Diorganotin(IV) complexes of dideprotonated pyridoxine (PN, vitamin B_6). The crystal structures of [SnEt$_2$(PN–2H)]·CH$_3$OH, [SnEt$_2$(PN–2H)(DMSO)] and [SnBu$_2$(PN–2H)]

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Abstract

The reactions of dimethyl-, diethyl- and dibutyltin(IV) oxides with pyridoxine (PN) in toluene/ethanol led to the formation of compounds [SnR$_2$(PN–2H)] which were characterized by EI and FAB mass spectrometry and by IR, Raman, Mössbauer and ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. The structures of [SnEt$_2$(PN–2H)]·CH$_3$OH, [SnBu$_2$(PN–2H)] and [SnEt$_2$(PN–2H)(DMSO)] were determined by X-ray diffractometry. The first two contain dimeric [SnR$_2$(PN–2H)]$_2$ units in which two bridging-chelating pyridoxinate anions link the Sn atoms, while in [SnEt$_2$(PN–2H)(DMSO)] the DMSO coordinates to the tin atom via its O atom in a similar dimeric unit.
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1. Introduction

As a part of a broad study of the interactions of diorganotin compounds with vitamins [1] we have recently described the interactions of pyridoxine (PN, vitamin B_6) with dimethyltin(IV) and diethyltin(IV) cations [2,3], and for comparison with the corresponding pyridoxine complexes we also prepared dimethyl-, diethyl-, dibutyl- and diphenyltin(IV) complexes of *N*-methylpyridoxine (MePN) [4]. The reactions of PN in ethanol–water containing chloride, nitrate or acetate anions afforded compounds of types [SnR$_2$(PN–H)]X or [SnR$_2$(PN–2H)] comprising dimeric [SnR$_2$(PN–H)]$_2^{2+}$ or [SnR$_2$(PN–2H)]$_2$ units in which monodeprotonated or dideprotonated pyridoxine (PN–H and PN–2H, respectively) coordinated to tin through the deprotonated C(4)–CH$_2$OH and phenolic OH groups, the N atom being protonated in PN–H but not in PN–2H (Scheme 1). No compounds were obtained in which the ligand coordinated through the N atom. The iodide of *N*-methyl pyridoxine afforded complexes of type [SnR$_2$(MePN–H)]I with structures differing only slightly from those of [SnR$_2$(PN–H)]X.

The only compounds of type [SnR$_2$(PN–2H)] that we were able to obtain were [SnEt$_2$(PN–2H)] and [SnMe$_2$(H$_2$O)(PN–2H)]·0.5H$_2$O, in which a water molecule is coordinated to the tin atom; due to a hydrolytic process, the butyl derivative was elusive. Given the interest of a complete structural characterization of [SnBu$_2$(PN–2H)], which has antitumoral activity against the P388 and L1210 cells [5] we have now prepared it by the method of Gielen et al. [5] (reaction of SnR$_2$O with PN) and for comparative purposes have also prepared the methyl and ethyl derivatives by the same method.

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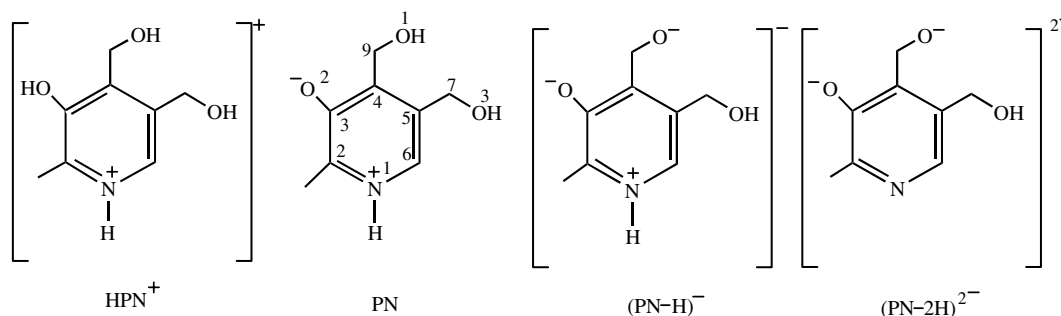
Scheme 1.

Here we describe these reactions and report the crystal structures of [SnEt$_2$(PN–2H)]·CH$_3$OH, [SnEt$_2$(PN–2H)(DMSO)] and [SnBu$_2$(PN–2H)].

2. Experimental

2.1. Material and methods

Pyridoxine, dibutyltin oxide (Aldrich) and dimethyltin oxide (Alfa) were used as received. Diethyltin oxide was obtained by treating diethyltin dichloride with sodium hydroxide [6]. Elemental analysis was performed with a Fisons 1108 microanalyser. Melting points were determined with a Büchi apparatus and are uncorrected. Mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS90 system and operating under either EI conditions (direct insertion probe, 70 eV, 250 °C) or in FAB mode (*m*-nitrobenzyl alcohol, Xe, 8 eV; ca. 1.28×10^{-15} J); ions were identified by DS90 software and the intensities of the metallated peaks were calculated for the isotope ^{120}Sn. IR spectra (KBr pellets or Nujol mulls) and Raman spectra (polycrystalline samples) were recorded on a Bruker IFS66V FT-IR spectrometer equipped with an FRA-106 Raman accessory and are reported in the synthesis section using the following abbreviations: br, broad; m, medium; s, strong; sh, shoulder; vs, very strong; w, weak. Mössbauer spectra were recorded at 80.0 K in a Harwell cryostat; the Ca^{119m}SnO$_3$ source (15 mCi, NEN) was kept at room temperature and moved with a triangular velocity wave form, and Lorentzian lineshapes were fitted to the experimental data. ^{1}H and ^{13}C NMR spectra in solution were recorded at room temperature on a Bruker AMX 300 operating at 300.14 and 75.40 MHz, respectively, using 5 mm o.d. tubes; chemical shifts are reported relative to TMS using the solvent signal (δ ^{1}H = 2.50 ppm; δ ^{13}C = 39.5 ppm) as reference. ^{119}Sn NMR spectra were recorded at 186.50 MHz on a Bruker AMX 500 spectrometer using 5 mm o.d. tubes and are reported relative to external neat Sn(CH$_3$)$_4$ (δ ^{119}Sn = 0 ppm). The conductivities of 10^{-3} M solutions

in dmf were measured in a Crison MicroCM2202 conductivity meter. Elemental analysis, mass, IR, Raman, NMR and X-ray data were obtained at CACTUS (University of Santiago de Compostela) and CACTI (University of Vigo).

2.2. Synthesis of the compounds

2.2.1. [SnMe$_2$(PN–2H)] (1)

Solid dimethyltin(IV) oxide (0.83 g, 5 mmol) was added to a solution of PN (0.85 g, 5 mmol) in a 3:1 (v/v) mixture of toluene and absolute ethanol (200 ml). After refluxing for 24 h water was removed by azeotropic distillation in a Dean–Stark funnel, and the white solid formed was filtered out and vacuum dried. Yield 95%. M.p. >300 °C. Found: C, 38.1; N, 4.4; H, 4.9%. [SnMe$_2$(PN–2H)] requires: C, 38.0; N, 4.4; H, 4.8. The main metallated signals in the EI spectrum are at m/e (ion, intensity) 316 ([SnMe$_2$(PN–2H)], 20.1); 286 ([SnMe$_2$(PN-CH$_2$OH)], 13.6); 150 ([SnMe$_2$], 17.2); 135 ([SnMe], 100) and 120 ([Sn], 35.9). Besides these signals the EI spectrum shows signals for pyridoxine and its fragments, and the FAB spectrum shows the same metallated signals and a signal at 632 ([SnMe$_2$(PN–2H)]$_2$, 5.0). Infrared and Raman (in parentheses) (cm^{-1}): 1559s (1560w), 1374sh (1375w), 1266w (1267w), 1226sh (1225w), v(ring); 1026vs (1025w), v(CO); 572m (572m), v_{asym}(Sn–C); 521m (525vs), v_{sym}(Sn–C). Mössbauer: I.S. 1.39, Q.S. 3.48, Γ 0.97 mm s^{-1}, $A_{2/1}$ 0.96. NMR data (DMSO-d$_6$, see Scheme 1 for numbering). ^{1}H: δ[C(6)H] 7.60s(1); δ[O(3)H] 4.97t(1), ^3J = 5.3 Hz; δ[C(9)H$_2$] 4.76s(2), ^3J(^{1}H–^{119}Sn) = 38 Hz; δ[C(7)H$_2$] 4.38d(2), ^3J = 5.3 Hz; δ[C(8)H$_3$] 2.25s(3); δ[CH$_3$–Sn] 0.55s(6), ^2J(^{1}H–$^{119/117}$Sn) = 86.2 Hz. ^{13}C: δ[C(3)] 155.9; δ[C(2)] 148.6; δ[C(6)] 135.9; δ[C(4)] 134.6; δ[C(5)] 131.2; δ[C(7)] 58.9; δ[C(9)] 59.0; δ[C(8)] 19.4; δ[C–Sn] 3.7. ^{119}Sn: δ −204.7, −216.7.

Crystallization in a 5:2 (v/v) mixture of absolute methanol and DMSO afforded crystals that X-ray crystallography showed be identical to those obtained previously [2], [SnMe$_2$(H$_2$O)(PN–2H)]·0.5H$_2$O.

2.2.2. [SnEt₂(PN–2H)] (2)

Solid diethyltin(IV) oxide (0.92 g, 5 mmol) was added to a solution of PN (0.85 g, 5 mmol) in a 75:25 (v/v) mixture of toluene and absolute ethanol (200 ml). After refluxing for 24 h, water was removed by azeotropic distillation in a Dean–Stark funnel and the white solid formed was filtered out and vacuum dried. Yield 95%. M.p. = 275 °C. Found: C, 41.7; N, 4.0; H, 5.5%. [SnEt₂(PN–2H)] requires: C, 41.8; N, 4.1; H, 5.6. The main metallated signals in the EI spectrum are at m/e (ion, intensity) 344 ([SnEt₂(PN–2H], 10.0); 327 ([SnEt₂(PN–2H–OH)], 48.6); 268 ([SnEt₂(PN–2H–2CH₂OH–CH₃)], 57.0); 240 ([SnEt(PN–H–2CH₂OH–CH₃)], 27.2); 195 ([SnEt₂OH], 6.7); 149 ([SnEt], 23.7) and 120 ([Sn], 46.1). Besides these signals the EI spectrum shows signals for pyridoxine and its fragments, and the FAB spectrum signals at 344 ([SnEt₂(PN–2H)], 100) and 688 ([{SnEt₂(PN–2H)}₂], 23). Infrared and Raman (in parentheses) (cm⁻¹): 1556m (1557w), 1463m (1455w), 1404m, 1371m, ν(ring); 982vs, ν(CO); 517m (525w), ν_{as}(Sn–C); 490sh (476vs), ν_{sym}(Sn–C). Mössbauer: I.S. 1.44, Q.S. 3.07, Γ 0.96 mm s⁻¹, $A_{2/1}$ 1.01. NMR data (DMSO-d₆). ¹H: δ[C(6)H] 7.60s(1); δ[O(3)H] 4.96t(1), ^3J = 5.0 Hz; δ[C(9)H₂] 4.79s(2), ^3J(¹H–¹¹⁹Sn) = 39 Hz; δ[C(7)H₂] 4.38d(2), ^3J = 5.3 Hz; δ[C(8)H₃] 2.28s(3); δ[CH(α)–Sn] 1.26s,br(4); δ[CH(β)–Sn] 1.15t(6), ^3J(¹H–¹¹⁹/¹¹⁷Sn) = 132.9/127.4 Hz. ¹³C: δ[C(3)] 149.6; δ[C(2)] 145.9; δ[C(6)] 138.9; δ[C(4)] 133.1; δ[C(5)] 131.2; δ[C(7)] 56.5; δ[C(9)] 58.8; δ[C(8)] 19.3; δ[C(α)–Sn] 15.7; δ[C(β)–Sn] 9.6. ¹¹⁹Sn: δ –250.4.

Crystallization from absolute methanol afforded crystals suitable for X-ray diffraction which proved to be [SnEt₂(PN–2H)]·CH₃OH (2·CH₃OH). The solution of 2 that had been used for NMR spectroscopy afforded crystals that X-ray crystallography showed to be [SnEt₂(PN–2H) (DMSO)] (3).

2.2.3. [SnBu₂(PN–2H)] (4)

Solid dibutyltin(IV) oxide (1.25 g, 5 mmol) was added to a solution of PN (0.85 g, 5 mmol) in a 75:25 (v/v) mixture of toluene and absolute ethanol (200 ml). After refluxing for 24 h, water was removed by azeotropic distillation in a Dean–Stark funnel and the white solid formed was filtered out and vacuum dried. Yield 95%. M.p. = 226 °C. Found: C, 48.1; N, 3.7; H, 7.2%. [SnBu₂(PN–2H)] requires: C, 48.0; N, 3.5; H, 6.8. The main metallated signals in the EI spectrum are at m/e (ion, intensity) 384 ([SnBu₂(PN–2H–OH)], 31.5); 268 ([SnBu(PN–H–2CH₂OH–CH₃)], 76.0); 240 ([Sn(PN–H–CH₂OH–OH)], 27.5); 177 ([SnBu], 14.0) and 120 ([Sn], 43.5). Besides these signals the EI spectrum shows signals for pyridoxine and its fragments, and the FAB spectrum signals at 398 ([SnBu₂ (PN–2H)-2H], 100) and 800 ([{SnBu₂(PN–2H)}₂], 100). Infrared and Raman (in parentheses) (cm⁻¹): 1556m (1556w), 1462m, 1404w, 1373m, ν(ring); 987vs (896m), ν(CO); 680m, ν_{as}(Sn–C);

616w, ν_{sym}(Sn–C). Mössbauer: I.S. 1.40, Q.S. 2.91, Γ 0.93 mm s⁻¹, $A_{2/1}$ 1.04. NMR data (DMSO-d₆). ¹H: δ[C(6)H] 7.60s(1); δ[O(3)H] 4.98t(1), ^3J = 4.8 Hz; δ[C(9)H₂] 4.79s(2), ^3J(¹H–¹¹⁹Sn) = 36.8 Hz; δ[C(7)H₂] 4.38d(2), ^3J = 5.4 Hz; δ[C(8)H₃] 2.28s(3); δ[CH(α)–Sn] 1.33t(4); δ[CH(β)–Sn] 1.53m(4); δ[CH(γ)–Sn] 1.25m(4); δ[CH(δ)–Sn] 0.78t(6). ¹³C: δ[C(3)] 156.3; δ[C(2)] 148.4; δ[C(6)] 136.8; δ[C(4)] 136.8; δ[C(5)] 131.1; δ[C(7)] 59.1; δ[C(9)] 59.9; δ[C(8)] 19.1; δ[C(α)–Sn] 23.2; δ[C(β)–Sn] 26.7; δ[C(γ)–Sn] 26.1; δ[C(δ)–Sn] 13.4. ¹¹⁹Sn: δ –235.9. Λ_M (dmf), 1.7 S cm² mol⁻¹.

Crystals suitable for X-ray diffractometry were obtained from a solution in absolute methanol.

2.3. Crystal structure determination

2.3.1. X-ray data collection and reduction

Crystals were mounted on glass fibres for data collection in a Bruker CCD Smart diffractometer (2·CH₃OH and 3) or an Enraf-Nonius MACH3 [7] diffractometer (4) Data were collected by the ω-scan technique at 293 K using Mo Kα radiation (λ = 0.71073 Å), and were corrected for Lorentz and polarization effects [8]. MultiScan (SADABS) [9a] or ψ scan [9b] semi-empirical absorption corrections were also made.

2.3.2. Structure solution and refinement

The structure was solved by direct methods [10] and subsequent Fourier maps, and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [11]. All hydrogen atoms were located from difference Fourier maps and refined as riders [11] except those belonging to the –OH groups in 2·CH₃OH and 4, which were refined isotropically in positions previously determined from the corresponding Fourier map. Atomic scattering factors were taken from *International Tables for Crystallography* [12]. Molecular graphics were generated with PLATON98 [13] and PLATON99 [14]. Crystal data, experimental details and refinement results are summarized in Table 1.

3. Results and discussion

3.1. Synthesis

The complexes [SnR₂(PN–2H)] were synthesized using the procedure described by Gielen et al. [5] based on direct reaction of PN with the diorganotin(IV) oxide. The product obtained when R = Et was analytically and spectroscopically identical with that prepared by the method described in [3]. Recrystallization of 1 afforded crystals identical to those described in [2], and recrystallization of 2 gave a solvate with methanol; both were studied by X-ray diffraction crystallography. The solution of 2 in DMSO-d₆ used for NMR spectroscopy

Table 1
Crystal data collection and structure refinement parameters

	$2 \cdot CH_3OH$	3	4
Empirical formula	$C_{13}H_{23}NO_4Sn$	$C_{14}H_{21}NO_4SSn$	$C_{16}H_{27}NO_3Sn$
Formula weight	376.01	426.12	400.08
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (no. 1)	$P2_1/c$ (no.14)	$P2_1/a$ (no.14)
Unit cell dimensions			
a (Å)	8.3145(9)	10.111(2)	10.399(6)
b (Å)	9.4270(10)	13.309(3)	17.967(3)
c (Å)	10.5821(12)	14.329(3)	10.172(2)
α (°)	86.397(2)		
β (°)	67.772(2)	110.659(3)	106.821(19)
γ (°)	74.786(2)		
V (Å^3)	740.27(14)	1804.0(7)	1819.2(11)
Z	2	4	2
D_c (Mg cm^{-3})	1.687	1.569	1.461
$F(000)$	380	840	816
μ (mm^{-1})	1.735	1.544	1.413
Crystal size (mm)	$0.06 \times 0.13 \times 0.24$	$0.07 \times 0.16 \times 0.17$	$0.25 \times 0.20 \times 0.15$
θ Range for data collection (°)	2.08–28.08	2.15–28.08	2.71–26.30
θ Range (25 reflections) (°)	$28.08 < \theta < 92.6$	$28.08 < \theta < 95.2$	$8.946 < \theta < 18.081$
Index ranges	$-10 \leqslant h \leqslant 10, -12 \leqslant k \leqslant 10,$ $-13 \leqslant l \leqslant 9$	$-12 \leqslant h \leqslant 13, -17 \leqslant k \leqslant 15,$ $-18 \leqslant l \leqslant 18$	$-12 \leqslant h \leqslant 12, -22 \leqslant k \leqslant 0,$ $-12 \leqslant l \leqslant 12$
Reflections collected	4811	10658	3898
Unique reflections	3331 [$R_{int} = 0.0412$]	4175 [$R_{int} = 0.1162$]	3685 [$R_{int} = 0.0816$]
Absorption correction	none	empirical	ψ-scan
Maximum, minimum transmission	1.000000, 0.769095	1.0000, 0.5835	0.816, 0.7189
Data, restraints, parameters	3331, 0, 180	4175, 0, 192	3685, 0, 194
Goodness-of-fit on F^2	0.896	0.905	0.940
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0360, wR_2 = 0.066$	$R_1 = 0.0581, wR_2 = 0.1268$	$R_1 = 0.0574, wR_2 = 0.1126$
R indices (all data)	$R_1 = 0.0484, wR_2 = 0.09690$	$R_1 = 0.1086, wR_2 = 0.1406$	$R_1 = 0.2280, wR_2 = 0.1544$
Largest difference peak, hole (e Å^{-3})	1.022, −0.439	0.966, −0.711	0.724, −0.731

afforded crystals **3** that X-ray crystallography showed to contain DMSO coordinated to the metal. [SnBu$_2$(PN–2H)] (**4**) was isolated as a pure compound.

Mode EI mass spectrometry positive ion showed the molecular ion for all compounds and all the FAB spectra show the signal of the dimer (besides organotin fragments such as [SnR$_2$]$^+$ and [SnR]$^+$).

3.2. Solid state structures

3.2.1. [SnEt$_2$(PN–2H)] · CH$_3$OH (**2** · CH$_3$OH)

Crystals of **2** · CH$_3$OH are composed of dimeric [SnEt$_2$(PN–2H)]$_2$ units and methanol molecules. Fig. 1 shows the structure of the dimer and the numbering scheme used. Selected bond lengths and angles are listed in Table 2.

In each dimer the two pyridoxinate anions bridge between the two tin atoms via their deprotonated 4-CH$_2$OH groups while chelating one of them through this O and the likewise deprotonated phenolic OH, creating a structure based on an Sn$_2$O$_2$ ring that is similar to those detected previously in diorganotin compounds with N-protonated or N-methylated pyri-
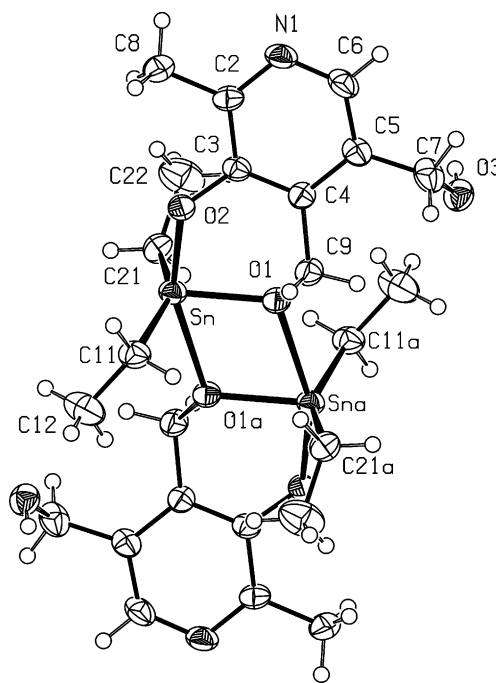

Fig. 1. The molecular structure of [SnEt$_2$(PN–2H)] in (**2** · CH$_3$OH), showing the numbering scheme.

Table 2
Selected bond lengths (Å) and angles (°) in [SnEt$_2$(PN–2H)]·CH$_3$OH (**2**·CH$_3$OH), [SnEt$_2$(PN–2H)(DMSO)] (**3**) and [SnBu$_2$(PN–2H)] (**4**), with e.s.d.'s in parentheses[a]

	2·CH$_3$OH	**3**	**4**
(a) Tin environment			
Sn–O(1)	2.061(2)	2.072(4)	2.027(6)
Sn–O(2)	2.075(2)	2.093(4)	2.075(6)
Sn–C(11)	2.110(4)	2.111(7)	2.109(9)
Sn–C(21)	2.123(4)	2.131(7)	2.100(11)
Sn–O(1)[#1]	2.386(2)	2.330(4)	2.268(6)
Sn–X[b]	2.805(3)	2.588(5)	
O(1)–Sn–C(11)	105.09(13)	100.7(2)	112.1(4)
O(1)–Sn–C(21)	102.97(13)	102.1(2)	115.7(4)
O(1)–Sn–O(2)	86.68(9)	86.05(16)	86.1(2)
O(1)–Sn–O(1)[#1]	71.48(10)	70.12(17)	69.7(3)
O(2)–Sn–C(11)	94.02(13)	95.0(2)	100.6(3)
O(2)–Sn–C(21)	102.66(13)	100.4(2)	96.2(4)
O(2)–Sn–O(1)[#1]	157.33(9)	155.97(16)	155.7(2)
C(11)–Sn–C(21)	148.02(16)	153.2(3)	130.3(5)
C(11)–Sn–O(1)[#1]	86.14(13)	86.6(2)	90.7(3)
C(21)–Sn–O(1)[#1]	88.48(12)	88.0(2)	92.6(4)
C(11)–Sn–X	75.71(9)	81.9(2)	
C(21)–Sn–X	78.14(13)	77.6(3)	
O(2)–Sn–X	75.71(9)	85.30(19)	
O(1)[#1]–Sn–X	126.39(9)	118.61(18)	
(b) Pyridoxine ligand			
O(1)–C(9)	1.439(4)	1.461(7)	1.421(9)
C(4)–C(9)	1.516(5)	1.502(8)	1.519(12)
C(3)–C(4)	1.391(5)	1.405(8)	1.405(13)
C(3)–O(2)	1.339(4)	1.344(7)	1.324(11)
N(1)–C(2)	1.339(5)	1.320(8)	1.334(12)
N(1)–C(6)	1.338(5)	1.341(8)	1.326(12)
O(1)–C(9)–C(4)	112.2(3)	109.1(5)	111.9(7)
C(3)–C(4)–C(9)	117.8(3)	120.9(6)	118.1(9)
C(5)–C(4)–C(3)	119.0(3)	117.0(6)	119.0(9)
C(5)–C(4)–C(9)	123.1(3)	122.0(6)	122.9(10)
O(2)–C(3)–C(4)	122.5(3)	120.8(5)	120.6(9)
O(2)–C(3)–C(2)	118.5(3)	119.1(5)	120.4(10)
C(2)–C(3)–C(4)	119.0(3)	120.1(6)	118.9(10)

[a] Symmetry operations: for **2**·CH$_3$OH, $-x, -y + 1, -z + 1$ (#1) and $x + 1, y, z$ (#2) for **3**, $-x + 2, -y + 1, -z$; and for **4** $-x, -y - 1, -z - 1$.
[b] X = O(3)[#2] for **2**·CH$_3$OH and O(11) for **3**.

doxine [2–4]. The different lengths of the Sn–O bonds make the ring slightly asymmetric. Each tin atom coordinates octahedrally to two ethyl C atoms, to the O(2) of a deprotonated phenolic hydroxyl group, to the O(1) of the deprotonated 4-CH$_2$OH group of the same PN–2H molecule, to the similarly deprotonated O(1^i) of the other pyridoxinate anion in its dimer, and to the O(3) atom of a neighbouring dimer [(Sn–O(3): 2.805(3) Å]. Whereas Sn–O(1), Sn–O(2) and Sn–O(1)[#1] have normal covalent bond lengths (the sum of the covalent radii of Sn and O is 2.13 Å [15]) the Sn–O(3) bond is longer, although still in the range found in other systems [16]. In particular, Sn–O(3) is close to the 2.802(3) Å found in [SnMe$_2$(PN–H)]·NO$_3$·2H$_2$O [2], a methyltin(IV) complex in which Sn has a very similar distorted octahedral environment in spite of its PN ligand being only monodeprotonated and in spite of its different R.

As in [SnMe$_2$(PN–H)]·NO$_3$·2H$_2$O [2], the Sn–O(3) bond results in the formation of Sn$_2$O$_4$C$_8$ rings that link the dimers in polymeric chains in which the Sn$_2$O$_2$ rings are not coplanar but stepped, although the distance between successive Sn$_2$O$_2$ planes is less than in the dimethyl derivative [2] (1.07(1) as against 1.711 Å).

The methanol molecules included in the lattice stabilize the crystal through the formation of hydrogen bonds via their O atoms: one with a C(5)–CH$_2$OH–OH group [O(3)–H(3)···O(41)[#1]: 0.77(4), 2.04(4), 2.797(5); 168(5)°. # 1 = $-x, -y + 1, -z + 1$], and another with the N(1) atom of a neighbouring molecule [O(41)–H(41)···N(1)[#3]: 0.77(5), 2.13(5), 2.866(5); 160(5)°. # 3: $x, y + 1, z + 1$]. Through these moderate [17] hydrogen bonds the methanol molecules link the chains described above to form a two-dimensional polymeric network.

3.2.2. [SnEt$_2$(PN–2H)(DMSO)] (3)

Crystals of **3** are composed of dimeric [SnEt$_2$(PN–2H)(DMSO)]$_2$ units. Fig. 2 shows their structure and the numbering scheme used, and selected bond lengths and angles are listed in Table 2.

As in **2**·CH$_3$OH, the two pyridoxinato ligands in each dimer coordinate to the tin centres via O(2) and bridging O(1) atoms, and the tin atoms have a distorted octahedral environment. The Sn$_2$O$_2$ ring is more symmetrical than in **2**·CH$_3$OH. The Sn–C bond lengths are similar in the two compounds, but Sn–O(11) is shorter than Sn–O(3) is in **2**·CH$_3$OH, which makes C–Sn–C wider [153.2 (3)° as against 148.02 (16)°].

The lengths and angles in the coordinated DMSO molecule are unremarkable [18], and the structural parameters of PN–2H are close to those found in **2**·CH$_3$OH. Although the C(5)–CH$_2$OH group is not
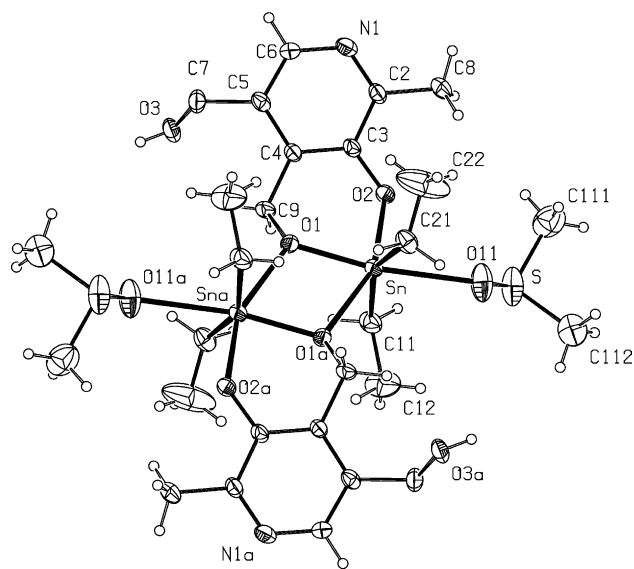

Fig. 2. The molecular structure of [SnEt$_2$(PN–2H)(DMSO)] (**3**), showing the numbering scheme.

coordinated in **3** (although it does form a hydrogen bond with the N atom of a neighbouring dimer) O(3)–C(7) is only slightly shorter in **3** than in **2** · CH$_3$OH [1.405(8) as against 1.426(5) Å] and the O(3)–C(7)–C(5) angle only slightly narrower [110.3(6)° as against 114.0(3)°].

The only hydrogen bond detected is that mentioned above [O(3)–H(30)···N(1)$^{#2}$: 0.82, 1.95, 2.762(7); 171.4°. # 2: $-x + 3, y - 1/2, -z + 1/2$]. This moderate [17] hydrogen bond connects the dimers in a polymeric structure.

3.2.3. [SnBu$_2$(PN–2H)] (4)

Crystals of **4** are composed of [SnBu$_2$(PN–2H)]$_2$ units. Fig. 3 shows their structure and the numbering scheme used, and selected bond lengths and angles are listed in Table 2. Although these dimers are also based on Sn$_2$O$_2$ rings, being formed through PN–2H bridges involving bridging O(1) and also O(2) atoms, the environment of the tin atoms is different from those of **2** · CH$_3$OH and **3**, the coordination number now being 5 instead of 6. The Sn–C, Sn–O(1) and Sn–O(2) bond lengths are similar to those found in **2** · CH$_3$OH and **3**, but the absence of an O atom in the position previously occupied by O(3) or O(11), and the large volume of the butyl group and its repulsion from the PN–2H ligand, result in a C–Sn–C angle of 130.3 (5)°, the narrowest found by us in diorganotin derivatives of pyridoxine or its *N*-methyl derivative [2–4]. The value of the parameter τ [19], 0.46, means that the coordination polyhedron is almost exactly half way between a square pyramid ($\tau = 0$) and a trigonal bipyramid ($\tau = 1$). The formation

Fig. 3. The molecular structure of [SnBu$_2$(PN–2H)] (**4**), showing the numbering scheme.

of a hydrogen bond between the C(5)–CH$_2$OH group and the N atom of a neighbouring pyridine ring [O(3)–H(3)···N(1)$^{#2}$: 1.06, 1.81, 2.823(10); 158.0°. # 2: $x, -y - 1/2, z - 1/2$] affects the structural parameters of the C(5)–CH$_2$OH group in a similar way as in **3**.

3.3. Spectral characteristics

Besides the bands indicated in Section 2, the IR and Raman spectra of the compounds exhibit medium–strong bands attributed to the ν(CH$_3$–, CH$_2$–) vibrations of the alkyl groups of the SnR$_2$ fragment. In the 1650–1450 cm^{-1} region the pyridine ring bands are slightly shifted from their positions in the spectra of the free ligand. Also, as expected, neither the two weak Raman bands typical of the N-protonated ring nor the strong band at 1530 cm^{-1}, also characteristic of this system [20], is present in the spectra of the complexes. All the Mössbauer spectra consist of well resolved, slightly asymmetric doublets with isomer shifts and quadrupole splittings that are typical of diorganotin(IV) compounds. The values obtained for the butyl derivative are lower than those found in [SnBu$_2$(MePN–H)]I (which has a similar SnC$_2$O$_3$ kernel) possibly because of differences in the donor capacities of the ligands and the distortion of the kernel (specially as regards the C–Sn–C angle, which is significantly wider in the MePN compound than in **4**). In the case of **4**, the fact that the C–Sn–C bond angle, 130.3(5)°, is close to the theoretical value for a tbp structure allows the p.q.s. value for the organic groups in the equatorial positions, −1.13 mm s^{-1}, to be used to calculate a value of 2.96 mm s^{-1} for Q.S. which agrees very well with the experimental value, 2.91 mm s^{-1}.

3.4. Structures in solution

The ^{1}H and ^{13}C NMR data for [SnEt$_2$(PN–2H)] and [SnBu$_2$(PN–2H)] in DMSO-d$_6$ agree with those previously found [3,5c] and suggest that PN–2H remains coordinated in solution. The signals attributed to the PN–2H fragment occupy practically the same positions in the spectra of all three derivatives suggesting that in solution the coordination mode of the ligand is similar in all three. The signals of **1** are slightly shifted respect to those previously found for [SnMe$_2$(H$_2$O)(PN–2H)] · 0.5H$_2$O [2].

The ^{119}Sn spectra of **2** and **4** each exhibit a single resonance, at −250.4 and −235.9 ppm, respectively, showing that these complexes each have only one type of organotin moiety. Although ^{119}Sn chemical shifts are influenced by several factors [21], the coordination mode of the tin atom is one of the most important [22]; the values obtained for **2** and **4** are in the range reported [23] for pentacoordinated tin, which is compatible especially in the case of the ethyl derivative, with there
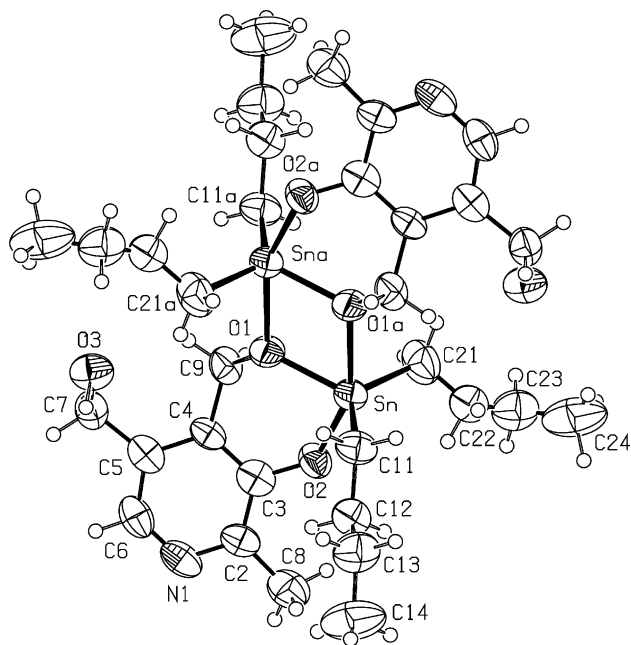
being significant coordination of DMSO (as is also suggested by the formation of **3**). Complex **1** presents two signals located at −204.7 and −216.7, suggesting the presence of two slightly different types of molecule in solution.

4. Supplementary data

Crystallographic data have been deposited with The Director, CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-366033; e-mail: deposit@ ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) and are available on request, quoting the deposition number 215053, 215054 and 215055 for the **2·CH₃OH**, **3** and **4**, respectively.

Acknowledgements

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