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Rangoli with Tin Drums: C−H- - -O Bond-Assisted Supramolecular Grids Involving Organostannoxane Clusters[†]

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*Summary: The reaction of n-BuSn(O)OH with RCOOH affords hexameric compounds [n-BuSn(O)OC(O)R]$_6$, R = $CH_2C_5H_4FeC_5H_5$ (**1**) and 2,4,6-$Me_3C_6H_2$ (**2**). The compounds **1** and **2** have drum-like structures with a prismane type Sn_6O_6 core. Both **1** and **2** form supramolecular 2D grid-like assemblies as a result of intermolecular C−H- - -O bonds between the ferrocenyl C−H and the carboxylate oxygen in the case of compound **1** and the C−H of the p-CH_3 group and the carboxylate oxygen in the case of compound **2**. In each case six stannoxane molecules surround a central hexameric stannoxane in a highly symmetric manner, although C−H- - -O bonds connect only four molecules together. The overall architecture of the supramolecular assembly is reminiscent of a highly repetitive decorative pattern.*

Introduction

There is a great deal of contemporary interest in the assembly of ordered supramolecular structures through crystal engineering because of the potential for realizing new types of functional solids.[1] For inorganic compounds the most attractive route for the realization of supramolecular assemblies has been through coordinate covalent bonds involving an appropriate difunctional ligand and a suitable metal ion.[2] These combinations have led to different types of structural motifs such as diamondoid, honeycomb grid, square grid, ladder, brick wall, or octahedral.[3] The concept and importance of weak hydrogen bonds particularly in organic and biological systems has been very successfully and forcefully elaborated in recent years, including its application in crystal engineering leading to the assembly of porous solids.[4] However, the application of these structural principles to inorganic and organometallic compounds has been limited to very few systems.[5] Among main group organometallic compounds organostannoxanes occupy a prominent place in view of the extensive structural diversity that they possess.[6]A large variety of cluster types such as drums, ladders, cubes, football cages, etc., are known.[7] There is also considerable interest in the preparation of oligomeric units of these clusters by covalent[8] or coordinative interactions.[9] However, utilization of covalent interactions *alone* may be a limiting factor for realizing larger aggregates of these clusters. In contrast, application of the principles of supramolecular chemistry is likely to be more profitable and can lead to the formation of well-defined polymeric arrays in the solid state. We have deliberately chosen organotin clusters that adopt *prismane* or *drum* type of structures to probe the formation of supramolecular grids. Herein we report two examples of such supramolecular assemblies with grid-like structures involving hexameric stannoxanes. Interestingly in both these instances the structure direction arises not out of coordinative interactions but from intermolecular C−H- - -O bonding. These represent the first examples of this type for this family of compounds.

Experimental Data

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 reaction. *n*-Butyltin hydroxide oxide (Aldrich) and 2,4,6-trimethylbenzoic acid (Fluka) were used as such without any further purification. Ferrocenylacetic acid was prepared according to the literature procedure.[10] Melting points were measured using a JSGW melting point apparatus and are uncorrected. Elemental

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[†] *Rangoli* is a repetitive decorative pattern drawn in front of many homes in India during festive seasons.

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Table 1. Crystal Data and Structure Refinement for 1 and 2

parameter	**1**	**2**
empirical formula	$C_{96}H_{120}Fe_6O_{18}Sn_6$	$C_{43}H_{61}Cl_3O_9Sn_3$
fw	2609.16	1184.34
temperature	293(2) K	213(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	*P*2(1)/*n*
unit cell dimens	$a = 23.7724(4)$ Å, $\alpha = 90°$	$a = 14.1807(4)$ Å, $\alpha = 90°$
	$b = 15.2901(10)$ Å, $\beta = 90°$	$b = 17.4637(5)$ Å, $\beta = 96.642(1)°$
	$c = 26.8663(5)$ Å, $\gamma = 90°$	$c = 20.7182(6)$ Å, $\gamma = 90°$
volume, *Z*	9765.4(7) Å^3, 4	5096.4(6) Å^3, 4
density (calcd)	1.775 Mg/m^3	1.544 Mg/m^3
abs coeff	2.432 mm^{-1}	1.663 mm^{-1}
F(000)	5184	2368
cryst size	$0.32 \times 0.06 \times 0.06$ mm^3	$0.46 \times 0.68 \times 0.76$ mm^3
θ range for data collection	2.17 to 25.98°	1.53 to 28.24°
limiting indices	$-29 \leq h \leq 29, -16 \leq k \leq 16, -33 \leq l \leq 33$	$-15 \leq h \leq 18, -22 \leq k \leq 16, -27 \leq l \leq 24$
no. of reflns collected	9305	31 218
no. of ind reflns	9305 ($R_{int} = 0.073$)	11 973 ($R_{int} = 0.1044$)
abs corr	empirical, R. A. Jacobson, MS Corp, 1998	none
refinement method	full-matrix least-squares of F^2	full-matrix least-squares of F^2
no. of data/restraints/params	9305/0/547	7271/0/524
goodness-of-fit on F^2	1.151	0.989
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0650, wR2 = 0.1314	R1 = 0.0473, wR2 = 0.0970
R indices (all data)	R1 = 0.1276, wR2 = 0.1648	R1 = 0.0991, wR2 = 0.1328
largest diff peak and hole	2.184 and −0.648 e Å^3	1.258 and −1.415 e Å^3

analyses were carried out using a Thermoquest CE instruments model EA/110 CHNS-O elemental analyzer. ^{1}H and ^{119}Sn NMR spectra were obtained on a JEOL-JNM LAMBDA 400 model spectrometer using $CDCl_3$ as the solvent. Tetramethylsilane (^{1}H) and tetramethyltin (^{119}Sn) were used as internal reference. Cyclic voltammetric and differential pulse voltammetric studies were performed on a PAR model 273A polarographic analyzer utilizing the three-electrode configuration of a Pt (Beckman) working electrode, a Pt mesh counter electrode, and a commercially available saturated calomel electrode as the reference electrode interfaced with the computer. Half-wave potentials were measured as the average of the cathodic and the anodic peak potentials. The voltammograms were recorded in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, and the potential was scanned from −1.5 to +1.5 V at various scan rates ranging from 25 to 200 mV s^{-1}.

Synthesis of [*n*-BuSn(O)OC(O)CH$_2$C$_5$H$_4$FeC$_5$H$_5$]$_6$, 1. A mixture of *n*-BuSn(O)OH (0.37 g, 1.8 mmol) and ferrocenyl acetic acid (0.43 g, 1.8 mmol) in benzene (100 mL) was heated under reflux for 6 h using a Dean−Stark apparatus to remove by azotropic distillation the water formed in the reaction. The reaction mixture was filtered and the solvent removed from the filtrate in vacuo to afford shiny brownish yellow flakes. Yield: 0.66 g (86.7%). Mp: 92 °C. Anal. Calcd for $C_{96}H_{120}O_{18}Sn_6Fe_6$: C, 44.19; H, 4.64. Found: C, 43.98; H, 4.89. ^{1}H NMR (400 MHz, $CDCl_3$): 0.76 (t, *J* = 7.1 Hz, 18H, $-CH_3$); 1.06−1.64 (m, 36H, butyl CH$_2$'s); 3.27 (s, 12H, CH$_2$); 4.00−4.35 (m, 54H, ferrocenyl). ^{119}Sn NMR (150 MHz, $CDCl_3$): −483.2 (s).

Synthesis of [*n*-BuSn(O)OC(O)C$_6$H$_2$-2,4,6-Me$_3$]$_6$, 2. Compound **2** was synthesized using the same procedure as given for **1**. The stoichiometries of the reactants used are as follows: *n*-BuSn(O)OH (0.42 g, 2.0 mmol) and 2,4,6-trimethylbenzoic acid (0.33 g, 2.0 mmol). Yield of **2**: 0.64 g (89.6%). Mp: 273 °C. A solvent-free sample (for analysis) was obtained by pumping the sample thoroughly for about 6−8 h. Anal. Calcd for $C_{84}H_{120}O_{18}Sn_6$: C, 47.36; H, 5.68. Found: C, 47.29; H, 5.6. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, 18H, $-CH_3$); 2.0−1.1 (m, 36H, butyl CH$_2$'s); 2.21 (s, 18H, aromatic methyl); 2.28 (s, 36H, aromatic methyl); 6.75 (s, 12H, aromatic). ^{119}Sn NMR (150 MHz, $CDCl_3$): δ −482.0 (s).

Scheme 1. Synthesis of 1 and 2

$$6n\text{-BuSn(O)OH} + 6\text{RC(O)OH} \xrightarrow[-6H_2O]{C_6H_6,\ \Delta} [n\text{-BuSn(O)OC(O)R}]_6$$

R = CH$_2$C$_5$H$_4$FeC$_5$H$_5$, **1**; R = 2,4,6-Me$_3$C$_6$H$_2$, **2**

X-ray Structure Determination of 1 and 2. By slow evaporation of the dichloromethane solution of **1** at room temperature, dark brown needle-shaped crystals suitable for single-crystal X-ray studies were obtained. A crystal of dimensions 0.32 × 0.06 × 0.06 mm was loaded on a Mercury CCD-AFC8S at 293(2) K, and the details pertaining to data collection and refinement are given in Table 1. The structure was solved by direct methods using the SHELXS-97 program and refined by full matrix least squares on F^2 using SHELXL-97.[11] Colorless diamond-shaped crystals of **2** were obtained by cooling a 1:1 solution of chloroform and *n*-hexane at 5 °C. A crystal of dimensions 0.46 × 0.68 × 0.76 mm was mounted on a Siemens SMART system, complete with a three-circle goniometer and CCD detector operating at −53 °C. The data sets were collected at 213(2) K. The other details pertaining to data collection and refinement for this are given Table 1. The structure was solved and refined using the SHELXTL program.[12] Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters.

Results and Discussion

The reaction of *n*-BuSn(O)OH with ferrocene acetic acid or 2,4,6-trimethylbenzoic acid afforded hexameric compounds [*n*-BuSn(O)OCOR)]$_6$ (R = CH$_2$C$_5$H$_4$FeC$_5$H$_5$ (**1**) and R = 2,4,6-Me$_3$C$_6$H$_2$ for (**2**)) in quantitative yields (Scheme 1). The structures of **1** and **2** resemble the well-known drum structures[6] and show a central hexameric stannoxane core (Sn$_6$O$_6$) that is supported by a periphery of six-ferrocene acetoxy or mesityl carboxylate bridges (Figure 1). A closer inspection of **1** and **2** reveals

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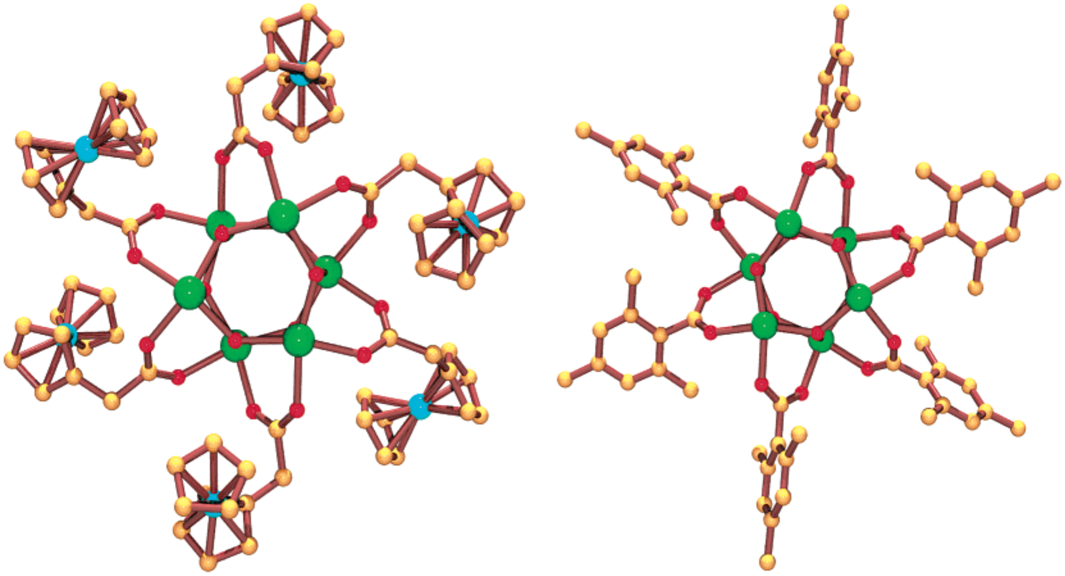

Figure 1. Pov-Ray structures of **1** and **2**. The *n*-butyl groups on tin are omitted for clarity. Red: oxygen; green: tin; yellow: carbon; blue: iron.

the presence of extensive *intermolecular* C−H- - -O interactions. Each stannoxane drum interacts with four neighboring molecules involving two *proton acceptor* and two *proton donor* type C−H- - -O bonding. Thus, two bridging carboxylate oxygens of every stannoxane interact with the protons of the ferrocenyl (C−H) or the mesityl (CH_3) substituents of two neighboring molecules (proton acceptor interaction). Similarly the converse interaction (proton donor) also occurs between each stannoxane drum and two other neighbors. The metric parameters observed for these hydrogen-bonding interactions are quite reasonable.[13] Thus while for **1** the H- - -O distance is 2.735(5) Å and the C−H- - -O angle is 152.30(84)°, for **2** these are 2.486(7) Å and 152.41(2)°. The cumulative effect of these interactions is the generation of a highly symmetric supramolecular grid-like structure (Figure 3), which is reminiscent of a decorative repetitive pattern. Each grid is represented by the presence of columns and rows of molecules. The inter-centroid distances are 15.456 and 14.725 Å for **1** and **2** in these nearly square grids. Within each column in **1** the stannoxane molecules are displaced by about 7.73 Å to facilitate the hydrogen bonding. In this respect the presence of the CH_2 spacer between the ferrocene unit and the stannoxane core is important, as this allows the ferrocene units to adjust to the needs of the hydrogen-bonding interactions.[14] In **2** the presence of the *p*-CH_3 obviates this structural necessity. Thus in **2** the translational displacement of molecules within the column is only about 3.68 Å. Second the C−H- - -O bond in **2** is also stronger, as indicated by the shorter H- - -O bond. Interestingly for the analogous compound [*n*-BuSn(O)OCO-C_6H_2-2,6-Me_2]$_6$ we could not detect intermolecular C−H- - -O bonding even up to the limit of 2.9 Å.[15] The absence of supramolecular grid formation in the latter reveals that the optimum centroid distances observed for **1** and **2** cannot be achieved in this molecule because it does not contain a favorably situated interacting group such as the *p*-CH_3 group or a flexible spacer such as the CH_2. Another interesting detail in the supramolecular formation of **1** and **2** is worth noting. In every row the adjacent molecules are tilted away from each other (while the diagonally related molecules have the same orientation). This *tilt* as measured by the dihedral angles of the Sn_3O_3 planes of adjacent molecules in a row is 14.8° for **1** and 52.8° for **2**. The

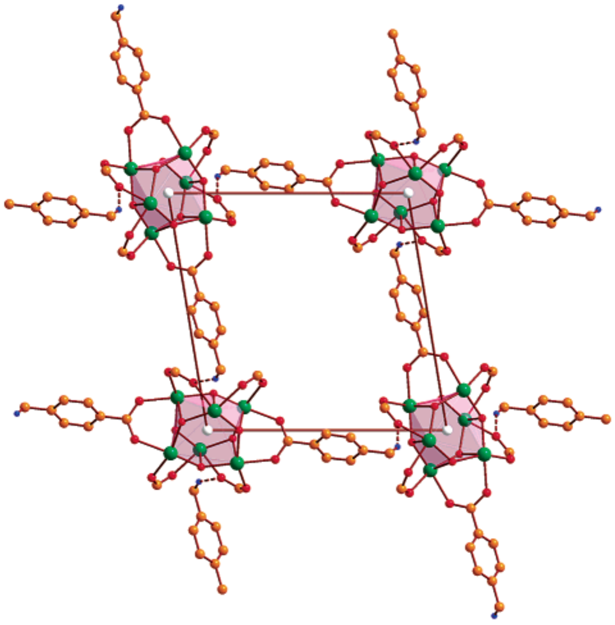

Figure 2. Intermolecular proton-acceptor and proton-donor interactions in **2** involving the carboxylate oxygens and the *p*-CH_3 group of the mesityl groups. Only four molecules are shown for illustration.

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[13] Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290.

[14] In [*n*-BuSn(O)OCOC$_5H_4FeC_5H_5$]$_6$, which does not have the CH_2 spacer group as **1**, the formation of a regular square grid is not noticed, although C−H- - -O interactions between the substituted ferrocenyl C−H and carboxylate oxygens is observed (C−H 1.000(12), O- - -H 2.741(16), C- - -O 3.647(25) Å, C−H- - -O 150.71(46)°, and the symmetry is 1−*x*, 2−*y*, 1−*z*; C−H 1.000(12), O- - -H 2.765(17), C- - -O 3.681(27) Å, C−H- - -O 152.40(37)°, and the symmetry is 1−*x*, 1−*y*, 1−*z*). Further, there is considerable tilt among adjacent molecules in a row as indicated by the dihedral angles between the corresponding Sn_3O_3 planes, viz., 93.76°.

[15] Chandrasekhar, V.; Nagendran, S.; Steiner, A.; Zacchini, S. Unpublished results.

[16] Chandrasekhar, V.; Nagendran, S.; Bansal, S.; Kozee, M. A.; Powell, D. R. *Angew. Chem., Int. Ed.* **2000**, *39*, 1833.

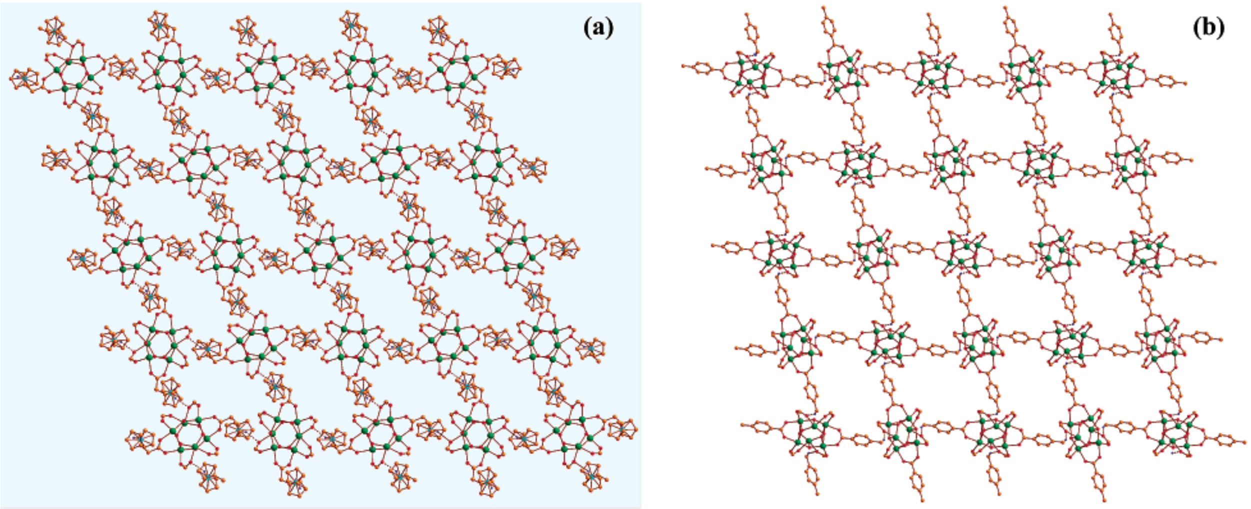

Figure 3. Views of the supramolecular grids of (a) **1** and (b) **2** stabilized by C−H- - -O bonds. The metric parameters for **1**: C−H 0.930(13), O−H 2.735(5), C−O 3.584(14) Å and C−H- - -O 152.30(84)°. The symmetry is $1-x$, $0.5+y$, $0.5-z$. The metric parameters for **2**: C−H 0.970(1), O−H 2.486(7), C−O 3.375(6) Å and C−H- - -O 152.41(2)°. The symmetry is $-0.5+x$, $1.5-y$, $-0.5+z$. The *n*-butyl groups on tin and the noninteracting $CH_2C_5H_4FeC_5H_5$ or mesityl groups have been removed for clarity. Blue: hydrogen.

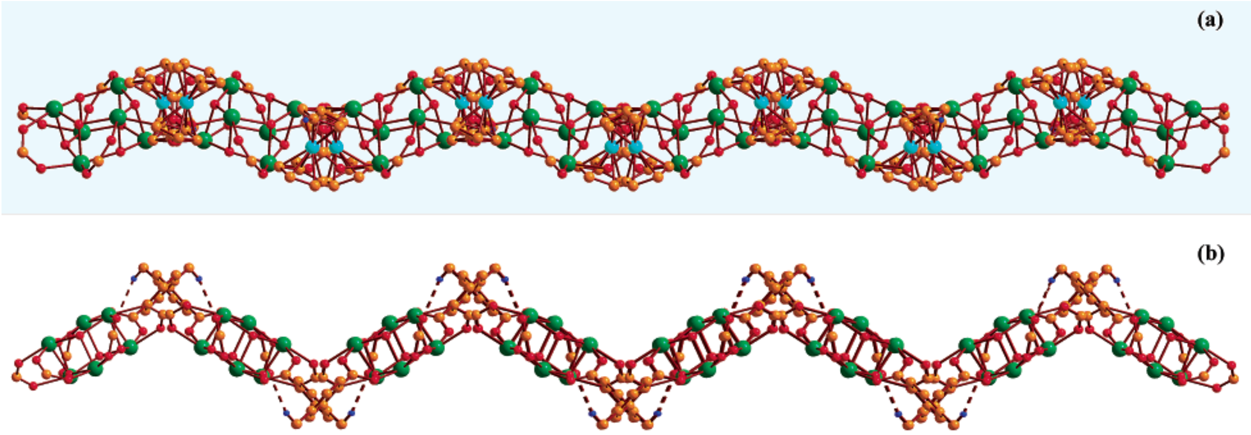

Figure 4. Zigzag tape like structures of (a) **1** and (b) **2** arising out of a tilt between adjacent molecules in the rows of the supramolecular grids. In **1** the tilt is 14.8°, and in **2** the tilt is 52.8°.

consequence of such a *tilt* is a zigzag tape-like arrangement of molecules in each row (Figure 4). In addition to the interesting structural array that **1** and **2** adopt, **1** is also of interest from an electrochemical point of view. Cyclic voltammetric studies on compound **1** show a quasi-reversible peak with an $E_{1/2}$ value of 0.50 V (vs SCE). This is suggestive of the fact that all six ferrocene units are oxidized at the same potential. In addition the voltammogram is reproduced even after several cycles, indicating that the cluster is robust and does not decompose upon oxidation. This is also supported by the nonvariance of the oxidation potential upon performing the cyclic voltammetric experiment in a wide scan range (25−200 mV). In this respect the behavior of **1** is reminiscent of $[n\text{-BuSn(O)OC(O)C}_5\text{H}_4\text{FeC}_5\text{H}_5]_6$.[16]

In conclusion the presence of multiply interacting structural units such as C−H and C−O can lead to the formation of interesting supramolecular solids in hexameric organostannoxanes. Modulation of the architecture of these assemblies appears to be possible by varying the nature of the carboxylic acid and by changing the type of organostannoxane. The delineation of this hypothesis is being currently pursued.

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Supporting Information Available: Comparable Rangoli diagrams for the table of contents picture and for Figure 3 (Figures S1 and S2), central stannoxane core of **1** and **2** (Figures S3 and S4), tables giving atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters for **1** and **2** (Tables S1 to S10). These materials are available free of charge via the Internet at http://pubs.acs.org.

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