

The Ru—P bond lengths of 2.254 (2) Å (*trans* to H<sub>2</sub>O) and 2.245 (2) and 2.259 (2) Å (*trans* to O<sub>2</sub>CCF<sub>3</sub>) in (I) are all within the range of previously reported Ru—P bond lengths *trans* to oxygen donor ligands (Albers, Liles, Singleton & Stead, 1986a; Ashworth, Nolte & Singleton, 1976, 1977; Jones, Wilkinson, Galas, Hursthouse & Malik, 1980; Skapski & Stephens, 1974), but are shorter than those reported as unexpectedly long (2.339–2.361 Å) for [Ru(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>(MeOH)] (Dobson & Robinson, 1977). The Ru—O(trifluoroacetato) bond lengths of 2.158 (4) and 2.179 (4) Å are longer than those of 2.092 (6) to 2.104 (6) Å for the monodentate trifluoroacetato ligands *trans* to oxygen donor ligands in [ $L_2$ Ru(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>( $\mu$ -O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>( $\mu$ -OH<sub>2</sub>)] [ $L_2$  = cycloocta-1,5-diene (Albers *et al.*, 1984);  $L$  = PMe<sub>2</sub>Ph (Albers, Liles, Singleton & Stead, 1986a)], thus displaying the *trans* influence of the tertiary phosphine ligands. In contrast, no particular *trans* influence was observed in the structure of [Ru(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>(MeOH)] (Dobson & Robinson, 1977). The reason for this is not immediately apparent.

The reaction of [ $(\eta^3$ -C<sub>8</sub>H<sub>13</sub>)Ru(PMe<sub>3</sub>)<sub>3</sub>]PF<sub>6</sub> (Ashworth *et al.*, 1984) with trifluoroacetic acid in air gives a purple compound of stoichiometry [ $\{Ru(O_2CCF_3)(PMe_3)_3\}_2O$ ] (II), the precursor to (I). (II) is an analogue of the ruthenium(III) complex [ $\{Ru(PPh_3)(O_2CCH_3)_2\}_2(\mu-O)$ ] (III) proposed to have the structure shown (Mitchell, Spencer & Wilkinson, 1973), and is also related to the recently reported dinuclear oxo-bridged diiron(III) hemerythrin models (Armstrong, Spool, Papefthymiou, Frankel & Lippard, 1984). (II) converts slowly in ethanol solution to the colourless crystalline (I), but we have as yet been

unable to determine the mechanism of this unusual conversion.

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### Structure of Bis(1-butanethiolato)mercury(II)

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**Abstract.** [Hg(C<sub>4</sub>H<sub>9</sub>S)<sub>2</sub>],  $M_r = 378.95$ , tetragonal,  $I4_1/a$ ,  $a = 27.10$  (1),  $c = 13.28$  (1) Å,  $V = 9754$  (8) Å<sup>3</sup>,  $Z = 32$ ,  $D_x = 2.06$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 129$  cm<sup>-1</sup>,  $F(000) = 5696$ ,  $T = 207$  K,  $R = 0.036$  for 1533 unique observed reflections. The two independent Hg atoms are tetrahedrally coordinated by the thiolate ligands. The HgS<sub>4</sub> tetrahedra share corners and edges

forming spirals running parallel to **c** and with the organic residues in the cavities.

**Introduction.** When Zeise (1834*a,b*) synthesized ethanethiol, he recognized immediately that it was the first member of a new class of compounds, closely related to alcohols, the so-called thioalcohols RSH, or thiols. He also discovered (Zeise, 1834*c–e*) their extreme affinity towards mercuric compounds to yield very stable,

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water-insoluble compounds  $\text{Hg}(\text{SR})_2$ . Based on these observations, he gave them a second name, mercaptanes, which he derived from the latin description of these compounds as corpora MERcurium CAP-TANtes, *i.e.* the 'mercury snatchers'.

A great deal of scientific work has been carried out since those early days to describe and explain the extreme stability of the mercury-sulfur bond in this type of system. Simple solid neutral  $\text{Hg}(\text{SR})_2$  complexes have been extensively investigated by spectroscopy and structure determination. In the series with  $R = {}^n\text{C}_x\text{H}_{2x+1}$  structural data were reported by Wells (1937) for the compounds with  $x = 2-8$ . He found that these compounds form a monoclinic isomorphous series with one exception, the  $\text{Hg}(\text{SC}_4\text{H}_9)_2$  compound. In more recent studies, the structures of  $\text{Hg}(\text{SCH}_3)_2$  and  $\text{Hg}(\text{SC}_2\text{H}_5)_2$  (Bradley & Kuncher; 1963, 1964) and of the branched compound  $\text{Hg}(\text{S}'\text{C}_4\text{H}_9)_2$  (Kuncher, 1964) have been refined. In the row  $\text{Hg}(\text{SR})_2$  for unbranched alkyl groups  $R$ , structural data on the compound  $\text{Hg}(\text{SC}_4\text{H}_9)_2$  that Wells pointed out as exceptional are still missing and the purpose of this work is to complete the structural data by filling this gap.

**Experimental.** The compound was precipitated from an aqueous methanolic solution of mercury(II) perchlorate on addition of excess of the free thiol, and single crystals were obtained by slow cooling of a warm saturated acetonitrile solution. A transparent, tetragonal bipyramidal crystal of volume  $0.60 \times 10^{-2} \text{ mm}^3$  was enclosed in a thin-wall capillary. CAD-4 diffractometer, graphite-monochromatized  $\text{Mo K}\alpha$  radiation, variable speed,  $\omega-2\theta$  scans of width  $(0.70 + 0.50 \tan \theta)$ , max. recording time 120 s. Three standard reflections, no significant variations. Lattice parameters from 25 diffractometer  $\theta$  values. Cell data at 295 K,  $a = 26.967$  (7),  $c = 13.99$  (1) Å,  $V = 10175$  (7) Å<sup>3</sup>, close to data given by Wells (1937). From data collected at room temperature the Hg and S atoms were found by direct methods with *MULTAN80* (Main *et al.*, 1980), but as refinements gave high temperature factors a new data set was collected at 207 K. Lower temperature gave broad scan peaks. Intensities of 2012 independent reflections within  $\sin \theta / \lambda \leq 0.482 \text{ \AA}^{-1}$  ( $0 \leq h, k \leq 25$ ,  $0 \leq l \leq 12$ ), 1533 with  $I \geq 3\sigma(I)$ . Lp and absorption corrections, transmission factors 0.07-0.37. C atoms located by difference Fourier maps, full-matrix least-squares refinements, minimizing  $\sum w(\Delta F)^2$ ,  $w = [\sigma^2(F_o) + (0.035F_o)^2 + 1.00]^{-1}$ , anisotropic temperature factors for Hg and S, isotropic for C, methylene H atoms included with fixed parameters in calculated positions [ $d(\text{C}-\text{H}) = 1.00 \text{ \AA}$ ]. One of the four organic groups was found with a disordered hydrocarbon chain and refined as two partly occupied chains. Two pairs of overlapping atoms [C(41a), C(41b); C(43a), C(44b)] could not be resolved and were therefore included with

fixed positions found from difference Fourier synthesis. Final refinement with 1533 reflections, 124 variables,  $R = 0.036$ ,  $wR = 0.048$ ,  $S = 1.11$ . Corrections for secondary extinction (Zachariasen, 1967),  $g = 0.50$  (12)  $\times 10^{-4}$ ;  $(\Delta/\sigma)_{\text{max}} = 0.03$ , final  $\Delta\rho$  excursions  $\leq 10.75 \text{ e \AA}^{-3}$ . Scattering factors and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974). Program used: see Lundgren (1982).

Table 1. Atomic coordinates and isotropic temperature factors (Å<sup>2</sup>)

	$x$	$y$	$z$	$U_{\text{iso}}/U_{\text{eq}}$
	$U_{\text{eq}} = \frac{1}{3} \text{trace } U_{ij}$			
Hg(1)	0.18732 (2)	0.23501 (2)	0.73321 (6)	0.0470 (3)
Hg(2)	0.07009 (3)	0.32023 (3)	0.65616 (7)	0.0543 (3)
S(1)	0.25026 (16)	0.27542 (17)	0.61686 (40)	0.0500 (18)
S(2)	0.15421 (15)	0.15523 (16)	0.67106 (40)	0.0495 (18)
S(3)	0.13185 (15)	0.30329 (16)	0.79523 (38)	0.0474 (18)
S(4)	-0.01309 (16)	0.31893 (16)	0.74161 (41)	0.0515 (19)
C(11)	0.2301 (6)	0.3399 (6)	0.6225 (14)	0.053 (5)
C(12)	0.2687 (8)	0.3745 (7)	0.5751 (17)	0.075 (6)
C(13)	0.2504 (9)	0.4287 (9)	0.5766 (21)	0.105 (9)
C(14)	0.2871 (13)	0.4612 (12)	0.5281 (28)	0.158 (13)
C(21)	0.1910 (6)	0.1427 (6)	0.5602 (15)	0.052 (5)
C(22)	0.2431 (7)	0.1266 (7)	0.5843 (15)	0.059 (5)
C(23)	0.2747 (8)	0.1143 (8)	0.4947 (19)	0.090 (7)
C(24)	0.3279 (9)	0.0936 (9)	0.5179 (20)	0.098 (8)
C(31)	0.0920 (7)	0.2755 (7)	0.8911 (15)	0.059 (6)
C(32)	0.1181 (10)	0.2429 (9)	0.9618 (21)	0.111 (9)
C(33)	0.0871 (9)	0.2225 (9)	1.0447 (21)	0.101 (8)
C(34)	0.1163 (17)	0.1859 (15)	1.1189 (35)	0.218 (18)
C(41a)*	-0.0110	0.3820	0.7830	0.096 (25)
C(42a)	-0.0515 (18)	0.3879 (18)	0.8572 (42)	0.071 (15)
C(43a)	-0.0490	0.4410	0.9073	0.105 (21)
C(44a)	-0.0968 (37)	0.4494 (29)	0.9623 (70)	0.170 (34)
C(41b)	-0.0221	0.3830	0.7830	0.057 (12)
C(42b)	0.0038 (13)	0.3898 (13)	0.8773 (28)	0.077 (11)
C(43b)	-0.0063 (15)	0.4426 (15)	0.9272 (34)	0.103 (14)
C(44b)	-0.0612	0.4530	0.9679	0.156 (22)

\* Site-occupation factor 0.40 for C(41a)-C(44a) and 0.60 for C(41b)-C(44b).

Table 2. Selected distances (Å) and angles (°) in the mercury-sulfur network

Hg(1)-S(2)	2.482 (5)	S(1)-Hg(1)-S(1 <sup>l</sup> )	94.3 (2)
Hg(1)-S(3)	2.522 (4)	S(1)-Hg(1)-S(2)	114.5 (2)
Hg(1)-S(1)	2.549 (5)	S(1)-Hg(1)-S(3)	106.4 (2)
Hg(1)-S(1 <sup>l</sup> )	2.628 (5)	S(1 <sup>l</sup> )-Hg(1)-S(2)	113.0 (2)
		S(1 <sup>l</sup> )-Hg(1)-S(3)	102.4 (2)
Hg(2)-S(4 <sup>h</sup> )	2.500 (5)	S(2)-Hg(1)-S(3)	122.2 (1)
Hg(2)-S(4)	2.524 (5)		
Hg(2)-S(3)	2.535 (5)	S(2 <sup>h</sup> )-Hg(2)-S(3)	106.1 (2)
Hg(2)-S(2 <sup>h</sup> )	2.584 (4)	S(2 <sup>h</sup> )-Hg(2)-S(4)	115.0 (1)
		S(2 <sup>h</sup> )-Hg(2)-S(4 <sup>h</sup> )	103.7 (2)
Hg(1)-Hg(1 <sup>l</sup> )	3.521 (2) Å	S(3)-Hg(2)-S(4)	105.0 (2)
Hg(2)-Hg(2)	$\geq 3.892$ (2) Å	S(3)-Hg(2)-S(4 <sup>h</sup> )	117.9 (2)
Hg(1)-Hg(2)	$\geq 3.965$ (1) Å	S(4)-Hg(2)-S(4 <sup>h</sup> )	109.5 (2)
Hg(1)-S(1)-Hg(1 <sup>l</sup> )	85.7 (2)		
Hg(1)-S(2)-Hg(2 <sup>h</sup> )	103.0 (2)		
Hg(1)-S(3)-Hg(2)	106.8 (2)		
Hg(2)-S(4)-Hg(2 <sup>h</sup> )	101.5 (2)		

Symmetry code: (i)  $\frac{1}{2}-x, \frac{1}{2}-y, \frac{3}{2}-z$ ; (ii)  $-\frac{1}{4}+y, \frac{1}{4}-x, \frac{5}{4}-z$ ; (iii)  $\frac{1}{4}-y, \frac{1}{4}+x, \frac{3}{4}-z$ ; (iv)  $x, \frac{1}{2}-y, \frac{3}{4}-z$ .

**Discussion.** Final atomic coordinates and temperature factors are listed in Table 1;\* selected interatomic distances and bond angles are given in Table 2. The two independent Hg atoms are both coordinated to four thiolate ligands ( $\text{Hg-S} = 2.48\text{--}2.63 \text{ \AA}$ ) in distorted tetrahedra (Fig. 1). The  $\text{HgS}_4$  tetrahedra are linked by corner- and edge-sharing to helical chains (Fig. 2) running parallel to *c*. The edge-sharing occurs between two  $\text{Hg(1)S}_4$  tetrahedra. Each of the four helices in the unit cell requires 12 tetrahedra to fulfill a complete turn and shares a pair of  $\text{Hg(1)}$  tetrahedra with its four neighbouring helices. The 'tubes', which are formed by the helices, are filled up by hydrocarbon chains (not included in Fig. 2) bonded to the S atoms. The structure thus exhibits a clear separation between regions of metal-chalcogen interactions and regions with only van der Waals contacts between the hydrocarbon groups. Of the four organic ligands, one has an orientationally disordered hydrocarbon chain, occupying both the normal coplanar [C(41*a*)–C(44*a*)] and a

*gauche* [C(41*b*)–C(44*b*)] conformation. Distances and angles within the ligands are normal.

$\text{Hg}^{\text{II}}$  usually forms complexes that are either linear two- or tetrahedral four-coordinated. The  $\text{HgS}_4$  tetrahedra can be isolated as found in *e.g.* monomeric  $\text{Hg}(\text{SC}_6\text{H}_4\text{Cl})_4$  (Choudhury, Dance, Guerne & Rae, 1983) with  $\text{Hg-S}$  distances of  $2.537\text{--}2.552 \text{ \AA}$ , and as  $\text{HgS}_4^{6-}$  ions in  $\text{K}_6[\text{HgS}_4]$  (Sommer & Hoppe, 1978);  $\text{Hg-S}$   $2.54\text{--}2.59 \text{ \AA}$ . Dimers and trimers of edge-sharing tetrahedra are found in  $(\text{Et}_4\text{N})[\text{Hg}_2(\text{SMe})_6]$  (Bowmaker, Dance, Dobson & Rogers, 1984) and in  $(\text{PPh}_4)_2[\text{Hg}_3(\text{SCH}_2\text{CH}_2\text{S})_4]$  (Henkel, Betz & Krebs, 1985) in which the  $\text{Hg-S}$  distances vary in the ranges  $2.44\text{--}2.71 \text{ \AA}$  and  $2.36\text{--}2.86 \text{ \AA}$ , respectively. Chains of edge-sharing  $\text{HgS}_4$  tetrahedra are the building element in  $\text{Hg}(\text{S}'\text{C}_4\text{H}_9)_2$  (Kuncher, 1964), in which the  $\text{Hg-S}$  distances are  $2.59\text{--}2.66 \text{ \AA}$  and the  $\text{S-Hg-S}$  angles vary between  $87$  and  $121^\circ$ .

A three-dimensional network composed of both corner- and edge-sharing  $\text{HgS}_4$  tetrahedra, as found in the present structure, has not been observed previously. Corner-sharing  $\text{HgS}_4$  tetrahedra are, however, the building elements in the zinc blende structure of  $\text{HgS}$  (metacinnabarite), in which the  $\text{Hg-S}$  distances are  $2.53 \text{ \AA}$  (Aurivillius, 1964, 1965).

\* Lists of structure factors, anisotropic thermal parameters, calculated H-atom positions together with distances and angles within the organic ligands have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43626 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

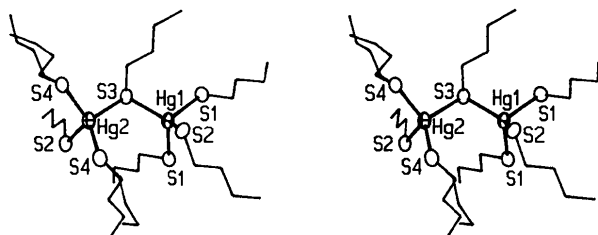


Fig. 1. Stereoview of the environment of the Hg atoms. The atomic numbering scheme is given in Table 2.

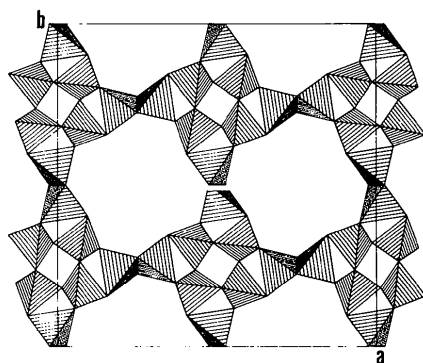


Fig. 2. Projection along *c* showing the  $\text{Hg-S}$  network of tetrahedra. Edge-sharing occurs between  $\text{Hg(1)S}_4$  groups. The tetrahedra in the middle are separated by one unit translation along *c*.

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