Inorg. Chem. **2008**, *47*, 5930−5935

Inorganic Chemistry
Article

Synthesis, Characterization, and Structural Studies of Mixed-Ligand Diorganotin Esters, $[R_2Sn(OP(O)(OH)Ph)(OS(O)_2R^1)]_n$ [R = *n*-Bu, R^1 = Me (1), *n*-Pr (2); R = Et, R^1 = Me (3)] with 1D and 3D Coordination Polymeric Motifs

Ravi Shankar,*,† Atul Pratap Singh,† Archana Jain,† Mary F. Mahon,‡ and Kieran C. Molloy‡

Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi 110016, and India Department of Chemistry, University of Bath, Bath BA2 7AY, U.K.

Received February 7, 2008

Mixed-ligand diorganotin esters, $[R_2Sn(OP(O)(OH)Ph)(OS(O)_2R^1)]_n$ [R = *n*-Bu, R^1 = Me (**1**), *n*-Pr (**2**); R = Et, R^1 = Me (**3**)], have been synthesized by reacting the tin precursors, $R_2Sn(OR^1)OS(O)_2R^1$ with an equimolar amount of phenylphosphonic acid under mild conditions (room temperature, 6−8 h, CH_2Cl_2). These have been characterized by IR, multinuclear (^1H, $^{13}C\{^1H\}$, ^{31}P, and ^{119}Sn) NMR, and single crystal X-ray diffraction studies. The asymmetric unit of **1** is comprised of a tetramer with four crystallographically unique tin atoms. The structure reveals a central eight-membered $(Sn-O-S-O)_2$ cyclic ring with two exocyclic tin atoms, which results from μ_3-binding of the two methanesulfonate groups. The remaining two sulfonates are monodentate and contribute in O···HO(P) hydrogen bonding. The molecular structure is extended into a 3D coordination polymer with the aid of hydrogenphenylphosphonate group on each tin atom, acting in a μ_2-O_2P mode and forms a series of eight-membered $(Sn-O-P-O)_2$ rings in the structural framework. **2** and **3** are isostructural and represent linear 1D coordination polymers via μ_2-binding mode of both alkanesulfonate and hydrogenphenylphosphonate groups.

Introduction

The coordination chemistry of ambidentate ligands, namely sulfonate (RSO_3^-) and phosphonate $[RP(O)(OH)O^-/RPO_3^{2-}]$, toward transition and main-group metal ions has expanded rapidly in recent years.[1,2] This upsurge is partly attributed to the ability of these ligands to structurally organize hybrid inorganic−organic solids and metal−organic frameworks in varying dimensionalities. Whereas these tetrahedral ligands have a strong structural analogy, the sulfonate group is generally regarded as weakly coordinating and functions cooperatively with metal ions in primary and/or secondary spheres in the presence of a co-ligand.[1a,3] An interesting variation in the ligand design in which both sulfonate and/or phosphonate groups are attached on the same organic scaffold has also been pursued in the quest for new multidimensional metal−organic networks.[3b,4]

Among the tetravalent metal ions, organotin phosphonates/sulfonates have received considerable attention.[2] In the former class, there are only a few structurally known examples, which include homoleptic $[n\text{-}Bu_2Sn(OP(O)(OH)Me)_2]_2$[5] (dimer), $[Me_3Sn(OP(O)(OH)Ph)]_n$[6] (helical polymer), and $[n\text{-}[(BuSn)_2O(O_2P(OH)\text{-}t\text{-}Bu)_4]_2$[7] (cluster). In

---

* To whom correspondence should be addressed. E-mail: shankar@chemistry.iitd.ac.in.

† Indian Institute of Technology.

‡ University of Bath.

(1) (a) Côté, A. P.; Shimizu, G. K. H. *Coord. Chem. Rev.* **2003**, *245*, 49. (b) Cai, J. *Coord. Chem. Rev.* **2004**, *248*, 1061. (c) Clearfield, A. Metal Phosphonate Chemistry. In *Progress in Inorganic Chemistry*; Karlin, K. D. , Ed.; John Wiley & Sons: New York, 1998; Vol. *47*, p 371.

(2) (a) Jain, V. K. *Coord. Chem. Rev.* **1994**, *135/136*, 809. (b) Chandrasekhar, V.; Nagendran, S.; Baskar, V. *Coord. Chem. Rev.* **2002**, *235*, 1. (c) Walawalkar, M. G.; Roesky, H. W.; Murugavel, R. *Acc. Chem. Res.* **1999**, *32*, 117.

(3) (a) Chandrasekhar, V.; Singh, P.; Gopal, K. *Organometallics* **2007**, *26*, 2833. (b) Chandrasekhar, V.; Boomishankar, R.; Steiner, A.; Bickley, J. F. *Organometallics* **2003**, *22*, 3342.

(4) (a) Videnova-Adrabinska, V. *Coord. Chem. Rev.* **2007**, *251*, 1987. (b) Du, Z.-Y.; Xu, H.-B.; Mao, J.-G. *Inorg. Chem.* **2006**, *45*, 6424. (c) Sharma, C. V. K.; Clearfield, A. *J. Am. Chem. Soc.* **2001**, *123*, 2885. (d) Liang, J.; Shimizu, G. K. H. *Inorg. Chem.* **2007**, *46*, 10449. (e) Du, Z.-Y.; Prosvirin, A. V.; Mao, J.-G. *Inorg. Chem.* **2007**, *46*, 9884.

(5) Ribot, F.; Sanchez, C.; Biesemans, M.; Mercier, F. A. G.; Martins, J. C.; Gielen, M.; Willem, R. *Organometallics* **2001**, *20*, 2593.

(6) Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Cunningham, D.; Zuckerman, J. J. *Inorg. Chem.* **1981**, *20*, 2402.

(7) Kumara Swamy, K. C.; Schmid, C. G.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *121*, 223.

10.1021/ic8002433 CCC: $40.75

all cases, the hydrogenphosphonate ligand acts in bridging bidentate mode. The dianionic, tridentate mode of the phosphonate groups has been observed in an organotin phosphonate cluster, $[Na_6(CH_3OH)_2(H_2O)]$ $[\{(BzSn)_3(PhPO_3)_5(\mu_3\text{-}O)(CH_3O)\}_2Bz_2Sn]CH_3OH$, which has been synthesized by the solvothermal route.[8] Structural studies of di/triorganotin arenesulfonates reveal that the ligand character is either ionic or weakly coordinating, depending upon the steric bulk of organic substituents on tin and/or the ligand and results in the formation of 1D and 2D polymeric assemblies with the aid of hydrogen bonding interactions.[9] To our knowledge, the construction of a 3D coordination polymer has not been realized so far among these classes of organotin phosphonates and/or sulfonates.

Recently, we have developed a new synthetic approach for the mixed-ligand diorganotin esters bearing both an alkanesulfonate and phosphonate/carboxylate/β-diketonate group on the same tin center.[10,11] The synthetic protocol involves a one-pot reaction between di-*n*-butyltin oxide and dialkylsulfite, $(RO)_2S{=}O$ (R = Me, Et, *n*-Pr) in the presence of an alkyl iodide, which affords the corresponding di-*n*-butyltin(alkoxy)alkanesulfonate. These compounds undergo a displacement reaction with an appropriate protic ligand to yield the desired mixed-ligand diorganotin esters. Structural studies of the tin derivatives $[n\text{-}Bu_2Sn(OP(O)(OH)Me)(OS(O)_2R)]_n$ (R = Me, Et) have revealed a synergy in the bonding modes of alkanesulfonate and hydrogenmethylphosphonate groups, which results in the formation of 1D and 2D coordination polymeric assemblies.[11] The structural difference is governed by subtle variations of the alkyl group on the sulfonate moiety. These preliminary findings have stimulated our interest to comprehend the steric attributes of organic substituents on the ligands and/or tin atom in the structural organization among this class of mixed-ligand diorganotin esters. Herein, we report on the synthesis and structural characterization of analogous diorganotin derivatives, $[R_2Sn(OP(O)(OH)Ph)(OS(O)_2R^1)]_n$ [R = *n*-Bu, R^1 = Me (**1**), *n*-Pr (**2**); R = Et, R^1 = Me (**3**)], incorporating the hydrogenphenylphosphonate ligand and varying the substituents on the sulfonate or tin center. The structure of **1** represents the first example of a 3D coordination polymeric assembly among the mixed-ligand diorganotin ester derivatives.

Results and Discussion

Synthesis and characterization of 1−3. Following our earlier approach,[11] the synthesis of **1**−**3** has been achieved by reacting the diorganotin precursor $R_2Sn(OR^1)OS(O)_2R^1$ (R = *n*-Bu, Et; R^1 = Me, *n*-Pr) with an equimolar quantity of phenylphosphonic acid under mild conditions.

$$R_2Sn(OR^1)OS(O)_2R^1 \xrightarrow[CH_2Cl_2,\text{rt},6-8\text{h}]{PhP(O)(OH)_2} [R_2Sn(OP(O)(OH)Ph)(OS(O)_2R^1)]_n + R^1OH$$

$$R = n\text{-Bu},\ R^1 = \text{Me } (1), n\text{-Pr } (2);\ R = \text{Et},\ R^1 = \text{Me } (3) \quad (1)$$

These compounds are obtained as white crystalline solids. Whereas **1** and **2** are soluble in common organic solvents such as dichloromethane, chloroform, and so forth, **3** dissolves only in coordinating solvents such as CH_3OH, DMSO, DMF, and so forth. A characteristic feature of the IR spectra (KBr optics) of all the compounds is the appearance of a medium intensity band at 2359 cm^{-1}, which is ascribed to a hydrogen bonded −OH functionality associated with hydrogenphenylphosphonate groups. However, the observed IR absorptions in the region 940−1200 cm^{-1} are overlapping νSO_3 and νPO_3 stretching modes and are thus not informative in evaluating the coordination modes of these ligands. The NMR spectra for **1**, **2**, and **3** have been studied in $CDCl_3$ and DMSO-d_6 respectively. ^1H and $^{13}C\{^1H\}$ NMR spectra are in accord with structural composition. In the ^1H NMR spectra, characteristic signals at δ 2.3−2.8 (SCH_2/SCH_3), 7.4−7.8 (P−Ph) and 0.8−1.7 (Et_2Sn/$n\text{-}Bu_2Sn$) appear in a 1:1:1 integrated ratio. From the observed tin satellites in the ^{13}C NMR spectra, the $^1J(^{13}C\text{-}^{119}Sn)$ coupling constant values for **1**−**3** have been calculated as 642, 634, and 1008 Hz, respectively, whereas the corresponding ^{119}Sn NMR chemical shifts appear at δ −244 (**1**, **2**) and −348 (**3**). These values are suggestive of a six-coordinate tin environment in solution.[12,13] The ^{31}P NMR spectra of **1**−**3** show a single peak in each case at δ 11.5, 12.8, and 7.8, respectively, and are comparable with that of di-*n*-butyltin bis(hydrogenphenylphosphonate) reported earlier.[5]

X-ray Crystal Structures. Slow diffusion of diethyl ether into a solution of **1**, **2** in dichloromethane, and **3** in methanol results in the formation of crops of crystals suitable for X-ray crystallographic studies. The crystal data of **1**−**3** are summarized in Table 1, whereas selected bond lengths and angles are given in Tables 2, 3, and 4, respectively.

The crystal structure of **1** (part a of Figure 1) reveals that the asymmetric unit is composed of a tetrameric tin assembly with four crystallographically unique tin atoms (Sn(1) to Sn(4)) in which the methanesulfonate groups associated with S(2) and S(3) act in μ_3-tridentate coordination mode. The structure thus generates a central eight-membered $[Sn{-}O{-}S{-}O]_2$ puckered ring by virtue of two μ_2-O_2S bridges, with the exocyclic Sn(1) and Sn(4) atoms being held by O(12) and O(18) respectively, thereby completing their μ_3-bridging role. The endocyclic O−Sn−O angles and Sn−O bond lengths associated with the cyclic ring are found to

---

(8) Song, S.-Y.; Ma, J.-F.; Yang, J.; Gao, L.-L.; Su, Z.-M. *Organometallics* **2007**, *26*, 2125.

(9) (a) Harrison, P. G.; Phillips, R. C.; Richards, J. A. *J. Organomet. Chem.* **1976**, *114*, 47. (b) Kapoor, R.; Gupta, A.; Kapoor, P.; Venugopalan, P. *J. Organomet. Chem.* **2001**, *619*, 157. (c) Chandrasekhar, V.; Basker, V.; Boomishankar, R.; Gopal, K.; Zacchini, S.; Bickley, J. F.; Steiner, A. *Organometallics* **2003**, *22*, 3710.

(10) (a) Narula, S. P.; Kaur, S.; Shankar, R.; Verma, S.; Venugopalan, P.; Sharma, S. K. *Inorg. Chem.* **1999**, *38*, 4777. (b) Shankar, R.; Kumar, M.; Chadha, R. K.; Hundal, G. *Inorg. Chem.* **2003**, *42*, 8585. (c) Shankar, R.; Kumar, M.; Narula, S. P.; Chadha, R. K. *J. Organomet. Chem.* **2003**, *671*, 35. (d) Shankar, R.; Singh, A. P.; Hundal, G.; Butcher, R. J. *J. Organomet. Chem.* **2007**, *692*, 5555.

(11) Shankar, R.; Singh, A. P.; Upreti, S. *Inorg. Chem.* **2006**, *45*, 9166.

(12) Holeěek, J.; Nádvorník, M.; Handlíř, K.; Lyěka, A. *J. Organomet. Chem.* **1986**, *315*, 299.

(13) Howard, W. F., Jr.; Crecely, R. W.; Nelson, W. H. *Inorg. Chem.* **1985**, *24*, 2204.

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

	1	**2**	**3**
empirical formula	$C_{60}H_{105}O_{24}P_4S_4Sn_4$	$C_{17}H_{31}O_6PSSn$	$C_{11}H_{19}O_6PSSn$
fw	1937.32	513.14	429.01
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	13.0210(1)	9.8494(2)	8.65210(10)
b, Å	18.8670(2)	14.0400(3)	9.96560(10)
c, Å	19.7880(2)	16.3432(4)	10.7760(2)
α, deg	104.981(1)	90	72.9260(10)
β, deg	107.287(1)	97.3380(10)	67.4340(10)
γ, deg	109.017(1)	90	69.5950(10)
Z	2	4	2
V, Å^3	4034.08(7)	2241.52(9)	790.340(19)
ρcalcd./Mg m^{-3}	1.595	1.521	1.803
F(000)	1962	1048	428
Crystal size/mm	0.15 × 0.10 × 0.07	0.13 × 0.13 × 0.13	0.20 × 0.17 × 0.15
θ (deg)	3.52 - 27.50	2.95 - 27.49	3.31−30.06
reflns collected/unique	70 609/49 698	27 896/5127	16 259/4615
R_{int} value		0.0541	0.0309
data/restraints/params	49 698/17/866	5127/1/268	4615/0/205
μ, mm^{-1}	1.053	1.094	1.145
Final R, wR2 indices [$I > 2\sigma(I)$]	0.0765, 0.1733	0.0344, 0.0744	0.0234, 0.0563
Final R, wR2 indices (all data)	0.1147, 0.1954	0.0509, 0.0811	0.0247, 0.0571

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for **1**

Sn(1)−C(1)	2.109(5)	Sn(1)−C(5)	2.110(5)
Sn(1)−O(1)	2.116(3)	Sn(1)−O(2)^a	2.093(3)
Sn(1)−O(4)	2.416(4)	Sn(1)−O(12)	2.640(4)
Sn(2)−C(16)	2.112(6)	Sn(2)−C(20)	2.091(6)
Sn(2)−O(7)	2.105(3)	Sn(2)−O(8)^b	2.116(3)
Sn(2)−O(10)	2.445(4)	Sn(2)−O(17)	2.352(4)
Sn(3)−C(31)	2.078(6)	Sn(3)−C(35)	2.088(5)
Sn(3)−O(11)	2.463(3)	Sn(3)−O(13)	2.090(3)
Sn(3)−O(15)^c	2.087(3)	Sn(3)−O(16)	2.568(4)
Sn(4)−C(46)	2.136(8)	Sn(4)−C(50)	2.103(5)
Sn(4)−O(18)	2.443(4)	Sn(4)−O(19)	2.103(3)
Sn(4)−O(21)^d	2.117(4)	Sn(4)−O(23)	2.443(4)
C(1)−Sn(1)−C(5)	154.1(2)	O(2)^a-Sn(1)−O(1)	86.81(13)
O(4)−Sn(1)−O(12)	109.82(12)	O(2)^a-Sn(1)−O(4)	81.72(13)
O(1)−Sn(1)−O(12)	81.25(13)	O(1)−P(1)−O(2)	115.00(21)
C(20)−Sn(2)−C(16)	167.2(2)	O(7)−Sn(2)−O(8)^b	92.54(18)
O(7)−Sn(2)−O(17)	83.21(16)	O(8)^b-Sn(2)−O(10)	90.03(14)
O(17)−Sn(2)−O(10)	94.22(16)	O(8)−P(2)−O(7)	114.2(2)
O(10)−S(2)−O(11)	110.5(2)	O(16)−S(3)−O(17)	112.0(3)
C(31)−Sn(3)−C(35)	153.6(2)	O(15)^c-Sn(3)−O(13)	88.20(14)
O(13)−Sn(3)−O(11)	74.73(13)	O(15)^c-Sn(3)−O(16)	79.05(13)
O(11)−Sn(3)−O(16)	117.99(12)	O(13)−P(3)−O(15)	114.6(2)
C(50)−Sn(4)−C(46)	150.7(3)	O(21)^d-Sn(4)−O(18)	81.83(17)
O(19)−Sn(4)−O(23)	84.26(14)	O(18)−Sn(4)−O(23)	105.52(17)
O(19)−Sn(4)−O(21)^d	88.19(14)	O(21)−P(4)−O(19)	115.1(2)

Symmetry transformations used to generate equivalent atoms: ^{a} $-x + 1, -y + 2, -z + 2$. ^{b} $-x + 1, -y + 2, -z + 1$. ^{c} $-x + 2, -y + 3, -z + 2$. ^{d} $-x + 1, -y + 3, -z + 1$.

Table 3. Selected Bond Lengths (Angstroms) and Angles (Degrees) for **2**

Sn−O(1)	2.084(2)	Sn−O(3)^a	2.115(19)
Sn−O(4)	2.496(2)	Sn−O(5)^b	2.508(2)
Sn−C(1)	2.120(3)	Sn−C(5)	2.113(3)
C(1)−Sn−C(5)	154.26(12)	O(1)−Sn−O(5)^b	81.27(8)
O(4)−Sn−O(5)^b	109.31(8)	O(3)^a−Sn−O(4)	81.23(8)
O(1)−Sn−O(3)^a	87.91(8)	O(1)−P−O(3)	115.54(12)
O(5)−S−O(4)	112.82(15)		

Symmetry transformations used to generate equivalent atoms: ^{a} $-x + 2, -y + 1, -z + 1$. ^{b} $-x + 1, -y + 1, -z + 1$.

Table 4. Selected Bond Lengths (Angstroms) and Angles (Degrees) for **3**

Sn−C(1)	2.1122(18)	Sn−C(3)	2.1143(19)
Sn−O(4)	2.0850(12)	Sn−O(1)	2.4818(13)
Sn−O(6)^a	2.1017(12)	Sn−O(2)^b	2.5328(14)
C(1)−Sn−C(3)	157.92(9)	O(4)−Sn−O(6)^a	88.81(5)
O(4)−Sn−O(1)	80.79(5)	O(6)^a−Sn−O(2)^b	84.94(5)
O(1)−Sn−O(2)^b	105.08(5)	O(4)−P−O(6)	115.27(7)
O(2)−S−O(1)	112.66(9)		

Symmetry transformations used to generate equivalent atoms: ^{a} $-x + 2, -y + 1, -z + 1$. ^{b} $-x + 2, -y + 2, -z + 1$.

vary significantly (O(17)−Sn(2)−O(10) = 94.22(16), O(11)−Sn(3)−O(16) = 117.99(12)°; Sn(2)−O(10) = 2.445(4), Sn(2)−O(17) = 2.353(4), Sn(3)−O(11) = 2.463(3), Sn(3)−O(16) = 2.568(4) Å).

The directional effect of the μ_3-methanesulfonate ligand-binding mode gives rise to a unique spatial disposition such that Sn(2), Sn(3), Sn(4), and Sn(1), Sn(2), Sn(3) atoms form two triangular planes with Sn(2) and Sn(3) atoms forming the junction. These planes are oriented by 55.95° with respect to each other and are important in the organization of 3D coordination polymer assembly. The hydrogenphenylphosphonate groups bonded to Sn(2) (P(2)) and Sn(3) (P(3)) atoms form μ_2-O_2P bridges and associate similar tin atoms of the adjacent asymmetric units to extend the structure into the 1D domain with alternate eight-membered (Sn−O−P−O)$_2$ and (Sn−O−S−O)$_2$ cyclic rings forming the polymeric chains (part b of Figure 1). This structural arrangement finds a close analogy with those of [n-Bu$_2$Sn(OP(O)(OH)Me)(OS(O)$_2$Et)]$_n$[11] as well as **2** and **3** reported herein (vide infra). The metrical parameters [O(8)−P(2)−O(7) = 114.2(2), O(13)−P(3)−O(15) = 114.6(2)°; Sn(2)−O(7) = 2.105(3), Sn(2)−O(8) = 2.116(3), Sn(3)−O(13) = 2.090(3), Sn(3)−O(15) = 2.087(3) Å)] are similar for both phosphonate groups and reflect the centrosymmetric nature of the (Sn−O−P−O)$_2$ rings. The phosphonate groups associated with Sn(4) atoms (P(4)) act as a linker between the chains via the formation of centrosymmetric eight-membered (Sn−O−P−O)$_2$ rings [O(21)−P(4)−O(19) = 115.1(2)°; Sn(4)−O(19) = 2.103(3), Sn(4)−O(21) = 2.117(4) Å] and give a layered connectivity in the bc plane (part b of Figure 1). The layered structures are interlinked by the Sn(1) atoms involving μ_2-O_2P bridges and extend the

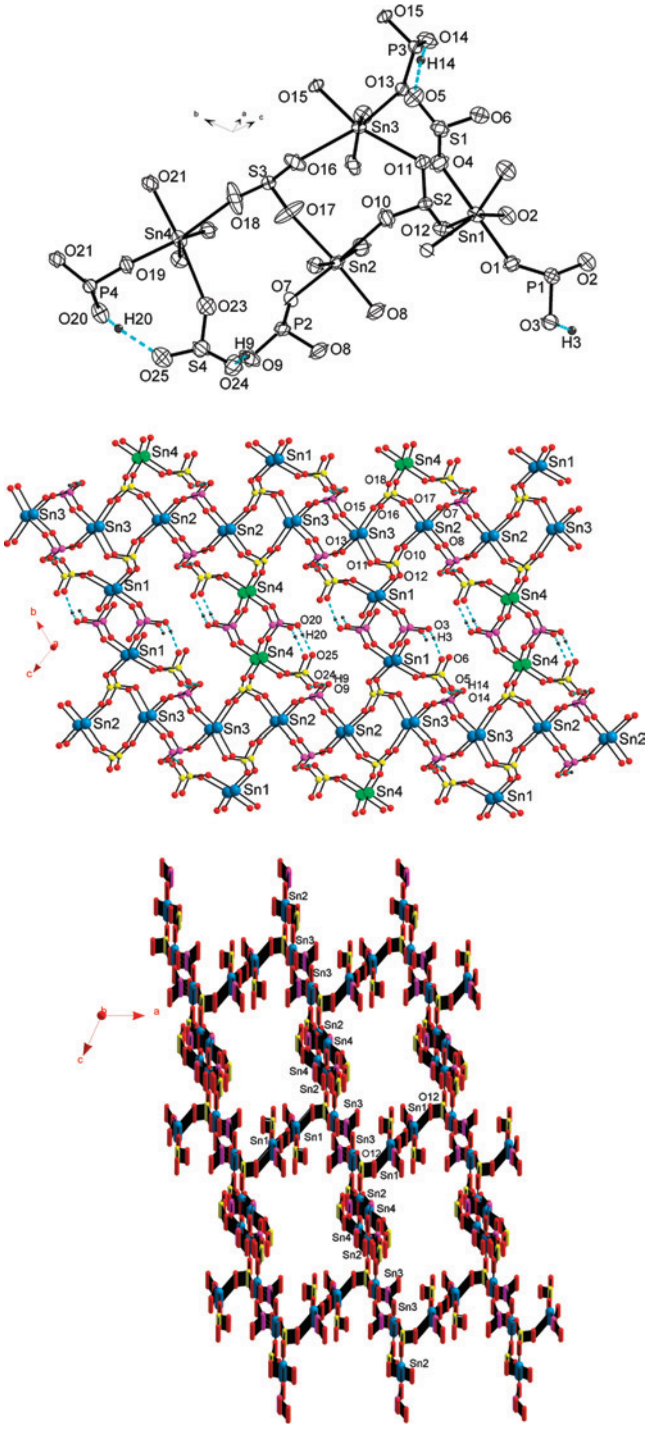

Figure 1. (a) ORTEP view of **1**. The thermal ellipsoids are set at 30% probability; *n*-Bu, Me, Ph groups, and hydrogen atoms (except for H(3), H(9), H(14), and H(20)) are omitted for clarity, 3D structure of **1** in *bc* plane. The *n*-Bu, Me, and Ph groups and hydrogen atoms (except H(3), H(9), H(14) and H(20)) are omitted for clarity, 3D structure of **1** in ac-plane. The *n*-Bu, Me, and Ph groups and hydrogen atoms are omitted for clarity.

Table 5. Hydrogen-Bonding Parameters for **1**−**3**

D−H−A	D−H (Å)	H−A (Å)	D−A (Å)	D−H−A (deg)
		1		
O(14)−H(14)−O(5)	0.841(3)	1.795(5)	2.618(6)	166.01(32)
O(3)−H(3)−O(6)	0.842(4)	1.901(4)	2.577(6)	136.30(29)
O(9)−H(9)−O(24)	0.840(4)	1.776(6)	2.589(7)	162.41(33)
O(20)−H(20)−O(25)	0.840(4)	1.760(5)	2.591(7)	169.64(32)
		2		
O(2)−H(2)−O(6)	0.814(22)	1.815(21)	2.619(3)	169.18(214)
		3		
O(5)−H(5)−O(3)	0.758(31)	1.874(33)	2.628(2)	172.27(309)

assembly into a 3D coordination polymeric motif. The methanesulfonate groups associated with S(1) and S(4) remain unidentate in nature and involve their uncoordinated oxygen atoms (O(5), O(6) or O(24), O(25)) in hydrogen bonding with the −OH functionalities of two phosphonate groups, one of which belong to the same tin, for example, O(20)−H(20)···O(25), the other to that of a different tin atom, for example, O(9)−H(9)···O(24). This results in the formation of eight- and twelve-membered rings, respectively. The metrical parameters associated with these hydrogen bonds are shown in Table 5.

The overall 3D coordination polymeric assembly thus comprises of the tin atoms, which are associated with a series of connected (Sn−O−P−O)$_2$ and (Sn−O−S−O)$_2$ eight-membered rings, which involve all of the four phosphonate groups of the asymmetric unit and two methanesulfonate groups (linked to Sn(2), Sn(3)) in μ_2-O$_2$P and μ_3-O$_3$S bonding modes, respectively. As a result, each tin atom adopts a distorted octahedral geometry with SnO$_4$ core occupying the basal plane (360 ± 0.62°) and trans disposition of *n*-butyl groups. However, varying degrees of distortion in O−Sn−O and C−Sn−C angles (C−Sn−C = 151−167°) are discernible on each tin atom (Table 2). The mean Sn−O$_S$ bond lengths (2.35−2.64 Å) across the four sulfonate groups are found to be much larger than those observed for Sn−O$_P$ bonds (2.09−2.12 Å). However, these metrical parameters are comparable with those of related 1D and 2D mixed-ligand di-*n*-butyltin assemblies reported earlier.[11] A top down view of **1** along the *ac* plane (part c of Figure 1) reveals the formation of a series of parallelogram frameworks of dimension 13.2 × 20.2 Å with Sn(3) atoms occupying the corners and form infinite channels along the *b* axis. The topological arrangement is however not flat, and the Sn(1), Sn(2), and Sn(4) atoms lie above and below the interconnected macrocycle mean planes. The voids are occupied by the *n*-butyl, phenyl, and methyl groups.

To comprehend the steric role of the alkyl groups on the sulfonate or tin moiety in the organization of the structural motif, the X-ray structures of [*n*-Bu$_2$Sn(OP(O)(OH)Ph)-(OS(O)$_2$Pr)]$_n$, **2** and [Et$_2$Sn(OP(O)(OH)Ph)(OS(O)$_2$Me)]$_n$, **3** have also been determined. The crystal data are summarized in Table 1, while selected bond lengths and angles are given in Tables 3 and 4, respectively. In contrast to **1**, both these molecules are isostructural (Figures 2 and 3) featuring μ_2-O$_2$S and μ_2-O$_2$P coordination of the *n*-propane/methanesulfonate and hydrogenphenylphosphonate groups, respectively. This results in the formation of alternate (Sn−O−S-O)$_2$ and (Sn−O−P-O)$_2$ eight-membered rings and constitutes one-dimensional polymeric chains which run parallel to one another along *a*-axis (for **2**) and *b*-axis (for **3**). However, these polymeric chains do not have any interaction between them. Although, the O−Sn−O bite angles subtended by hydrogenphenylphosphonate moieties to the tin atoms are quite similar [O(1)−Sn-O(3) = 87.91(8)° (for **2**), O(4)−Sn-

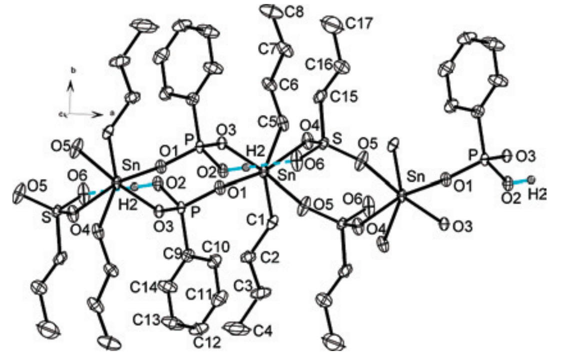

Figure 2. ORTEP view of **2**. The thermal ellipsoids are set at 30% probability, and the hydrogen atoms (except H(2)) are omitted for clarity.

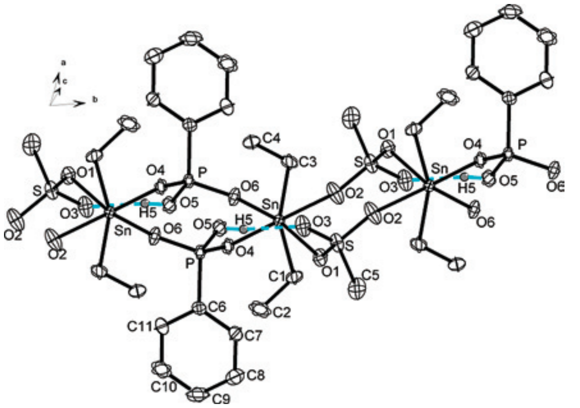

Figure 3. ORTEP view of **3**. The thermal ellipsoids are set at 30% probability, and the hydrogen atoms (except H(5)) are omitted for clarity.

O(6) = 88.81(5)° (for **3**)], these are much narrower than those observed for the sulfonate groups [O(4)−Sn-O(5) = 109.31(8)° (**2**), O(1)−Sn(1)−O(2)#2 = 105.08(5)° (**3**)]. The C−Sn−C angles are found to be 154.26(12)° and 157.92(9)°, respectively. The Sn−O_P (2.08−2.12 Å) and Sn−O_S (2.48−2.53 Å) bond lengths are however comparable with those observed in **1**. In addition, strong P−OH···O=S hydrogen bonding interactions are evident involving the O(6)/O(3) atoms of the sulfonate groups (Table 5).

An analysis of the structures of **1**, **2**, and **3** reveals a few significant features. It is evident that the steric effect of the substituents on the tin or sulfonate moieties plays a prominent role in modulating the bonding behavior of the methanesulfonate groups and O−H···O hydrogen bonds derived there from. In **1**, the methanesulfonate groups act both as μ_1 and μ_3 modes and the uncoordinated oxygen (O(24), O(25)/O(5), O(6)) atoms of each monodentate ligand form two hydrogen bonds with the (P)OH moieties, the later being derived from the phosphonate groups bonded to the same or different tin atom. On the other hand, the bonding behavior of sulfonate groups in **2** and **3** is invariably bridging bidentate (μ_2) in nature, and the OH···O hydrogen bonding involves the uncoordinated O(6) (for **2**)/O(3) (for **3**) oxygen and (P)OH group of the phosphonate ligand which is bonded to the same tin center. Although, the structural similarity of **1** and **2**,**3** in the 1D domain is apparent; the polymeric chains in **2** and **3** run parallel to each other but do not have any interaction. Nonetheless, the 1D chains in **1** are bridged by Sn(1) and Sn(4) atoms, which link with themselves to form the phosphonated $(SnOPO)_2$ rings and direct the assembly in a 3D motif.

Experimental Section

All operations were carried out using standard Schlenk line techniques under dry nitrogen atmosphere. Solvents were freshly distilled over phosphorus pentoxide (dichloromethane and hexane). Glasswares were dried in an oven at 110−120 °C and further flame dried under vacuum prior to use. ^1H, ^{13}C, and ^{31}P spectra were recorded on a BRUKER DPX-300 and ^{119}Sn NMR on BRUKER AVANCE II 400 spectrometers at 300, 75.48, 121.50, 149.19 MHz, respectively. ^1H and ^{13}C chemical shifts are quoted with respect to the residual protons of the solvents ($CDCl_3$ or DMSO-d_6) and ^{119}Sn and ^{31}P NMR data are given using tetramethyltin and 85% H_3PO_4 as the external standards, respectively. IR spectra were recorded on Nicolet protege 460 ESP spectrometer using KBr optics. Elemental analysis (C, H) was performed on a PerkinElmer model 2400 CHN elemental analyzer.

Synthesis of [$R_2Sn\{OP(O)(OH)Ph\}\{OS(O)_2R^1\}]_n$ [R = *n*-Bu, R^1 = Me (1), *n*-Pr (2); R = Et, R^1 = Me (3)]. To a stirred solution of di-*n*-butyltin(methoxy)methanesulfonate (0.50 g, 1.39 mmol)/ di-*n*-butyltin(propoxy)propanesulfonate (0.58 g, 1.39 mmol) in dichloromethane was added phenylphosphonic acid (0.22 g, 1.39 mmol), and the clear solution was stirred for 6−8 h at room temperature. Thereafter, the solvent was removed under vacuum, and *n*-hexane (30 mL) was added to afford a white solid in each case which was identified as **1** and **2,** respectively. Analogous reaction of diethyltin(methoxy)methanesulfonate (0.42 g, 1.39 mmol) with phenylphosphonic acid (0.22 g, 1.39 mmol) in dichloromethane results in the precipitation of a white solid which was filtered and dried under vacuum. The compound was identified as **3**.

1. [*n*-$Bu_2Sn(OP(O)(OH)Ph)(OS(O)_2Me)]_n$. Yield: 79%. ^1H NMR ($CDCl_3$): δ 7.80−7.70 (m, 2H, H-3/H-5), 7.47 (t, $^3J_{H-H}$ = 7.1 Hz, 1H, H-4), 7.37 (m, 2H, H-2/H-6), 2.67 (s, 3H, SCH_3), 1.64 (br, 8H, $Sn(CH_2)_2$), 1.25 (br, 4H, $Sn(CH_2)_2CH_2$), 0.80 (t, $^3J_{H-H}$ = 7.0 Hz, 6H, $Sn(CH_2)_3CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 132.09 (s, C-4), 130.92 (d, $^2J_{C-P}$ = 11 Hz, C-2/C-6), 130.52 (d, $^1J_{C-P}$ = 197 Hz, C-1), 128.34 (d, $^3J_{C-P}$ = 16 Hz, C-3/C5), 39.34 (S-CH_3), 28.93 ($SnCH_2$, $^1J_{Sn-C}$ = 642 Hz), 26.50 ($SnCH_2(CH_2)_2$, $^2J_{Sn-C}$ = 28 Hz, $^3J_{Sn-C}$ = 109 Hz), 13.47 ($Sn(CH_2)_3CH_3$). ^{119}Sn NMR ($CDCl_3$): δ -244. ^{31}P NMR ($CDCl_3$): δ 11.5. IR (KBr, cm^{-1}) 945, 1017, 1059, 1134, 1193 (ν(SO_3) and ν(PO_3)), 2361 (ν(PO-H), hydrogen bonded). Anal. Calcd for $C_{15}H_{27}O_6PSSn$: C, 37.14; H, 5.61; found: C, 37.11; H, 5.67.

2. [*n*-$Bu_2Sn(OP(O)(OH)Ph)(OS(O)_2Pr)]_n$. Yield: 74%. ^1H NMR ($CDCl_3$): δ 7.83−7.75 (m, 2H, H-3/H-5), 7.53 (t, $^3J_{H-H}$ = 6.9 Hz, 1H, H-4), 7.42 (m, 2H, H-2/H-6), 2.79 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, SCH_2), 1.69 (br, 10H, $Sn(CH_2)_2$ + SCH_2CH_2), 1.30−1.28 (m, 4H, $Sn(CH_2)_2CH_2$), 0.95 (t, $^3J_{H-H}$ = 6.9 Hz, 3H, $S(CH_2)_2CH_3$), 0.86 (br, $^3J_{H-H}$ = 7.2 Hz, 6H, $Sn(CH_2)_3CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 132.17 (s, C-4), 130.95 (d, $^2J_{C-P}$ = 11 Hz, C-2/C-6), 130.29 (d, $^1J_{P-C}$ = 197 Hz, C-1), 128.36 (d, $^3J_{C-P}$ = 16 Hz, C-3/C-5), 53.59 (S-CH_2), 29.06 ($SnCH_2$, $^1J_{Sn-C}$ = 634 Hz), 26.48 ($SnCH_2(CH_2)_2$, $^2J_{Sn-C}$ = 28 Hz, $^3J_{Sn-C}$ = 107 Hz), 17.92 (SCH_2CH_2), 13.03 ($S(CH_2)_2CH_3$), 13.46 ($Sn(CH_2)_3CH_3$). ^{119}Sn NMR ($CDCl_3$): δ - 244. ^{31}P NMR ($CDCl_3$): δ 12.8. IR (KBr, cm^{-1}) 944, 1065, 1137, 1186 (ν(SO_3) and ν(PO_3)), 2359 (ν(PO-H), hydrogen bonded). Anal. Calcd for $C_{17}H_{31}O_6PSSn$: C, 39.79; H, 6.09; found: C, 39.61; H, 6.24.

3. [$Et_2Sn(OP(O)(OH)Ph)(OS(O)_2Me)]_n$. Yield: 80%. ^1H NMR(DMSO-d_6): δ 7.71−7.67 (m, 2H, H-3/H-5), 7.48−7.43 (m, 3H, H-2/H-4/H-6), 2.30 (s, 3H, SCH_3), 1.45 (br, 4H, SnCH_2), 1.18 (br, 6H, SnCH_2CH_3). $^{13}C\{^1H\}$ NMR(DMSO-d_6): δ 130.81 (s, C-4), 130.55 (d, $^2J_{C-P} = 10$ Hz, C-2/C-6), 134.56 (d, $^1J_{C-P} = 196$ Hz, C-1), 128.08 (d, $^3J_{C-P} = 14$ Hz, C-3/C-5), 39.51 (S-CH_3, merged in DMSO peak), 26.40 (SnCH_2, $^1J_{Sn-C} = 1008$ Hz), 10.04 ($SnCH_2CH_3$, $^2J_{Sn-C} = 54$ Hz,). ^{119}Sn NMR (DMSO-d_6): δ - 348. ^{31}P NMR (DMSO-d_6): δ 7.8. IR (KBr, cm^{-1}) 944, 1045, 1141, 1186 ($\nu(SO_3)$ and $\nu(PO_3)$), 2354 (ν(PO-H), hydrogen bonded). Anal. Calcd for $C_{11}H_{19}O_6PSSn$: C, 30.80; H, 4.46; found: C, 30.51; H, 4.48.

X-ray Crystallography. The intensity data were collected on Bruker AXS CCD (for **1**) and Nonius Kappa CCD diffractometer (for **2** and **3**) diffractometers equipped with a molybdenum sealed tube (Mo Kα radiation, $\lambda = 0.71073$ Å) and a graphite monochromator at $T = 150$ K by ω, φ, and 2θ rotation at 10 s per frame. Cell parameters, data reduction, and absorption corrections were performed with *Nonius* software (*DENZO* and *SCALEPACK*).[14] The structures were solved by direct methods using *SHELXS-97* (for **1**) and *SIR97* (**2** and **3**)[15] and refined by full matrix least-squares method on F^2 using *SHELXL-97*.[16] All of the calculations were performed using *SHELXL-97/2* (for **1**)[17] and *WinGx* (for **2** and **3**).[18]

For **1**, diffraction data were pseudomerohedrally twinned (28%) about the 0, −1, −1 reciprocal axis direction, and model refinement as presented accounts for same. Some *n*-butyl groups also exhibited disorder. In particular, C(32)−(34) are disordered over 2 sites in a 1:1 ratio, C(36)−(38) are disordered over 2 locations in a 60:40 ratio, and C(46)−(50) are disordered in a 65:35 ratio. C−C distances in these disordered fragments were restrained to idealized values in the final least-squares cycles. Partial atoms were refined isotropically. Residual electron density in this structure is not chemically significant and is a legacy of crystal twinning. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions using a riding model. For **2**, all three carbons of propanesulfonate ligand (C(15), C(16), and C(17)) are disordered over two locations in a 1:1 ratio, and for **3** two carbons of ethyl groups (C(2) and C(4)) showed high thermal parameters and splitting in two locations in a 66:34 ratio.

Acknowledgment. This research was supported by grants from CSIR and DST (India). We thank IIT Delhi for providing a Senior Research Fellowship to A.P.S. and SAIF (Panjab University) Chandigarh for ^{119}Sn NMR data.

Supporting Information Available: Crystallographic data for the structural analysis (in CIF format) have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 676760 (for **1**), 676761 (for **2**), and 676762 (for **3**). Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44−1233−336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk). This material is available free of charge via the Internet at http://pubs.acs.org.

IC8002433

---

(14) *HKL DENZO* and *SCALEPACK* vl.96: Otwinowski, Z.; Minor, W. *Processing of X-ray Diffraction Data Collected in Oscillation Mode; Methods in Enzymology, Vol. 276: Macromolecular Crystallography*, Part A. ; Carter, C. W., Jr., Sweet, R. M. , Eds.; Academic Press: San Diego, CA, 1997; p 307.

(15) ltornare, A.; Burla, M. C.; Carnalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagan, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(16) Sheldrick, G. *SHELXL-97, Program for Crystal Structure Refinement*; Institüt für Anorganische Chemie der Universität: Tammanstrasse 4, D-3400 Göttingen, Germany.

(17) Sheldrick, G. M. *SHELXL 97−2: Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(18) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.