

Note

Synthesis, characterization and crystal structure of $(C_3H_5N_2)_2[Sn_2(NO_3)_4(\mu-OH)_2Me_4]$, a di- μ -hydroxo-bridged compound with heptacoordinated tin(IV)

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(Received August 12, 1993; revised October 15, 1993)

Abstract

$[Sn_2(NO_3)_2(\mu-OH)_2Me_4]$ reacts with imidazole in nitric acid media to give $(C_3H_5N_2)_2[Sn_2(NO_3)_4(\mu-OH)_2Me_4]$, the structure of which was determined by X-ray diffraction and refined to $R=0.032$ using 1711 observed reflections. The compound is monoclinic, space group $P2_1/c$, with $a=9.315(1)$, $b=16.107(5)$, $c=8.147(2)$ Å, $\beta=101.94(1)^\circ$, $Z=2$. The crystal consists of imidazolium $[C_3H_5N_2]^+$ cations and $[Sn_2(NO_3)_4(\mu-OH)_2Me_4]^{2-}$ anions with the imidazolium rings hydrogen-bonded to nitrate groups of neighbouring units and to the hydroxyl bridging groups of the anion. Each hydroxyl group is also hydrogen bonded to one nitrate group of a neighbouring anion. In the anion each tin atom is seven-coordinated to two methyl groups, one asymmetrically bidentate nitrate anion, one monodentate nitrate anion and two bridging hydroxyl groups. IR and Mossbauer data are discussed on the basis of the above coordination scheme.

Key words Crystal structures; Tin complexes; Hydroxo complexes; Dinuclear complexes

Introduction

Biological and industrial applications of organotin(IV) compounds have increased interest in the hydrolytic equilibria of dialkyltin(IV) and trialkyltin(IV) cations [1]. Potentiometric studies of the hydrolysis of SnR_2^{2+} ions in aqueous solution ($R=Me, Et$) [2] have shown that the dinuclear species $[(SnR_2)_2(\mu-OH)_2]^{2+}$ exists at $pH \approx 4$ and high organometal ion concentration. Although it has recently [3] been shown that the hydroxo

species initially formed in the reaction of dibutyltin oxides with carboxylic acids lose a water molecule to yield isolatable tetraorganodistannoxanes when the steric demands of the butyl group on the tin atom are not severe, di- μ -hydroxobis[*dimethyl*tin(IV)], $[Sn_2(NO_3)_2(\mu-OH)_2Me_4]$, is isolated when dimethyltin oxide is dissolved in nitric acid and the solvent is partially evaporated [4, 5]. The tin atoms in this latter compound are five-coordinate, as in $[Sn_2^+Bu_4(O_2CCH_3)_2(\mu-OH)_2]$ [3b] and most distannoxanes [6], but coordination numbers of six in chloromonooorganotin dihydroxy-bridged species [6], and seven in the aryltin(IV) $[Sn_2(NO_3)_4(\mu-OH)_2Ph_4]^{2-}$ anion [7], have also been reported. To investigate further the stabilization of the $[(SnMe_2)_2(\mu-OH)_2]^{2+}$ unit and the possibility of increasing the coordination number of its tin atoms while preserving its integrity, we reacted $[Sn_2(NO_3)_2(\mu-OH)_2Me_4]$ with imidazole in an aqueous nitric acid medium, obtaining $(C_3H_5N_2)_2[Sn_2(NO_3)_4(\mu-OH)_2Me_4]$ (I), in which each tin in the dinuclear anion was shown by X-ray diffraction to be seven-coordinate.

Experimental

Materials

Imidazole (Ega), nitric acid (65%, Merck), silver nitrate (Probus) and dimethyltin dichloride (Ventron) were used as supplied. Solvents were purified by the usual methods.

Synthesis

Compound I is an air-stable colourless crystalline solid prepared by reaction of $[Sn_2(NO_3)_2(\mu-OH)_2Me_4]$ [5] (0.65 mmol) with imidazole (1.31 mmol) in aqueous nitric acid (0.54 ml, 2.5 M). Upon partial elimination of solvent, crystals were obtained. *Anal.* Found: C, 16.7; H, 3.5; N, 15.8. Calc. for I: C, 16.7; H, 3.4; N, 15.6%. M.p. 178 °C. I was alternatively prepared as follows: $AgNO_3$ (1.90 mmol) in water (*c.* 5 ml) was added to $SnMe_2Cl_2$ (0.95 mmol) in water (*c.* 5 ml); once the $AgCl$ formed was filtered off, imidazole (1.90 mmol) in water (*c.* 5 ml) was added, the white solid formed ($pH=5.5$) was redissolved by addition of nitric acid (final $pH=3$) and crystals were obtained by partial elimination of solvent. Crystals suitable for X-ray analysis were obtained from isopropyl alcohol solution by slow evaporation of the solvent.

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Physical measurements

Elemental analyses were performed with a Carlo-Erba 1108 apparatus. The melting point was measured in a Büchi apparatus. IR spectra were recorded in KBr discs on a Perkin-Elmer 180 spectrophotometer. The ^1H NMR spectrum was recorded at room temperature on a Bruker WM-250 spectrometer at 250.13 MHz, in D_2O and referred to DSS. The Mossbauer spectrum was recorded on a Laben Master 4000 instrument at 80 K using a Harwell cryostat. The $\text{Ca}^{119}\text{SnO}_3$ source (15 mCi, New England Nuclear) at room temperature was moved at constant acceleration and with a triangular wave form. Suitable computer programs were employed in the fitting procedure of the experimental spectrum to Lorentzian line-shapes. δ was referred to r.t. SnO_2 .

Crystal structure determination

A colourless prismatic crystal of dimensions $0.20 \times 0.20 \times 0.08$ mm was mounted in an Enraf-Nonius CAD-4 diffractometer. The unit cell (Table 1) was determined and refined from angular data of 25 randomly selected reflections in the range $8 < \theta < 14^\circ$. Intensities were measured at 293 K with filtered Mo $K\alpha$ radiation ($\lambda = 0.70930 \text{ \AA}$) using $\omega/2\theta$ scans for $3 < \theta < 26^\circ$. 2590 reflections were collected in the range $h 0 \rightarrow 10$, $k 0 \rightarrow 19$, $l -11 \rightarrow 11$. 2254 reflections were unique ($R_{\text{int}} = 0.019$). 1711 with $I > 3 \sigma(I)$ were used in structure determination and refinement. The intensities of two standard reflections ($-4, 0, 2$ and $-5, -1, 3$) measured every 60 min showed no variation. Lorentz polarization corrections were applied, as well as an empirical absorption correction (absorption: minimum 0.899, maximum 1.235, average 1.005) [8]. Structure solution was by direct methods [9], least-squares and Fourier techniques, and refinement (on F) by full-matrix least-squares with unit weights and anisotropic displacement parameters for non-H atoms [10]. H atoms from difference Fourier synthesis were included in structure factor calculations with B_{iso} fixed at 4.0 \AA^2 , but not refined. A secondary extinction coefficient refined to

TABLE 1. Crystal data for I

Formula	$\text{C}_{10}\text{H}_{24}\text{N}_8\text{O}_{14}\text{Sn}_2$
Formula weight	717.73
System	monoclinic
Space group	$P2_1/c$
Cell constants	
a (\AA)	9.315(1)
b (\AA)	16.107(5)
c (\AA)	8.147(2)
β ($^\circ$)	101.94(1)
V (\AA^3)	1195.8(4)
Density (calc), D_x (g cm^{-3})	1.994
Molecules per cell, Z	2
Absorption (Mo $K\alpha$), μ (cm^{-1})	43.4

$g = 5.869 \times 10^{-7} (F_c = F_c/[1 + g(F_c)^2 \text{Lp}])$ [11]. After all shift/e.s.d. ratios $(\Delta/\sigma)_{\text{max}}$ were less than 0.001, the refinement converged to the agreement factors of $R = 0.032$, $R_w = 0.036$ for 155 parameters. Max. height in final ΔF map $(\Delta\rho)_{\text{max}}$: 0.679 e \AA^{-3} . Error in an observation of unit weight (S): 1.80. Atomic scattering factors were taken from International Tables for X-ray Crystallography [12]. Calculations were performed on a DEC MicroVAXII computer. Plots from ORTEP [13]. Positional and thermal parameters are given in Table 2.

Results and discussion

Compound I was synthesized not only from di- μ -hydroxobis[dimethylnitratotin(IV)], in which the $\text{Sn}(\mu\text{-OH})_2\text{Sn}$ framework is already present, but also from SnMe_2Cl_2 in an aqueous medium of a pH at which a high concentration of $[\text{SnR}_2(\mu\text{-OH})_2]^{2+}$ has been postulated on the basis of potentiometric measurements [2]. The formation of the $\text{Sn}(\mu\text{-OH})_2\text{Sn}$ framework in water thus appears to take place with considerable readiness, as also happens in organic [7, 14, 15] or organic-aqueous [16] media.

Figure 1 shows the molecular structure of I, together with the numbering scheme used. The structure consists of imidazolium $[\text{C}_3\text{H}_5\text{N}_2]^+$ cations and $[\text{Sn}_2(\text{NO}_3)_4(\mu\text{-OH})_2\text{Me}_4]^{2-}$ anions. The imidazolium rings are essentially planar, with no carbon atom more than 0.003 \AA from the least-squares plane. Bond distances and angles (Table 3) are not very different from those of coordinated imidazole [17, 18], although the N(1)–C(3) bond is slightly shorter. These rings are hydrogen bonded to nitrate groups of neighbouring units (bond distances N(1)–H(1) = $0.876(6)$; H(1)–O(31) $^{\text{ii}}$ = $2.371(5)$; N(1)–

TABLE 2. Positional parameters and their e.s.d.s in parentheses

Atom	x	y	z	B_{eq}^a
Sn	0.60917(4)	0.05112(2)	0.16255(5)	2.067(6)
O(1)	0.5386(4)	−0.0699(2)	0.0767(5)	2.35(8)
O(31)	0.6520(6)	0.2085(3)	0.1566(7)	5.1(1)
O(32)	0.6362(6)	0.3337(3)	0.2367(7)	4.9(1)
O(33)	0.4432(6)	0.2624(5)	0.165(1)	8.2(2)
O(41)	0.7395(5)	−0.0371(3)	0.3837(6)	3.5(1)
O(42)	0.7997(5)	0.0876(3)	0.4618(7)	4.3(1)
O(43)	1.1109(6)	0.0136(4)	0.3772(6)	5.1(1)
N(1)	1.0442(7)	−0.2114(6)	0.2097(9)	6.6(2)
N(2)	0.8197(7)	−0.1871(5)	0.136(1)	6.0(2)
N(3)	0.5750(6)	0.2684(4)	0.1856(7)	3.3(1)
N(4)	1.1886(6)	−0.0126(4)	0.5082(7)	3.1(1)
C(1)	0.8023(6)	0.0576(4)	0.0681(8)	3.0(1)
C(2)	0.4562(8)	0.0760(5)	0.3119(9)	4.2(2)
C(3)	0.947(1)	−0.1569(6)	0.206(1)	5.8(2)
C(4)	0.982(1)	−0.2794(6)	0.142(1)	7.1(2)
C(5)	0.837(1)	−0.2662(5)	0.092(1)	5.3(2)

$^a B_{\text{eq}} = 4/3(B_{11}a^{*2} + B_{22}b^{*2} + B_{33}c^{*2})$.

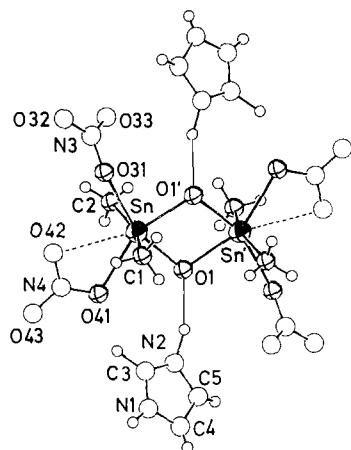


Fig. 1. View of **I** showing a partial atom labelling scheme.

TABLE 3. Selected bond distances (Å) and angles (°)

Sn–O(1)	2.129(4)	N(1)–C(4)	1.31(1)
Sn–O(1')	2.162(4)	N(2)–C(3)	1.30(1)
Sn–O(31)	2.569(5)	N(2)–C(5)	1.34(1)
Sn–O(41)	2.415(4)	C(4)–C(5)	1.35(1)
Sn–O(42)	2.765(5)	N(1)–H(1)	0.876(6)
Sn–C(1)	2.100(6)	H(1)–O(31) ⁱⁱ	2.371(5)
Sn–C(2)	2.095(8)	H(1)–O(32) ⁱⁱⁱ	2.178(6)
O(31)–N(3)	1.254(8)	N(1)–O(31) ⁱⁱⁱ	3.096(9)
O(32)–N(3)	1.227(8)	N(1)–O(32) ⁱⁱⁱ	3.007(9)
O(33)–N(3)	1.208(8)	N(2)–H(2)	1.124(8)
O(41)–N(4)	1.274(7)	H(2)–O(1)	2.104(4)
O(42)–N(4)	1.233(8)	N(2)–O(1)	3.183(8)
O(43)–N(4)	1.233(7)	O(1)–O(32) ⁱⁱⁱ	2.898(7)
N(1)–C(3)	1.25(1)		
O(1)–Sn–O(1')	74.7(1)	C(3)–N(2)–C(5)	108.9(8)
O(1)–Sn–O(31)	159.4(2)	O(31)–N(3)–O(32)	118.8(6)
O(1)–Sn–O(41)	77.3(1)	O(31)–N(3)–O(33)	121.1(6)
O(1)–Sn–C(1)	98.9(2)	O(32)–N(3)–O(33)	120.2(7)
O(1)–Sn–C(2)	99.5(2)	O(41)–N(4)–O(42)	117.8(5)
O(1)–Sn–O(31)	85.2(2)	O(41)–N(4)–O(43)	120.9(6)
O(1)–Sn–O(41)	152.0(1)	O(42)–N(4)–O(43)	121.4(6)
O(1)–Sn–C(1)	95.5(2)	N(1)–C(3)–N(2)	109.6(9)
O(1)–Sn–C(2)	96.6(3)	N(1)–C(4)–C(5)	109.2(8)
O(31)–Sn–O(41)	122.7(2)	N(2)–C(5)–C(4)	103.6(7)
O(31)–Sn–C(1)	78.3(2)	O(31) ⁱⁱⁱ –H(1)–O(32) ⁱⁱⁱ	55.8(2)
O(31)–Sn–C(2)	87.1(3)	O(31) ⁱⁱⁱ –H(1)–N(1)	140.4(6)
O(41)–Sn–C(1)	88.1(3)	O(32) ⁱⁱⁱ –H(1)–N(1)	157.6(6)
O(41)–Sn–C(2)	88.7(2)	O(1)–H(2)–N(2)	159.9(4)
C(1)–Sn–C(2)	160.1(3)	O(31) ⁱⁱⁱ –N(1)–O(32) ⁱⁱⁱ	41.0(2)
C(3)–N(1)–C(4)	108.7(8)		

Symmetry code: ⁱ = 1 – x, – y, – z; ⁱⁱ = 2 – x, y – 0.5, 0.5 – z, ⁱⁱⁱ = 1 – x, y – 0.5, 0.5 – z

O(31)ⁱⁱⁱ = 3.096(9) Å; N(1)–H(1)–O(31)ⁱⁱⁱ angle = 140.4(6)°; bond distances: N(1)–H(1) = 0.876(6); H(1)–O(32)ⁱⁱⁱ = 2.178(6); N(1)–O(32)ⁱⁱⁱ = 3.007(9) Å; N(1)–H(1)–O(32)ⁱⁱⁱ angle = 157.6(6)°; symmetry code ⁱⁱ = 2 – x, y – 0.5, 0.5 – z) and to the hydroxyl bridging groups of the anion (Fig. 1). Each hydroxyl group is also hydrogen bonded to one nitrate group of a neighbouring anion (O(1)–O(32)ⁱⁱⁱ = 2.898(7) Å; symmetry code ⁱⁱⁱ = 1 – x, y – 0.5, 0.5 – z). Figure 2 shows a stereoscopic view of the unit cell.

In the anion, each tin atom is seven-coordinated to two methyl groups, one asymmetrically bidentate nitrate anion, one monodentate nitrate anion and two bridging hydroxyl groups, an environment very similar to that found in the related aryl anion $[\text{Sn}_2(\text{NO}_3)_4(\mu\text{-OH})_2\text{Ph}_4]^{2-}$ [7]. Comparison of the main bond distances for the two anions shows that in the methyl derivative the Sn–C distances are shorter (2.100(6), 2.095(8) versus 2.137(3) Å), whereas the five Sn–O distances are longer (2.129(4) versus 2.108(5) for the shortest and 2.765(5) versus 2.752(6) Å for the longest). Although the Sn–O bond distances in the Sn_2O_2 ring are longer in the methyl derivative, the Sn–Sn distance is shorter (3.4109(5) versus 3.463(2) Å) due to the different ring angles (O–Sn–O, 74.7(1) versus 70.6(2)° and Sn–O–Sn 105.3(2) versus 109.5(3)°); the Sn–O–Sn angle lies at the high end of the range found for the Sn_2O_2 ring in other systems [6, 16]. Comparison of the main distances and angles of the anion $[\text{Sn}_2(\text{NO}_3)_4(\mu\text{-OH})_2\text{Me}_4]^{2-}$ with those of the parent $[\text{Sn}_2(\text{NO}_3)_2(\mu\text{-OH})_2\text{Me}_4]$ [5] shows that in the former the Sn–C distances are slightly shorter (2.096(8) versus 2.12(4) Å), the nitrate groups are farther from the tin atom (2.415(4) versus 2.30(3) Å), the C–Sn–C angle is wider (160.1(3) versus 139.9(1.4)°) and the four-membered Sn_2O_2 ring, without differing greatly in angles and distances, is more symmetric.

The IR spectrum in KBr shows bands at: 3220sh, 3160vs, $\nu(\text{OH})$; 1760w, 1380s,b, 1040m, 820m, $\nu(\text{NO}_3^-)$; 790m,b, $\rho(\text{Me})$; 565m, $\nu(\text{Sn-C})$; 530s,b, $\nu(\text{Sn-O})$. The pattern of the NO_3^- bands is indicative of an ionic nitrate [7, 19] which is not shown by the X-ray data and may be the result of partial hydrolysis [7].

The Mossbauer spectrum of the title compound is composed of a slightly distorted quadrupole split doublet with parameters: $\delta = 1.56 \text{ mm s}^{-1}$; $\Delta E_{\text{O}} = 4.14 \text{ mm s}^{-1}$; $I^{\text{r}} = 0.96$ and $I^{\text{s}} = 0.90 \text{ mm s}^{-1}$. The average value of the linewidth is small enough to suggest (within the sensitivity of the Mössbauer technique) that at 80 K there is just a single kind of tin site, as was shown to hold at room temperature by the X-ray diffraction study. It is well known that Mössbauer data alone cannot discriminate between hexa- and hepta-coordinate tin(IV) complexes, but these results are in full agreement with those for the few hepta-coordinate complexes already reported in the literature [20]. The isomer shift is slightly greater than those of $\text{SnPh}_2(\text{NO}_3)_2 \cdot \text{Ph}_3\text{XO}$ (X = P or As) (1.36 and 1.32 mm s^{-1} , respectively [20]), reflecting the different electronegativities of the ligands and different bond lengths. Within the limits of the point charge model, the experimental C–Sn–C bond angle can be used to calculate a theoretical ΔE_{O} under the hypothesis that the equatorial ligands do not play an important role in the imbalance of the p-electron cloud around the tin nucleus. If -1.09 mm s^{-1} is taken

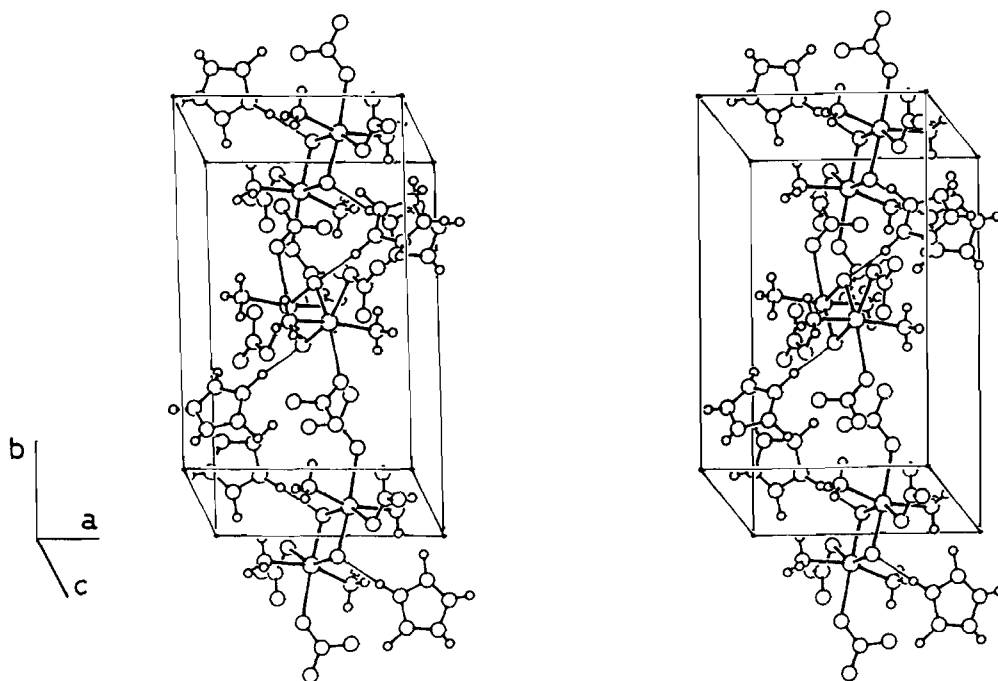


Fig 2 Stereoscopic view of I

as the PQS value for the alkyl groups in seven-coordinate complexes with low denticity substituents [20], the calculated ΔE_Q coincides exactly with the experimental value, which supports the accuracy of the few data so far available for calculation of the PQS .

The scant solubility of I in organic solvents prevented detailed study of its NMR behaviour in these media. The similarity between the ^1H NMR spectra of 0.05 M solutions of $[\text{Sn}(\text{NO}_3)_2(\mu\text{-OH})_2\text{Me}_4]$ and I in D_2O ($[\text{Sn}(\text{NO}_3)_2(\mu\text{-OH})_2\text{Me}_4]$: $\delta(\text{Me-Sn})=0.71$ ppm, $^2J(^{119}\text{Sn-}^1\text{H})=93.1$ Hz. I: $\delta(\text{Me-Sn})=0.76$ ppm, $^2J(^{119}\text{Sn-}^1\text{H})=94.3$ Hz; $(\text{C}_3\text{H}_5\text{N}_2)^+$, $\delta(\text{H}_{4,5})=7.32$ and $\delta(\text{H}_2)=8.53$ ppm) suggests that I undergoes a dissociative equilibrium in this solvent.

Acknowledgements

This work was partially financed by the Xunta de Galicia, Spain (Project XUGA 20314B91) and Programa de Acciones Integradas (HI 110).

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