

Trapping a Discrete $[R_2Sn(\mu-OH)SnR_2]$ Motif. Synthesis and Structural Characterization of $\{[(Phen)(NO_3)Me_2Sn(\mu-OH)SnMe_2(NO_3)(Phen)]\{NO_3\}\}$ (Phen = 1,10-Phenanthroline)

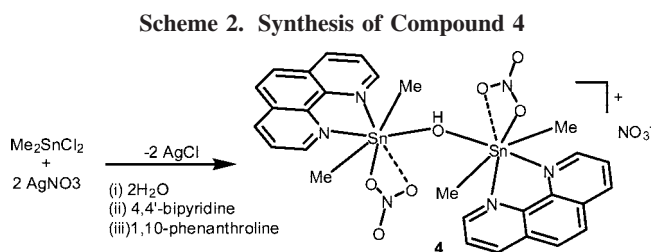
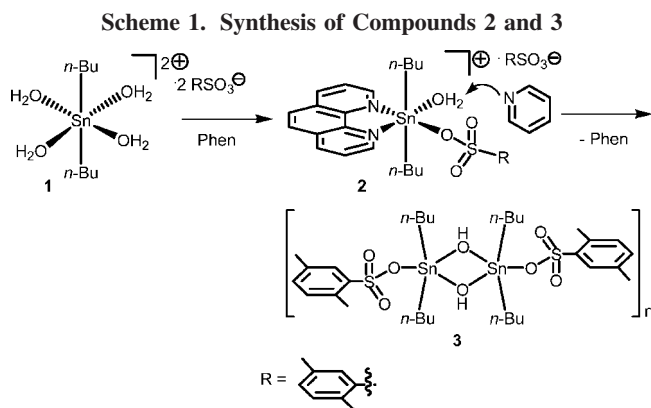
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The reaction of Me_2SnCl_2 with 2 equiv of silver nitrate in methanol followed by treatment with 2 equiv of water and 1 equiv of 4,4'-bipyridine in presence of 1,10-phenanthroline afforded the hydrolyzed product $[(NO_3)(Phen)Me_2Sn(\mu-OH)SnMe_2(Phen)(NO_3)]^+ [NO_3]^-$ (**4**), containing a $[R_2Sn(\mu-OH)SnR_2]$ unit where two diorganotin units are bridged by an unsupported hydroxide ligand.

Many complex and diverse structural forms of organostannoxane assemblies have been discovered in recent years.^{1–3} Many of these have been prepared by the reactions of organotin oxides, hydroxides, and oxide hydroxides and their condensation products with protic acids such as carboxylic acids, phosphonic acids, sulfonic acids, and phosphonic acids.^{1–3} The Sn–O frameworks of the organostannoxanes, thus assembled, are built from the bridging coordination action of oxide and/or hydroxide ligands. Among triorganotin compounds, motifs containing $[Sn_2(\mu-O)]$ and $[Sn_2(\mu-OH)]$ have been structurally characterized. An example of the latter is $[(C_2H_5)_3Sn(\mu-OH)Sn(C_2H_5)_3][B(C_6H_5)_4]$, which is a hydrolysis product of a triorganotin cation.⁴ Among diorganotin compounds the most common structural building block is the four-membered $[Sn_2O_2]$ ring comprising a hydroxide or an oxide ligand. The isolation and identification of discrete diorganotin compounds that *only* contain the acyclic $[Sn_2(\mu-OH)]$ unit is still elusive. The coordination polymer $\{[(Me_2Sn)_2(OH)_3]\{ClO_4\}\}_n$ has been characterized earlier, containing both di- and monohydroxo bridging motifs, viz. $[Sn_2(\mu-OH)_2]$ and $[Sn_2(\mu-OH)]$, alternating with each other.⁵ With a view to developing strategies for the isolation of $[R_2Sn(\mu-OH)SnR_2]$ motifs among molecular diorganotin compounds, we have recently embarked on a *direct hydrolysis methodology* of organotin cations. Although we were able to isolate $[n-Bu_2Sn(OH_2)(Phen)(2,5-Me_2C_6H_3SO_3)]^+ [2,5-Me_2C_6H_3SO_3]^-$ (**2**; Phen = 1,10-phenanthroline), further hydrolysis of this compound, aided by a mild base such as pyridine, afforded a coordination polymer (**3**), containing the $[Sn_2(\mu-OH)_2]$ motif (Scheme 1).⁶ We reasoned that replacement of the sulfonate by the nitrate group would enhance the isolation of



the rare $[R_2Sn(\mu-OH)SnR_2]$ motif because of the chelating coordination mode of the nitrate ligand. Accordingly, herein we report the isolation and structural characterization of the discrete dimeric monocationic complex $\{[(Phen)(NO_3)Me_2Sn(\mu-OH)SnMe_2(NO_3)(Phen)]\{NO_3\}\}$ (**4**), where the two tin centers are linked by an unsupported hydroxide bridging ligand.

Results and Discussion

Dimethyltin dichloride was reacted with 2 equiv of silver nitrate in methanol in the presence of 2 equiv of water. We were unable to isolate and characterize the product formed in the above reaction. We proceeded to treat the above with 1 equiv of 1,10-phenanthroline in the presence of 1 equiv of 4,4'-bipyridine, which afforded a pinkish white solid. Recrystallization of the latter from acetonitrile afforded **4** (Scheme 2). The rationale for the choice of 4,4'-bipyridine was that it would bring about a template effect whereby two tin centers are held in proximity so that the isolation of a hydroxide-bridged dimer

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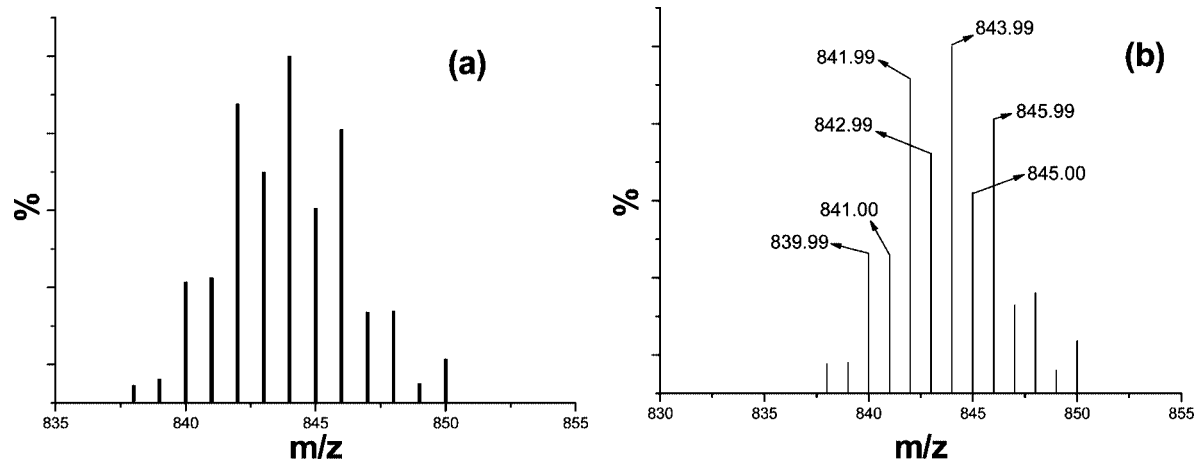


Figure 1. ESI-MS spectra of $[(C_{12}H_8N_2)_2(CH_3)_4Sn_2(OH)(NO_3)_2 + CH_3CH_2NH_2]^+$: (a) simulated; (b) experimental.

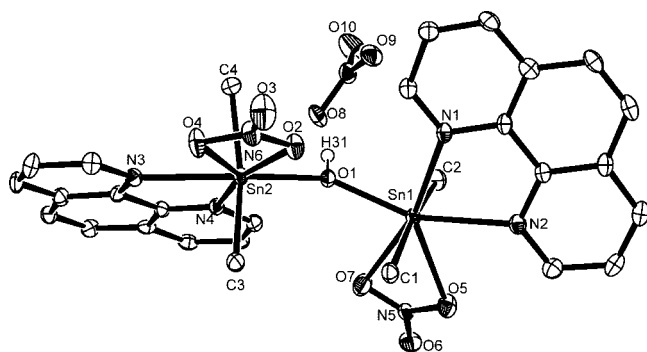


Figure 2. ORTEP representation of compound **4**, with ellipsoids at the 50% probability level.

Table 1. Selected Bond Parameters of **4**

Bond Distances (Å)			
Sn(1)–O(7)	2.171(2)	Sn(2)–C(3)	2.101(3)
Sn(1)–O(5)	2.132(2)	Sn(2)–C(4)	2.121(3)
Sn(1)–N(2)	2.094(3)	Sn(2)–N(3)	2.474(3)
Sn(1)–N(1)	2.108(3)	Sn(2)–N(4)	2.344(3)
Sn(1)–C(2)	2.344(3)	Sn(2)–O(2)	2.449(2)
Sn(1)–C(1)	2.457(3)	Sn(2)–O(4)	2.719(3)
Sn(2)–O(1)	2.473(2)	O(1)–H(31)	0.78(4)
Sn(1)–O(1)	2.584(2)		
Bond Angles (deg)			
Sn(2)–O(1)–Sn(1)	147.07(13)	C(3)–Sn(2)–C(4)	164.56(14)
Sn(2)–O(1)–H(31)	103(3)	C(3)–Sn(2)–O(1)	98.69(11)
Sn(1)–O(1)–H(31)	110(3)	C(4)–Sn(2)–O(1)	93.85(11)
C(1)–Sn(1)–C(2)	168.18(13)	C(3)–Sn(2)–O(4)	92.88(11)
C(1)–Sn(1)–O(1)	91.93(11)	C(4)–Sn(2)–N(4)	96.91(11)
C(2)–Sn(1)–O(1)	93.69(11)	O(1)–Sn(2)–N(4)	86.28(9)
C(1)–Sn(1)–N(1)	100.64(11)	C(3)–Sn(2)–O(2)	87.33(11)
C(2)–Sn(1)–N(1)	90.05(11)	C(4)–Sn(2)–O(2)	86.20(11)
O(1)–Sn(1)–N(1)	86.82(9)	O(1)–Sn(2)–O(2)	79.19(8)
C(1)–Sn(1)–N(2)	91.35(11)	N(4)–Sn(2)–O(2)	165.32(8)
C(2)–Sn(1)–N(2)	87.70(11)	C(3)–Sn(2)–N(3)	88.89(11)
O(1)–Sn(1)–N(2)	156.15(9)	C(4)–Sn(2)–N(3)	83.56(11)
N(1)–Sn(1)–N(2)	69.37(9)	O(1)–Sn(2)–N(3)	154.46(9)
O(1)–Sn(1)–O(5)	129.77(9)	N(4)–Sn(2)–N(3)	68.92(9)
N(1)–Sn(1)–O(5)	143.24(8)	O(2)–Sn(2)–N(3)	125.75(8)
N(2)–Sn(1)–O(5)	74.08(8)		

compound would become possible. This anticipation was realized in the isolation of **4**. $^{119}Sn\{^1H\}$ NMR of **4** showed a single peak at -387.6 ppm, which is suggestive of heptacoordination.⁷ The ESI-MS spectrum of this compound in the positive ion mode shows a peak at m/z 843.99 (Figure 1b) corresponding to the species $[(C_{12}H_8N_2)_2(CH_3)_4Sn_2(OH)(NO_3)_2$

Table 2. Hydrogen-Bonding Parameters of **4**

D–H–A	D–H (Å)	H–A (Å)	D–A (Å)	D–H–A (deg)	symmetry
O1–H31–O8	0.78(4)	1.944(4)	2.713(3)	166.12(43)	x, y, z
C27–H27–O8	0.930(4)	2.613(3)	3.214(5)	122.83(22)	$1 - x, -y, -z$
C24–H24–O9	0.930(4)	2.645(2)	3.343(4)	132.36(23)	$x, y, 1 + z$
C24–H24–O10	0.930(4)	2.514(4)	3.439(5)	173.11(23)	$x, y, -1 + z$

$+ CH_3CH_2NH_2]^+$, underscoring the stability of the dinuclear species in solution. The presence of $CH_3CH_2NH_2$ in the species detected by ESI-MS is due to the reduction of the solvate acetonitrile under positive ion mode conditions.⁸ The molecular structure of **4** was confirmed by a single crystal X-ray analysis.

The molecular structure of **4** (Figure 2) shows the presence of two crystallographically independent tin atoms which are bridged to each other solely by a μ -OH ligand. The Sn1–O1–Sn2 bond angle found for this motif is $147.05(11)^\circ$ (Table 1), which is larger than that found in $[(Me_2Sn)_2(OH)_3\{ClO_4\}]_n$ ($135.5(2)^\circ$).⁵ In compounds containing the four-membered-ring $[Sn_2(\mu-OH)_2]$ unit, the Sn–O–Sn angles are far more acute.⁹ For example, in **3**, the corresponding bond angle is $117.51(11)^\circ$.⁶

Each tin atom in **4** is heptacoordinate (2N, 2C, 3O) in an approximately pentagonal bipyramidal geometry. The two methyl groups occupy the apical positions. The bond angles C1–Sn1–C2 and C3–Sn2–C4 are $168.18(13)$ and $164.56(14)^\circ$, respectively (Table 1). The equatorial plane around each tin is occupied by a chelating phenanthroline ligand, a chelating anisobidentate nitrate ligand, and the oxygen atom of the hydroxide bridging ligand.

The Sn–O bond distances involving the bridging hydroxide ligand (Sn1–O1, 2.171(2) Å; Sn2–O1, 2.132(2) Å) (Table 1) are comparable to those found in $[(n-Bu_2Sn(\mu-OH)(O_3SC_6H_3-2,5-Me_2))_2]_n$ ⁶ and $[(CF_3SO_3)(H_2O)n-Bu_2Sn(OH)]_2$.¹⁰ These latter compounds contain doubly bridged four-membered $[Sn_2(OH)_2]_2$ motifs. In addition to the chelating nitrate, **4** also contains one nitrate group as a counteranion which is strongly hydrogen-bonded to the hydroxide ligand (Figure 2).

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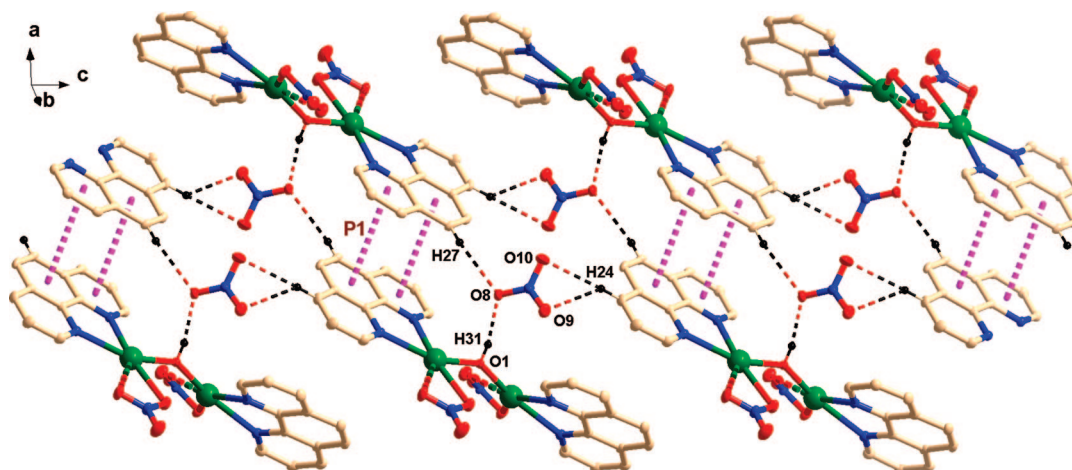


Figure 3. One-dimensional polymer chain of the three-dimensional supramolecular structure of **4** mediated by O–H–O and C–H–O hydrogen bonding and π – π interactions. P1 denotes N3, N4, C17–C28; $\pi_{\text{cent}}-\pi_{\text{cent}} = 3.84(2)$ Å.

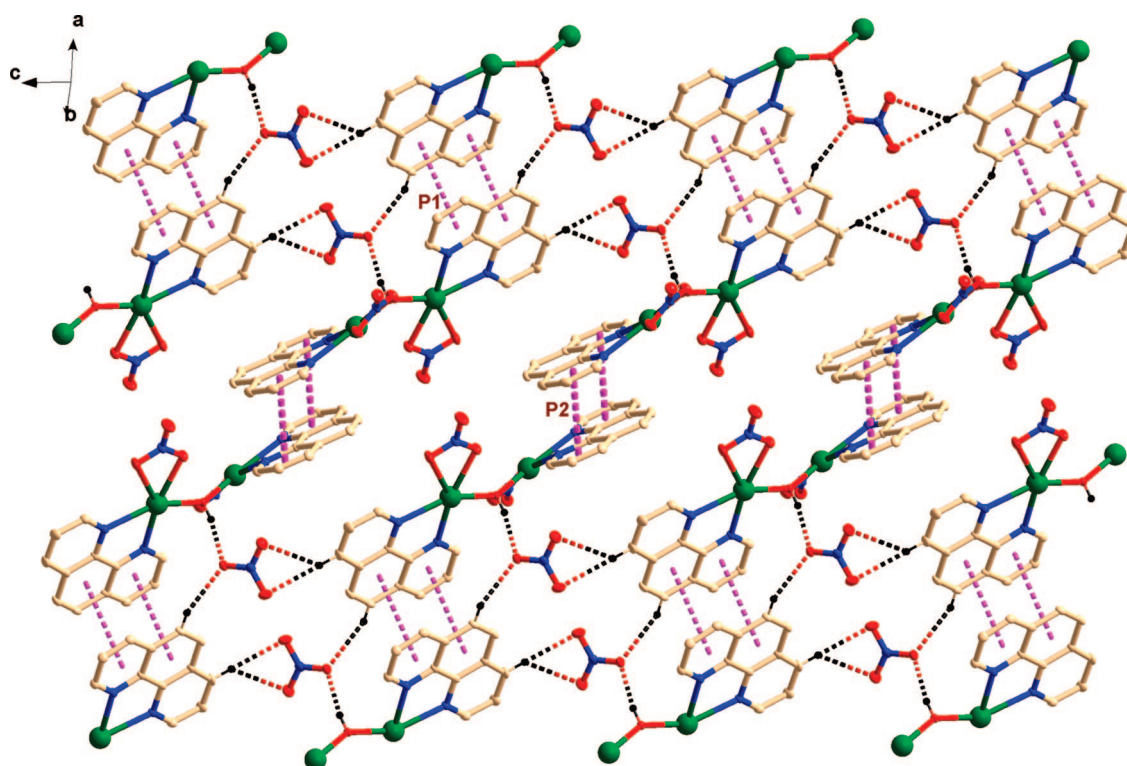


Figure 4. Two-dimensional assembly of the three-dimensional supramolecular structure of **4** assisted by π – π interactions. P2 denotes N1, N2, C5–C16; $\pi_{\text{cent}}-\pi_{\text{cent}} = 3.74(2)$ Å.

The crystal structure of **4** reveals the presence of a three-dimensional supramolecular assembly which is built with a combination of O–H \cdots O, C–H \cdots O, $\pi\cdots\pi$, and O $\cdots\pi$ interactions. Hydrogen-bonding parameters are given in Table 2. The formation of the supramolecular assembly is initiated by strong O–H \cdots O and C–H \cdots O bonds between two cationic units and the nitrate counteranions. Such dimers are associated by $\pi\cdots\pi$ interactions (labeled P1 in Figure 3) between phenanthroline groups (N3, N4, C17–C28; $\pi_{\text{cent}}\cdots\pi_{\text{cent}} = 3.84(2)$ Å). Adjacent dimers are associated by C–H \cdots O interactions involving a hydrogen atom of the phenanthroline ligand and an oxygen atom of the nitrate counteranion to form a one-dimensional chain (Figure 3). Two such chains interact with each other as a result of another $\pi\cdots\pi$ interaction (labeled P2 in Figure 4) involving the other phenanthroline unit (N1, N2, C5–C16; $\pi_{\text{cent}}-\pi_{\text{cent}} = 3.74(2)$ Å) of the molecule to form

a two-dimensional sheet (Figure 4). These sheets are taken into the third dimension with the help of bifurcated O– π interactions involving a free oxygen atom of one of the coordinating nitrate groups (O6) of one sheet with the phenanthroline centroids of two different molecules of an adjacent chain of another sheet (Figure 5).

In conclusion, we have successfully applied the strategy of hydrolysis of organotin cations to isolate the molecular species **4**, where two diorganotin units are bridged by an unsupported hydroxide ligand. The formation of **4** can be rationalized as follows. On the basis of our previous studies, it is reasonable to postulate the formation of $[Me_2Sn(Phen)(NO_3)(H_2O)][NO_3]$ as being similar to that of **2**, which was structurally characterized.⁶ Deprotonation of the coordinated water leads to a hydroxide ligand on one molecule which can displace the water molecule on another to generate a Sn–O–Sn linkage through

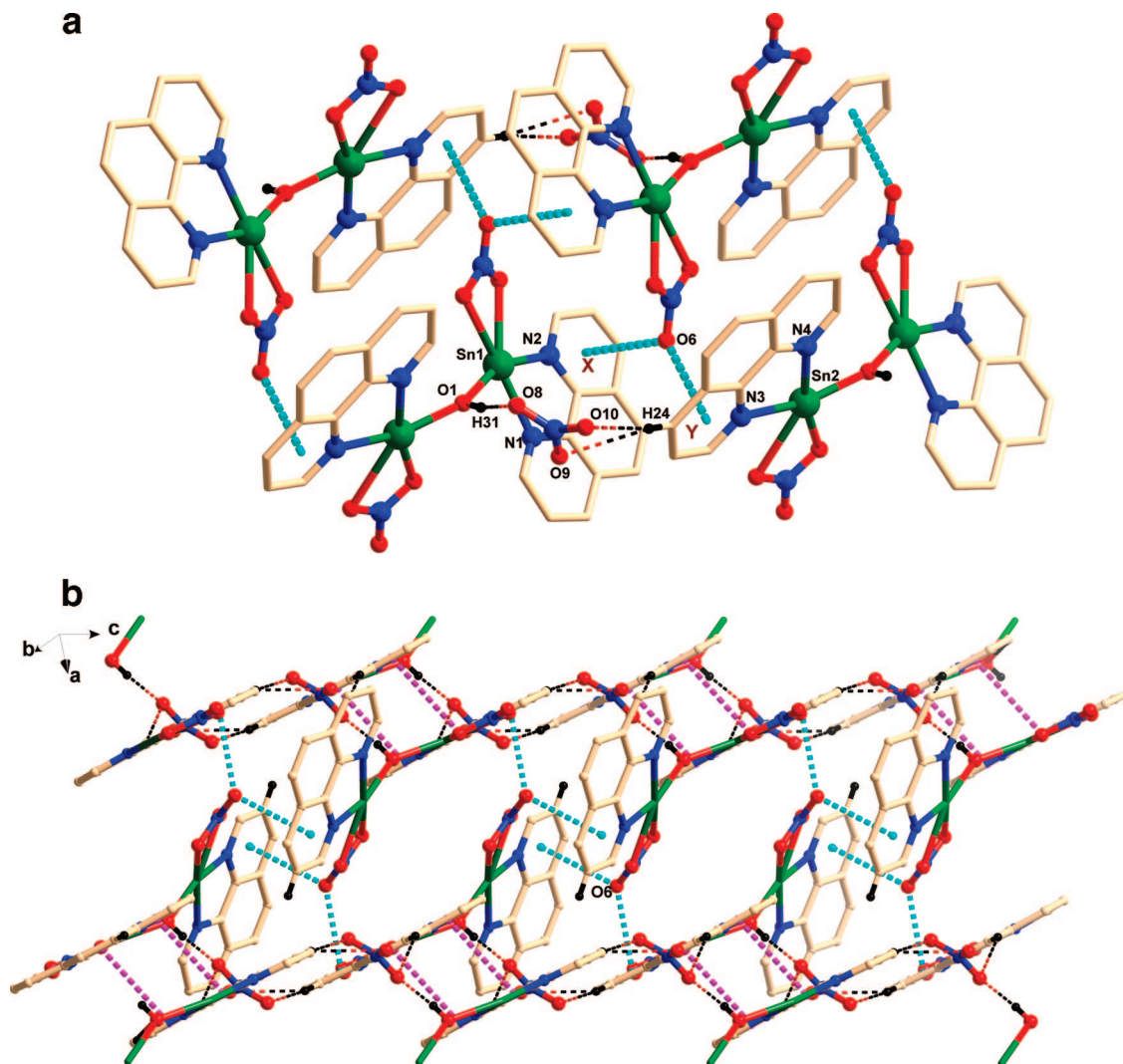


Figure 5. (a) O- π interactions bringing together four molecules of adjacent layers. The parameters for O- π interactions are as follows: $O6-\pi_{\text{cent}_X} = 3.25(2)$ Å (X denotes N2, C5-C9); $O6-\pi_{\text{cent}_Y} = 3.12(2)$ Å (Y denotes N3, C22-C26). (b) Three-dimensional supramolecular structure of **4**. O- π interactions are shown which take the structure into the third dimension.

μ -OH. Formation of a double bridge is prevented because of the presence of two chelating ligands on tin. The absence of such chelating ligands leads to the formation of the doubly bridged compound $[\text{Me}_2\text{Sn}(\text{OH})(\text{NO}_3)]_2$, as reported previously.¹¹

Experimental Section

General Remarks. Solvents were distilled prior to use according to standard procedures. Me_2SnCl_2 , 1,10-phenanthroline (Phen), and 4,4'-bipyridine (Aldrich) and AgNO_3 (sd-fine, India) were purchased and used as such without any further purification. 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. Infrared spectra were recorded as KBr pellets on a FT-IR Bruker-Vector model. ^1H and ^{119}Sn NMR spectra were obtained on a JEOL-JNM LAMBDA 400 model spectrometer using CDCl_3 or CD_3CN solutions with chemical shifts referenced to tetramethylsilane (for ^1H NMR) and tetramethyltin (for ^{119}Sn NMR), respectively. ^{119}Sn NMR spectra were recorded under broadband-decoupled conditions. ESI-MS spectra were recorded on a

MICROMASS QUATTRO II triple-quadrupole mass spectrometer. The ionization mechanism used was electrospray in positive ion full scan mode using acetonitrile as solvent and nitrogen gas for desolvation. The capillary voltage was maintained at 3 kV, and the cone voltage was kept at 30 V.

Synthesis of 4. A mixture of Me_2SnCl_2 (0.110 g 0.5 mmol) and AgNO_3 (0.170 g, 1mmol) was stirred in 40 mL of dry methanol for 15 min. The white precipitate of AgCl was removed by filtration, and to the filtrate was added water (18×10^{-3} mL, 1 mmol) and 4,4'-bipyridine (0.080 g, 0.5 mmol). The reaction mixture was stirred for 5 min, followed by addition of 1,10-phenanthroline (0.090 g, 0.5 mmol). The reaction mixture was stirred for 20 h and then evaporated in vacuo to give a pinkish white solid (**4**). The solid was washed with 2 mL of dichloromethane. Single crystals were obtained from slow evaporation of a solution of **4** in acetonitrile. Yield: 0.11 g (49%, isolated crystal). Mp: 182 °C. Anal. Calcd for $\text{C}_{28}\text{H}_{29}\text{O}_{10}\text{N}_7\text{Sn}_2$ (860.96 g): C, 39.06, H, 3.40, N, 11.39. Found: C, 39.57, H, 3.81, N, 10.99. IR (KBr, cm^{-1}): 3439 (m,b, $\nu(\text{OH})$ asym str), 1493 (m, $\nu(\text{NO}_3)$ asym str), 1288 (m, $\nu(\text{NO}_3)$ sym str), 1429 (s, $\nu(\text{NO}_3)$ sym str), 1384 (s, $\nu(\text{NO}_3(\text{anionic}))$), 1030 (s, $\nu(\text{NO}_3(\text{anionic}))$), 994 (w, $\delta(\text{NO}_2)$), 804 (m, $\delta(\text{NO}_2)$), 3064, 2922, and 2854 (m, $\nu(\text{CH})$). ^1H NMR (400 MHz, CD_3CN): δ 1.075–1.088 (6H, SnCH_3), 7.74 (m, 2H, Phen CH), 8.14 (m, 2H, Phen CH), 8.71 (d, 2H, Phen CH), 9.47 (d, 2H, Phen CH). ^{119}Sn NMR (150 MHz, $\text{CDCl}_3/\text{CH}_3\text{OH}$): δ -387.61 (s). ESI-MS: $[(\text{NO}_3)_2(\text{C}_{12}$ -

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$H_8N_2)_2(CH_3)_4Sn_2(OH) + CH_3CH_2NH_2]^+$ 843.99, $[(CH_3)_2Sn(OH)_2(OH)]^+$ 203.05, $[(C_{12}H_8N_2)(CH_3)_2Sn(OH)(OH_2)]^+$ 364.97 $[(C_{12}H_8N_2)(CH_3)_2Sn(OH)_2(OH)]^+$ 383.12, $[(C_{12}H_8N_2)(CH_3)_2Sn(NO_3)]^+$ 391.99, $[(C_{12}H_8N_2) + 1]^+$ 181.05.

X-ray Crystallographic Study. The crystal data for compound **4** was collected on a Bruker SMART APEX CCD diffractometer. The SMART software package (version 5.628) was used for collecting data frames, the SAINT software package (version 6.45) for integration of the intensity and scaling, and SADABS for absorption correction. Details pertaining to the data collection and refinement of the crystal are as follows for **4**: size $0.2 \times 0.1 \times 0.1$ mm³; triclinic; $P\bar{1}$; $a = 11.0753(7)$ Å, $b = 12.0391(8)$ Å, $c = 12.0906(8)$ Å; $\alpha = 90.121(10)^\circ$, $\beta = 98.3850(10)^\circ$, $\gamma = 101.5990(10)^\circ$; $V = 1562.50(18)$ Å³; $T = 273(2)$ K; $Z = 2$; $D_{\text{calcd}} = 1.831$ Mg m⁻³; θ range $4.14 - 25.03^\circ$; 8060 reflections collected; 5403 independent reflections ($R_{\text{int}} = 0.0144$); $R1 = 0.0242$, $wR2 = 0.0624$ (for $I > 2\sigma(I)$); $R1 = 0.0258$, $wR2 = 0.0665$ (for all data); $GOF = 1.086$; largest difference peak and hole 0.600 and -0.472 e Å⁻³. The structure was solved and refined by full-matrix least squares on F^2 using the SHELXTL software package.¹² Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom of the hydroxyl group was located from the difference map, and its position was refined isotropically.

(12) Sheldrick, G. M., SHELXTL version 6.14; Bruker AXS Inc., Madison, WI, 2003.

All other hydrogen atoms were included in idealized positions, and their positions were refined isotropically using a riding model. CCDC 679216 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax (internat.) +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk). Figures 2–5 and their bonding parameters were obtained from the DIAMOND 3.1f software package.¹³

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Supporting Information Available: A figure giving the ORTEP diagram of compound **4** and a CIF file giving crystal data for compound **4** (CCDC 679216). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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