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## Tetramethylammonium Tris(thiobenzoato-O,S)mercury(II)

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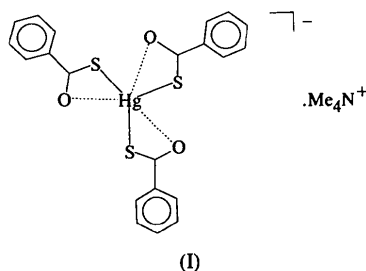
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### Abstract

The synthesis and structure for the title compound,  $(C_4H_{12}N)[Hg(C_7H_5OS)_3]$ , are reported. In the  $[Hg\{S(O)CPh\}_3]^-$  anion, the Hg<sup>II</sup> atom is located at the center of the triangle of S atoms. The Hg—S distances are 2.432 (3), 2.442 (4) and 2.555 (3) Å. In addition, there are weak intramolecular interactions between the Hg and carbonyl O atoms [Hg···O 2.767 (7), 2.915 (8) and 3.051 (9) Å].

### Comment

In earlier work, we reported the chemistry and structures of anionic thiobenzoate complexes of the type  $[M\{S(O)CPh\}_3]^-$ , where *M* is Zn, Cd and Hg (Vittal & Dean, 1996*a*), Sn (Vittal & Dean, 1996*b*) or Pb (Burnett, Dean & Vittal, 1994). Also, from  $[Cd\{S(O)CPh\}_3]^-$  in the presence of Na<sup>+</sup> ions, we have isolated the anion  $[Na\{Cd\{S(O)CPh\}_3\}_2]^-$ , in which the Cd<sup>II</sup> atom is preferentially bound to the S atoms and the Na<sup>+</sup> cation is attached to six O atoms (Vittal & Dean, 1993). In an attempt to isolate a similar trimetallic Hg derivative from a mixture of HgCl<sub>2</sub>, Na<sup>+</sup>.S(O)CPh<sup>-</sup> and Me<sub>4</sub>NCl, the title compound, (I), was obtained in high yield.



The single-crystal X-ray diffraction analysis of (I) shows that  $(Me_4N)[Hg\{S(O)CPh\}_3]$  consists of discrete anions and cations. There is no crystallographically imposed symmetry present in the anion or cation. A view of the anion is shown in Fig. 1. The three S(O)CPh<sup>-</sup> ligands are bonded to the Hg<sup>II</sup> atom primarily through their S atoms. Neglecting the weak interactions from the O atoms, the coordination sphere

around the Hg atom can be described as trigonal planar, with the three S atoms occupying the corners and the Hg<sup>II</sup> atom at the center. The Hg—S distances [2.432 (2), 2.442 (4) and 2.555 (3) Å] are comparable to those of 2.402 (2)–2.533 (2) Å found for the Ph<sub>4</sub>P<sup>+</sup> salt (Vittal & Dean, 1996*a*). The S—Hg—S angles are 109.1 (1), 112.4 (1) and 138.0 (1)°. The Hg···O distances [2.767 (7), 2.915 (8) and 3.051 (9) Å] are also close to the range of 2.858 (6)–3.364 (5) Å observed in the Ph<sub>4</sub>P<sup>+</sup> salt (Vittal & Dean, 1996*a*). These are approximately within the limits of the sum of the van der Waals radii (3.0 Å; Bondi, 1964). If we take into account these weak Hg···O bonds, then the coordination geometry of the Hg<sup>II</sup> atom is best described as a distorted octahedron.

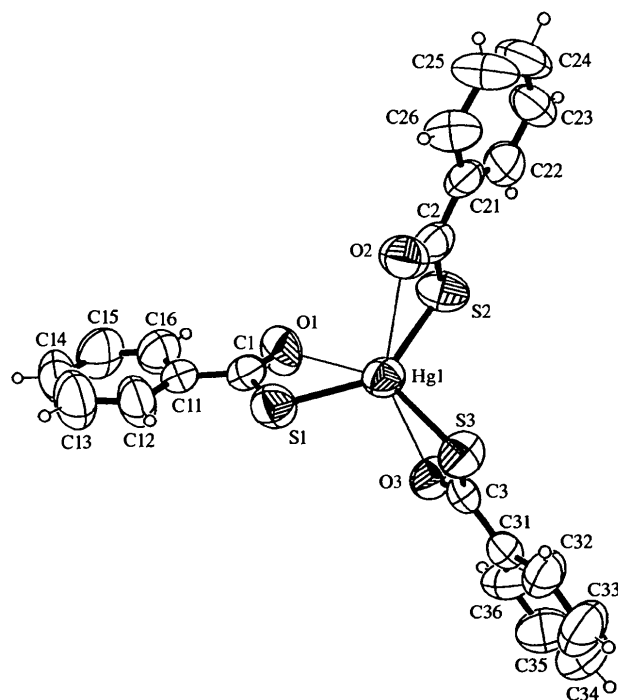


Fig. 1. A view of the  $[Hg\{S(O)CPh\}_3]^-$  anion showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

Although changing the cation from Ph<sub>4</sub>P<sup>+</sup> to Me<sub>4</sub>N<sup>+</sup> does not change the planarity of the HgS<sub>3</sub> skeleton, there are some dissimilarities between the structures of the anions in the Ph<sub>4</sub>P<sup>+</sup> and Me<sub>4</sub>N<sup>+</sup> salts. These differences arise from differing orientations of the PhCO fragments with respect to the HgS<sub>3</sub> plane.

The methyl groups of the Me<sub>4</sub>N<sup>+</sup> cation are disordered. The disorder model includes two different orientations of the methyl C atoms (occupancies of 0.65

and 0.35). The large void available for the cation may account for its orientational disorder. A similar case is observed in the structure of (Me<sub>4</sub>N)[Sn{S(O)CPh}<sub>3</sub>] (Vittal & Dean, 1996b).

## Experimental

All the chemicals were of reagent grade and were used as received. The synthesis was carried out under an argon atmosphere. Thiobenzoic acid (2.47 g, 17.85 mmol) in 15 ml methanol was added to NaOMe prepared *in situ* by dissolving sodium metal (0.37 g, 16.06 mmol) in 10 ml methanol to produce Na<sup>+</sup>S(O)CPh<sup>-</sup>. The resulting yellow solution was added with stirring to a solution containing HgCl<sub>2</sub> (1.45 g, 5.35 mmol) dissolved in 20 ml methanol producing a yellow precipitate. This turned into a white precipitate on addition of a solution containing Me<sub>4</sub>NCl (0.58 g, 5.35 mmol) in 20 ml methanol. The mixture was stirred for 10 min, then 10 ml H<sub>2</sub>O was added, followed by 25 ml MeCN. Warming the mixture to 313 K for 30 min gave a colorless clear solution, which was filtered hot and left to crystallize at 278 K. Colorless crystals were separated by decantation, washed with methanol and diethyl ether and dried in a stream of argon. A second crop of crystals was obtained from the mixture of mother liquor and washings (total yield 3.0 g; 81.6%). Single crystals were grown from a mixture of acetone and diethyl ether by diffusion.

### Crystal data

(C<sub>4</sub>H<sub>12</sub>N)[Hg(C<sub>7</sub>H<sub>5</sub>OS)<sub>3</sub>]  
*M<sub>r</sub>* = 686.25  
 Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 11.480 (2) Å  
*b* = 15.846 (3) Å  
*c* = 15.140 (3) Å  
 $\beta$  = 91.50 (3)°  
*V* = 2753.2 (10) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.656 Mg m<sup>-3</sup>  
*D<sub>m</sub>* = 1.67 (5) Mg m<sup>-3</sup>  
*D<sub>m</sub>* measured by flotation in  
 1,2-dibromoethane/hexane

### Data collection

Enraf-Nonius CAD-4  
 diffractometer  
 $\omega$  scans  
 Absorption correction:  
 face indexing, Gaussian  
 method (Siemens, 1995)  
*T<sub>min</sub>* = 0.291, *T<sub>max</sub>* = 0.334  
 8304 measured reflections  
 3830 independent reflections

### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.0485  
*wR*(*F*<sup>2</sup>) = 0.1037

*S* = 1.124  
 3829 reflections  
 303 parameters  
 H atoms: riding model  
 $w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 5.4047P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none  
 Scattering factors from  
*International Tables for  
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Hg1—S1	2.432 (3)	S3—C3	1.730 (11)
Hg1—S2	2.442 (4)	O1—C1	1.205 (12)
Hg1—S3	2.555 (3)	O2—C2	1.197 (13)
Hg1—O3	2.767 (7)	O3—C3	1.234 (12)
Hg1—O2	2.915 (8)	C1—C11	1.486 (14)
Hg1—O1	3.051 (9)	C2—C21	1.486 (16)
S1—C1	1.730 (11)	C3—C31	1.482 (15)
S2—C2	1.705 (12)		
S1—Hg1—S2	137.98 (12)	C1—S1—Hg1	99.4 (4)
S1—Hg1—S3	112.42 (11)	C2—S2—Hg1	94.5 (5)
S2—Hg1—S3	109.06 (12)	C3—S3—Hg1	88.8 (4)
S1—Hg1—O3	102.9 (2)	C1—O1—Hg1	86.2 (7)
S2—Hg1—O3	104.2 (2)	C2—O2—Hg1	86.7 (8)
S3—Hg1—O3	58.3 (2)	C3—O3—Hg1	91.3 (6)
S1—Hg1—O2	107.1 (2)	O1—C1—C11	123.8 (11)
S2—Hg1—O2	56.2 (2)	O1—C1—S1	120.0 (9)
S3—Hg1—O2	102.8 (2)	C11—C1—S1	116.2 (9)
O3—Hg1—O2	149.2 (2)	O2—C2—C21	120.4 (12)
S1—Hg1—O1	54.1 (2)	O2—C2—S2	122.7 (11)
S2—Hg1—O1	90.5 (2)	C21—C2—S2	117.0 (10)
S3—Hg1—O1	151.9 (2)	O3—C3—C31	121.7 (10)
O3—Hg1—O1	98.2 (2)	O3—C3—S3	121.6 (9)
O2—Hg1—O1	104.9 (2)	C31—C3—S3	116.7 (9)

The data were not collected beyond 23° on  $\theta$  because there were very few observed data in the 21–23° shell.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL (Siemens, 1995). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1233). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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