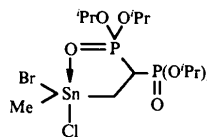


- Kosturko, L. D., Folzer, C. & Stewart, R. F. (1974). *Biochemistry*, **13**, 3949–3952.
- Paige, C. R. & Richardson, M. F. (1984). *Can. J. Chem.* **62**, 332–335.
- Skrzypczak-Jankun, E. & Smith, D. A. (1994). *Acta Cryst.* **C50**, 91–93.
- Smith, D. A., Cramer, S., Suheck, S. & Skrzypczak-Jankun, E. (1992). *Tetrahedron Lett.* **33**, 7765–7768.
- Smith, D. A., Suheck, S. & Pinkerton, A. A. (1992). *J. Chem. Soc. Chem. Commun.* pp. 367–368.
- Suheck, S., Finnen, D. C., Pinkerton, A. A., Skrzypczak-Jankun, E., Vijayakumar, S. & Smith, D. A. (1991). *Am. Crystallogr. Assoc. Meet.*, Toledo, 21–26 July. Abstract PJ17.
- Taylor, D. (1977). *Aust. J. Chem.* **30**, 2647–2654.
- Zachariassen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.



The donor character of the Sn1—O6 [2.427 (2) Å] and Sn1—O1ⁱ [2.497 (2) Å] bonds [symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$] results in a lengthening effect (typical Sn—O single bonds = 2.15 Å; Harrison, 1989), and in accordance with this, the double-bond character of the bonds P1—O1 [1.472 (2) Å] and P2—O6 [1.484 (2) Å] is stronger than for the other P—O bonds [P1—O2 1.566 (2), P1—O3 1.567 (2), P2—O4 1.558 (2), P2—O5 1.568 (2) Å]; a typical P—O single bond = 1.62 Å (Rademacher, 1987). The bridging O atom O1 is almost linearly coordinated [Sn1—O1ⁱ—P1ⁱ 174.69 (15)°]. In most of the compounds with an Sn—O—P unit, this angle adopts values between 125 and 170° (Cambridge Structural Database; Allen *et al.*, 1979). The Sn—O—P angle in (1) is in the upper range, which is rarely observed. A similar structure to that of (1) is adopted by Me₂SnClCH₂CH[P(O)(OⁱPr)₂][P(O)Ph₂] (Richter, Weichmann, Freitag & Herbst-Irmer, 1994), in which the Sn atom is five-coordinate and no dimerization is found. Since the Lewis acidity resulting from an Sn—Br bond is greater than that from an Sn—Me bond, compound (1) displays sixfold coordination.

Acta Cryst. (1994). **C50**, 1588–1590

Tetraisopropyl 2-[(Bromo)(chloro)(methyl)-stannyl]-1,1-ethanediphosphonate at 153 K

STEFANIE FREITAG AND REGINE HERBST-IRMER

*Institut für Anorganische Chemie,
Universität Göttingen, Tammannstrasse 4,
37077 Göttingen, Germany*

FRANK U. RICHTER AND HORST WEICHMANN

*Institut für Anorganische Chemie,
Universität Halle-Wittenberg, Weinbergweg 16,
06120 Halle(Saale), Germany*

(Received 3 February 1994; accepted 18 April 1994)

Abstract

The structure of the title compound, [SnBrCl(CH₃)(C₁₄H₃₁O₆P₂)], is reported. As a result of an Sn—O interaction, dimers are formed in the crystal. The bridging O atom is almost linearly coordinated.

Comment

Syntheses and NMR studies of tetraisopropyl 2-[(bromo)(chloro)(methyl)stannyl]-1,1-ethanediphosphonate, (1), are discussed elsewhere (Richter, Weichmann, Krug, Hartung & Zeigan, 1994). The crystal structure of (1) consists of dimeric molecules, with an inversion centre in the middle of each dimer. The Sn atoms are coordinated by two C, two O, one Cl and one Br atom, forming distorted octahedra. As a result of the donor interaction of O6 with Sn1, a five-membered ring is formed. This ring adopts a twist conformation in which C2 lies 0.310 (6) Å above and C3 0.214 (6) Å below the plane formed by Sn1, P2 and O6.

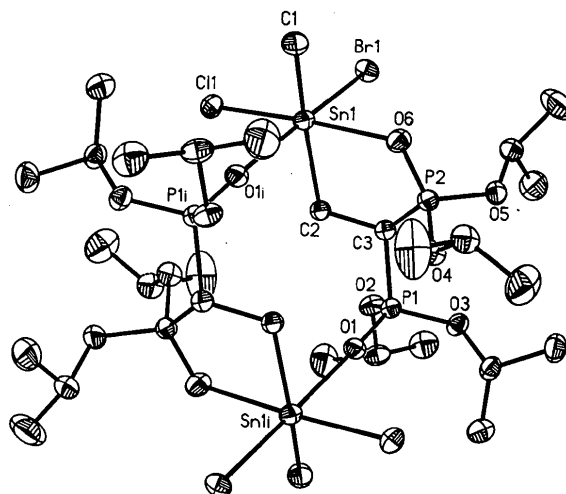


Fig. 1. Structure of (1) showing 50% probability displacement ellipsoids. The H atoms have been omitted for clarity. Atoms of the ⁱPr groups are not labelled.

Experimental

Crystal data

[SnBrCl(CH₃)(C₁₄H₃₁O₆P₂)]
M_r = 606.41

Mo *K*α radiation
λ = 0.71073 Å

Monoclinic
 $C2/c$
 $a = 13.5640 (10) \text{ \AA}$
 $b = 16.812 (2) \text{ \AA}$
 $c = 22.887 (2) \text{ \AA}$
 $\beta = 106.250 (10)^\circ$
 $V = 5010.6 (8) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.608 \text{ Mg m}^{-3}$

Data collection

Stoe Siemens AED-2
 diffractometer
 Profile data from $2\theta/\omega$ scans
 Absorption correction:
 semi-empirical
 $T_{\min} = 0.485$, $T_{\max} = 0.517$
 6586 measured reflections
 5646 independent reflections
 4772 observed reflections
 $[I > 2\sigma(I)]$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0320$
 $wR(F^2) = 0.0705$
 $S = 1.077$
 5634 reflections
 250 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 20.6362P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Cell parameters from 72
 reflections
 $\theta = 10\text{--}12.5^\circ$
 $\mu = 2.873 \text{ mm}^{-1}$
 $T = 153 (2) \text{ K}$
 Block
 $0.4 \times 0.4 \times 0.3 \text{ mm}$
 Colourless

$R_{\text{int}} = 0.0543$
 $\theta_{\text{max}} = 27.35^\circ$
 $h = -17 \rightarrow 17$
 $k = -19 \rightarrow 21$
 $l = -29 \rightarrow 29$
 3 standard reflections
 frequency: 90 min
 intensity variation: none

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.920 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.747 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors
 from *International Tables*
 for *Crystallography* (1992,
 Vol. C, Tables 4.2.6.8 and
 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Sn1	0.52597 (2)	0.174128 (13)	0.436096 (10)	0.02210 (7)
Br1	0.3474 (3)	0.2147 (2)	0.4460 (2)	0.0249 (4)
Cl2	0.3524 (9)	0.2010 (5)	0.4488 (6)	0.0249 (4)
Cl1	0.4881 (24)	0.2211 (15)	0.3289 (10)	0.0295 (7)
Br2	0.4879 (10)	0.2295 (6)	0.3289 (4)	0.0295 (7)
C1	0.5030 (3)	0.0507 (2)	0.4201 (2)	0.0335 (8)
C2	0.6061 (2)	0.2783 (2)	0.47807 (14)	0.0220 (6)
C3	0.6056 (2)	0.2922 (2)	0.54460 (14)	0.0204 (6)
P1	0.69505 (6)	0.36992 (5)	0.57908 (4)	0.0202 (2)
O1	0.7997 (2)	0.35861 (14)	0.57363 (11)	0.0257 (5)
O2	0.6363 (2)	0.44337 (13)	0.54377 (11)	0.0261 (5)
C4	0.6716 (3)	0.5250 (2)	0.5620 (2)	0.0302 (8)
C5	0.5985 (3)	0.5608 (2)	0.5931 (2)	0.0426 (10)
C6	0.6740 (4)	0.5683 (3)	0.5050 (2)	0.0578 (13)
O3	0.6888 (2)	0.38147 (14)	0.64587 (10)	0.0253 (5)
C7	0.7735 (3)	0.3659 (2)	0.70163 (15)	0.0268 (7)
C8	0.7205 (3)	0.3482 (3)	0.7501 (2)	0.0394 (9)
C9	0.8428 (3)	0.4375 (2)	0.7157 (2)	0.0373 (9)
P2	0.61328 (7)	0.19989 (5)	0.58621 (4)	0.0227 (2)
O4	0.7277 (2)	0.18790 (14)	0.62302 (11)	0.0273 (5)
C10	0.7578 (3)	0.1122 (2)	0.6575 (2)	0.0329 (8)
C11	0.8333 (5)	0.0718 (3)	0.6306 (3)	0.078 (2)
C12	0.8010 (4)	0.1332 (3)	0.7229 (2)	0.0583 (13)
O5	0.5584 (2)	0.2116 (2)	0.63745 (11)	0.0294 (5)
C13	0.4464 (3)	0.2258 (3)	0.6230 (2)	0.0354 (9)
C14	0.4008 (4)	0.1589 (3)	0.6507 (3)	0.0622 (14)
C15	0.4319 (3)	0.3060 (3)	0.6478 (2)	0.0482 (11)
O6	0.5690 (2)	0.13546 (14)	0.54243 (11)	0.0297 (5)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Sn1—C1	2.115 (4)	C3—P1	1.807 (3)
Sn1—C2	2.142 (3)	C3—P2	1.808 (3)
Sn1—O6	2.427 (2)	P1—O1	1.472 (2)
Sn1—Cl1	2.49 (2)	P1—O2	1.566 (2)
Sn1—Cl2	2.494 (12)	P1—O3	1.567 (2)
Sn1—O1 ⁱ	2.497 (2)	P2—O6	1.484 (2)
Sn1—Br2	2.538 (9)	P2—O4	1.558 (2)
Sn1—Br1	2.587 (4)	P2—O5	1.568 (2)
C2—C3	1.542 (4)		
Cl1—Sn1—C2	155.73 (14)	O6—Sn1—Br2	173.8 (2)
Cl1—Sn1—O6	83.85 (12)	Cl2—Sn1—Br2	95.9 (4)
C2—Sn1—O6	79.63 (10)	O1 ⁱ —Sn1—Br2	86.3 (3)
Cl1—Sn1—Cl1	99.3 (6)	Cl1—Sn1—Br1	100.20 (13)
C2—Sn1—Cl1	97.0 (6)	C2—Sn1—Br1	96.63 (12)
O6—Sn1—Cl1	176.6 (6)	O6—Sn1—Br1	87.19 (12)
Cl1—Sn1—Cl2	95.7 (2)	Cl1—Sn1—Br1	93.6 (7)
C2—Sn1—Cl2	100.2 (3)	O1 ⁱ —Sn1—Br1	177.45 (9)
O6—Sn1—Cl2	84.4 (3)	C3—C2—Sn1	115.1 (2)
Cl1—Sn1—O1 ⁱ	82.30 (12)	C2—C3—P1	110.6 (2)
C2—Sn1—O1 ⁱ	81.13 (10)	C2—C3—P2	112.0 (2)
O6—Sn1—O1 ⁱ	93.57 (8)	P1—C3—P2	117.2 (2)
Cl1—Sn1—O1 ⁱ	85.5 (7)	P1—O1—Sn1 ⁱ	174.69 (15)
Cl2—Sn1—O1 ⁱ	177.3 (2)	O6—P2—C3	108.55 (14)
Cl1—Sn1—Br2	102.3 (3)	P2—O6—Sn1	114.83 (13)
C2—Sn1—Br2	94.2 (3)		

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

The Cl and Br atoms are disordered over two sites. The occupancy for each site was refined at first, then fixed at 50%. The Sn—Br and Sn—Cl bond lengths were restrained to be equal within an effective standard deviation of 0.03 \AA . The U_{ij} values of the disordered Cl and Br atoms on the same sites were constrained to be equal. H atoms were included in calculated positions and refined using a riding model with U fixed at either $1.2 \times U_{\text{eq}}$ (CH, CH₂) or $1.5 \times U_{\text{eq}}$ (CH₃) of the corresponding C atom. Data collection and cell refinement: *DIF4* (Stoe & Cie, 1988a). Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: SH1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Allen, F. H., Bellard, S., Brice, M. D., Cartwright, B. A., Doubleday, A., Higgs, H., Hummelink, T., Hummelink-Peters, B. G., Kennard, O., Motherwell, W. D. S., Rodgers, J. R. & Watson, D. G. (1979). *Acta Cryst.* B35, 2331–2339.
- Harrison, P. G. (1989). In *Chemistry of Tin*. Glasgow: Blackie.
- Rademacher, P. (1987). *Strukturen organischer Moleküle. Physikalische Organische Chemie*, Vol. 2, edited by M. Klessinger. Weinheim: VCH.
- Richter, J., Weichmann, H., Freitag, S. & Herbst-Irmer, R. (1994). *J. Organomet. Chem.* In preparation.
- Richter, J., Weichmann, H., Krug, A., Hartung, H. & Zeigan, D. (1994). *Main Group Metal Chem.* In the press.
- Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
- Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. Univ. of Göttingen, Germany.
 Stoe & Cie (1988a). *DIF4. Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
 Stoe & Cie (1988b). *REDU4. Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1994). **C50**, 1590–1592

A New Dimercurated Derivative of Acetylacetonone, [Hg₂(C₅H₆O₂)Cl₂].CH₃CN

CHRISTIAN BONHOMME,* PAUL TOLEDANO AND JACQUES LIVAGE

Laboratoire de Chimie de la Matière Condensée, Université P. et M. Curie, 4 Place Jussieu, Tour 54, 75252 Paris CEDEX 05, France

(Received 14 December 1993; accepted 28 March 1994)

Abstract

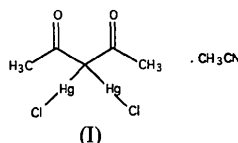
The unit cell of the title compound μ -diacetyl-methylene-1:2 κ^2 C-bis[chloromercury(II)]-acetonitrile (1/1), [Hg₂(C₅H₆O₂)Cl₂].C₂H₃N, contains four discrete asymmetric units. Each unit contains one dimercurated acetylacetonone moiety and one associated acetonitrile molecule. Hg—C bond lengths are 2.11 (1) Å and Hg—Cl bond lengths are in the range 2.306 (4)–2.326 (3) Å. C—Hg—Cl bond angles are in the range 172.5 (3)–174.5 (3)°, in agreement with the near linearity of the three atoms. Hg···O and Hg···N contacts in the range 2.844 (9)–3.12 (2) Å are also observed.

Comment

The mercurated derivatives of β -diketones and β -keto esters have been studied widely over the last two decades, especially by vibrational spectroscopic and solution-NMR techniques. However, the bonding of the Hg atoms remained unclear. Some authors have suggested that mercury should be bonded to the O atoms of β -diketone moieties, while others indicated that mercury was bound to the methylene C atom. Some compounds have been characterized by X-ray diffraction, e.g. bis(dipivaloylmethyl)mercury (Allmann, Flatau & Musso, 1972), dipivaloylmethylmercury acetate (Allmann & Musso, 1973) and 3,3-bis(chloromercury)-2,4-pentanedione (McCandlish & Macklin, 1975), and these show the formation of Hg—C bonds in all cases. More recently, two novel crystallographic structures involving monomercurated acetylacetonone molecules and dimercurated ethyl

acetoacetate molecules were proposed (Toledano, Bonhomme, Henry & Livage, 1993).

The present paper describes the structure of a new dimercurated acetylacetonone derivative (I), which is comparable with a similar structure published by McCandlish & Macklin (1975).



Figs. 1 and 2 show the molecular structure of the [Hg₂(C₅H₆O₂)Cl₂].CH₃CN asymmetric unit and a packing diagram, respectively.

The structure of this dimercurated compound consists of discrete entities having intermolecular interactions. Two Hg atoms replace the two H atoms on the C(3) atom of acetylacetonone. Hg—Cl bond lengths are in the range 2.306 (4)–2.326 (3) Å. Such distances have been observed for similar compounds (Matković-Calogović, 1987; Matković-Calogović, Popović & Korpar-Colig, 1992). The C—Hg—Cl bond angles are 174.5 (3) and 172.5 (3)°. This deviation from linearity is significant and may be attributed to secondary interactions with electronegative atoms surrounding the Hg atoms. Actually, each Hg atom is connected to an O atom of a symmetry related molecule and two Hg···O contacts are observed: Hg(1)···O(1ⁱ) 2.88 (1) and Hg(2)···O(2ⁱⁱ) 2.844 (9) Å [symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, -z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$]. These distances are smaller than the sum of the van der Waals radii of Hg and O [≈ 2.94 Å (Grdenic & Bruvo, 1982)]. The Hg···O contacts link the different acetylacetonone moieties and suggest a 'polymeric' structure in the *ab* plane. Acetonitrile molecules are then oriented along the *c* axis of the crystal. Two Hg···N contacts are observed: Hg(1)···N 3.07 (2) and Hg(2)···N

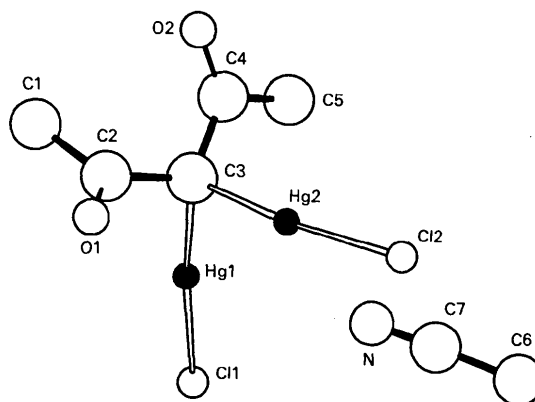


Fig. 1. ORTEP (Johnson, 1965) view of the structure of [Hg₂(C₅H₆O₂)Cl₂].CH₃CN, showing the atom-labelling scheme. H atoms are omitted.