

## Reinvestigation of bis(trimethylsilyl)-mercury

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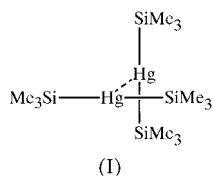
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In the course of work on main-group silyl compounds, crystals of the title compound,  $[\text{Hg}(\text{C}_3\text{H}_9\text{Si})_2]_2$ , were prepared. An earlier X-ray analysis of this compound failed to give a full structural characterization. Here, the title compound is found to consist of dimers with 222 crystallographic symmetry formed by two molecules of  $(\text{Me}_3\text{Si})_2\text{Hg}$  linked by a weak  $\text{Hg}\cdots\text{Hg}$  interaction with an interatomic distance of 3.1463 (6) Å. Each Si—Hg—Si frame is nearly linear and has an Hg—Si distance of 2.4913 (18) Å.

### Comment

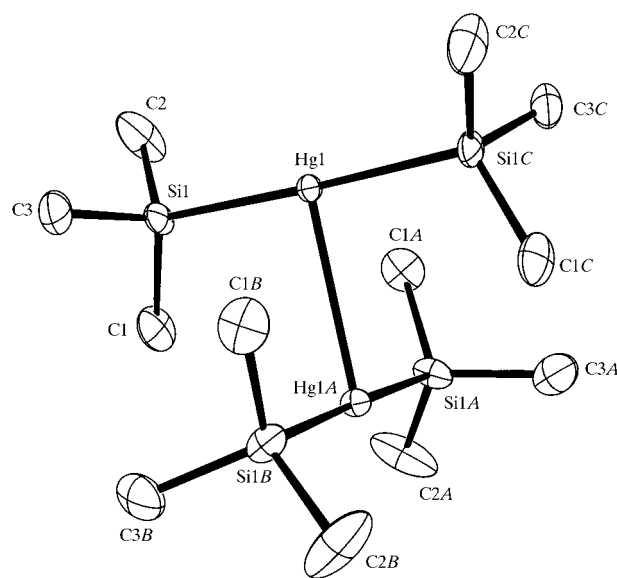
Mercury-bis(silyl) compounds have been known for many years and have been used extensively as silylating agents in the preparation of main-group silyl compounds. A single-crystal X-ray structural determination was undertaken previously on the title compound, bis(trimethylsilyl)mercury,  $(\text{Me}_3\text{Si})_2\text{Hg}$ , (I); however, only a partial solution was obtained (Bleckmann



*et al.*, 1976). The only other mercury-bis(silyl) compounds to have been structurally characterized include bis(triphenylsilyl)mercury,  $(\text{Ph}_3\text{Si})_2\text{Hg}$ , (II) (Ilsley *et al.*, 1980), bis(tri-*tert*-butylsilyl)mercury,  $(\text{tBu}_3\text{Si})_2\text{Hg}$ , (III) (Wiberg *et al.*, 1997), in which  $\text{tBu}_3\text{Si}$  is a supersilyl ligand, and bis[tris(trimethylsilyl)silyl]mercury,  $[(\text{SiMe}_3)_3\text{Si}]_2\text{Hg}$ , (IV), containing the hypersilyl ligand  $(\text{SiMe}_3)_3\text{Si}$  (Klinkhammer & Weidlein, 1996). Like bis(trimethylsilyl)mercury, compounds (II), (III) and (IV) all adopt a linear configuration about mercury. Also worth mentioning is the related cyclic compound 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasilolane-1,5-dimercuracyclo-octane, (V), which is a centrosymmetric molecule containing two linear Si—Hg—Si moieties linked by methylene groups (Ilsley *et al.*, 1980).

The results of a single-crystal X-ray analysis of the title compound, (I), are shown in Fig. 1. The molecular structure of (I) consists of dimers formed by two molecules of  $(\text{Me}_3\text{Si})_2\text{Hg}$  linked by a weak  $\text{Hg}\cdots\text{Hg}$  interaction with an interatomic distance of 3.1463 (6) Å, the midpoint of this interaction having crystallographic 222 symmetry. Each Si—Hg—Si frame is nearly linear [ $178.04(8)^\circ$ ] about the Hg atom. The Hg—Si interatomic distance of 2.4913 (8) Å is in good agreement with that determined by the original data collection [2.500 (5) Å]. This value is close to the Hg—Si interatomic distances seen in (II), (III), (IV) and (V) [2.490 (4), 2.495 (2), 2.469 (2) and 2.501 (4)/2.505 (4) Å, respectively]. Surprisingly, (I) and (V), possessing the less bulky silyl ligands, have the longest Hg—Si interatomic distances; these differences can most likely be attributed to the electron-withdrawing effect of the triphenylsilyl ligands in (II), the supersilyl ligands in (III) and the hypersilyl ligands in (IV). The Si—C interatomic distances seen in (I) [1.876 (9), 1.872 (7) and 1.866 (8) Å] are very similar to those of Si—C bonds adjacent to an Hg atom in other mercury-bis(silyl) compounds.

The geometry about the Si atom deviates very slightly from that of an ideal tetrahedron, with angles ranging from  $106.9(5)$  to  $112.9(3)^\circ$ . The Hg—Si—C angles are all larger than ideal angles, while all the C—Si—C angles are somewhat smaller than the ideal. A similar effect has also been noted in previously structurally characterized mercury-bis(silyl) compounds and is due to the large size of the Hg atom. One further point of interest is that within the crystal structure, two molecules of bis(trimethylsilyl)mercury are in very close proximity, with the two Si—Hg—Si planes of neighboring molecules lying perpendicular to each other about the Hg atoms, as shown in Fig. 1. The  $\text{Hg}\cdots\text{Hg}$  interatomic distance [3.1463 (6) Å] appears to be close to the sum of the covalent radii for two Hg atoms [the reported atomic radius of Hg is



**Figure 1**  
Displacement ellipsoid (30% probability) representation of the solid-state structure of (I), as determined by single-crystal X-ray diffraction analysis. All H atoms have been omitted from the representation for clarity.

1.57 Å (Ilsley *et al.*, 1980)]. For most structurally characterized compounds possessing an Hg—Hg bond, the interatomic distance is of the order of 2.5–2.7 Å; however, there are also reports of compounds possessing abnormally long Hg··Hg interactions, as in the case of the dimercury platinum cluster [Pt<sub>3</sub>Hg(CO)<sub>3</sub>(PPh<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>]<sub>2</sub> (Albinati *et al.*, 1982), which has a slightly longer distance [3.225 (1) Å] than that seen in (I). Due to the cyclic nature of (V), this compound also possesses a close Hg··Hg interaction, albeit an intramolecular interaction. On the basis of other structurally characterized compounds containing Hg··Hg interactions, the Hg··Hg interaction in (V) [3.286 (2) Å], which is slightly longer than the sum of the atomic radii, and that in (I), are considered to constitute real Hg—Hg bonds.

## Experimental

The title compound, (I), was prepared according to the literature method of Rösch & Erb (1979). Aluminium powder (20.0 g), mercury (20.0 g) and 130 ml of SiMe<sub>3</sub>Cl were placed in a 500 ml round-bottomed flask and 130 ml of tetrahydrofuran was added. The resulting reaction solution was allowed to reflux for 5 h with stirring. The solvent volume was removed by vacuum pump and the residue redissolved in pentane. The solution was filtered through celite and the solvent volume reduced. After keeping at 238 K for several days, a crop of bright-yellow crystals was obtained. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.200 p.p.m. (s, H, SiMe<sub>3</sub>).

### Crystal data

[Hg(C <sub>3</sub> H <sub>9</sub> Si) <sub>2</sub> ] <sub>2</sub>	Mo K $\alpha$ radiation
$M_r = 693.94$	Cell parameters from 3392 reflections
Orthorhombic, <i>Ccca</i>	$\theta = 2.32\text{--}25.00^\circ$
$a = 14.9958$ (10) Å	$\mu = 13.10$ mm <sup>-1</sup>
$b = 17.5356$ (12) Å	$T = 173$ K
$c = 9.0327$ (6) Å	Plate, bright yellow
$V = 2375.2$ (3) Å <sup>3</sup>	0.272 × 0.119 × 0.102 mm
$Z = 4$	
$D_x = 1.941$ Mg m <sup>-3</sup>	

**Table 1**

Selected geometric parameters (Å, °).

Hg1—Si2	2.4913 (18)	Si2—C1	1.872 (7)
Hg1··Hg1 <sup>i</sup>	3.1463 (6)	Si2—C3	1.876 (9)
Si2—C2	1.866 (8)		
Si2—Hg1—Si2 <sup>ii</sup>	178.04 (8)	C1—Si2—C3	107.2 (4)
Si2—Hg1··Hg1 <sup>i</sup>	90.98 (4)	C2—Si2—Hg1	110.9 (3)
C2—Si2—C1	106.9 (5)	C1—Si2—Hg1	112.9 (3)
C2—Si2—C3	108.0 (5)	C3—Si2—Hg1	110.8 (3)

Symmetry codes: (i)  $-x, \frac{1}{2} - y, z$ ; (ii)  $x, \frac{1}{2} - y, \frac{3}{2} - z$ .

### Data collection

Siemens SMART 1K CCD diffractometer	1058 independent reflections
$\omega$ scans	764 reflections with $I > 2\sigma(I)$
Absorption correction: based on symmetry-related measurements (Blessing, 1995)	$R_{\text{int}} = 0.054$
$T_{\text{min}} = 0.13, T_{\text{max}} = 0.35$	$\theta_{\text{max}} = 25^\circ$
5829 measured reflections	$h = -17 \rightarrow 16$
	$k = -20 \rightarrow 13$
	$l = -10 \rightarrow 10$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.028$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.074$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.985$	$\Delta\rho_{\text{max}} = 2.14$ e Å <sup>-3</sup>
1058 reflections	$\Delta\rho_{\text{min}} = -1.02$ e Å <sup>-3</sup>
46 parameters	Extinction correction: <i>SHELXTL</i>
H atoms: riding; one variable $U_{\text{iso}}$ per methyl group	(Sheldrick, 1995)
	Extinction coefficient:
	$3.3(6) \times 10^{-4}$

The largest electron-density peak and deepest electron-density hole are 1.00 and 0.78 Å, respectively, from the Hg1 atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1496). Services for accessing these data are described at the back of the journal.

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