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Synthesis, spectroscopic and structural aspects of some tetraorganodistannoxanes with internally functionalized oxime. 2. Crystal and molecular structure of $[\{Me_2Sn(ON{=}C(Me)C_5H_4N)\}_2O\}]_2 \cdot 2[2\text{-}NC_5H_4(Me)C{=}NOH]$

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Abstract

The title compound $[\{Me_2Sn(ON{=}C(Me)C_5H_4N)\}_2O\}]_2 \cdot 2[2\text{-}NC_5H_4(Me)C{=}NOH]$ was obtained during the reaction of Me_2SnCl_2 with the sodium salt of the ligand in 1:2 molar ratio in a refluxing methanol–benzene mixture. X-ray diffraction analysis of the compound reveals that it is the first tetraorganodistannoxane structural motif in which two molecules of free oxime are connected to the stannoxane framework and the two Sn–O distances of the four-membered planar Sn_2O_2 ring are identical.

Keywords: Tetraorganodistannoxanes; Internally functionalized oxime; Crystal structures

1. Introduction

In our earlier studies on tetra-organodistannoxanes $[\{R_2SnL)_2O\}]_2$, it was shown that subtle variations in the R group on tin or in the ligand moiety, usually result in different structural patterns in the solid state [1,2]. In continuation of our work on these compounds, we report on the structure of $[\{Me_2Sn(ON{=}C(Me)C_5H_4N)\}_2O\}]_2 \cdot 2[2\text{-}NC_5H_4(Me)C{=}NOH]$.

2. Results and discussion

When the preparation of $[Me_2Sn\{ONC(Me)Py\}_2]$ was attempted by the reaction of Me_2SnCl_2 with the sodium salt of the ligand in 1:2 molar ratio in refluxing benzene–methanol followed by recrystallization from benzene–hexane, $[\{Me_2Sn(ON{=}C(Me)C_5H_4N)\}_2O\}]_2 \cdot 2[2\text{-}NC_5H_4(Me)C{=}NOH]$ was isolated. This hydrolysis product is essentially a tetraorganodistannoxane dimer in which two molecules of free oxime are hydrogen bonded to the ring nitrogen of the dangling oximate group.

Not surprisingly, the NMR (^1H, ^{13}C, ^{119}Sn) and IR data of this complex are similar to those of $[\{Me_2Sn(ON{=}C(Me)C_5H_4N)\}_2O\}]_2$ and the free ligand, so they do not provide unambiguous characterization. However, the ^1H NMR chemical shift for the OH proton is deshielded by ~0.5 ppm from the free oxime and the melting point differs.

The molecular structure has been unambiguously established by single crystal X-ray diffraction analysis. Selected bond lengths and angles are given in Table 2 and an ORTEP diagram is shown in Fig. 1. A comparison of this result with those reported earlier for stannoxanes derived from 2-acetyl pyridyl oxime [1] as well as other stannoxanes [2–13] affords interesting structural varia-

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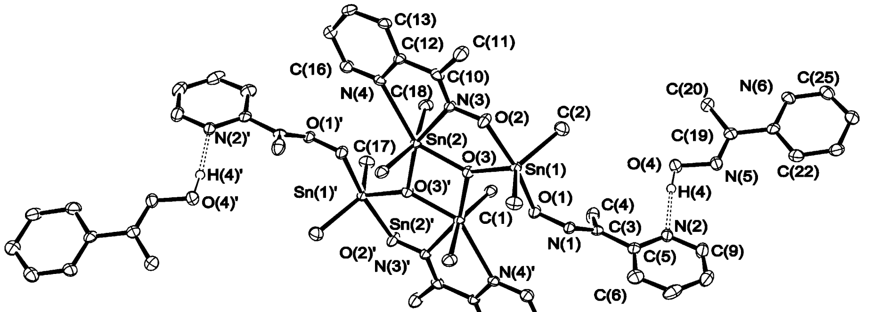

Fig. 1. ORTEP plot of the molecule $[\{Me_2Sn(ON{=}C(Me)C_5H_4N)\}_2O\}]_2 \cdot 2[2\text{-}NC_5H_4(Me)C{=}NOH]$. The atoms are drawn with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

tions. The basic structure is very similar to that of the corresponding $[\{Et_2Sn(ON{=}C(Me)C_5H_4N)\}_2O\}]$ derivative, but with the addition of two free oximes that are hydrogen bonded to the ring nitrogen atom of the oximate anion bonded to the exocyclic tin atom. This is the first structural motif in which two free oximes are connected to the stannoxanes framework in this manner. The two Sn–O distances of the four-membered planar Sn_2O_2 ring are identical (2.039 Å). This contrasts with the majority of such structures of tetraorganodistannoxanes, which usually contain different Sn–O bond distances in the planar Sn_2O_2 ring [2]. Each of the exocyclic tin atoms is bonded to two oximate anions and the oxime nitrogen of one of the anions is coordinated to the endocyclic tin atoms. The interesting feature of this structure is that the ring nitrogen of the same ligand moiety, which was not taking part in coordination, is now coordinating to the endocyclic tin atom [1]. The Sn(2)–N(4) bond distance (2.513(2) Å) is considerably shorter than the sum of the van der Waals radii of Sn and N atoms (3.75 Å) [11,12], but is longer than the Sn(2)–N(3) bond distance (2.265(3) Å), indicating weaker coordination through the ring N atom in comparison to the oxime nitrogen of the ligand with the endocyclic tin center.

The geometry around each endocyclic tin atom is distorted octahedral, with the methyl groups in *trans* positions [C(17)–Sn(2)–C(18); 158.11(12)°]. The exocyclic tin atoms are in distorted trigonal bipyramidal environments with the methyl groups in equatorial positions (130.89(13)°). The axial Sn(1)–O(1) and Sn(1)–O(2) bond distances are 1.994(2) and 2.046(2) Å, respectively, which are shorter than the sum of the van der Waals radii of Sn and O atoms (3.70 Å) [11]. The oximate ligand bond distances are only slightly changed on complexation [1].

It is interesting to compare the degree of hydrogen bonding in the complex with that in the free acid. In the solid state structure of the latter, the O···N distance is 2.762(3) with O–H 1.02(2) and H···N 1.75(3) Å and an O–H—N angle of 171(3)°. The hydrogen bonding is weaker in the complex where O(4)···N(2) is 2.906(4) with O(4)–H(4) 1.01(5) and H(4)···N(2) 1.903(4) Å, and with an O(4)–H(4)—N(2) angle of 173(3)°. Consistent with the above observation, the hydroxo band appeared at 3360 cm^{-1} in the IR spectra of the complex as compared to that in the free acid (3300 cm^{-1}).

3. Experimental

All the experimental conditions and spectroscopic techniques are the same as described earlier [1].

3.1. Preparation of $[\{Me_2Sn(ON{=}C(Me)C_5H_4N)\}_2O\}]_2 \cdot 2[2\text{-}NC_5H_4(Me)C{=}NOH]$

2-Acetylpyridyloxime (1.017 g, 7.47 mmol) was added to a MeOH solution of sodium (172 mg, 7.48 mmol) and heated at reflux for 2.5 h. To this solution was added Me_2SnCl_2 (829 mg, 3.77 mmol) in benzene and the mixture was refluxed for 5 h. The NaCl (400 mg, 6.84 mmol) formed during the reaction was filtered off and the filtrate was concentrated in vacuo to give a pinkish solid, which was recrystallized from a benzene–hexane mixture to give crystals of the hydrolyzed product, $[\{Me_2Sn(ON{=}C(Me)C_5H_4N)\}_2O\}]_2 \cdot 2[2\text{-}NC_5H_4(Me)C{=}NOH]$. M.p. 145°C; Anal. Found: C, 41.56; H, 4.61; N, 11.51; Sn, 32.88. Calc. for $C_{50}H_{68}N_{12}O_8Sn_4$: C, 41.66; H, 4.77; N, 11.67%. ^1H-NMR in $CDCl_3$ δ: 0.65 $[^2J(^{119}Sn{-}^1H) = 74.1$ Hz], 0.84 $[^2J(^{119}Sn{-}^1H) = 64.6$ Hz] (each s, Sn–Me); 2.34 (s, oxime-Me); 7.16 (t, 5.5 Hz, CH-4); 7.61 (t, 7.1 Hz, CH-5); 7.77 (d, 7.3 Hz, CH-3); 8.55 (br, CH-6); 9.54 (br, OH). $^{13}C\{^1H\}$-NMR in $CDCl_3$ δ: 3.7 $[^1J(^{119/117}Sn{-}^{13}C) = 667$ Hz], 10.4 $[^1J$(Sn–C) could not be resolved due to the low intensity of the Sn–C resonance] (each s, Sn–Me); 10.7 (s, oxime–Me); 120.3 (C-5); 122.7 (C-3); 136.1 (C-4); 148.3 (C-6); 154.8 (br, C-2 and C=N). $^{119}Sn\{^1H\}$-NMR in $CDCl_3$ δ: −192.3, −239.0.

NMR data for free oxime; ^1H-NMR in $CDCl_3$ δ: 2.44 (s, Me); 7.25 (td, 1.1 Hz(d), 6.1 Hz (t), H-4); 7.68 (td, 1.8

Hz (d), 8 Hz (t), H-5); 7.83 (dt, 9 Hz (t), 8 Hz (d), H-3); 8.63 (m, H-6); 9.08 (br, s, OH). $^{13}C\{^1H\}$-NMR in $CDCl_3$ δ: 10.7 (Me); 120.6 (C-5); 123.4 (C-3); 136.3 (C-4); 148.8 (C-6); 154.6 (C-2); 1565 (C=N).

NMR data for $[\{Me_2Sn(ON{=}C(Me)C_5H_4N)\}_2O\}]_2$; ^1H-NMR in $CDCl_3$ δ: 0.66 $[^2J(^{119}Sn-^1H) = 94$ Hz], 0.85 $[^2J(^{119}Sn-^1H) = 83$ Hz] (each s, Sn–Me); 2.34 (s, oxime-Me); 7.16 (t, 5.0 Hz, CH-4); 7.60 (d, 7.0 Hz, CH-5); 7.78 (br, CH-3); 8.58 (br, CH-6). $^{13}C\{^1H\}$-NMR in $CDCl_3$ δ: 3.7, 10.0 (each s, Sn–Me, $^1J(^{119}Sn-^{13}C)$ could not be resolved due to the low intensity of the Sn–C resonances); 10.8 (s, oxime-Me); 120.3 (C-5); 122.8 (C-3); 136.1 (C-4); 148.3 (C-6); 154.9 (br, C-2 and C=N). $^{119}Sn\{^1H\}$-NMR in $CDCl_3$ δ: −190.8, −239.4.

3.2. X-ray diffraction analysis

A colorless block crystal of $[\{Me_2Sn(ON{=}C(Me)C_5H_4N)\}_2O\}]_2 \cdot 2[2\text{-}NC_5H_4(Me)C{=}NOH]$ was mounted on a glass fiber. Data was collected on an Enraf–Nonius KappaCCD area detector with ϕ and ω scans chosen to give a complete asymmetric unit. Data collection and cell refinement [14] gave cell constants corresponding to a monoclinic cell whose dimensions are given in Table 1 along with other experimental parameters. An absorption correction was applied [15], which resulted in transmission factors ranging from 0.9963 to 0.8391.

Table 1
Crystal data and structure refinement for $[\{Me_2Sn(ON{=}C(Me)py)\}_2O]_2 \cdot 2(2\text{-}NC_5H_4(Me)C{=}NOH)$

Empirical formula	$C_{50}H_{68}N_{12}O_8Sn_4$
Formula weight	1439.92
Temperature (°C)	−120(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	8.1000(16)
b (Å)	17.601(4)
c (Å)	20.061(4)
β (°)	98.89(3)
V (Å^3)	2825.6(10)
Z	2
D_{calc} (g cm^{-3})	1.692
Absorption coefficient (mm^{-1})	1.809
F(000)	1432
Crystal size (mm^3)	0.10 × 0.04 × 0.04
θ range for data collection (°)	2.84–29.80
Index ranges	$-10 \le h \le 9$, $-22 \le k \le 22$, $-25 \le l \le 26$
Reflections collected	30 219
Independent reflections	6506 [$R_{int} = 0.0667$]
Max/min transmission	0.9963 and 0.8391
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6506/0/346
Goodness-of-fit on F^2	1.009
Final R indices [$F^2 > 4\sigma(F^2)$]	$R_1 = 0.0338$, $wR_2 = 0.0656$
R indices (all data)	$R_1 = 0.0549$, $wR_2 = 0.0717$
Extinction coefficient	0.00065(11)
Largest difference peak and hole (e Å^{-3})	0.952 and −1.011

Table 2
Selected bond lengths (Å) and angles (°) for $\{Me_2Sn(ON{=}C(Me)py)\}_2O]_2 \cdot 2(2\text{-}NC_5H_4(Me)C{=}NOH)$ [a]

Bond lengths			
Sn(1)–O(1)	1.994(2)	Sn(2)–O(3)	2.039(2)
Sn(1)–O(2)	2.046(2)	Sn(2)–O(3)=	2.039(2)
Sn(1)–O(3)	1.956(2)	Sn(2)–N(3)	2.265(3)
		Sn(2)–N(4)	2.513(2)
Sn(1)–C(1)	2.243(3)	Sn(2)–C(17)	2.242(3)
Sn(1)–C(2)	2.205(3)	Sn(2)–C(18)	2.251(3)
O(1)–N(1)	1.398(3)	O(2)–N(3)	1.351(3)
N(1)–C(3)	1.304(4)	N(3)–C(10)	1.222(4)
N(2)–C(5)	1.403(4)	N(4)–C(12)	1.285(4)
N(2)–C(9)	1.346(4)	N(4)–C(16)	1.331(4)
C(3)–C(4)	1.558(5)	C(10)–C(11)	1.426(4)
C(3)–C(5)	1.482(4)	C(10)–C(12)	1.475(4)
N(2)···H(4)	2.906(4)	O(4)–H(4)	1.01(5)
O(4)–N(5)	1.409(4)	N(5)–C(19)	1.334(4)
N(6)–C(21)	1.390(4)	N(6)–C(25)	1.346(4)
C(19)–C(20)	1.537(5)	C(19)–C(21)	1.487(5)
Bond angles			
O(1)–Sn(1)–O(2)	165.75(9)	C(17)–Sn(2)–C(18)	158.11(12)
C(1)–Sn(1)–C(2)	130.89(13)	O(3)=–Sn(2)–N(3)	152.96(8)
O(3)–Sn(1)–C(1)	114.87(11)	O(3)–Sn(2)–N(4)	144.29(8)
O(3)–Sn(1)–C(2)	114.24(12)	O(3)=1–Sn(2)–N(4)	138.68(8)
O(1)–Sn(1)–C(1)	96.46(11)	O(3)–Sn(2)–C(17)	101.01(10)
O(2)–Sn(1)–C(2)	93.95(11)	O(3)–Sn(2)–C(18)	100.73(11)
O(2)–Sn(1)–C(1)	91.68(11)	N(3)–Sn(2)–C(18)	98.34(11)
O(1)–Sn(1)–C(2)	89.55(11)	O(3)=–Sn(2)–C(18)	92.05(10)
O(1)–Sn(1)–O(3)	83.24(9)	O(3)=–Sn(2)–C(17)	90.55(10)
O(2)–Sn(1)–O(3)	82.72(8)	C(17)–Sn(2)–N(3)	88.97(11)
N(1)–O(1)–Sn(1)	109.11(16)	C(17)–Sn(2)–N(4)	86.70(10)
C(3)–N(1)–O(1)	111.2(3)	C(18)–Sn(2)–N(4)	77.07(10)
N(1)–C(3)–C(4)	126.0(3)	O(3)–Sn(2)–N(3)	76.99(9)
N(1)–C(3)–C(5)	113.2(3)	O(3)=–Sn(2)–O(3)	76.58(9)
C(4)–C(3)–C(5)	120.8(3)	N(3)–Sn(2)–N(4)	68.26(9)
C(5)–N(2)–C(9)	115.5(3)	C(10)–N(3)–Sn(2)	122.8(2)
N(2)–C(5)–C(3)	113.3(3)	O(2)–N(3)–Sn(2)	120.43(16)
N(2)–C(5)–C(6)	124.5(3)	C(12)–N(4)–Sn(2)	111.0(2)
N(2)–C(9)–C(8)	122.8(3)	C(16)–N(4)–Sn(2)	127.81(19)
Sn(1)–O(3)–Sn(2)	134.19(11)	Sn(1)–O(3)–Sn(2)=	121.10(10)
N(2)–H(4)–O(4)	173.0(3)	Sn(2)=–O(3)–Sn(2)	103.42(9)
N(5)–O(4)–H(4)	98.90(2)	N(3)–O(2)–Sn(1)	123.58(16)
C(19)–N(5)–O(4)	112.9(3)	C(10)–N(3)–O(2)	116.3(3)
N(5)–C(19)–C(20)	126.5(3)	N(3)–C(10)–C(11)	118.3(3)
N(5)–C(19)–C(21)	115.4(3)	N(3)–C(10)–C(12)	118.2(3)
C(20)–C(19)–C(21)	118.1(3)	C(11)–C(10)–C(12)	123.5(3)
C(21)–N(6)–C(25)	117.8(3)	C(12)–N(4)–C(16)	121.0(3)
N(6)–C(21)–C(19)	116.6(3)	N(4)–C(12)–C(10)	119.5(3)
N(6)–C(21)–C(22)	124.1(3)	N(4)–C(12)–C(13)	117.4(3)
N(6)–C(25)–C(24)	121.7(3)	N(4)–C(16)–C(15)	125.3(3)

[a] Symmetry equivalent position $(-x+1, -y+2, -z+1)$ given by a prime.

The structure was solved by direct methods [16], and the structure was refined using the WinGX version [17] of SHELX-97 [18]. All of the non-hydrogen atoms were treated anisotropically. All hydrogen atoms, with the exception of H(4) attached to O(4), which was located in the difference map and refined isotropically, were included in idealized positions with C–H set at 0.95 Å and with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement [18] was based on 6506 observed reflections (5062 for $F^2 > 4\sigma F^2$)) and 346 variable parameters and converged (largest parameter shift was 0.001 times its estimated S.D.). Selected bond distances and angles are given in Table 2 and the molecule is displayed in the ORTEP diagram in Fig. 1.

4. Supplementary material

The final atomic coordinates for all atoms, thermal parameters, and a complete listing of bond distances and angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 192458. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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