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Crystal structure of octabutyl-μ-dichloro-μ_3-dioxodichlorotetratin(IV)

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Abstract

An X-ray diffraction study has shown that Sn atoms in octabutyl-μ-dichloro-μ_3-dioxodichlorotetratin(IV) have distorted trigonal bipyramidal geometry with *cis*-equatorial butyl groups. Sn(1)–C(but) and Sn(2)–C(but) bonds are 2.077(21), 2.111(26) and 2.097(23), 2.114(22) Å, respectively. The distances of the triply-bridging O atom from Sn atoms are 2.151(9), 2.018(9) and 2.069(9) Å, and those of the bridging Cl atom are 2.666(5) and 2.831(6) Å. The distance Cl(term)–Sn(2) is 2.426(5) Å. Refinement of the structure, based on 1828 observed reflections, converged to an R factor of 0.049 and a weighted R of 0.053. Crystal data for the compound are: a 13.672(6), b 19.529(9), c 8.999(2) Å, β 102.66(3)°, space group $P2_1/c$, $Z = 2$, $M_r = 1105.49$ for $[Sn_4(C_4H_9)_8Cl_4O_2]$, V 2344(2) Å^3, D_x 1.464 gcm^{-3}, $F(000) = 1096$, λ(Mo-K_α) 0.71069 Å, μ 22.1 cm^{-1} and T 293 K.

Introduction

Tin has a rich organometallic chemistry with many practical applications. The tin atom exhibits two- to eight-coordination in neutral, cationic, or anionic species giving rise to dimers and other oligomers. This variety in structural properties can lead to ambiguity in symmetry type and coordination number even in relatively simple systems. We have prepared some selected alkyltin compounds, of which only the title compound has to date yielded suitable crystals for X-ray diffraction analyses.

Experimental

The compound was prepared by treating 0.01 mole of dibutyltin dichloride (Aldrich) in acetylacetone with 30 ml of 1.0 M NaOH solution. The mixture was gently warmed on a water bath then the white precipitate was filtered off and dried in air. It was recrystallized in acetone at room temperature. Cell dimensions from

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least-squares refinement of 18 reflections centred on a Nicolet P3 diffractometer with $9 < 2\theta < 23°$. The space group $P2_1/c$ was uniquely determined by the observed systematic absences $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$). Intensity data were collected from crystal $0.30 \times 0.30 \times 0.30$ mm. Mo-K_α radiation and graphite monochromator were used. 4339 unique intensities between $4.0 < 2\theta < 50°$ with ω-scan and variable scan rate 2.0 to 30.0° min^{-1}; maximum $\sin\theta/\lambda$ 0.594 Å^{-1}. $h, k, \pm l$ set with maximum values 15, 22, 10, respectively. Two standard reflections examined after every 68 measurements showed no significant variation. Lorentz and polarization corrections were applied together with an empirical absorption correction based on the ϕ-scan method (min. 0.78, max. 1.00). No correction was made for secondary extinction. The structure was solved by MULTAN 80 [1] and Fourier methods of XRAY 76 program system [2]. Anisotropic least-squares refinement for non-hydrogen atoms reduced R value to 0.049, $R_w = 0.053$ and $(\Delta/\sigma)_{\max} = 0.46$. Final max and min electron densities 0.53 and -0.48 eÅ^{-3}. A total of 1828 reflections with $|F_o| \geq 6.0\sigma(|F_o|)$ were used in the refinement. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$ based on counting statistics. Atomic scattering factors from Cromer and Mann [3]. The anomalous dispersion corrections specified by Cromer & Liberman [4] were included for Sn and Cl atoms. The infrared spectrum was recorded on a Perkin–Elmer 577 spectrophotometer with KBr pellets.

Discussion

The atomic coordinates with equivalent isotropic temperature factors [5] are presented in Table 1 and interatomic distances and angles in Table 2. A perspective

Table 1

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^\star a_j^\star a_i a_j$

	x	y	z	U_{eq} (Å^2)
Sn(1)	5009(1)	−402(1)	1639(1)	0.089
Sn(2)	4988(1)	1541(1)	1523(1)	0.093
Cl(1)	5024(5)	−1767(2)	1588(6)	0.128
Cl(2)	5000(5)	1034(3)	3988(6)	0.144
O(1)	4989(8)	596(5)	620(10)	0.084
C(1)	6431(18)	−351(11)	3045(24)	0.140
C(2)	7279(25)	−620(17)	2763(34)	0.225
C(3)	8238(25)	−551(19)	4018(42)	0.235
C(4)	8968(30)	−723(25)	3334(45)	0.307
C(5)	3569(18)	−336(11)	2122(25)	0.146
C(6)	2781(25)	−687(17)	1413(38)	0.231
C(7)	1784(29)	−613(24)	1881(50)	0.253
C(8)	949(40)	−507(31)	751(63)	0.396
C(9)	6419(17)	1982(11)	1883(24)	0.127
C(10)	7134(24)	1738(15)	3132(35)	0.186
C(11)	8206(33)	2061(23)	3274(45)	0.245
C(12)	8985(36)	1804(24)	4226(58)	0.311
C(13)	3524(16)	1952(11)	933(24)	0.131
C(14)	2855(23)	1768(15)	1857(32)	0.192
C(15)	1799(29)	2064(21)	1215(46)	0.250
C(16)	1070(33)	1780(28)	1689(58)	0.365

Table 2

Interatomic distances (Å) and angles (°)

Sn(1)–Cl(1)	2.666(5)	C(1)–Sn(1)–C(5)	131.5(9)
Sn(1)–O(1)	2.151(9)	C(1)–Sn(1)–O(1^{i})	113.9(7)
Sn(1)–C(1)	2.077(21)	C(5)–Sn(1)–O(1^{i})	114.6(6)
Sn(1)–C(5)	2.111(26)	Cl(2)–Sn(2)–O(1)	89.6(3)
Sn(2)–Cl(2)	2.426(5)	Cl(2)–Sn(2)–C(9)	102.0(6)
Sn(2)–O(1)	2.018(9)	Cl(2)–Sn(2)–C(13)	101.6(6)
Sn(2)–C(9)	2.097(23)	Cl(2)–Sn(2)–Cl(1^{i})	164.8(3)
Sn(2)–C(13)	2.114(22)	O(1)–Sn(2)–Cl(1^{i})	75.4(3)
Sn(2)–Cl(1^{i}) [a]	2.831(6)	O(1)–Sn(2)–C(9)	110.8(7)
Sn(1)–O(1^{i})	2.069(9)	O(1)–Sn(2)–C(13)	109.3(6)
C(1)–C(2)	1.346(43)	C(9)–Sn(2)–C(13)	133.1(8)
C(2)–C(3)	1.538(43)	C(9)–Sn(2)–Cl(1^{i})	83.8(4)
C(3)–C(4)	1.326(60)	C(13)–Sn(2)–Cl(1^{i})	80.8(5)
C(5)–C(6)	1.318(38)	Sn(1)–C(1)–C(2)	126.6(18)
C(6)–C(7)	1.519(57)	Sn(1)–C(5)–C(6)	124.6(22)
C(7)–C(8)	1.368(62)	C(1)–C(2)–C(3)	117.3(28)
C(9)–C(10)	1.402(35)	C(2)–C(3)–C(4)	104.2(32)
C(10)–C(11)	1.574(55)	C(5)–C(6)–C(7)	120.3(31)
C(11)–C(12)	1.312(60)	C(6)–C(7)–C(8)	117.5(42)
C(13)–C(14)	1.411(41)	Sn(2)–C(9)–C(10)	116.6(19)
C(14)–C(15)	1.545(48)	Sn(2)–C(13)–C(14)	117.1(16)
C(15)–C(16)	1.292(67)	C(9)–C(10)–C(11)	113.7(27)
		C(10)–C(11)–C(12)	120.5(39)
Cl(1)–Sn(1)–O(1^{i})	78.4(3)	C(13)–C(14)–C(15)	110.9(26)
Cl(1)–Sn(1)–O(1)	153.9(3)	C(14)–C(15)–C(16)	116.1(37)
Cl(1)–Sn(1)–C(1)	92.8(6)		
Cl(1)–Sn(1)–C(5)	94.4(6)		
Sn(1)–O(1)–Sn(2)	131.2(5)		
Sn(1)–O(1)–Sn(1^{i})	104.6(4)		
Sn(1)–Cl(1)–Sn(2^{i})	82.3(5)		
Sn(2)–O(1)–Sn(1^{i})	124.3(4)		
O(1)–Sn(1)–C(1)	98.0(6)		
O(1)–Sn(1)–O(1^{i})	75.4(3)		

[a] $i = -x+1, -y, -z$.

view of the molecule with labelled atoms is given in Fig. 1. Lists of thermal parameters and structure factors are available from the authors. The centrosymmetric molecule contains two $Sn_2Bu_4Cl_2O$ units joined together by bridging Cl and triply bridging O atoms. Another Sn-coordinated Cl atom in the asymmetric unit is terminal. Each Sn atom is in a distorted trigonal bipyramidal environment with *cis* equatorial butyl groups.

Together the four Sn, two bridging Cl, and two triply-bridging O atoms form a planar structure made up of three quadrilaterals. The non-linear chlorine bridges involve fairly long Sn–Cl distances of 2.666(5) and 2.831(6) Å. The bridging Sn–Cl–Sn angle is only 82.3(5)°, while the axial Cl–Sn(2)–Cl angle has a value of 164.8(3)°. The two distances of the bridging O atom from the Sn atoms, 2.151(9), 2.069(9) Å, and the angle Sn–O–Sn 104.6(4)° in the central Sn_2O_2 ring are comparable to the values reported for dimeric oxotrifluoroacetatovinyltin compound [6].

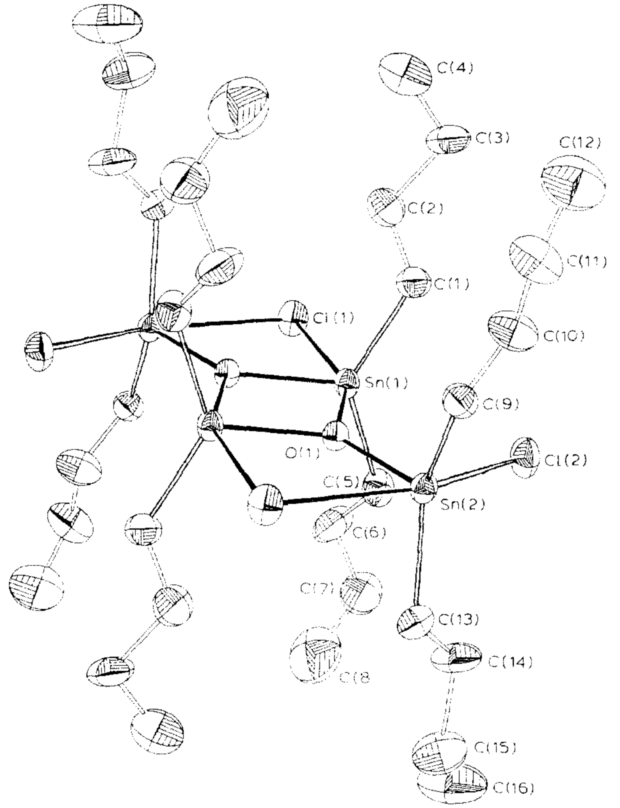

Fig. 1. An ORTEP drawing of the molecule and the atom labelling of the asymmetric unit.

The Sn–C values falling between 2.077(21) and 2.114(22) Å, are consistent with the generalisation that the Sn–C bond tends to be shorter when the Sn is also attached to chlorine [7]. The shortest Sn...Sn distance is 3.338(2) Å, between Sn(1) and Sn(1^i), where i = $-x+1, -y, -z$. There are no intermolecular contacts below

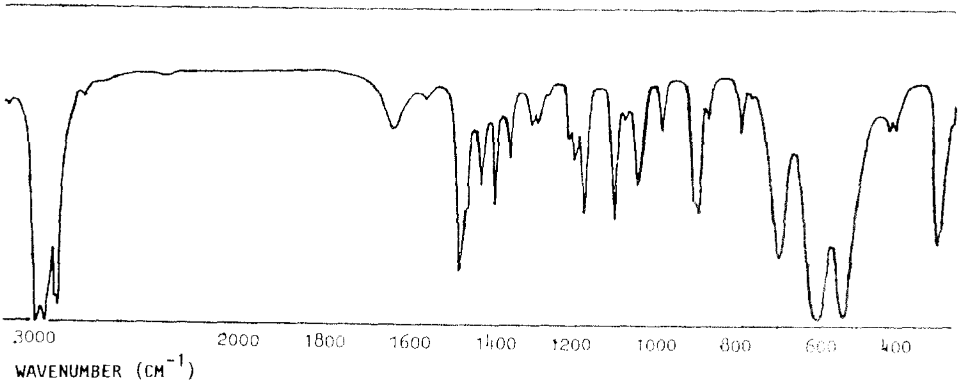

Fig. 2. Infrared spectrum of [$Sn_4(C_4H_9)_8Cl_4O_2$].

3.30 Å. As expected, the infrared spectrum (Fig. 2) contains bands at 600 and 540 cm^{-1} in the Sn–C stretching region, where the higher-frequency band corresponds to the asymmetric Sn–C stretch [8]. A single band of 310 cm^{-1} is attributable to Sn–Cl stretching frequencies. Symmetric and asymmetric stretching modes of Sn–O–Sn bridges are assigned at ca. 410–430 and 700 cm^{-1} in agreement with corresponding assignments in the $[Sn_3O_2Cl_4(ClO_4)_4]_2$ spectrum [9].

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