NMR (150 MHz, ppm): −532.7 (m), −551.3 (m), −563.6 (m).

3: *n*-BuSn(O)(OH) (1.32 g, 6.32 mmol), HO-C_6H_4-4-Br (1.10 g, 6.32 mmol), and H_3PO_3 (0.34 g, 4.21 mmol). Yield: 0.32 g (13%).[17] Mp: 306 °C (dec). Anal. Calcd (%) for $C_{60}H_{82}O_{20}Br_6P_4Sn_6$: C 29.54, H 3.38. Found: C 29.45, H 3.20. ^{1}H NMR (400 MHz, ppm): 0.50−0.72 (m, 18H, CH_3 of *n*-Bu), 0.80−1.40 (m, 36H, CH_2 of *n*-Bu), 6.83−7.35 (m, 24H, phenyl), 7.13 (d, 4H, ^1J(H−P) = 690 Hz). ^{31}P NMR (162 MHz, ppm): 0.54 (d, ^1J(P−H) = 688 Hz). ^{119}Sn NMR (150 MHz, ppm): −532.7 (m), −551.3 (m), −563.6 (m).

4: *n*-BuSn(O)(OH) (1.32 g, 6.34 mmol), HO-C_6H_4-4-I (1.40 g, 6.34 mmol), and H_3PO_3 (0.35 g, 4.23 mmol). Yield: 0.80 g (30%).[17] Mp: 100 °C (slight change in morphology of the solid) and 308 °C (major dec). Anal. Calcd (%) for $C_{72}H_{92}O_{22}I_8P_4Sn_6$: C 26.52, H 2.78. Found: C 26.41, H 2.89. ^{1}H NMR (400 MHz, ppm): 0.50−0.73 (m, 18H, CH_3 of *n-Bu*), 0.80−1.46 (m, 36H, CH_2 of *n-Bu*), 6.76−7.51(m, 24H, phenyl), 6.56 (d, 2H, free iodo phenol), 7.43 (d, 2H, free iodo phenol), 7.13 (d, 4H, ^1J(H−P) = 690 Hz). ^{31}P NMR (162 MHz, ppm): 0.57 (d, ^1J(P−H) = 688 Hz). ^{119}Sn NMR (150 MHz, ppm): −532.7 (m), −551.3 (m), −563.6 (m).

X-ray Crystallography. Colorless block-like crystals suitable for single-crystal X-ray diffraction were loaded on a Bruker AXS Smart Apex CCD diffractometer. The details pertaining to the data collection and refinement are given in Table 2. The structures were solved by direct methods and refined by using full-matrix least-squares on F^2 (SHELX97).[18] The hydrogen on the phosphorus atom was located from the difference maps, and their positions were refined. All the other hydrogens were fixed at calculated positions. The compounds **2** and **3** crystallized with a molecule of toluene, and compound **4** crystallized with a molecule of CH_2Cl_2 (disordered) as solvent of crystallization. The CCDC numbers for the crystal structures **1**−**4** are 192010, 268235, 268236, and 268237, respectively. Figures and bonding parameters were obtained from the DIAMOND 3.0 software package.[19]

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Supporting Information Available: ORTEP diagrams, figures of supramolecular assemblies, and crystallographic information files (CIF) for compounds **2**−**4**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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[17] Yields are based on the crystals isolated from their reaction mixture.

[18] Sheldrick, G. M. *SHELX97, Programs for the Solution and Refinement of Crystal Structures*; Institut für Anorganische Chemie der Universität Göttingen: Göttingen, Germany, 1998.

[19] *DIAMOND* version 3.0; Crystal Impact GbR: Bonn, Germany, 2004.