Crystal Structure of Bis[acetatotetrabutyl- μ -hydroxy- μ_3 -oxoditin], [(AcO)Bu₂Sn(OH)OSnBu₂]₂

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The title compound comprises two slightly different types of [(AcO)Bu₂Sn(OH)OSnBu₂]₂ units, which are hydrogen bonded via the μ -OH and AcO groups, giving a polymeric structure.

(Received July 31, 2006; Accepted November 9, 2006; Published on web July 13, 2007)

In the last two decades there has been considerable interest in the chemistry of organotin-oxo clusters.¹ Tetraorganodistannoxanes are of current interest owing to their potential as homogeneous catalysts for a variety of organic reactions.² The title compound (Fig. 1) was obtained by the reaction of pyridoxine hydrochloride with SnBu₂Cl₂ in ethanol-water, in an attempt to obtain a dibutyltin derivative of pyridoxine.^{3,4} Anal. Found: C, 38.7; H, 7.2. Calcd. for C₉H₂₀O₂Sn: C, 38.8; H, 7.1. IR (cm⁻¹) selected bands were: 3315(s), ν (OH); 1607(vs), ν_{asym} (COO⁻); 1387(vs), ν_{sym} (COO⁻); 668(m), ν_{asym} (Sn-C); 581(br), ν_{sym} (Sn-C), ν (Sn-O). ¹H NMR (CDCl₃; δ): 1.35 (m, 4, H_a); 1.63 (m, 4, H_b); 1.35 (m, 4, H_c); 0.90 (t, 3, H_d), 0.87 (t, 3, H_e); 1.91 (s, 3, CH₃-COO⁻).

The crystal structure was solved by direct methods and refined by full-matrix least squares. Intensity data were collected at 293(2)K from a 0.40 $\times$ 0.32 $\times$ 0.16 mm crystal in an Enraf-Nonius MACH3 diffractometer. The C atoms of the Bu groups are disordered, and in the final refinement a displacement coefficient restricted to 0.08 was used for the three butyl C atoms that are not bound to the tin atom, which were then refined isotropically.

A summary of the crystal along with further details of the structure determination and refinement are given in Table 1. The atomic coordinates, along with their equivalent isotropic displacement parameters, are presented in Table 2. The selected

bond lengths and bond angles are listed in Table 3.

The asymmetric unit of the structure contains two crystallographically independent [(AcO)Bu₂Sn(OH)OSnBu₂]₂ molecules, which are both centrosymmetric. Figure 2 shows an ORTEP drawing of one of them. In each, as in the very similar diethyltin derivative of perfluorophenylacetato,⁵ there are two different kinds of tin atoms. Both coordinate to two butyl C atoms, a bridging hydroxy O atom, a bridging oxo O and one other O atom, but for Sn(2) this third O atom belongs to the acetato group, while for Sn(1) it is the oxo O atom of the other half of the molecule. The environments of both Sn(1) and Sn(2) are distorted square pyramids with O(1) apical. The different

Fig. 1 Chemical diagram.

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Table 1 Crystal and experimental data

Empirical formula: C ₃₆ H ₈₀ O ₈ Sn ₄	
Formula weight = 1115.76	
Crystal system: monoclinic	
Space group: C2/c (No.15)	Z = 8
a = 24.949(12) Å	
b = 11.606(16) Å	
c = 35.202(15) Å	
β = 91.207(5)°	
V = 10191.2(16) Å ³	
D _{cal} = 1.454 Mg/m ³	
μ = 1.975 mm ⁻¹	
F(0 0 0) = 4480	
θ range for data collection : 1.16 to 27.45°	
Reflections collected / unique: 11634 / 11634 [R(int) = 0.0476]	
Absorption correction : ϕ -scan	
Max. and min. transmission: 0.962 and 0.891	
Goodness-of-fit on F ² = 1.109	
Final R indices [I > 2 σ (I)] R1 = 0.0383, wR2 = 0.1603	
Measurement: Enraf-Nonius MACH 3	
Program system: Nonius BV. CAD4-EXPRESS	
Structure determination: direct methods (SHELXS97)	
Refinement: full matrix least-squares on F ² (SHELXL97)	

CCDC 252524 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Fig. 2 Molecular structure of one $[(\text{AcO})\text{Bu}_2\text{Sn}(\text{OH})\text{OSnBu}_2]_2$ molecule. For clarity the carbon atoms of the butyl groups have been miniaturized, by fixing the displacement parameters.

Table 2 Atomic coordinates ($\times 10^2$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U_{eq}
Sn(1)	576(1)	593(1)	2752(1)	111(1)
Sn(2)	-442(1)	591(1)	3356(1)	119(1)
O(1)	-241(1)	562(2)	2809(1)	107(1)
O(2)	427(1)	630(3)	3349(1)	159(1)
O(11)	-1234(1)	589(2)	3113(1)	124(1)
O(12)	-1597(1)	803(1)	3659(1)	80(1)
C(10)	-1625(1)	664(2)	3316(1)	82(1)
C(11)	924(1)	-1128(2)	2690(1)	80(1)
C(12)	732(1)	-2032(2)	2810(1)	82(1)
C(13)	1015(1)	-3248(2)	2807(1)	78(1)
C(14)	1469(1)	-3104(2)	2600(1)	81(1)
C(15)	959(1)	2245(2)	2721(1)	81(1)
C(16)	1356(1)	2831(2)	3058(1)	82(1)
C(17)	1778(1)	2053(2)	3074(1)	82(1)
C(18)	2073(1)	2618(2)	3426(1)	80(1)
C(20)	-2122(1)	550(2)	3140(1)	82(1)
C(21)	-495(1)	-1139(2)	3562(1)	81(1)
C(22)	-256(1)	-1642(2)	3901(1)	76(1)
C(23)	-310(1)	-827(2)	4208(1)	80(1)
C(24)	-97(1)	-1473(2)	4591(1)	82(1)
C(25)	-459(1)	2340(2)	3561(1)	81(1)
C(26)	-360(1)	3296(2)	3282(1)	81(1)
C(27)	-437(1)	4297(2)	3489(1)	78(1)
C(28)	-462(1)	5177(2)	3243(1)	76(1)
Sn(3)	2157(1)	1523(1)	247(1)	96(1)
Sn(4)	2915(1)	3091(1)	853(1)	105(1)
O(3)	2711(1)	2806(2)	301(1)	105(1)
O(4)	2332(1)	1663(3)	841(1)	131(5)
O(31)	3398(1)	4434(2)	599(1)	130(5)
O(32)	3800(1)	4818(2)	1140(1)	92(1)
C(30)	3700(1)	5027(2)	847(1)	95(1)
C(31)	3542(1)	2012(2)	1100(1)	94(1)
C(32)	3687(1)	1039(2)	859(1)	93(1)
C(33)	4092(1)	265(2)	981(1)	91(1)
C(34)	4161(1)	-698(2)	727(1)	92(1)
C(35)	2390(1)	4318(2)	1094(1)	96(1)
C(36)	2228(1)	4154(2)	1423(1)	90(1)
C(37)	2472(1)	3788(2)	1744(1)	91(1)
C(38)	2147(1)	4176(2)	2104(1)	91(1)
C(40)	3997(1)	5983(2)	631(1)	94(1)
C(41)	1339(1)	1963(2)	275(1)	93(1)
C(42)	1227(1)	3285(2)	351(1)	97(1)
C(43)	639(1)	3523(2)	347(1)	95(1)
C(44)	743(1)	4761(2)	343(1)	93(1)
C(45)	2464(1)	-145(2)	159(1)	92(1)
C(46)	2407(1)	-1072(2)	451(1)	96(1)
C(47)	1892(1)	-1479(2)	454(1)	93(1)
C(48)	1893(1)	-2432(2)	779(1)	94(1)

Table 3 Selected bond lengths ($\text{\AA}$) and angles ($^\circ$)

Sn(1)-O(1)	2.053(2)
Sn(1)-O(1a)	2.129(2)
Sn(1)-O(2)	2.142(3)
Sn(1)-C(15)	2.147(2)
Sn(1)-C(11)	2.191(2)
Sn(2)-O(1)	2.000(2)
Sn(2)-O(11)	2.135(3)
Sn(2)-C(21)	2.139(2)
Sn(2)-C(25)	2.156(2)
Sn(2)-O(2)	2.171(4)
O(1)-Sn(1)-O(1a)	73.67(9)
O(1)-Sn(1)-O(2)	73.28(11)
O(1a)-Sn(1)-O(2)	146.94(11)
O(1)-Sn(1)-C(15)	117.71(8)
O(1a)-Sn(1)-C(15)	97.68(7)
O(2)-Sn(1)-C(15)	96.83(12)
O(1)-Sn(1)-C(11)	113.01(8)
O(1a)-Sn(1)-C(11)	92.34(8)
O(2)-Sn(1)-C(11)	101.17(10)
C(15)-Sn(1)-C(11)	129.12(8)
O(1)-Sn(2)-O(11)	82.14(8)
O(1)-Sn(2)-C(21)	109.18(8)
O(11)-Sn(2)-C(21)	94.13(9)
O(1)-Sn(2)-C(25)	110.25(8)
O(11)-Sn(2)-C(25)	96.38(9)
C(21)-Sn(2)-C(25)	140.19(7)
O(1)-Sn(2)-O(2)	73.66(9)
O(11)-Sn(2)-O(2)	155.75(9)
C(21)-Sn(2)-O(2)	95.26(10)
C(25)-Sn(2)-O(2)	90.59(11)

a: $-x, y, -z+1/2$

environments of the tin atoms determine the differences in the bond angles, especially regarding the C-Sn-C angles [$129.12(8)^\circ$ at Sn(1), $140.1(3)^\circ$ at Sn(2)]. The $[(\text{AcO})\text{Bu}_2\text{Sn}(\text{OH})\text{OSnBu}_2]_2$ molecules are hydrogen-bonded *via* their OH and AcO groups, creating a polymeric structure $[\text{O}(2)\cdots\text{H}(2)\cdots\text{O}(32)]^{\text{iii}}$: $0.93, 1.95, 2.775(3)\text{\AA}$, 146.7° ; $\text{O}(4)\cdots\text{H}(4)\cdots\text{O}(12)$: $0.93, 1.92, 2.756(3)\text{\AA}$, 148.6° . i: $-x, y, -z+1/2$; iii: $-x+1/2, y-1/2, -z+1/2$.

Acknowledgements

We thank the Xunta de Galicia, Spain, for support under projects PGIDIT03PXIC20306PN and PGIDIT03PXIC30103PN.

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