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4-(Tri-*tert*-butoxysilylthiomercurio)benzoic acid

Jaroslaw Chojnacki,[a]* Agnieszka Walaszewska,[a] Elke Baum[b] and Wieslaw Wojnowski[a]

[a]Department of Chemistry, Technical University of Gdańsk, 11/12 G. Narutowicz St., 80952-PL Gdańsk, Poland, and [b]Institut für Anorganische Chemie der Universität Karlsruhe, TH Engesserstr. Geb. 30.45, D-76128 Karlsruhe, Germany

Correspondence e-mail:
jarekch@chem.pg.gda.pl

Key indicators

Single-crystal X-ray study
T = 200 K
Mean *σ*(C–C) = 0.009 Å
R factor = 0.031
wR factor = 0.057
Data-to-parameter ratio = 18.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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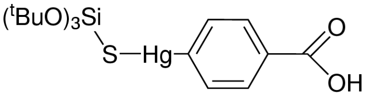
Contributions to the Chemistry of Silicon–Sulfur Compounds, Part 80.

The title compound, $[Hg(C_7H_5O_2)(C_{12}H_{27}O_3SSi)]$, was obtained by the reaction of 4-hydroxymercuriobenzoic acid with tri-*tert*-butoxysilanethiol. There are two independent molecules in the asymmetric unit, which are linked by hydrogen bonds involving the carboxylic acid groups. Two heterocubane-like Hg_4S_4 supramolecular arrangements are formed by weak Hg$\cdots$S interactions.

Comment

2-Hydroxymercuriobenzoic acid has been used for the volumetric determination of sulfur in sulfides, mercaptans and silanethiols (Wojnowska & Wojnowski, 1973). The structures of the products formed during the analysis of silanethiols have been postulated but never precisely measured. Determination of the structures of silanethiolanes has been the subject of research for many years (*e.g.* Wojnowski & Wojnowska, 1973; Wojnowski, Wojnowska, Peters *et al.*, 1985; Becker *et al.*, 2002; Kovacs *et al.*, 2000; Komuro *et al.*, 2002). Now we have turned our attention to the constitution and the geometry of compounds formed during mercurimetric titrations. The product of the reaction of 2-hydroxymercuriobenzoic acid with tri-*tert*-butoxysilanethiol is relatively stable and resistant to hydrolysis, allowing analytical procedures to be performed. Nevertheless, growing a good quality single crystal from this material has failed so far. It was decided to carry out the experiment with the closely related 4-hydroxymercuriobenzoic acid, the *para* isomer, which is also used in mercurimetry. It was found that its derivative with tri-*tert*-butoxysilanethiol was not only more stable, but also gave better quality single crystals.



(I)

The molecular structure of the title compound, (I), is shown in Fig. 1. The asymmetric unit contains two independent molecules, *viz*. *A*, involving atoms Hg1 and S1, and *B*, involving atoms Hg2 and S2. They are linked by hydrogen bonds; two COOH groups form O—H$\cdots$O bridges common for structures of simple organic acids. Additionally, Hg$\cdots$S contacts in four adjacent molecules produce two heterocubane Hg_4S_4 cores with two carboxylic ends on each side. The first heterocubane is formed entirely from atoms Hg1 and S1 and the symmetry-equivalent atoms, and the second consists of atoms Hg2 and S2 and the symmetry-equivalent atoms (see Table 1). This results in long threads of symmetrically non-equivalent thiolate molecules, linked by hydrogen bonds on one side and Hg$\cdots$S contacts on the other (see Fig. 2).

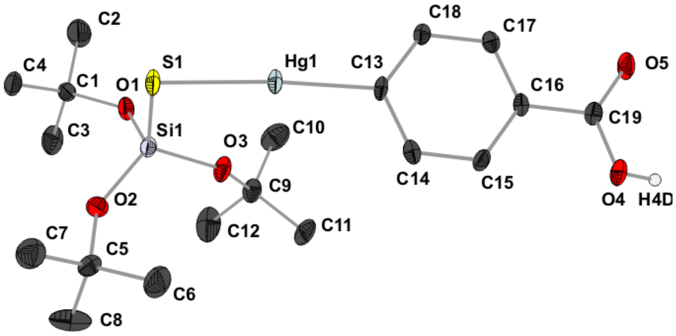


Figure 1
The structure and the labeling scheme of [HOOC–C_6H_4–HgSSi(O^tBu)$_3$]. Only one molecule of the asymmetric unit is shown. Displacement ellipsoids are at the 25% probabilty level. H atoms on C atoms have been omitted for clarity.

The valence angles at the S atoms [95.80 (6) and 96.74 (7)°] are similar to that observed in [(^{t}BuO)$_3$SiS]$_2$Hg (Wojnowski, Wojnowska, von Schnering & Noltemeyer, 1985), *viz.* 95.6 (1)°. There is a small deviation from linearity of the coordination of the Hg atoms: 175.74 (15)° at Hg1 and 177.22 (17) Å at Hg2. It appears that the O atoms have a weak chelating effect. The contacts Hg1···O3 and Hg2···O7 are 2.833 (2) and 2.929 (2) Å, respectively.

Experimental

The title compound was obtained by the following procedure: 0.381 g (1.12 mmol) of 4-hydroxymercuriobenzoic acid were dissolved in 30 ml of a 0.1 *M* solution of NaOH. To this were added 20 ml of freshly prepared ammonium salt solution, obtained from 0.33 ml of (^{t}BuO)$_3$SiSH (Piekos & Wojnowski, 1962) and 1 ml of concentrated aqueous NH_3 in 2-propanol. The mixture was neutralized dropwise with 0.1 *M* nitric acid and the contents extracted twice with 20 ml of toluene. The collected extracts were dried with $MgSO_4$ and filtered. The solvent was partially removed in a rotary evaporator to a volume of *ca* 4 ml, then left overnight for crystallization; yield 0.5 g (74%) of colourless crystals. The substance decomposes at 473–483 K without melting. Microanalysis, found: C 39.1 (1), H 5.4 (3), S 5.1 (1)%; calculated for $C_{19}H_{32}HgO_5SSi$: C 38.0, H 5.4, S 5.3%. Recrystallization of the crude product from toluene afforded colourless cube-like crystals suitable for X-ray diffraction analysis.

Crystal data

[Hg($C_7H_5O_2$)($C_{12}H_{27}O_3SSi$)]
M_r = 601.19
Tetragonal, $I4_1/a$
a = 22.5989 (13) Å
c = 39.015 (3) Å
V = 19926 (2) Å^3
Z = 32
D_x = 1.603 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 8000 reflections
θ = 1.5–25°
μ = 6.33 mm^{-1}
T = 200 (2) K
Plate, colourless
0.60 × 0.30 × 0.25 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1997)
T_{min} = 0.090, T_{max} = 0.293
21 819 measured reflections
9345 independent reflections
5930 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 25.9°
h = −27 → 20
k = −25 → 27
l = −26 → 47

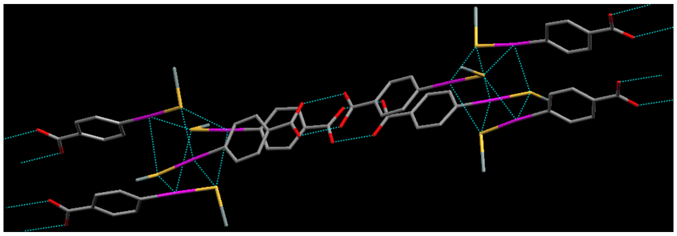


Figure 2
The crystal packing of [HOOC–C_6H_4–HgSSi(O^tBu)$_3$]. Contact lengths in the two heterocubanes are: (*a*) Hg1···S1^i 3.246 (2) Å and Hg1···S1^{ii} 3.382 (2) Å, and (*b*) Hg2···S2^{iii} 3.237 (2) Å and Hg2···S2^{iv} 3.726 (2) Å; the symmetry codes are as in Table 1.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.057
S = 0.83
9345 reflections
511 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.87 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Hg1···S1^i	3.2465 (15)	C19—O5	1.266 (6)
Hg1···S1^{ii}	3.3737 (15)	C19—O4	1.272 (7)
Hg2···S2^{iii}	3.2365 (16)	Hg2—C32	2.080 (5)
Hg2···S2^{iv}	3.7255 (18)	Hg2—S2	2.3508 (14)
Hg1—C13	2.078 (5)	S2—Si2	2.122 (2)
Hg1—S1	2.3685 (13)	Si2—O6	1.595 (4)
S1—Si1	2.119 (2)	Si2—O7	1.617 (4)
Si1—O2	1.611 (4)	Si2—O8	1.620 (4)
Si1—O1	1.614 (4)	C35—C38	1.480 (7)
Si1—O3	1.625 (4)	C38—O9	1.260 (6)
O1—C1	1.444 (6)	C38—O10	1.272 (7)
C16—C19	1.482 (7)		
C13—Hg1—S1	175.74 (15)	C32—Hg2—S2	177.22 (17)
Si1—S1—Hg1	95.80 (6)	Si2—S2—Hg2	96.74 (7)
O5—C19—O4	123.3 (5)	O9—C38—O10	123.3 (5)

Symmetry codes: (i) $y - \frac{1}{4}, \frac{5}{4} - x, \frac{1}{4} - z$; (ii) $\frac{5}{4} - y, \frac{1}{4} + x, \frac{1}{4} - z$; (iii) $\frac{3}{4} + y, \frac{5}{4} - x, \frac{1}{4} - z$; (iv) $\frac{5}{4} - y, x - \frac{3}{4}, \frac{1}{4} - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4D···O9^v	0.81 (2)	1.81 (2)	2.610 (5)	171 (7)
O10—H10D···O5^{vi}	0.79 (2)	1.93 (2)	2.703 (5)	167 (6)

Symmetry codes: (v) $\frac{1}{4} + y, \frac{7}{4} - x, -\frac{1}{4} - z$; (vi) $\frac{7}{4} - y, x - \frac{1}{4}, -\frac{1}{4} - z$.

All H atoms on C atoms were placed geometrically and allowed to ride on their parent atoms. For the carboxyl H atom, the O—H distance was restrained to 0.80 (2) Å and the other parameters were free to vary. The maximum electron-density peak is located 0.83 Å from atom Hg2.

Data collection: *IPDS* (Stoe & Cie, 1997); cell refinement: *IPDS*; data reduction: *X-RED* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *RESVIEW* (Schwenk, 1998) and *MERCURY* (CCDC, 2002); software used to prepare material for publication: *SHELXL*97.

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