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Facile Synthesis of Novel Two- And Three-Dimensional Coordination Polymers Containing Dialkyltin Phosphonate-Based Tri/Tetra-Nuclear Clusters with Appended Sulfonate Groups

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The coordination-driven self-assemblies of mixed-ligand dialkyltin derivatives, $[(Et_2Sn)_4\ (O_2P(OH)Me)_2(O_3PMe)_2(OSO_2Et)_2 \cdot 2H_2O]_n$ **1**, $[(Et_2Sn)_3(O_3PMe)_2(OSO_2Me)_2 \cdot CHCl_3]_n$ **2**, and $[(Me_2Sn)_3(O_3PBu^t)_2(OSO_2Me)_2 \cdot 2CHCl_3]_n$ **3** have been achieved by reacting the tin precursors, $[R_2Sn(OR^1)(OSO_2R^1)]_n$ (R = Et, R^1 = Et (**1a**), Me (**2a**); R = Me, R^1 = Me (**3a**)) with an equimolar amount of methylphosphonic/*t*-butylphosphonic acid under mild conditions (rt, 8 h, CH_2Cl_2). These have been characterized by IR and multinuclear (^1H, ^{13}C, ^{31}P, and ^{119}Sn) NMR spectroscopy as well as single crystal X-ray diffraction. The asymmetric unit of **1** is composed of a tetranuclear, $Sn_4(\mu_2\text{-}PO_2)_2(\mu_3\text{-}PO_3)_2$ core bearing an appended ethanesulfonate group on each terminal tin (Sn2) atom and two $P(OH)\cdots O$ hydrogen bonded water molecules. The ladder-like structural motif thus formed is extended into one-dimensional polymeric chains by virtue of bridging bidentate mode of the sulfonate groups. These chains are linked by $O-H\cdots O(S)$ hydrogen bonds involving H_2O molecules and oxygen atoms of the sulfonate groups. The asymmetric units of **2** and **3** are composed of trinuclear tin clusters with a $Sn_3(\mu_3\text{-}PO_3)_2$ core and two dangling methanesulfonate groups which are covalently bonded to the tin centers. The construction of three-dimensional self-assemblies is effected by variable bonding modes (μ_2, μ_3 in **2**; μ_2 in **3**) of the methanesulfonate groups. Both the structural motifs possess five- and six-coordinated tin atoms and form rectangular channels which are occupied by $CHCl_3$ molecules.

Introduction

The chemistry of metal-organic frameworks (MOFs) involving transition-metal ions is an area of active research interest in recent years owing to their potential applications in catalysis, gas storage, ion exchange, intercalation, and material chemistry.[1−4] In this context, phosphonate ligands, both in monoanionic ($RHPO_3^-$) and dianionic (RPO_3^{2-}) forms, in conjunction with a wide variety of organic ligands are being extensively used to synthesize metal-organic frameworks of varying dimensionalities, such as cages, clusters, and porous three-dimensional (3D) networks.[5] In the domain of main group chemistry,[6] much of the current efforts have been devoted to the development of synthetic methods for group 13 (B, Al, Ga, In) based metal phospho-

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nates and their structural elucidation by X-ray crystallography. A number of such metal phosphonates representing clusters of varying nuclearity are now known. A perusal of literature, however, reveals that there are only a few structurally known examples of organotin phosphonates.[7] These include homoleptic $[n\text{-}Bu_2Sn(OP(O)(OH)Me)_2]_2$[8a] (dimer), $[Me_3Sn(OP(O)(OH)Ph)]_n$[8b] (helical polymer), $[(n\text{-}BuSn)_2O(OP(O)(OH)\text{-}t\text{-}Bu)_4]_2$[8c] (cluster), and $[Na_6(CH_3OH)_2(H_2O)][\{(BzSn)_3(PhPO_3)_5(\mu_3\text{-}O)(CH_3O)\}_2Bz_2Sn]CH_3OH$[8d] (oligomer).

To our knowledge, the construction of higher dimensionality diorganotin phosphonate-based MOFs has not been realized until our recent reports on the self-assembled coordination polymers, involving mixed-ligand diorganotin derivatives, $[n\text{-}Bu_2Sn(OP(O)(OH)R)(OSO_2R^1)]_n$ (R = Me, Ph; R^1 = Me, Et, *n*-Pr),[9] bearing hydrogenphosphonate and alkanesulfonate groups on the same tin center. The synthetic method relies on the selective reactivity of the -OR group in the tin precursors, $[n\text{-}Bu_2Sn(OR^1)(OSO_2R^1)]_n$ (R^1 = Me, Et, *n*-Pr), toward phosphonic acids under mild conditions (rt, CH_2Cl_2). The ability of these tetrahedral ligands to act as multidentate donors to the Lewis acidic tin centers has given rise to extended one-dimensional (1D) (linear), two-dimensional (2D) (layered), and 3D structural motifs. In particular, the flexibility of the alkanesulfonate group to function as μ_1, μ_2, and μ_3-coordinating ligand, in conjunction with bridging bidentate hydrogenphosphonate groups, is the key feature of these well-defined diorganotin-based assemblies. The contribution arising from O−H···O hydrogen-bonding interactions has also been observed in all these compounds studied so far.

On the basis of this "sulfonate-phosphonate" ligand strategy, we report herein the synthesis and structural characterization of new dialkyltin-based 2D and 3D coordination polymeric assemblies, $[(Et_2Sn)_4(O_2P(OH)Me)_2(O_3PMe)_2(OSO_2Et)_2\cdot 2H_2O]_n$ **1**, $[(Et_2Sn)_3(O_3PMe)_2(OSO_2Me)_2\cdot CHCl_3]_n$ **2**, and $[(Me_2Sn)_3(O_3PBu^t)_2(OSO_2Me)_2\cdot 2CHCl_3]_n$ **3**. Interestingly, the secondary building units for these self-assemblies are composed of novel tetra-nuclear (for **1**) and trinuclear (for **2**, **3**) tin phosphonate clusters which incorporate two alkanesulfonate groups on the tin centers as the side arm functionalities. The striking difference in the structural features of the coordination-driven self-assemblies, **1**−**3**, derived from these clusters in comparison to those reported earlier[9] is illustrative of the potential of this simple methodology for the construction of porous diorganotin-based MOFs, involving phosphonate and sulfonate ligands.

Results and Discussion

Synthesis of 1−3. Following the synthetic method reported earlier,[9] the precursor tin complexes, $[R_2Sn(OR^{\mathbf{1}})(OSO_2R^{\mathbf{1}})]_n$ (R = Et, R^1 = Et (**1a**), Me (**2a**); R = R^1 = Me (**3a**)) have been synthesized from a direct reaction between dialkyltin oxide, R_2SnO (R = Et, Me) and excess diethyl/dimethyl sulfite in the presence of ethyl iodide/methyl iodide, respectively. The relevant spectroscopic data of these new compounds are summarized in the Experimental Section. Although the ^1H NMR data are in accord with the composition of each compound, the resonances due to ^{13}C and ^{119}Sn nuclei reveal a complex behavior. These results suggest the presence of a number of oligomeric species with 5- and/or 6-coordinated tin atoms which remain in equilibrium in solution state.[10] The precursor tin complexes, **1a**−**3a** react readily with an equimolar quantity of methylphosphonic or *t*-butylphosphonic acid in dichloromethane and result in the precipitation of a white solid in each case. Recrystallization of these products from a $CHCl_3/CH_3OH$ mixture affords **1**−**3**, respectively in analytically pure form, as shown in eqs 1 and 2. The entry of solvated water molecules in **1** is believed to arise from the traces of moisture in the solvent while inclusion of chloroform in **2** and **3** appears from the solvent of crystallization.

$$4nEt_2Sn(OEt)(OSO_2Et) + 4nMeP(O)(OH)_2 \xrightarrow[\text{rt, 8h}]{CH_2CL_2} [(Et_2Sn)_4(OP(O)(OH)Me)_2(O_3PMe)_2(OSO_2Et)_2\cdot 2H_2O]_n + 4nEtOH + 2nEtSO_3H \quad (1)$$

$$3nR_2Sn(OMe)(OSO_2Me) + 2nR^2P(O)(OH)_2 \xrightarrow[\text{rt, 8h}]{CH_2CI_2} [(R_2Sn)_3(O_3PR^2)_2(OSO_2Me)_2\cdot xCHCI_3]_n + 3nMeOH + nMeSO_3H \quad (2)$$

where R = Et, R^2 = Me, *x* = 1 (**2**) and R = Me, R^2 = Bu^t, *x* = 2 (**3**).

X-ray Crystal Structures. Single crystals of **1**−**3** suitable for X-ray structure analysis were grown by slow diffusion of diethyl ether into a solution of each compound in a $CHCl_3/CH_3OH$ solvent mixture. The crystal data of **1**−**3** are summarized in Table 1, while selected bond lengths and angles are given in Tables 2, 3, and 4, respectively.

The asymmetric unit of **1** reveals the presence of a centrosymmetric, tetranuclear tin assembly with a $Sn_4P_4O_{10}$ core, involving two μ_3-methylphosphonate (P1) and two μ_2-hydrogenmethylphosphonate (P2) groups (Figure 1a). The structure resembles a ladder-like motif by virtue of edge-sharing of the dianionic methylphosphonate groups, while each terminal Sn2 atom is linked to a covalently bonded ethanesulfonate group. The cluster also contains two solvated

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Table 1. Summary of Crystallographic Data for **1**−**3**

	1	**2**	**3**
empirical formula	$C_{24}H_{68}O_{20}P_4S_2Sn_4$	$C_{17}H_{43}Cl_3O_{12}P_2S_2Sn_3$	$C_{18}H_{44}Cl_6O_{12}P_2S_2Sn_3$
formula weight	1339.54	1027.99	1147.36
crystal system	triclinic	monoclinic	tetragonal
space group	$P\bar{1}$	$P12_1/c1$	$P4_12_12$
a (Å)	8.3684(3)	15.35460(10)	13.6286(1)
b (Å)	9.8461(4)	15.9150(2)	13.6286(1)
c (Å)	14.8985(6)	15.5604(2)	24.8038(3)
α (deg)	77.665(2)	90	90
β (deg)	87.625(2)	111.0400(10)	90
γ (deg)	87.683(2)	90	90
V (Å^3)	1197.58(8)	3548.96(7)	4607.03(7)
Z	1	4	4
ρ_{calcd} (Mg m^{-3})	1.857	1.924	1.654
μ (mm^{-1})	2.347	2.577	2.162
F (000)	664	2016	2248
crystal size (mm)	0.22 × 0.15 × 0.10	0.23 × 0.20 × 0.15	0.20 × 0.10 × 0.08
reflection collected/unique	17888/5499	84820/10359	92181/6715
R (int)	0.0509	0.0501	0.0667
data/restraints/parameters	5499/0/263	10359/0/384	6715/9/229
final R, wR2 indices [$I > 2\sigma(I)$]	0.0318, 0.0754	0.0289, 0.0611	0.0331, 0.0759
final R, wR2 indices (all data)	0.0383, 0.0795	0.0418, 0.0657	0.0430, 0.0801

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Sn1−C1	2.118(3)	Sn1−C3	2.124(3)
Sn1−O1	2.044(2)	Sn1−O3^a	2.158(2)
Sn1−O4	2.212(2)	Sn2−C5	2.114(3)
Sn2−C7	2.114(3)	Sn2−O2	2.061(2)
Sn2−O5	2.101(2)	Sn2−O7	2.389(2)
Sn2−O8^b	2.693(3)		
O1−Sn1−C1	101.76(11)	O1−Sn1−C3	112.22(11)
C1−Sn1−C3	146.03(13)	O3^a−Sn1−O4	172.77(9)
O1−Sn1−O3^a	88.02(9)	O1−Sn1−O4	84.75(9)
O2−Sn2−O5	91.17(9)	O2−Sn2−O7	84.10(9)
O7−Sn2−O8^b	105.16(8)	O5−Sn2−O8^b	79.52(8)
C5−Sn2−C7	151.23(14)		

[a] Symmetry transformations used to generate equivalent atoms: −x + 1, −y, −z + 2. [b] Symmetry transformations used to generate equivalent atoms: −x + 1, −y, −z + 3.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

Sn1−C1	2.120(2)	Sn1−C3	2.127(3)
Sn1−O1	2.0950(17)	Sn1−O4	2.0879(16)
Sn1−O8^a	2.4533(19)	Sn1−O7	2.5285(19)
Sn2−O3	2.1052(17)	Sn2−O6	2.0351(17)
Sn2−O10	2.3891(17)	Sn2−C7	2.121(3)
Sn2−C5	2.122(3)	Sn3−O2	2.0593(17)
Sn3−O5	2.0906(17)	Sn3−O11^b	2.5450(18)
Sn3−O12^c	2.593(2)	Sn3−C9	2.120(2)
Sn3−C11	2.121(2)		
O4−Sn1−O1	88.15(7)	O8^a−Sn1-O7	109.97(7)
O4−Sn1−O7	78.48(6)	O1−Sn1−O8^a	83.40(7)
C1−Sn1−C3	152.94(10)	O6−Sn2−C7	102.84(9)
O6−Sn2−C5	113.63(10)	C7−Sn2−C5	142.05(12)
O3−Sn2−O10	172.05(6)	O6−Sn2−O3	92.16(7)
O2−Sn3−O11^b	77.84(6)	O11^b−Sn3-O12^c	108.39(6)
O12^c−Sn3-O5	83.04(7)	O2−Sn3−O5	90.67(7)
C9−Sn3−C11	150.80(10)		

[a] Symmetry transformations used to generate equivalent atoms: −x, −y, −z. [b] Symmetry transformations used to generate equivalent atoms: x, −y + 1/2, z + 1/2. [c] Symmetry transformations used to generate equivalent atoms: 1 − x, y − 1/2, −z + 1/2.

Table 4. Selected Bond lengths (Å) and Bond angles (deg) for **3**

Sn1−O1^a	2.093(2)	Sn1−O1	2.093(2)
Sn(1)−C(1)	2.103(4)	Sn(1)−C(1)^a	2.103(4)
Sn(1)−O(5)^b	2.485(3)	Sn(1)−O(5)^c	2.485(3)
Sn(2)−O(2)^a	2.009(2)	Sn(2)−C(2)	2.084(4)
Sn(2)−C(3)	2.095(4)	Sn(2)−O(3)	2.128(2)
Sn(2)−O(4)	2.299(3)		
C1−Sn1−C1^a	158.1(2)	O1^a−Sn1−O1	90.93(14)
O1−Sn1−O5^b	81.56(10)	O1^a−Sn1−O5^c	81.56(10)
O5^b−Sn1−O5^c	106.02(13)	O2^a−Sn2−C2	106.31(15)
O2^a−Sn2−C3	113.63(15)	C2−Sn2−C3	138.84(17)
O3−Sn2−O4	168.72(10)	O2^a−Sn2−O3	92.16(10)

[a] Symmetry transformations used to generate equivalent atoms: x, y, −z. [b] Symmetry transformations used to generate equivalent atoms: x + 1/2, −y + 1/2, z + 1/4. [c] Symmetry transformations used to generate equivalent atoms: x + 1/2, −y + 1/2, −z − 1/4.

water molecules which are not bonded to the tin atoms but exhibit strong (P)O−H···O hydrogen bonding interactions [O6−H6 = 0.75(6), H6···O10 = 1.79(6), O6···O10 = 2.553(4) Å, O6−H6···O10 = 176(6)°]. The genesis of the ladder structural motif can be achieved by condensation of two μ_2-hydrogenmethylphosphonate bridged dimeric structural units, $[Et_2Sn(OP(O)(OH)Me)(OSO_2Et)]_2$ via the elimination of ethanesulfonic acid (Chart 1). The identity of such dimeric structures as the molecular building block for the construction of 1D and 2D coordination polymers has been reported recently.[9] In spite of large pK2 value (8.4) of the dibasic alkylphosphonic acids,[11] the generation of $MePO_3^{2-}$ dianion from the dimeric structure under mild conditions is facilitated by the ability of ethanesulfonate ligand to act as a leaving group.

The ethanesulfonate group on each Sn2 atom in the ladder functions in a μ_2-mode and coordinates with a symmetry-related tin atom of an adjacent unit to form 1D polymeric chains which run along the c-axis. The coordination polymer thus obtained consists of a series of eight membered $-(Sn-O-P-O-)_2$ and $-(Sn-O-S-O-)_2$ rings (Figure 1b). The geometry around each Sn1 atom is best described as distorted trigonal bipyramidal with SnC_2O equatorial plane (360 ± 0.01°) and trans disposition of O3, O4 atoms [O3^a−Sn1−O4 = 172.77(9)°]. On the other hand, the Sn2 atoms adopt a distorted octahedral geometry with a SnO_4 core as the basal plane (360 ± 0.05°) and trans-ethyl groups [C5−Sn2−C7 = 151.23(14)°]. The Sn−O(S) bond lengths [Sn2−O7 = 2.389(2), Sn2−O8^b = 2.693(3) Å] are found to be significantly larger than those observed for Sn−O(P)

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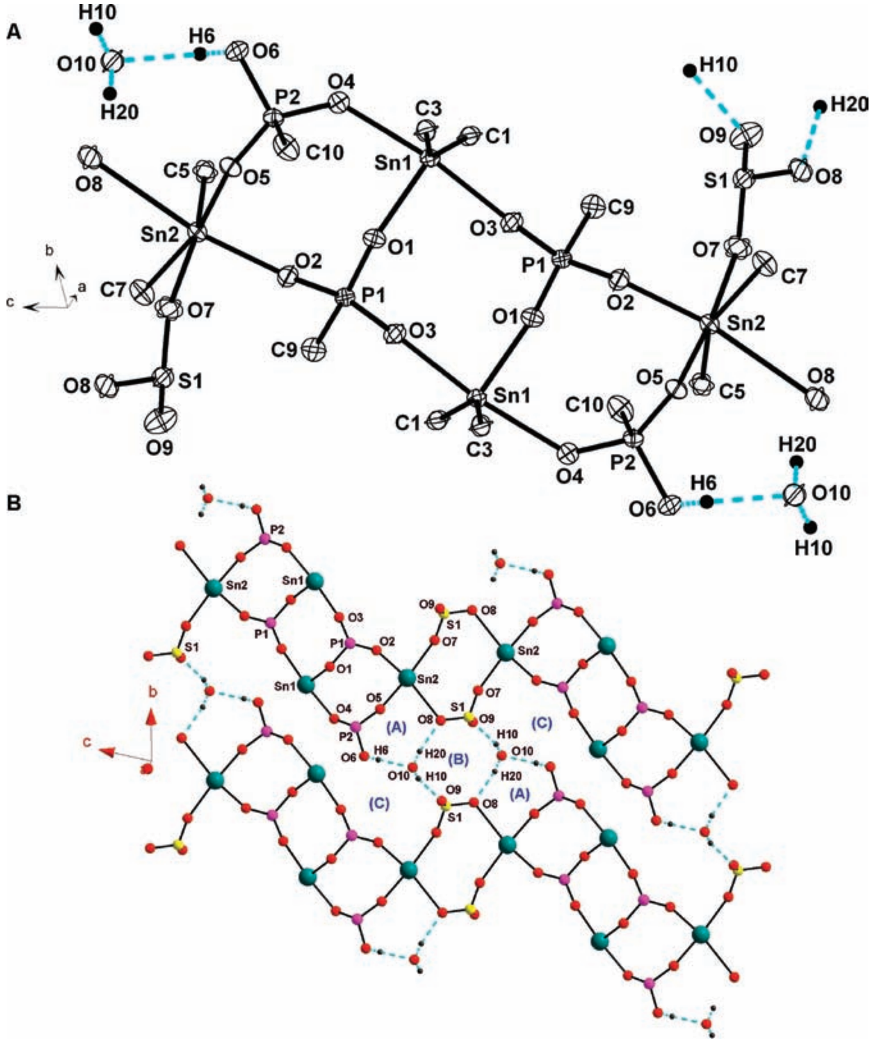
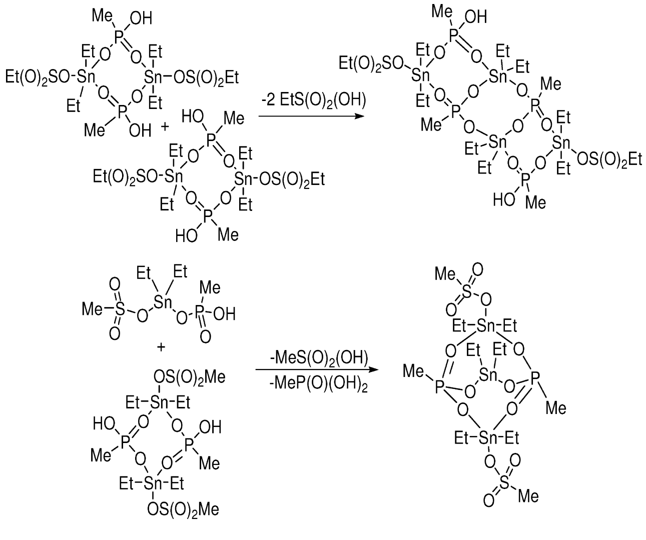


Figure 1. (a) ORTEP view of the asymmetric unit of **1**. The thermal ellipsoids are set at 50% probability. All the hydrogen (except H6, H10, and H20) and carbon (except Sn−C and P−C) atoms are omitted for clarity. (b) 2D structure of **1** in the *bc*-plane. All the hydrocarbon groups are omitted for clarity.

Chart 1. Proposed Mechanisms for the Generation of Asymmetric Units **1** and **2**



bonds [2.044(2)−2.212(2) Å]. These 1D chains are associated with one another by strong O−H···O hydrogen bonds involving water molecules and the sulfonate groups. Each water molecule acts as a hydrogen donor to the oxygen atoms (O8 and O9) of the sulfonate groups which are associated with adjacent 1D chains [O10−H10 = 0.78(7), H10···O9^c = 1.98(7), O10···O9^c = 2.735(5) Å, O10−H10···O9^c = 164(7)°; O10−H20 = 0.88(8), H20···O8^b = 1.91(8), O10···O8^b = 2.775(5) Å, O10−H20···O8^b = 169(8)°]. These interactions give rise to 8-membered $SnPO_4H_2$ (A) and 12-membered $S_2O_6H_4$ (B) rings, as well as 28-membered tetranuclear tin-containing macrocycles (C) and extend the assembly into a 2D motif in the *bc*-plane. The metrical parameters associated with the hydrogen bonds are consistent with those reported in literature.[12]

A notable feature of the crystal structure of **2** is the formation of an asymmetric unit composed of a trinuclear tin cluster of $Sn_3P_2O_6$ core with an additional methanesulfonate group (S1 and S2) on Sn1 and Sn2 atoms and a disordered $CHCl_3$ molecule (Figure 2a). The cluster represents two fused eight-membered −(Sn−O−P−O−)$_2$ rings which are constructed from μ_3-bonding of two methylphosphonate dianions, $MePO_3^{2-}$, to the tin centers. Putatively, the formation of this assembly may arise via a condensation

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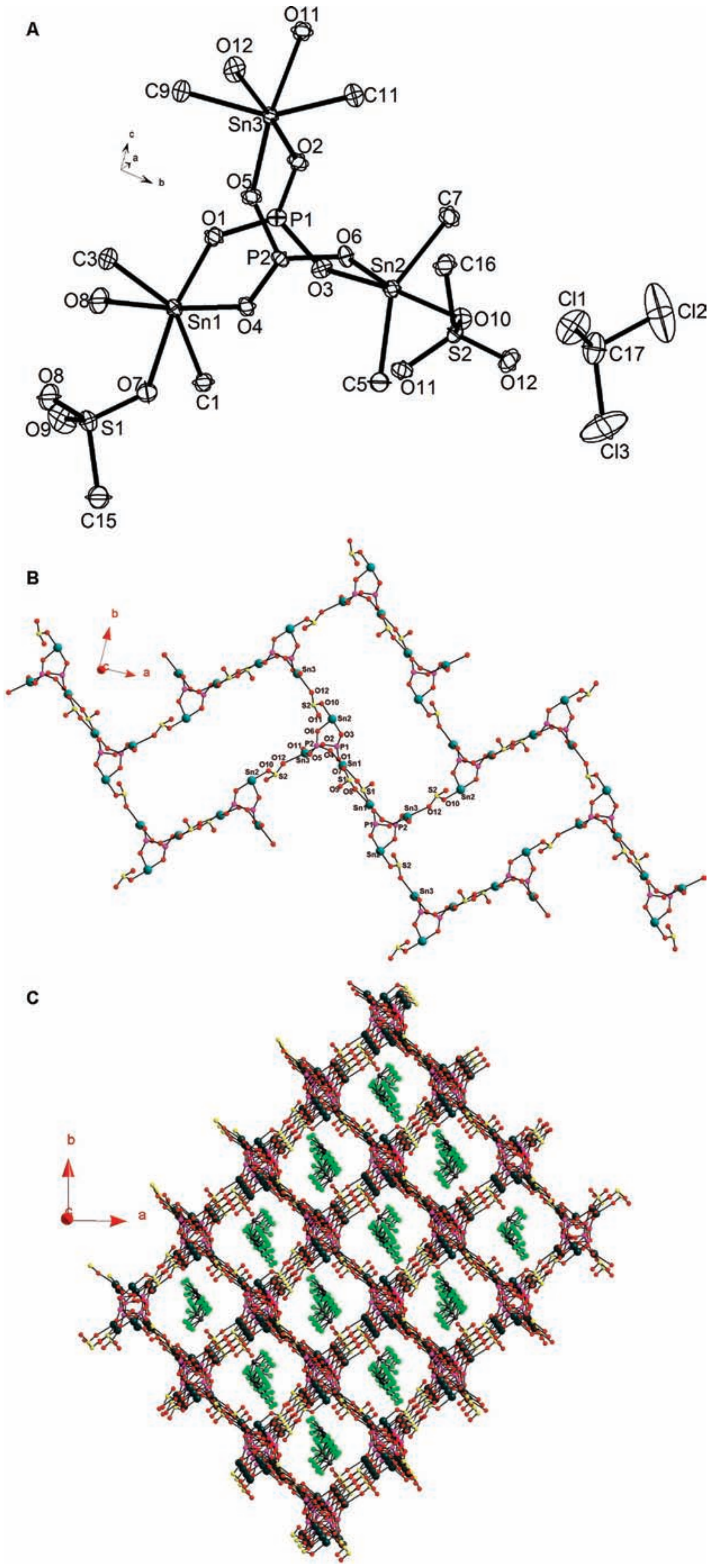

Figure 2. (a) ORTEP view of the asymmetric unit of **2**. The thermal ellipsoids are set at 50% probability. All the hydrocarbon groups (except Sn−C) are omitted for clarity. (b) 2D structure of **2** in the *ab*-plane. All the hydrocarbon groups are omitted for clarity. (c) 3D structure of **2**. All the hydrocarbon groups are omitted for clarity. The disordered chloroform molecules occupy the channels.

reaction between the dimer, $[Et_2Sn(OP(O)(OH)Me)(OSO_2Me)]_2$, and its monomeric analogue (Chart 1). The tin atom of the monomer undergoes a concerted attack of the uncoordinated oxygen atoms of two hydrogenmethylphosphonate groups associated with the dimer. This results in the deprotonation of the P(OH) moieties and formation of Sn−O covalent bonds via elimination of methanesulfonic acid and methylphosphonic acid from the monomer.

The asymmetric unit thus formed acts as a "secondary building unit" and utilizes varying coordination modes of the methanesulfonate groups to generate a self-assembled, 3D structural motif. The methanesulfonate group (S1) completes its role in the structural organization by μ_2-coordination via the O8 atom and formation of centrosymmetric dimeric entities. On the other hand, the methanesulfonate groups (S2) contribute in a μ_3-fashion and involve the O11 and O12 donor atoms to provide further connectivity to these dimers. The coordinative association of the O12 atoms to Sn3 atoms of the adjacent dimers results in the formation of a 2D layered assembly, composed of a network structure of rectangular frameworks in the *ab*-plane (Figure 2b), whereas the O11 atoms act as a bridge between the Sn3 atoms of the adjacent layers by forming eight-membered $-(Sn-O-S-O-)_2$ puckered rings and allow the assembly to extend in a 3D motif (Figure 2c). The offset arrangement of the adjacent layers leads to the formation of continuous channels of voids (10.75 × 11.77 Å) along the *c*-axis which are occupied by disordered $CHCl_3$ molecules. The 3D assembly exhibits two discrete geometries around the tin centers. The Sn1 and Sn3 atoms attain a distorted octahedral geometry with the SnO_4 core occupying the basal plane [360° (Sn1), 360 ± 0.06° (Sn3)] and trans disposition of ethyl groups [C1−Sn1−C3 = 152.94(10)°, C9−Sn3−C11 = 150.80(10)°]. On the contrary, each Sn2 atom adopts a distorted trigonal bipyramidal geometry with an SnC_2O equatorial atom set (360 ± 1.48°), and the axial positions are occupied by the O3 and O10 atoms which have their origin from phosphonate and sulfonate ligands respectively [O3−Sn2−O10 = 172.05(6)°]. The Sn−O(P) bond lengths [Sn1−O1 = 2.0950(17), Sn1−O4 = 2.0879(16), Sn2−O3 = 2.1052(17), Sn2−O6 = 2.0351(17), Sn3−O2 = 2.0593(17), Sn3−O5 = 2.0906(17) Å] lie in the range of Sn−O covalent bonds (2.0−2.1 Å).[13] The Sn−O(S) bond lengths [Sn1−O7 = 2.5285(19), Sn1−$O8^a$ = 2.4533(19), Sn2−O10 = 2.3891(17), Sn3−$O11^b$ = 2.5450(18), Sn3−$O12^d$ = 2.5930(2) Å] are comparatively large, suggesting appreciable ionic character.

The asymmetric unit of **3** resembles closely that observed for **2** in respect of the $Sn_3P_2O_6$ core structure which results from μ_3-bonding mode of two dianionic *t*-butylphosphonate groups (Figure 3a). The trinuclear tin cluster reveals two crystallographically unique tin atoms (Sn1 and Sn2), the latter being associated with covalently bonded methanesulfonate groups. The asymmetric unit also accommodates two disordered $CHCl_3$ molecules. Despite the structural similarity in the core atom arrangement, the preferred bonding of the sulfonate ligands in **3** is bridging bidentate (μ_2) in character involving O5 and Sn1 atoms exclusively, in contrast to μ_2- and μ_3-coordination of the ligand in **2** (vide supra). The bonding pattern which leads to the construction of a 3D assembly can be viewed as follows. One of the methanesulfonate groups of each cluster forms a μ_2-bridge with the Sn1 atom of the adjacent unit to afford zigzag polymeric chains. The interchain connectivity is accomplished by the uncoordinated sulfonate groups associated with alternate cluster units in the chains which results in the formation of a 2D layered structure (Figure 3b). The residual methanesulfonate groups are involved in forming bridges between the adjacent layers by associating with the Sn1 atoms and thus extend the assembly to a 3D motif. A top down view of **3** along the *a*- and *b*- axis (Figure 3c) reveals the formation of continuous channels of dimensions 15.70 × 9.22 Å, if one considers the centers of triangular tin-clusters as the vertices. These voids are occupied by disordered $CHCl_3$ molecules. The geometry around the Sn1 atoms is distorted octahedral with SnO_4 core as the basal plane (360 ± 0.07°) and trans-methyl groups [C1−Sn2−$C1^a$ = 158.1(2)°]. On the other hand, each Sn2 atom adopts a distorted trigonal bipyramidal geometry with SnC_2O equatorial plane (360 ± 1.22°) and trans disposition of O3, O4 atoms [O3−Sn2−O4 = 168.72(10)°]. The Sn−O(S) bond lengths [Sn1−O5 = 2.485(3), Sn2−O4 = 2.299(3) Å] are found to be significantly larger than those observed for Sn−O(P) bonds [2.009(2)−2.128(2) Å]. Other metrical parameters are comparable with those observed for **2**.

Spectroscopic Studies. The compounds **1**−**3** are readily soluble in coordinating solvents such as CH_3CN, CH_3OH, DMSO, and so forth. As a result, the NMR spectra have been studied in a mixture of $CDCl_3$ and DMSO-d_6, (unless otherwise stated) to understand the behavior of these assemblies in solution. ^1H and ^{13}C NMR spectra of **1**−**3** display characteristic signals due to the alkyl substituents associated with tin, as well as phosphonate and sulfonate groups (Experimental Section), and are in accord with the structural composition of each compound. As expected, the ^{31}P NMR spectra of **2** and **3** exhibit a single resonance at δ 21.1 and 26.3 respectively, with $^2J_{Sn-O-P}$ coupling constant of 121−126 Hz. For **1**, the ^{31}P NMR spectrum reveals only one resonance at δ 21.7, despite two non-equivalent (μ_2-, μ_3-) phosphonate groups in the solid state structure (vide supra). In addition, the spectrum is devoid of the Sn−O−P coupling, thereby suggesting structural changes in solution. The ^{119}Sn NMR spectra of **1**−**3** display a broad resonance in each case at δ −314, −285, and −278 whose peak widths at half-height ($W_{1/2}$) correspond to 1396, 372, and 248 Hz, respectively. The observed ^{119}Sn chemical shift values are suggestive of a hexa-coordinated environment around each tin center and is further supported by the $^1J(^{13}C-^{119}Sn)$ coupling constants [781 (for **1**), 920 (for **2**), and 980 (for **3**) Hz] obtained from the ^{13}C NMR spectra. It is, however, imperative to mention that the absence of ^{119}Sn resonance in the chemical shift

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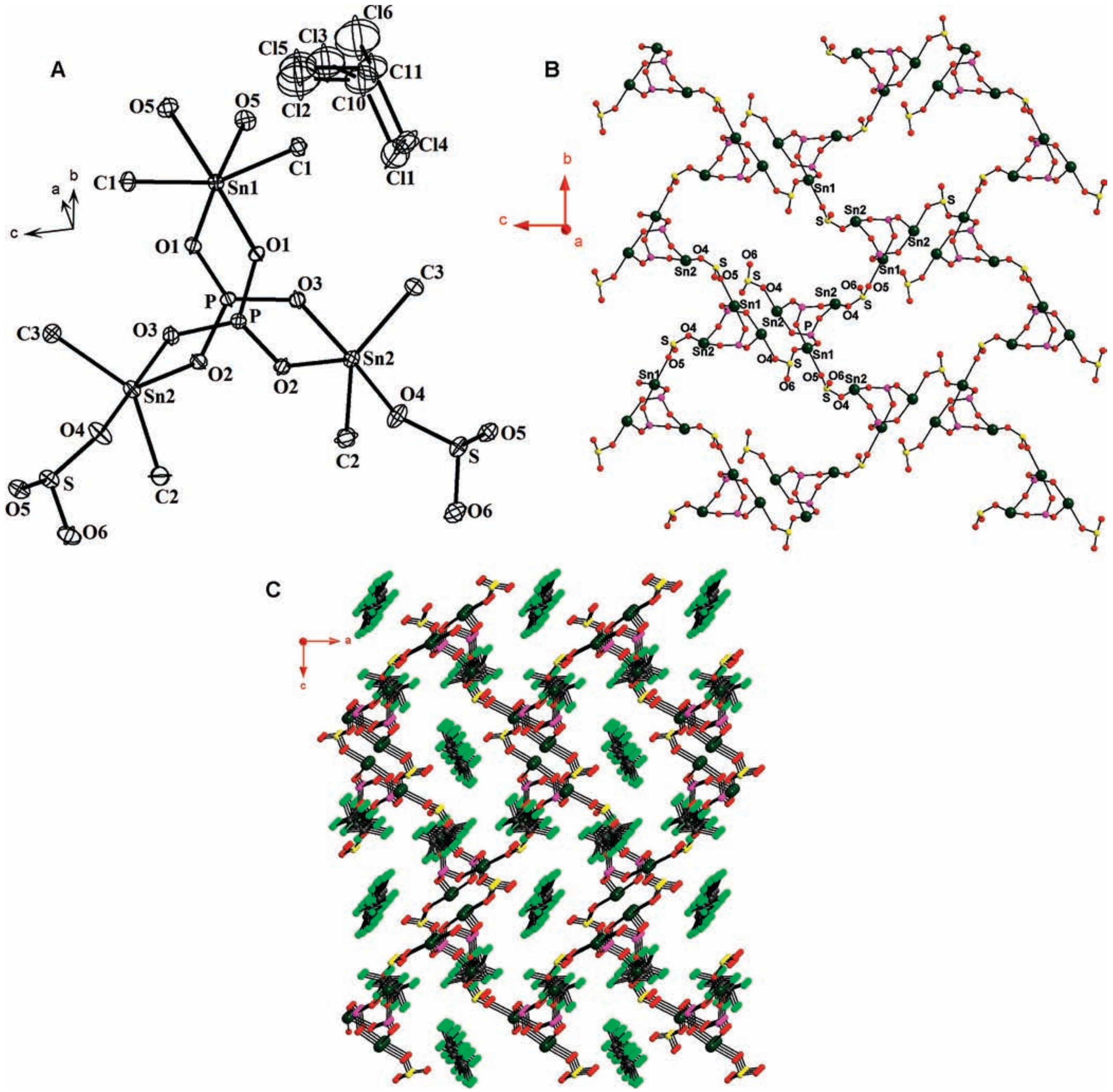

Figure 3. (a) ORTEP view of the asymmetric unit of **3**. The thermal ellipsoids are set at 30% probability. All the hydrocarbon groups (except Sn−C) are omitted for clarity. (b) 2D structure of **3** in the *bc*-plane. All the hydrocarbon groups are omitted for clarity. (c) 3D structure of **3** viewed along the *b*-axis. All the hydrocarbon groups are omitted for clarity. The disordered chloroform molecules occupy the channels.

domain of five-coordinate tin atoms,[14] as expected from the solid state structures of **1**−**3**, may point toward possible coordination of DMSO-d_6 with coordinatively unsaturated tin centers. For **1**, medium intensity IR absorptions at 3450 and 2360 cm^{-1} are suggestive of hydrogen bonded water and the P-(OH) group, respectively.[8a,9b] However, the observed IR absorptions in the region 940−1200 cm^{-1} are overlapping νSO_3 and νPO_3 stretching modes and are thus are not informative in evaluating the coordination modes of these ligands.

In summary, we have demonstrated that the coordination-driven 2D and 3D self-assemblies, **1**−**3** featuring sulfonate-functionalized tri/tetra-nuclear tin-phosphonate clusters, are accessible by following a simple synthetic protocol which involves the reaction of the tin precursors, $[R_2Sn(OR^1)(OSO_2R^1)]_n$ (R = Et, R^1 = Et (**1a**), Me (**2a**); R = R^1 = Me (**3a**)) with methylphosphonic/*t*-butylphosphonic acid under mild conditions. It is important to mention that the formation of **2** and **3** provides the first snapshot of 3D MOFs incorporating trinuclear tin-phosphonate clusters as integral part of the extended assemblies, although a few examples of discrete trinuclear tin clusters derived from carboxylate ligands have been reported recently.[15] In addition, the

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presence of coordinatively unsaturated, five coordinated tin centers in these MOFs are particularly attractive for the selective binding of appropriate guest molecules. Illustration of this concept has been reported earlier[16] by Yagi et al. in the extended porous framework of $Zn_3(BDC)_3\cdot 6CH_3OH$ (BDC = 1,4-benzendicarboxylate).

Experimental Section

All operations were carried out using standard Schlenk line techniques under dry nitrogen atmosphere. Solvents were freshly distilled over phosphorus pentoxide (dichloromethane, chloroform, and *n*-hexane), magnesium cake (methanol), and sodium wire (diethyl ether). Glasswares were dried in an oven at 110−120 °C and further flame dried under vacuum prior to use. Methylphosphonic acid, *t*-butylphosphonic acid, methyl iodide, and ethyl iodide (Aldrich) were used as supplied. Literature methods were used to prepare dimethyl/diethyltin oxide[17] and dimethyl/diethyl sulfite.[18]

^{1}H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectra were recorded on a BRUKER DPX-300 spectrometer at 300, 75.46, 121.50, and 111.88 MHz, respectively. ^{1}H and ^{13}C NMR chemical shifts are quoted with respect to the residual protons of the solvent while ^{119}Sn and ^{31}P NMR data are given using tetramethyltin and 85% H_3PO_4 as external standard, respectively. IR spectra were recorded on Nicolet protege 460 ESP spectrophotometer using KBr optics. Elemental analysis (C, H) was performed on a Perkin-Elmer model 2400 CHN elemental analyzer.

Synthesis of [$R_2Sn(OR^1)(OSO_2R^1)$]$_n$ R = Et, R^1 = Et (1a), Me (2a); R = Me, R^1 = Me (3a). Following the procedure reported earlier,[9] the reaction between diethyltin oxide (0.43 g, 2.20 mmol) and excess of diethyl sulfite (3.04 g, 22.0 mmol) was performed under refluxed conditions (100−110 °C, 40−45 h) in the presence of ethyl iodide (0.34 g, 2.20 mmol). The clear solution thus obtained was cooled, and *n*-hexane was added to precipitate a white solid which was filtered and dried under vacuum. The compound was identified as **1a**. The compounds **2a** and **3a** are obtained similarly by reacting diethyltin oxide/ dimethyltin oxide (0.64/0.55 g, 3.33 mmol) with excess of dimethyl sulfite (3.67 g, 33.3 mmol) in the presence of methyl iodide (0.47 g, 3.33 mmol).

1a. [$Et_2Sn(OEt)(OSO_2Et)$]$_n$. Yield: 61%. ^{1}H NMR ($CDCl_3$): δ 3.66 (q, $^{3}J_{H-H} = 6.9$ Hz, 2H, $OC\mathit{H}_2CH_3$), 2.84 (q, $^{3}J_{H-H} = 7.5$ Hz, 2H, $SC\mathit{H}_2CH_3$), 1.77−1.28 (m, 16H, $SnC\mathit{H}_2C\mathit{H}_3/SCH_2C\mathit{H}_3/OCH_2C\mathit{H}_3$). $^{13}C\{^{1}H\}$ NMR: δ 60.26, 58.16 ($O\mathit{C}H_2CH_3$), 45.93 ($S\mathit{C}H_2CH_3$), 21.06, 19.27 ($Sn\mathit{C}H_2CH_3$), 15.13, 14.80 ($OCH_2\mathit{C}H_3$), 10.02, 9.31 ($SnCH_2\mathit{C}H_3$), 9.03 ($SCH_2\mathit{C}H_3$). ^{119}Sn NMR: δ −139, −167, −176, −191, −210. IR (KBr, cm^{-1}): 1257, 1185, 1142, 1047 (νSO_3), 745 (νSCH_2CH_3). Anal. Calcd for $C_8H_{20}O_4SSn$: C, 29.03; H, 6.09. Found: C, 29.01; H, 6.17.

2a. [$Et_2Sn(OMe)(OSO_2Me)$]$_n$. Yield: 72%. ^{1}H NMR ($CDCl_3$): δ 3.49 (s, 3H, $OC\mathit{H}_3$), 2.84 (s, 3H, $SC\mathit{H}_3$), 1.86−1.36 (m, 10H, $SnC\mathit{H}_2C\mathit{H}_3$). $^{13}C\{^{1}H\}$ NMR: δ 52.86, 52.02 ($O\mathit{C}H_3$), 39.34 ($S\mathit{C}H_3$), 20.40, 18.55 ($Sn\mathit{C}H_2CH_3$), 12.66, 9.41 ($SnCH_2\mathit{C}H_3$). ^{119}Sn NMR: δ −142, −166, −170, −176, −186. IR (KBr, cm^{-1}): 1260, 1199, 1145, 1050 (νSO_3), 777 (νSCH_3). Anal. Calcd for $C_6H_{16}O_4SSn$: C, 23.79; H, 5.32. Found: C, 23.72; H, 5.41.

3a. [$Me_2Sn(OMe)(OSO_2Me)$]$_n$. Yield: 75%. ^{1}H NMR: δ 3.32 (s, 3H, OCH_3), 2.71 (s, 3H, SCH_3), 0.86 (br, 6H, $SnC\mathit{H}_3$). $^{13}C\{^{1}H\}$ NMR: δ 50.41 (OCH_3), 39.48 (SCH_3), 11.13 ($^{1}J_{Sn-C} = 974$, $SnCH_3$). ^{119}Sn NMR: δ −145, −150, −171, −190, −197, −249, −340. IR (KBr, cm^{-1}): 1262, 1199, 1130, 1036 (νSO_3), 780 (νSCH_3). Anal. Calcd for $C_4H_{12}O_4SSn$: C, 17.48; H, 4.40; Found: C, 17.45; H, 4.45.

Synthesis of 1−3. To a suspension of the tin precursor, **1a** (0.65 g, 1.96 mmol)/**2a** (0.59 g, 1.96 mmol) in dichloromethane (30 mL) was added methylphosphonic acid (0.19 g, 1.96 mmol) at room temperature with constant stirring. A clear solution was obtained instantly in each case which was followed by the precipitation of a white solid within 8−10 h. The solid thus obtained was filtered, dried under vacuum, and recrystallized from $CHCl_3/CH_3OH$ (3:1) solvent mixture to yield **1** and **2**, respectively, in analytically pure form. Following the similar procedure, the reaction of the tin precursor **3a** (0.63 g, 2.23 mmol) with *t*-butylphosphonic acid (0.32 g, 2.23 mmol) in dichloromethane solution affords the compound **3** as a white solid.

1. [$(Et_2Sn)_4(O_2P(OH)Me)_2(O_3PMe)_2(OSO_2Et)_2\cdot 2H_2O$]$_n$. Yield: 68%. ^{1}H NMR ($CDCl_3$): δ 2.93 (q, $^{3}J_{H-H} = 7.5$ Hz, 4H, $SC\mathit{H}_2CH_3$), 1.71 (q, $^{3}J_{H-H} = 8.1$ Hz, 16H, $SnC\mathit{H}_2CH_3$), 1.58 (d, $^{2}J_{P-H} = 18$ Hz, 12H, $PC\mathit{H}_3$), 1.39 (t, $^{3}J_{H-H} = 7.5$ Hz, 24H, $SnCH_2C\mathit{H}_3$), 1.34 (t, $^{3}J_{H-H} = 7.2$ Hz, 6H, $SCH_2C\mathit{H}_3$). $^{13}C\{^{1}H\}$ NMR: δ 45.75 ($S\mathit{C}H_2CH_3$), 22.21 ($Sn\mathit{C}H_2CH_3$, $^{1}J_{Sn-C} = 781$ Hz), 13.95 (d, $^{1}J_{P-C} = 146$ Hz, $P\mathit{C}H_3$), 9.33 ($SnCH_2\mathit{C}H_3$, $^{2}J_{Sn-C} = 43$ Hz), 9.05 ($SCH_2\mathit{C}H_3$). ^{119}Sn NMR: δ −314 (br, $W_{1/2} = 1396$ Hz). ^{31}P NMR ($CDCl_3$): δ 21.7. IR (KBr, cm^{-1}): 1184, 1065, 967 ($\nu(SO_3) + \nu(PO_3)$), 2360 (ν(PO-H), hydrogen bonded), 3450 (νH_2O). Anal. Calcd for $C_{24}H_{68}O_{20}P_4S_2Sn_4$: C, 21.52; H, 5.12. Found: C, 21.52; H, 5.14.

2. [$(Et_2Sn)_3(O_3PMe)_2(OSO_2Me)_2\cdot CHCl_3$]$_n$. Yield: 70%, ^{1}H NMR ($CDCl_3$): δ 2.79 (s, 6H, $SC\mathit{H}_3$), 1.66 (q, $^{3}J_{H-H} = 7.8$ Hz, 12H, $SnC\mathit{H}_2CH_3$), 1.51 (d, $^{2}J_{P-H} = 18$ Hz, 6H, $PC\mathit{H}_3$), 1.36 (t, $^{3}J_{H-H} = 7.7$ Hz, 18H, $SnCH_2C\mathit{H}_3$). $^{13}C\{^{1}H\}$ NMR: δ 39.50 ($S\mathit{C}H_3$), 25.12 ($Sn\mathit{C}H_2CH_3$, $^{1}J_{Sn-C} = 920$ Hz), 13.72 (d, $^{1}J_{P-C} = 145$ Hz, $P\mathit{C}H_3$), 9.31 ($SnCH_2\mathit{C}H_3$, $^{2}J_{Sn-C} = 57$ Hz). ^{119}Sn NMR: δ −285 (br, $W_{1/2} = 372$ Hz). ^{31}P NMR ($CDCl_3$): δ 21.1 (s,$^{2}J_{Sn-O-P} = 126$ Hz). IR (KBr, cm^{-1}): 1196, 1096, 1007 ($\nu(SO_3) + \nu(PO_3)$). Anal. Calcd for $C_{17}H_{43}O_{12}P_2S_2Cl_3Sn_3$: C, 19.86; H, 4.22. Found: C, 19.83; H, 4.28.

3. [$(Me_2Sn)_3(O_3PBu^t)_2(OSO_2Me)_2\cdot 2CHCl_3$]$_n$. Yield: 72%, ^{1}H NMR: δ 2.31 (s, 6H, $SC\mathit{H}_3$), 1.12 (d, $^{3}J_{P-H} = 18$ Hz, 18H, $PC(C\mathit{H}_3)_3$), 0.84 (s, $^{2}J_{Sn-H} = 108$ Hz, 18H, $SnC\mathit{H}_3$). $^{13}C\{^{1}H\}$ NMR: δ 39.36 ($S\mathit{C}H_3$), 30.84 (d, $^{1}J_{P-C} = 147$ Hz, $PC(CH_3)_3$), 24.67 (s, $PC(CH_3)_3$), 13.67 ($Sn\mathit{C}H_3$, $^{1}J_{Sn-C} = 980$ Hz). ^{119}Sn NMR: δ −278 (br, $W_{1/2} = 248$ Hz). ^{31}P NMR: δ 26.3 (s, $^{2}J_{Sn-O-P} = 122$ Hz). IR (KBr, cm^{-1}): 1215, 1163, 1069 ($\nu(SO_3) + \nu(PO_3)$). Anal. Calcd for $C_{18}H_{44}Cl_6O_{12}P_2S_2Sn_3$: C, 18.84; H, 3.87; Found: C, 18.83; H, 3.85.

X-ray Crystallography. The intensity data of **1**−**3** were collected on Nonius Kappa CCD diffractometer equipped with a molybdenum sealed tube (Mo Kα radiation, $\lambda = 0.71073$ Å) and a graphite monochromator at $T = 150(2)$ K. Cell parameters, data reduction, and absorption corrections were performed with Nonius software (DENZO and SCALEPACK).[19] The structures were solved by direct methods using SIR97,[20] and refined by full matrix

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least-squares method on F^2 using SHELXL-97.[21] All calculations were performed using WinGx.[22] For **2** and **3**, all three chlorine atoms showed high thermal parameters and splitting. The disorders were observed at two sites [90:10 (for **2**), 50:50 (for **3**) ratios]. C−Cl distances in these disordered fragments were restrained to idealized values in the final least-squares cycles. Partial atoms were refined isotropically. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions by using a riding model, except for those hydrogens which form part of P-OH or H_2O in **1** which were located and refined.

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Supporting Information Available: Crystallographic data in CIF file format. This material is available free of charge via the Internet at http://pubs.acs.org.

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