

Structure of the Dimer of Dibutylhydroxystannyl Perchlorate

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Abstract. Di- μ -hydroxo-bis(dibutylperchloratotin), $[\text{Sn}(\text{ClO}_4)(\text{OH})(\text{C}_4\text{H}_9)_2]$, $M_r = 349.38$, monoclinic, $P2_1/c$, $a = 11.749$ (3), $b = 8.300$ (2), $c = 14.725$ (2) Å, $\beta = 103.97$ (2)°, $V = 1393$ (1) Å³, $Z = 4$, $D_x = 1.665$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 20.3$ cm⁻¹, $F(000) = 696$, $T = 153$ K, $R = 0.032$ for 1568 reflections. Dibutylhydroxystannyl perchlorate exists as a dimer $[\text{Bu}_2(\text{OH})\text{SnClO}_4]_2$ consisting of a four-membered ring with alternating Sn and O atoms. The ring O atoms are protonated and the Sn atoms are the centers of very distorted trigonal bipyramids. The apical positions of each bipyramid are occupied by a perchlorato group with a very long Sn—O bond length and the ring O atom with a longer Sn—O bond distance. Two dimer molecules interact closely *via* hydrogen bonds between a perchlorate O atom of one dimer and a hydroxy H atom of the other. These interactions bring about the formation of continuous chains in the solid. There are no significant interactions between chains.

Introduction. The stannoxyl functionality, $-\text{R}_2\text{SnO}-$, readily forms four-membered rings (Sn_2O_2), which can be part of larger ladder and drum structures (Holmes, Shafieezad, Chandrasekhar, Holmes & Day, 1988; Holmes, 1989). In our attempts to obtain tricoordinate tin by the reaction of tributyltin chloride with silver perchlorate ($\text{Bu}_3\text{SnCl} + \text{AgClO}_4 \rightarrow \text{Bu}_3\text{Sn}^+ \cdot \text{ClO}_4^- + \text{AgCl}$), we obtained cubic crystals of $\text{Bu}_3\text{SnClO}_4$, which were unsuitable for X-ray studies (Lambert & Kuhlmann, 1992). From the crystallization product we observed crystals of a different habit, prismatic rather than cubic, which we were able to isolate and study by X-ray diffraction. These crystals proved to be the dimer of $\text{Bu}_2(\text{HO})\text{SnClO}_4$, in which one butyl group of $\text{Bu}_3\text{SnClO}_4$ has been replaced by hydroxyl. The molecule contains the Sn_2O_2 unit. Although our solutions were dried and all manipulations were carried out under vacuum, some water (no more than 10% with respect to substrate) was present. We could monitor the presence of water by the resonances of the observed hydrolysis product, $(\text{Bu}_3\text{Sn})_2\text{O}$, in the NMR spectra. Formal loss of butyl can occur by disproportionation. Alternatively, the product may have been derived from hydrolysis

of an impurity, Bu_2SnCl_2 . As this study was primarily structural rather than mechanistic, we did not explore the mechanism.

We report herein the crystal structure of this product, in which the common four-membered ring structure (O—Sn)₂ is distorted due to ionization of the perchlorate moiety by tin. Although the ring is relatively common with organic groups attached to the O atoms, there are only a few examples in which the bridge is OH. In these, the counterion has been nitrate (Domingos & Sheldrick, 1974), halide (Puff, Hevendehl, Höfer, Reuter & Schuh, 1985; Holmes *et al.*, 1988), or thiophosphate (Nasser, Hossain, van der Helm & Zuckerman, 1983). The perchlorate structure has not been reported previously. Moreover, the long Sn—O(perchlorate) distance suggests that this structure has the highest ionic character within this class.

Experimental. A colorless prismatic crystal of approximate dimensions $0.17 \times 0.14 \times 0.12$ mm, obtained from the reaction of tributyltin chloride with silver chloride, was mounted on a glass fiber. All measurements were made on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement from the setting angles of 25 carefully centered reflections in the range $19.4 < 2\theta < 23.8^\circ$ and corresponded to a monoclinic cell. Based on systematic absences, the space group was determined to be $P2_1/c$.

The data were collected at 153 K with the ω/θ technique to a maximum 2θ value of 45.9° . ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.30° with a take-off angle of 2.8° . Scans of $(1.00 + 0.35\tan\theta)^\circ$ were made at speeds ranging from 3.0 to $16.0^\circ \text{ min}^{-1}$ (in ω). Moving-crystal, moving-counter background measurements were made by scanning an additional 25% above and below the scan range. The counter aperture consisted of a variable horizontal slit with a width ranging from 2.0 to 2.5 mm and a vertical slit set at 2.0 mm. The diameter of the incident-beam collimator was 0.7 mm, and the crystal to detector distance was 21 cm. For intense

Table 1. Final atomic coordinates and thermal parameters (\AA^2) with e.s.d.'s in parentheses
$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B_{eq}
Sn	-0.00939 (4)	0.09529 (6)	0.39633 (3)	1.36 (2)
Cl	-0.0859 (2)	0.4871 (2)	0.3210 (1)	1.96 (7)
O(1)	-0.0613 (5)	0.4026 (6)	0.2424 (3)	2.3 (2)
O(2)	-0.0824 (4)	0.3687 (6)	0.3958 (3)	1.8 (2)
O(3)	-0.1975 (6)	0.5622 (9)	0.2978 (4)	5.0 (3)
O(4)	0.0051 (6)	0.6058 (7)	0.3525 (4)	4.2 (3)
O(5)	-0.0363 (5)	0.1252 (7)	0.5298 (4)	1.7 (2)
C(1)	0.1589 (6)	0.191 (1)	0.4016 (5)	1.8 (3)
C(2)	0.2048 (6)	0.308 (1)	0.4813 (6)	2.5 (3)
C(3)	0.3232 (8)	0.379 (1)	0.4772 (7)	3.7 (4)
C(4)	0.364 (1)	0.509 (2)	0.549 (1)	7.3 (7)
C(5)	-0.1745 (7)	0.029 (1)	0.3099 (5)	2.1 (3)
C(6)	-0.2773 (6)	0.070 (1)	0.3525 (6)	2.4 (3)
C(7)	-0.3934 (8)	0.001 (1)	0.2953 (7)	4.6 (5)
C(8)	-0.4951 (9)	0.035 (2)	0.339 (1)	6.2 (6)
H(19)	-0.037 (7)	0.22 (1)	0.545 (6)	3 (2)

Table 2. Selected interatomic distances (\AA) and angles ($^\circ$) of $[(\text{Bu}_2\text{SnOH})\text{ClO}_4]_2$ with e.s.d.'s in parentheses

Sn—O(2)	2.425 (5)	Cl—O(4)	1.446 (6)
Sn—O(5)	2.080 (5)	O(5)—H(19)	0.81 (9)
Sn—O(5)	2.131 (5)	C(1)—C(2)	1.52 (1)
Sn—C(1)	2.116 (7)	C(2)—C(3)	1.53 (1)
Sn—C(5)	2.120 (8)	C(3)—C(4)	1.50 (1)
Cl—C(1)	1.442 (5)	C(5)—C(6)	1.53 (1)
Cl—O(2)	1.469 (5)	C(6)—C(7)	1.53 (1)
Cl—O(3)	1.417 (6)	C(7)—C(8)	1.52 (1)
O(2)—Sn—O(5)	75.9 (2)	C(1)—Sn—C(5)	146.2 (3)
O(2)—Sn—O(5)	148.3 (2)	O(1)—Cl—O(2)	107.6 (3)
O(2)—Sn—C(1)	88.5 (2)	O(1)—Cl—O(3)	111.9 (4)
O(2)—Sn—C(5)	88.2 (3)	O(1)—Cl—O(4)	108.2 (4)
O(5)—Sn—O(5)	72.4 (2)	O(2)—Cl—O(3)	109.4 (3)
O(5)—Sn—C(1)	105.9 (2)	O(2)—Cl—O(4)	109.3 (4)
O(5)—Sn—C(5)	105.8 (3)	O(3)—Cl—O(4)	110.3 (4)
O(5)—Sn—C(1)	100.8 (3)	Sn—O(2)—Cl	125.1 (3)
O(5)—Sn—C(5)	99.5 (3)	Sn—O(5)—Sn	107.6 (2)
Sn—O(5)—H(19)	114 (6)	C(2)—C(3)—C(4)	113.1 (7)
Sn—O(5)—H(19)	134 (6)	Sn—C(5)—C(6)	113.2 (5)
Sn—C(1)—C(2)	115.0 (5)	C(5)—C(6)—C(7)	112.1 (7)
C(1)—C(2)—C(3)	112.0 (7)	C(6)—C(7)—C(8)	112.5 (8)

atoms were placed at calculated, idealized positions. All calculations were performed with the *TEXSAN* crystallographic package from Molecular Structure Corporation (1989). The final cycle of full-matrix least-squares refinement was based on 1568 observed reflections with $I > 3\sigma(I)$ and 141 parameters and converged with $R = 0.032$, $wR = 0.046$. The standard deviation of an observation of unit weight was 2.01; $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$, in which N_o is the number of observations and N_v is the number of variables. The weighting scheme was based on counting statistics and included a factor ($\rho = 0.03$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ vs $|F_o|$, reflection order in data collection, $\sin(\theta/\lambda)$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.75 and -0.88 e \AA^{-3} , respectively. Neutral-atom

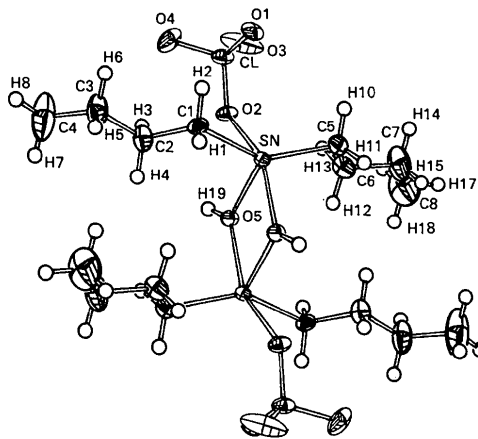


Fig. 1. Molecular structure and numbering scheme for bis(dibutylhydroxystannyl perchlorate).

reflections, an attenuator was automatically inserted in from the detector.

Of the 2188 reflections ($\pm h$, $-k$, $-l$; $-12 \leq h \leq 12$, $-9 \leq k \leq 0$, $-16 \leq l \leq 0$) that were collected, 2096 were unique ($R_{int} = 0.024$). The intensities of three representative reflections were measured after every 90 min of X-ray exposure and were found to remain constant throughout data collection, so no decay correction was applied. An analytical absorption correction was applied that resulted in transmission factors ranging from 0.75 to 0.82. The data were corrected for Lorentz and polarization effects, and correction for secondary extinction was applied (coefficient 1.40×10^{-7}).

The structure was solved by direct methods with *SHELXS86* (Sheldrick, 1986). The non-H atoms were refined anisotropically. Only the positions of hydroxyl H atoms were refined. The remaining H

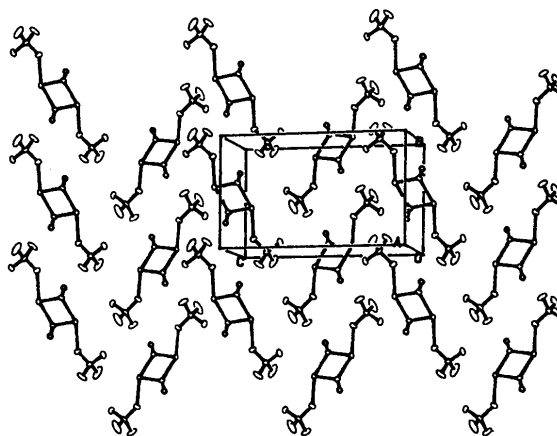


Fig. 2. Unit cell showing the chain structure of bis(dibutylhydroxystannyl perchlorate). The butyl groups are omitted for clarity.

Table 3. Comparison of structural parameters^a

X^b	Sn— X^c (Å)	Sn—OH ^d (Å)	Sn—OH ^e (Å)	Sn—O—Sn (°)	O—Sn—O (°)	X—Sn—O ^f (°)
OCIO ₃ ^g	2.425 (5)	2.080 (5)	2.131 (5)	107.6 (2)	72.4 (2)	148.3 (2)
ONO ₂ ^h	2.30 (3)	2.06 (3)	2.18 (3)	108.5	71.4	149.3
OP(S)(OPh) ₂ ⁱ	2.151 (2)	2.032 (2)	2.198 (2)	107.23 (8)	72.77 (7)	150.0
F ^j		2.012 (5)	2.199 (5)	109.9	70.1	155.4
Cl ^k		2.036 (6)	2.237 (9)	112.5	67.6	154.2
Br ^l		2.048 (1)	2.257 (2)	111.5	68.5	154.3

Notes: (a) All systems have the same ring (Sn—OH)₂; (b) X is the counterion attached to the apical position of Sn; (c) the Sn—O(2) bond in Fig. 1; (d) the shorter ring Sn—O(5) bond in Fig. 1, attached to an equatorial position of Sn; (e) the longer Sn—O(5) bond in Fig. 1, attached to an apical position of Sn; (f) the apical angle through Sn; (g) this work; (h) Domingos & Sheldrick (1974) (the organic groups at the equatorial positions of Sn are CH₃); (i) Nasser *et al.* (1983) (the organic groups at the equatorial position of Sn are phenyl rings); (j) Puff *et al.* (1985) (the organic groups at the equatorial position of Sn are *tert*-butyl).

scattering factors were taken from Cromer & Waber (1974). The maximum shift/e.s.d. in the final cycle was 0.03. Final atomic coordinates and thermal parameters are given in Table 1.* Important structural parameters are given in Table 2.

Discussion. In the crystal, dibutylhydroxystannyl perchlorate assumes a dimer structure with bridging hydroxyl groups (Fig. 1). The resulting four-membered ring can be named variously as bis(dibutylhydroxystannyl perchlorate), bis(dibutylstannyl hydroxide perchlorate), di- μ -hydroxobis(dibutylperchloratotin) or 2,2,4,4-tetrabutyl-1,3,2,4-dioxadistannetanium diperchlorate. The ring O atoms are protonated, with an O—H bond distance of 0.81 (9) Å [O(5)—H(19) in Table 2]. Each Sn atom is at the center of a distorted trigonal bipyramid, in which the apical positions are occupied by a perchlorate group and the bridging hydroxyl group having the longer Sn—O bond length [2.131 (5) Å]. The equatorial positions are occupied by the two butyl groups and the bridging hydroxyl group with the shorter Sn—O bond length [2.080 (5) Å]. The four-membered ring is a parallelogram with unequal Sn—O bond lengths, the smaller O—Sn—O bond angle being 72.4 (2)° [O(5)—Sn—O(5) in Table 3] and the larger Sn—O—Sn bond angle being 107.6 (2)°.

There is some vestige of the monomeric tin cation, which would be Bu₂(OH)Sn⁺, in the inequality of the two ring Sn—O bond lengths and in the long Sn—OCIO₄ bond length, 2.425 (5) Å. The normal Sn—O bond length falls in the range 1.9–2.1 Å even in penta- and hexacoordination (for a review, see Ho & Zuckerman, 1973). The observed bond distance exceeds this range by at least 0.3 Å but lies well

within the sum of the van der Waals radii for Sn and O of 3.62 Å (Dräger, 1976).

The O(4) atom of each perchlorate has a very short hydrogen-bonded distance to the hydroxyl H(19) atom of an adjacent dimer, 2.06 (9) Å. This interaction gives rise to an array of continuous chains (Fig. 2). The chains have no interaction with each other. The O(1) atom of each perchlorate has a relatively short distance of 2.870 (5) Å to the Sn atom of the adjacent ring in the chain. This interaction probably contributes to the large distortion of the Sn atom from a regular trigonal bipyramid.

Structures of similar molecules have been reported with a variety of counterions but not with perchlorate (Domingos & Sheldrick, 1974; Puff *et al.*, 1985; Nasser *et al.*, 1983), and with a variety of organic groups but not butyl. Comparative data for key structural parameters are summarized in Table 3. The Sn—X bond length (X is the counterion) provides a measure of the ionicity of the bond. The longest bond length is found for perchlorate, with nitrate having intermediate length and thiophosphonate the shortest. The halides are not directly comparable. The inequality of the two ring Sn—O bonds is also instructive. In every case, the bonds are unequal, so that the geometry is properly termed an oblique parallelogram rather than a rhombus (which has equal sides). The difference between the ring Sn—O bonds varies from 0.05 to 0.20 Å, the larger values being associated with the halogen systems. The obliqueness of the parallelogram is necessitated by the inequality of the angles within the ring.

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References

* Lists of anisotropic temperature factor coefficients, observed and calculated structure-factor moduli and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55757 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1020]

- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
DOMINGOS, A. M. & SHELDICK, G. M. (1974). *J. Chem. Soc. Dalton Trans.* pp. 475–477.

- DRÄGER, M. (1976). *Z. Anorg. Allg. Chem.* **423**, 53–65.
- HO, B. Y. K. & ZUCKERMAN, J. J. (1973). *J. Organomet. Chem.* **49**, 1–84.
- HOLMES, R. R. (1989). *Acc. Chem. Res.* **22**, 190–197.
- HOLMES, R. R., SHAFIEEZAD, S., CHANDRASEKHAR, V., HOLMES, J. M. & DAY, R. O. (1988). *J. Am. Chem. Soc.* **110**, 1174–1180.
- LAMBERT, J. B. & KUHLMANN, B. (1992). *J. Chem. Soc. Chem. Commun.* pp. 931–932.
- Molecular Structure Corporation. (1989). *TEXSAN. TEXRAY Structure Analysis Package*. Version 5.0. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
- NASSER, F. A. K., HOSSAIN, M. B. VAN DER HELM, D. & ZUCKERMAN, J. J. (1983). *Inorg. Chem.* **22**, 3107–3111.
- PUFF, H., HEVENEDEHL, H., HÖFER, K., REUTER, H. & SCHUH, W. (1985). *J. Organomet. Chem.* **287**, 163–178.
- SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Acta Cryst. (1993). **C49**, 890–893

Mixed Chelate Complexes. II. Structures of L-Alaninato(aqua)(4,7-diphenyl-1,10-phenanthroline)copper(II) Nitrite Monohydrate and Aqua(4,7-dimethyl-1,10-phenanthroline)(glycinato)(nitrate)copper(II) Monohydrate

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Abstract. $[\text{Cu}(\text{C}_3\text{H}_6\text{NO}_2)(\text{C}_{24}\text{H}_{16}\text{N}_2)(\text{H}_2\text{O})]\text{NO}_2 \cdot \text{H}_2\text{O}$ (I), $M_r = 566.1$, monoclinic, $P2_1$, $a = 11.864$ (3), $b = 7.726$ (2), $c = 14.832$ (3) Å, $\beta = 102.17$ (2)°, $V = 1329.0$ (9) Å³, $Z = 2$, $D_x = 1.414$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.868$ mm⁻¹, $T = 288$ K, $R = 0.064$ for 2061 reflections. $[\text{Cu}(\text{C}_2\text{H}_4\text{NO}_2)(\text{NO}_3)(\text{C}_{14}\text{H}_{12}\text{N}_2)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (II), $M_r = 443.9$, triclinic, $P\bar{1}$, $a = 14.138$ (3), $b = 10.016$ (2), $c = 7.565$ (2) Å, $\alpha = 104.83$ (2), $\beta = 83.47$ (2), $\gamma = 119.93$ (2)°, $V = 897.3$ (6) Å³, $Z = 2$, $D_x = 1.642$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.265$ mm⁻¹, $T = 288$ K, $R = 0.046$ for 1322 reflections. The Cu ion displays square pyramidal coordination with an apical water molecule for (I) and a distorted octahedral coordination in (II). The apical Cu—OH₂ bond lengths are 2.209 (11) Å for (I) and 2.458 (6) Å for (II). The lengthening in (II) may be due to the *trans* O—NO₂ ligand that blocks the sixth coordination site. The results obtained are compared with those for other aminoacidate copper(II) complexes.

Introduction. Compounds with general formula $[\text{Cu}(\text{N}-\text{N})(\text{O}-\text{N})\text{H}_2\text{O}]^+$, where (N—N) = 4,7-di-

phenyl-1,10-phenanthroline or 4,7-dimethyl-1,10-phenanthroline and (O—N) = alaninato or glycinato, have been synthesized and characterized by Ruiz-Ramírez, Martínez & Gasque (1992) who also determined their stability constants potentiometrically. The compounds are obtained from 1:1 mmol solutions of Cu^{II} ion and the (N—N) ligand in water, followed by the addition of L-alanine (I) or glycine (II); the pH is increased to 8 by addition of ammonium hydroxide. Concentration of the solution leads to precipitation of the mixed chelate complex. Blue crystals are grown from a water solution. In order to determine the coordination geometry of the Cu^{II} ions and confirm the chelating scheme, crystal structure determinations have been carried out on the title compounds (I) and (II).

Experimental. A similar method was followed in the determination of both crystal structures. Prismatic crystal of (I) (0.1 × 0.1 × 0.15 mm) and tabular crystal of (II) (0.1 × 0.1 × 0.08 mm) were selected and mounted on a Philips PW1100 four-circle diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used. Cell parameters were determined from 25 reflections ($4 < \theta < 12^\circ$) and refined by least squares. Intensities were collected with ω -scan technique, with scan width 1° and scan speed 0.03° s⁻¹.

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