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Journal of Organometallic Chemistry 651 (2002) 98–104

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis, spectroscopic and structural aspects of some tetraorganodistannoxanes with internally functionalized oxime: crystal and molecular structures of $[\{R_2Sn(ON{=}C(Me)py)\}_2O]_2$ ($R = Bu^n$ and Et) and $2\text{-}NC_5H_4C(Me){=}NOH$

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Received 8 October 2001; accepted 26 February 2002

Abstract

Diorganotin(IV) complexes of the type $[\{R_2Sn(ON{=}C(Me)py)\}_2O]_2$($R = Bu^n$ (**1**), Pr^n (**2**), Et (**3**) and Me (**4**)) have been synthesized by the condensation reaction of R_2SnO with $2\text{-}NC_5H_4(Me)C{=}NOH$ (**5**) in 1:1 molar ratio in refluxing anhydrous benzene–toluene and characterized by elemental analyses and IR and NMR (^1H, ^{13}C and ^{119}Sn) spectroscopy. Two sets of ^{119}Sn chemical shifts are observed in the ^{119}Sn-NMR spectra of all of these compounds indicating the presence of two types of environment around the tin atoms in solution. The crystal structures of **1**, **3** and **5** have been established by single crystal X-ray diffraction. The bonding in **1** differs from that in **3** but in both structures two different environments around the tin atoms are evident with the geometry around each tin atom being that of a distorted trigonal bipyramid with alkyl groups at the equatorial positions. The structure of **5** consists of chains of molecules arising from intermolecular hydrogen bonding involving the nitrogen atom of the ring.

Keywords: Tetraorganodistannoxane; Functionalized oxime; Multinuclear NMR; X-ray structures

1. Introduction

The chemistry of dimeric tetraorganodistannoxanes has attracted considerable attention during the last several years, because of their unique structural features (e.g. [1–10]) as well as their applications as biocides [11] and in homogenous catalysis [12]. In the solid state, they contain characteristic $Sn_4O_2X_2Y_2$ structural motifs with ladder or staircase arrangements, a planar four-membered Sn_2O_2 ring and, generally, penta-coordination around the tin atom [10,13,14]. Further, among main group organometallics, diorganotin(IV) complexes demonstrate considerably higher anti-cancer activity in vitro as well as lower toxicity than the well known *cis*-platin, $Pt(NH_3)_2Cl_2$ [15]. Of the many multidentate organic ligands, oximes are of particular importance, because of their remarkable structural diversity and biological implications [16]. In general oximes are weak acids that form numerous salts and complexes quite readily.

Recent research has been devoted to the influence of the nature and acidity of the entering nucleophile on the reactivity of distannoxanes and, more specifically, on the stability of their Sn_2O_2 cluster network. Considerable effort has been made to determine whether the presence of an additional donor atom in the internally functionalized oxime ligand has any effect on the structure adopted by organotinoximates [8,14a,17].

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0022-328X/02/$ - see front matter
PII: S0022-328X(02)01330-X

In this paper, we report on the synthesis and characterization of some novel tetraorganodistannoxanes with 2-acetylpyridyloxime. We also report the structures of the tetraorganodistannoxanes, $[\{Bu^n_2Sn(ON{=}C(Me)py)\}_2O]_2$ (**1**) and $[\{Et_2Sn(ON{=}C(Me)py)\}_2O]_2$ (**3**) as well as the free oxime, 2-$NC_5H_4(Me)C{=}NOH$ (**5**).

2. Result and discussion

Reaction of R_2SnO with 2-acetylpyridyloxime in 1:1 stoichiometry in refluxing anhydrous benzene–toluene readily gives $[\{R_2Sn(ON{=}C(Me)py)\}_2O]_2$ in 65–80% yield after recrystallization:

$$4R_2SnO + 4HON{=}C(Me)C_5H_4N\text{-}2 \rightarrow [\{R_2Sn(ON{=}C(Me)C_5H_4N)\}_2O]_2 + 2H_2O$$

(**1**, $R = n$Bu; **2**, $R = n$Pr; **3**, $R = $ Et and **4**, $R = $ Me)

All of the complexes are colorless crystalline solids and are soluble in common organic solvents. The synthetic details along with NMR spectral data are summarized in Section 3. The IR spectra of these complexes were interpreted by comparison with those of the free oxime **5**, diorganotin oxides and other related compounds [14,17]. The OH band (3300 cm^{-1} in the free oxime) is absent in the spectra of **1**–**4**. The medium to strong intensity band at 461 ± 3 cm^{-1} and the absorptions in the region 532–612 cm^{-1} (612 Bu^n–Sn, 611 Pr^n–Sn, 532 Et–Sn, 542 cm^{-1} Me–Sn) in the spectra of tetraorganodistannoxane, are assigned to ν_{Sn-O} and ν_{Sn-C}, respectively. The ^1H and $^{13}C\{^1H\}$-NMR spectra of these complexes exhibit characteristic signals and multiplicities for R–Sn and for the ligand protons and carbon atoms. The hydroxyl proton resonance that is present in the free oxime ligand is absent in the ^1H-NMR spectra of all the corresponding complexes, indicating the deprotonation of the OH group and formation of the Sn–O bond. A significant shift in the position of the methyl signal of the ligand moiety further supports Sn–O bonding. However, no appreciable shift is observed in the positions of the ring protons of the oxime ruling out the possibility of coordination through the pyridyl nitrogen atom. All of these complexes display two Sn–CH resonances with different $^2J(^{119/117}Sn-^1H)$ and $^1J(^{119/117}Sn-^{13}C)$ coupling constants in the ^1H and $^{13}C\{^1H\}$-NMR spectra, as is characteristic of dimeric tetraorganodistannoxanes [17]. In the case of the diethyltin complex **3**, the highfield $Sn-CH_2$ resonance with the larger value for $^1J(^{119/117}Sn-^{13}C)$ is assigned to the *exo*-cyclic Et_2Sn group and the lowfield $Sn-CH_2$ resonance with the smaller value of $^1J(^{119/117}Sn-^{13}C)$ to *endo*-cyclic Et_2Sn [14a]. The ^1H-NMR spectra of the dimethyltin derivative **4** shows two well separated $Sn-CH_3$ resonances with different $^1J(^{119/117}Sn-^1H)$ coupling constants (94 and 83 Hz). The butyl and propyl groups attached to the tin atoms in **1** and **2** exhibit multiplets at their expected positions. In the $^{13}C\{^1H\}$-NMR spectra of tetraorganodistannoxane complexes, C=N carbon in general is deshielded as compared with its position in the corresponding free ligand. However, other resonances are hardly changed indicating that the pyridyl nitrogen is not coordinated to tin. This is further substantiated by the X-ray structures of $[\{R_2Sn(ON{=}C(Me)py)\}_2O]_2(R{=}Bu^n$, Et) (**1** and **3**).

The ^{119}Sn-NMR spectra of all of these complexes display two well separated resonances (-190.8 to -220.4 and -219.9 to -239.4 ppm), as is observed for tetraorganodistannoxanes indicating dimeric structures in solution (e.g. [10,14,17,18]). Of these two signals, the low field signal is broad which may be due to the ‘Wagging motion’ of the *exo*-cyclic tin atoms in solution [5,9,18]. The values of the ^{119}Sn chemical shift for the dipropyltin derivative **2** (-203.2 and -221.7 ppm) indicate that the bonding should be similar to that of the dibutyltin derivative **1** (Fig. 1). However, the ^{119}Sn chemical shifts for the dimethyltin derivative **4** -190.8 and -239.4 ppm suggesting that the bonding should be similar to that of the diethyltin complex **3** (Fig. 2).

It has been reported that subtle variation in the R groups on tin or in the ligand moiety usually results in different structural motifs of tetraorganodistannoxanes in the solid state [14b]. However, in solution, weak intramolecular Sn–L interactions may be ruptured but the dimeric structure retained. This could be the cause for dynamic behavior in solution [2c,18]. Thus in solution, ligand proton and carbon signals appear as only one set of resonances inspite of their different bonding patterns within a stannoxane framework in the

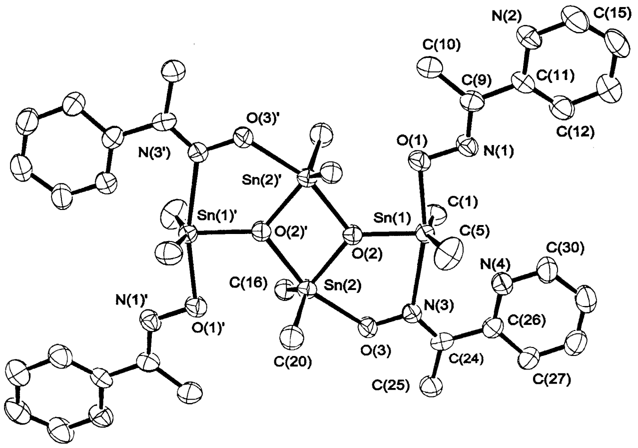

Fig. 1. ORTEP plot of the molecule $[\{Bu^n_2Sn(O{=}NC(Me)py)\}_2O]_2$ (**1**). The atoms are drawn with 20% probability ellipsoids. Carbon atoms of the butyl groups other than those attached to tin and hydrogen atoms excluded for clarity.

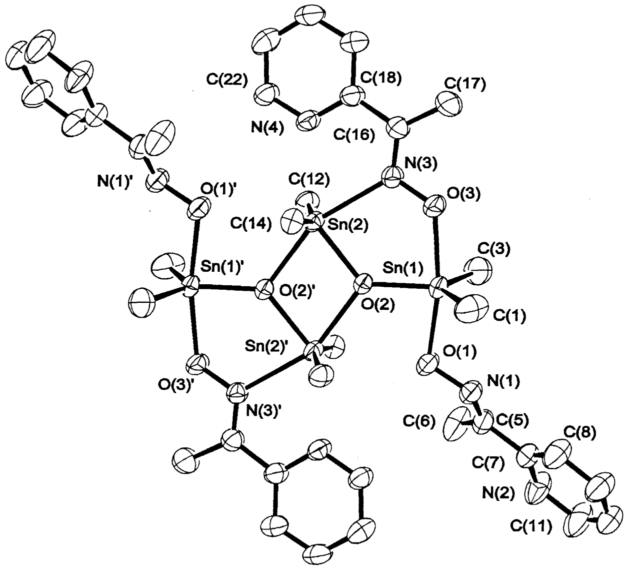

Fig. 2. ORTEP plot of the molecule $[\{Et_2Sn(ON{=}C(Me)py)\}_2O]_2$ (**3**). The atoms are drawn with 20% probability ellipsoids. Carbon atoms of the ethyl groups other than those attached to tin and hydrogen atoms excluded for clarity.

solid state [2,5,9,18]. It is likely that distannoxanes discussed here may have similar behavior as their NMR features can be compared with those reported earlier [2,18].

The molecular structures of $[\{Bu^n_2Sn(ON{=}C(Me)py)\}_2O]_2$ (**1**), $[\{Et_2Sn(ON{=}C(Me)py)\}_2O]_2$ (**3**) and $2\text{-}NC_5H_4(Me)C{=}NOH$ (**5**) have been unambiguously established by single crystal X-ray diffraction analyses. Selected bond lengths and angles are given in Tables 2–4 and ORTEP diagrams are shown in Figs. 1–3.

It is interesting to mention here that the reactions of the rather similar benzaldoxime with R_2SnO have been studied in detail [6]. In these cases, a completely different structure crystallizes out and a completely different cluster is formed than reported here.

A comparison of the present results with those reported earlier yields some interesting variations. For example, the structure of $[\{Bu^n_2Sn(ON{=}C(Me)py)\}_2O]_2$ (**1**) (Fig. 1), is very similar to the previously reported tetraorganodistannoxane structures (e.g. [2,5,9,17,18]). The axial Sn(2)–O(2)′ bond length at the *endo*-cyclic Sn(2) atom is 2.170(4) Å, which is much shorter than the sum of the van der Waals radii of Sn and O (3.70 Å) [19] and is greater than the equatorial Sn(2)–O(2) bond distance of (2.022(4) Å). For the *exo*-cyclic tin atom Sn(1), the axial Sn(1)–N(3) bond length is 2.406(5) Å, which is appreciably less than the sum of van der Waals radii of Sn and N (3.75 Å) [19]; indicating significant bonding between N(3) and Sn(1).

However, the structure of **3** (Fig. 2) differs from previously reported tetraorganodistannoxane structures. In contrast to $\{(R_2SnL)_2O\}_2$, where each tin is bonded to the uninegative ligand L, in the case of $[\{Et_2Sn(ON{=}C(Me)py)\}_2O]_2$ (**3**) each of the *exo*-cyclic tin atoms is bonded to two oximate anions and the oxime nitrogen of one of the anions is coordinated to the *endo*-cyclic tin atoms. Both *exo*- and *endo*-cyclic tin atoms acquire distorted trigonal bipyramidal configurations with the ethyl groups at the equatorial positions. The Sn(2)–N(3) distance (2.364(5) Å) is again considerably smaller than the sum of the van der Waals radii indicating considerable coordination of the oxime nitrogen atom with the *endo*-cyclic tin center.

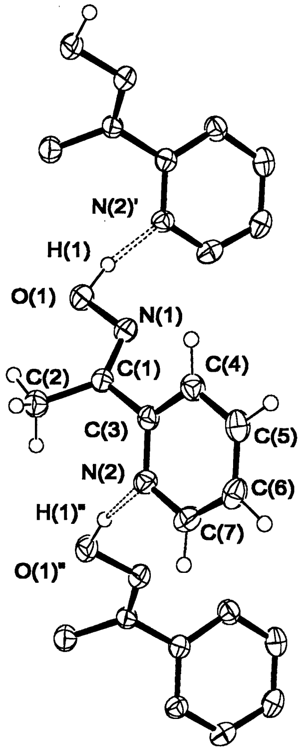

Fig. 3. ORTEP plot of the molecule $2\text{-}NC_5H_4(Me)C{=}NOH$ (**5**) showing hydrogen bonding. The atoms are drawn with 50% probability ellipsoids and hydrogen atoms attached to carbon atoms are only shown on the central molecule for clarity.

Both *endo*- and *exo*-cyclic tin atoms in **1** and **3** are in distorted trigonal bipyramidal configurations with the R groups occupying the equatorial positions. The asymmetric four-membered Sn_2O_2 ring is planar as is usually observed [10,13,14,17,18]; one of the ring Sn–O distances being shorter (2.068(3) in **3** and 2.022(4) Å in **1**) than the other (2.218 (4) in **3** and 2.17(4) Å in **1**). These molecules adopt a staircase conformation in the solid state. The Sn–C distances for *endo*-cyclic tin centers are essentially identical within experimental error. However, for the *exo*-cyclic tin, the two Sn–C distances are slightly different. All other interatomic parameters are similar to those expected for tetraorganodistannoxanes [2–4].

In the structure of the free oxime, $2\text{-}NC_5H_4(Me)C{=}NOH$ (**5**) (Fig. 3), hydrogen bonding involves the nitrogen atom of the ring to give O(1)–H(1)–N(2)′

linkages that lead to chains. This is in contrast to what was observed in the case of the corresponding thiophene derivative [20] in which dimeric units resulted from hydrogen bonds involving adjacent oxime nitrogen atoms. The C=N bond length is essentially unchanged on complexation, with C(1)–N(1) being 1.278(2) Å in **5** and an average of 1.278(8) Å in **1** and **3**. Consistent with this, the ^{13}C-NMR spectrum of the complexes indicates only a very slight downfield shift for the C=N carbon atom. However, an appreciable change has been observed in the O–N bond length on complexation, with O(1)–N(1) being 1.406(2) Å in the free oxime **5** and an average of 1.366 Å in complexes **1** and **3**. Similarly, a change in the angle O(1)–N(1)–C(1) (112.43(17)°) present in the free oxime **5**, was also observed on complexation in **1** (114.6(6); 114.8(5)°) and **3** (113.9(5); 115.4(5)°).

3. Experimental

Diorganotin oxides and 2-acetyl pyridine were obtained from commercial sources. 2-Acetylpyridyloxime, 2-NC_5H_4(Me)C=NOH (**5**) [melting point (m.p.) 102 °C, ^{1}H-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{^{1}H}-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); 156.5 (C=N)] was prepared according to the literature method [21]. IR spectra were recorded as Nujol mulls on a Bomem MB-102 FT-IR spectrophotometer. ^{1}H, ^{13}C{^{1}H}- and ^{119}Sn{^{1}H}-NMR spectra were recorded in 5 mm NMR tubes as freshly prepared $CDCl_3$ solutions on a Bruker DPX-300 NMR spectrometer operating at 300, 75.47 and 111.92 MHz, respectively. Spectra were referenced with the internal chloroform peak (δ 7.26 for^{1}H and 77.0 ppm for ^{13}C) and external 33% solution of Me_4Sn in $C_6D_6$for ^{119}Sn. Microanalyses were carried out by the Analytical Chemistry Division, BARC, Mumbai.

3.1. *Preparation of*[{$Bu^n_2Sn(ON{=}C(Me)py)\}_2O]_2$ (*1*)

2-Acetylpyridyl oxime (558 mg, 4.10 mmol) was added to a benzene suspension (60 ml) of Bu_2SnO (1.018 g, 4.09 mmol), then stirred and heated at reflux for 3 h. The water formed during the reaction was

Table 1
Crystal data and structure refinement for [{Bu^n_2Sn(ON=C(Me)py)}$_2$O]$_2$, (**1**) [{Et_2Sn(ON=C(Me)py)}$_2$O]$_2$ (**3**) and 2-NC_5H_4(Me)C=NOH (**5**)

Compound	1	3	5
Empirical formula	$C_{60}H_{100}N_8O_6Sn_4$	$C_{44}H_{68}N_8O_6Sn_4$	$C_7H_8N_2O$
Formula weight	1504.24	1279.82	136.15
Temperature (°C)	25(2)	25(2)	−123(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	9.7345(19)	9.1697(18)	7.9867(16)
b (Å)	14.206(3)	12.290(3)	8.0321(16)
c (Å)	14.552(3)	12.472(3)	10.594(2)
α (°)	104.10(3)	89.58(3)	
β (°)	106.90(3)	76.60(3)	95.53(3)
γ (°)	107.87(3)	75.70(3)	
V (Å^3)	1705.7(6)	1323.0(5)	676.4(2)
Z	1	1	4
D_{calc} (g cm^{-3})	1.464	1.606	1.337
Absorption coefficient (mm^{-1})	1.498	1.915	0.093
F(000)	764	636	288
Crystal size (mm)	0.25 × 0.20 × 0.20	0.10 × 0.03 × 0.03	0.10 × 0.10 × 0.09
θ Range for data collection (°)	2.96–25.02	3.21–25.03	3.19–27.43
Index ranges	$-11 \le h \le 11$, $-16 \le k \le 16$, $-17 \le l \le 17$	$-10 \le h \le 10$, $-14 \le k \le 14$, $-14 \le l \le 14$	$-10 \le h \le 10$, $-10 \le k \le 10$, $-13 \le l \le 11$
Reflections collected	22 632	12 510	9577
Independent reflections	5967 [$R_{int} = 0.0845$]	4642 [$R_{int} = 0.0654$]	1539 [$R_{int} = 0.1270$]
Max/min transmission	0.7538 and 0.7059	0.9448 and 0.8316	0.9917 and 0.9908
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	5967/9/359	4642/2/284	1539/0/113
Goodness-of-fit on F^2	1.008	1.015	0.935
Final R indices [$F^2 > 4\sigma(F^2)$]	$R_1 = 0.0500$, $wR_2 = 0.1269$	$R_1 = 0.0442$, $wR_2 = 0.1068$	$R_1 = 0.0486$, $wR_2 = 0.0988$
R indices (all data)	$R_1 = 0.0827$, $wR_2 = 0.1485$	$R_1 = 0.0670$, $wR_2 = 0.1195$	$R_1 = 0.1376$, $wR_2 = 0.1256$
Extinction coefficient	0.0027(8)	0.0013(9)	0.017(6)
Largest difference peak and hole (e Å^{-3})	0.823 and −0.756	0.794 and −0.833	0.221 and −0.268

fractionally removed azeotropically. The clear solution was filtered and the filtrate concentrated in vacua to give a pinkish solid, which was recrystallized from *n*-hexane at −10EC to give colorless crystals (1.230 g, 80% yield), m.p. 106 °C. Anal. Found: C, 47.3; H, 6.8; N, 6.7; Sn 31.1. Calc. for $C_{60}H_{100}N_8O_6Sn_4$: C, 47.9; H, 6.7; N, 7.4; Sn, 31.6%. ^{1}H-NMR in $CDCl_3$ δ: 0.87 (br, t, Sn−CCC*Me*); 1.37 (br, m, Sn−CCH_2CH_2); 1.66 (br, m, Sn−CH_2); 2.39 (s, oxime-Me); 7.24 (br, CH-4); 7.69 (t, CH-5); 7.89 (d, 8 Hz, CH-3), 8.63 (br, CH-6). $^{13}C\{^1H\}$-NMR in $CDCl_3$ δ: 10.7 (s, oxime-Me); 13.5 (s, Sn−CCCCH_3); 23.7 (s, Sn−CCCH_2); 26.9 (s, Sn−CCH_2); 27.6, 27.8 (each s, Sn−CH_2); 120.6 (C-5); 122.7 (C-3); 135.9 (C-4); 148.5 (C-6); 155.5 (C-2 and C=N). $^{119}Sn\{^1H\}$-NMR in $CDCl_3$ δ: −198.5, −219.9.

Similarly all other complexes were prepared with reactions carried out in refluxing toluene instead of benzene, and with the refluxing time being increased with decreasing chain length of the alkyl group on tin.

3.2. [{Pr^n_2Sn(ON=C(Me)py)}$_2$O]$_2$ (**2**)

Yield 70%; m.p. 128 °C; Anal. Found: C, 44.3; H, 6.3; N, 8.1; Sn, 34.0. Calc. for $C_{52}H_{84}N_8O_6Sn_4$: C, 44.9; H, 6.1; N, 8.0; Sn, 34.1%. ^{1}H-NMR in $CDCl_3$ δ: 0.93(m, Sn−CCCH_3); 1.38–1.74 (m, *Sn*−CH_2CH_2); 2.38 (s, oxime-Me); 7.16 (t, 5.6 Hz, CH-4); 7.59 (t, 7.5 Hz, CH-5); 7.82 (d, 5.5 Hz, CH-3); 8.59 (d, 3.0 Hz, CH-6). $^{13}C\{^1H\}$-NMR in $CDCl_3$ δ: 10.6 (oxime-Me); 18.4 (Sn−CCCH_3); 18.8 (Sn−$CH_2$$CH_2$); 26.8 and 30.3 (Sn−$CH_2$); 120.3 (C-5); 122.8 (C-3); 136.1 (C-4); 148.5 (C-6); 155.2 (C-2); 155.6 (C=N). $^{119}Sn\{^1H\}$-NMR in $CDCl_3$ δ: −203.2, −221.7.

3.3. [{Et_2Sn(ON=C(Me)py)}$_2$O]$_2$ (**3**)

Yield 65%; m.p. 126 °C; Anal. Found: C, 40.6; H, 5.4; N, 8.0; Sn, 37.0. Calc. for $C_{44}H_{68}N_8O_6Sn_4$, C, 41.3;H, 5.3; N, 8.7; Sn, 37.1%. ^{1}H-NMR in $CDCl_3$ δ: 1.22 (m, Sn−CCH_3); 1.37–1.61 (m, Sn−CH_2); 2.34 (s, oxime-Me); 7.14 (t, 5.4 Hz, CH-4); 7.63 (t, 7.2 Hz, CH-5); 7.81 (d, 7.6 Hz, CH-3); 8.55 (d, 3.0 Hz, CH-6). $^{13}C\{^1H\}$-NMR in $CDCl_3$ δ: 9.8 and 10.0 (each s, Sn−CCH_3); 10.9 (s, oxime-Me); 16.0 [$^1J(^{119/117}Sn-^{13}C) = 687$ Hz], 21.2 [$^1J(^{119/117}Sn-^{13}C) = 660$ Hz] (each s, Sn−CH_2); 120.1 (C-5); 122.4 (C-3); 136.1 (C-4); 148.3 (C-6); 154.4 (C-2); 155.7 (C=N). $^{119}Sn\{^1H\}$-NMR in $CDCl_3$ δ: −220.4, −238.8.

3.4. [{Me_2Sn(ON=C(Me)py}$_2$O]$_2$ (**4**)

Yield 70%; m.p. 175 °C; Anal. Found: C, 36.7; H, 4.1; N, 8.8; Sn, 40.4. Calc. for $C_{36}H_{52}N_8O_6Sn$: C, 37.0; H, 4.5; N, 9.6; Sn, 40.7%. ^{1}H-NMR in $CDCl_3$ δ: 0.66 [$^1J(^{119}Sn-^1H) = 94$ Hz], 0.85 [$^1J(^{119}Sn-^1H) = 83$ 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(Sn−C) could not be resolved due to low intensity of the Sn−C resonance); 10.8 (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.

3.5. X-ray diffraction analysis

Block crystals of [{Bu^n_2Sn(ON=C(Me)py)}$_2$O]$_2$ (**1**) and 2-NC_5H_4(Me)C=NOH (**5**) and a needle-like crystal of [{Et_2Sn(ON=C(Me)py)}$_2$O]$_2$ (**3**) were mounted on glass fibers. Data were collected on an Enraf Nonius KappaCCD area detector (ϕ scans and ω scans to fill Ewald sphere) at the University of Southampton EPSRC National Crystallography Service. Data collection and cell refinement [22] gave cell constants corresponded to triclinic cells for **1** and **3** and a monoclinic

Table 2
Selected bond lengths (Å) and angles (°) for [{Bu^n_2Sn(ON=C(Me)py)}$_2$O]$_2$, (**1**) [a]

Bond lengths			
Sn(1)–O(1)	2.134(4)	Sn(2)–O(2)	2.022(4)
Sn(1)–O(2)	2.047(4)	Sn(2)–O(2)′	2.170(4)
Sn(1)–N(3)	2.406(5)	Sn(2)–O(3)	2.164(4)
Sn(1)–C(1)	2.111(7)	Sn(2)–C(16)	2.109(6)
Sn(1)–C(5)	2.147(13)	Sn(2)–C(20)	2.101(7)
		O(2)–Sn(2)	2.170(4)
O(1)–N(1)	1.394(7)	O(3)–N(3)	1.337(7)
N(1)–C(9)	1.271(8)	N(3)–C(24)	1.269(8)
N(2)–C(11)	1.336(8)	N(4)–C(26)	1.328(9)
N(2)–C(15)	1.304(11)	N(4)–C(30)	1.309(10)
C(9)–C(10)	1.504(10)	C(24)–C(25)	1.471(9)
C(9)–C(11)	1.468(10)	C(24)–C(26)	1.506(10)
Bond angles			
O(1)–Sn(1)–N(3)	166.87(18)	O(2)–Sn(2)–O(3)	161.87(17)
O(2)–Sn(1)–C(1)	102.5(3)	O(2)–Sn(2)–C(16)	116.1(2)
O(2)–Sn(1)–C(5)	101.9(3)	O(2)–Sn(2)–C(20)	113.3(3)
C(1)–Sn(1)–C(5)	155.6(4)	C(16)–Sn(2)–C(20)	130.5(3)
O(2)–Sn(1)–O(1)	85.24(17)	O(2)–Sn(2)–O(2)	75.80(18)
C(1)–Sn(1)–O(1)	93.7(4)	C(16)–Sn(2)–O(2)	97.9(2)
C(5)–Sn(1)–O(1)	89.3(3)	C(20)–Sn(2)–O(2)	95.5(2)
O(2)–Sn(1)–N(3)	81.83(17)	O(2)–Sn(2)–O(3)	86.27(16)
C(1)–Sn(1)–N(3)	86.9(2)	C(16)–Sn(2)–O(3)	87.5(2)
C(5)–Sn(1)–N(3)	95.5(3)	C(20)–Sn(2)–O(3)	94.0(3)
C(24)–N(3)–Sn(1)	127.4(5)	Sn(2)–O(2)–Sn(1)	129.8(2)
O(3)–N(3)–Sn(1)	117.5(4)	Sn(2)–O(2)–Sn(2)	104.20(18)
Sn(1)–O(2)–Sn(2)	126.0(2)		
N(1)–O(1)–Sn(1)	104.5(3)	N(3)–O(3)–Sn(2)	123.7(4)
C(9)–N(1)–O(1)	114.6(6)	C(24)–N(3)–O(3)	114.8(5)
N(1)–C(9)–C(10)	123.4(7)	N(3)–C(24)–C(25)	124.0(7)
N(1)–C(9)–C(11)	116.6(6)	N(3)–C(24)–C(26)	116.2(6)
C(10)–C(9)–C(11)	120.0(6)	C(25)–C(24)–C(26)	119.7(6)
C(11)–N(2)–C(15)	117.4(8)	C(26)–N(4)–C(30)	118.8(7)
C(9)–C(11)–N(2)	116.3(7)	C(24)–C(26)–N(4)	118.1(6)
C(12)–C(11)–N(2)	121.5(7)	C(27)–C(26)–N(4)	121.6(7)
C(14)–C(15)–N(2)	124.6(8)	C(29)–C(30)–N(4)	125.0(9)

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

Table 3
Bond lengths (Å) and angles (°) for $[\{Et_2Sn(ON{=}C(Me)py)\}_2 0]_2$ (**3**) [a]

Bond lengths			
Sn(1)–O(1)	2.136(4)	Sn(2)–O(2)	2.068(3)
Sn(1)–O(2)	1.988(3)	Sn(2)–O(2)	2.218(4)
Sn(1)–O(3)	2.173(4)	Sn(2)–N(3)	2.364(5)
Sn(1)–C(1)	2.104(7)	Sn(2)–C(12)	2.119(5)
Sn(1)–C(3)	2.160(9)	Sn(2)–C(14)	2.137(5)
		O(2)–Sn(2)	2.218(4)
O(1)–N(1)	1.384(6)	O(3)–N(3)	1.351(5)
N(1)–C(5)	1.288(8)	N(3)–C(16)	1.285(7)
N(2)–C(7)	1.306(8)	N(4)–C(18)	1.337(8)
N(2)–C(11)	1.356(7)	N(4)–C(22)	1.330(7)
C(5)–C(6)	1.510(9)	C(16)–C(17)	1.493(9)
C(5)–C(7)	1.488(8)	C(16)–C(18)	1.473(8)
Bond angles			
O(1)–Sn(1)–O(3)	169.07(15)	O(2)–Sn(2)–N(3)	156.48(13)
O(2)–Sn(1)–C(1)	119.9(3)	O(2)–Sn(2)–C(12)	100.85(16)
O(2)–Sn(1)–C(3)	112.2(3)	O(2)–Sn(2)–C(14)	103.30(18)
C(1)–Sn(1)–C(3)	127.9(4)	C(12)–Sn(2)–C(14)	154.8(2)
O(2)–Sn(1)–O(1)	83.02(14)	O(2)–Sn(2)–O(2)	75.03(14)
C(1)–Sn(1)–O(1)	95.8(2)	C(12)–Sn(2)–O(2)	89.61(18)
O(1)–Sn(1)–C(3)	88.4(3)	C(14)–Sn(2)–O(2)	89.74(19)
O(2)–Sn(1)–O(3)	86.11(14)	O(2)–Sn(2)–N(3)	81.77(15)
C(1)–Sn(1)–O(3)	90.5(2)	C(12)–Sn(2)–N(3)	98.6(2)
C(3)–Sn(1)–O(3)	94.8(3)	C(14)–Sn(2)–N(3)	91.9(2)
Sn(1)–O(2)–Sn(2)	129.72(18)	C(16)–N(3)–Sn(2)	126.3(4)
Sn(1)–O(2)–Sn(2)	124.85(14)	O(3)–N(3)–Sn(2)	117.2(3)
N(1)–O(1)–Sn(1)	108.8(3)	Sn(2)–O(2)–Sn(2)	104.97(14)
C(5)–N(1)–O(1)	113.9(5)	N(3)–O(3)–Sn(1)	122.2(3)
N(1)–C(5)–C(6)	125.0(6)	C(16)–N(3)–O(3)	115.4(5)
N(1)–C(5)–C(7)	115.9(6)	N(3)–C(16)–C(17)	122.0(6)
C(6)–C(5)–C(7)	119.0(6)	N(3)–C(16)–C(18)	117.0(6)
C(7)–N(2)–C(11)	117.5(6)	C(17)–C(16)–C(18)	121.0(5)
C(5)–C(7)–N(2)	117.3(7)	C(18)–N(4)–C(22)	119.5(5)
C(8)–C(7)–N(2)	120.9(6)	C(16)–C(18)–N(4)	116.6(5)
C(10)–C(11)–N(2)	124.1(6)	C(19)–C(18)–N(4)	120.3(6)
		C(21)–C(22)–N(4)	122.7(7)

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

cell for **5**, whose dimensions are given in Table 1 along with other experimental parameters, Absorption corrections were applied [23] which resulted in transmission factors ranging from 0.7538 to 0.7059 for **1**, 0.9448–0.8316 for **3** and 0.9917–0.9908 for **5**.

The structures were solved by direct methods [24], and the structure refined using the WINGX version [25] of SHELX-97 [26]. All of the non-hydrogen atoms were treated anisotropically. In **1** and **3**, all hydrogen atoms 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. In **5**, hydrogen atoms on the methyl atom, C(2), were also included in idealized positions but the remaining hydrogen atoms were refined isotropically.

Some of the butyl and ethyl groups in **1** and **3** were badly disordered with high thermal parameters. Attempts were made to model different conformations of the chains, but with no success. Several C–C bonds were fixed at 1.51 Å, which was the average of the C–C distances that were not fixed.

Table 4
Selected bond lengths (Å) and angles (°) for 2-NC_5H_4(Me)ONOH (**5**) [a]

Bond lengths			
H(1)–O(1)	1.02(3)	H(1)–N(2)	1.77(4)2)
N(1)–C(1)	1.278(2)	O(1)–N(2)	2.765(3)
C(1)–C(2)	1.498(3)	N(2)–C(7)	1.344(3)
C(1)–C(3)	1.484(3)	C(3)–C(4)	1.400(3)
N(2)–C(3)	1.341(2)	C(4)–C(5)	1.382(3)
C(1)–C(3)	1.484(3)	C(5)–C(6)	1.384(3)
Bond angles			
H(1)–O(1)–N(1)	102.0(16)	O(1)–H(1)–N(2)	168(3)
O(1)–N(1)–C(1)	112.43(17)	C(1)–C(3)–C(4)	121.59(18)
N(1)–C(1)–C(2)	126.23(19)	C(3)–N(2)–C(7)	117.57(19)
N(1)–C(1)–C(3)	114.40(18)	N(2)–C(3)–C(1)	116.30(18)
C(2)–C(1)–C(3)	119.36(18)	N(2)–C(3)–C(4)	122.1(2)
		N(2)–C(7)–C(6)	123.9(2)

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

Bond distances and bond angles are given in Tables 2–4 and the molecules are displayed as ORTEP diagrams in Figs. 1–3.

4. Supplementary material

Additional material available from the Cambridge Crystallographic Data Center comprises the final atomic coordinates for all atoms, thermal parameters, and a complete listing of bond distances and angles. Copies of this information may be obtained free of charge on application to The Director, 12 Union Road, Cambridge CB2 2EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk)

Acknowledgements

We are grateful to DAE (BRNS Project Number 98/37/33) Mumbai, DST and UGC, New Delhi for financial support. We are also grateful to the Head, Analytical Chemistry Division, BARC for microanalysis of some of the complexes. One of us (J.E.D.) wishes to thank the Natural Sciences and Engineering Research Council of Canada for financial support. M.B.H. thanks the UK Engineering and Physical Sciences Research Council for support of the X-ray facilities at Southampton University.

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