

Di(2-thienyl)mercury

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Abstract. $C_8H_6HgS_2$, $Hg(C_4H_3S)_2$, monoclinic, $C2/c$, $a = 21.720$ (3), $b = 5.368$ (3), $c = 7.746$ (1) Å, $\beta = 103.63$ (1)°, $V = 877.8$ Å³, $Z = 4$, $D_m = 2.69$, $D_x = 2.776$ Mg m⁻³, $\mu(Cu K\alpha) = 36.22$ mm⁻¹. The atomic coordinates obtained on the basis of 586 diffractometrically measured reflexions were refined to a conventional R of 0.053. The molecule is centrosymmetric with an Hg–C bond length of 2.061 (18) Å.

Introduction. Colourless prismatic crystals of di(2-thienyl)mercury, prepared according to Steinkopf (1917), were grown by slow evaporation of a benzene solution at room temperature. The single crystal used was ground to a sphere of diameter 0.185 mm. The crystallographic and intensity data were measured on a Philips PW 1100 four-circle automatic computer-controlled diffractometer (graphite-monochromatized Cu $K\alpha$ radiation, $\lambda = 1.542$ Å) by ω - 2θ scans (scan speed 0.12° s⁻¹, scan range 4.8°) within the range 3° < 2θ < 68°. The intensity variation during the course of the data collection amounted to 1.1% as measured from reference reflexions (310, 202 and 312) every 2 h. The only systematic absences were hkl , $h + k = 2n + 1$ and $h0l$, $l = 2n + 1$, indicating the space groups Cc or $C2/c$. The latter was assumed and found to give satisfactory refinement. A total of 782 non-zero independent reflections were collected out of 806 possible reflections within the given range, and the intensities of 622 reflections with $I > 3\sigma(I)$ were used for the structure determination. The usual corrections

were made for Lorentz-polarization and absorption effects. Unit weights were allotted to all reflexions. The preliminary atomic coordinates, obtained by the heavy-atom method, were refined by a full-matrix least-squares procedure with isotropic thermal parameters to an R value of 0.067. The refinement with anisotropic thermal parameters in which the H atoms, at calculated positions ($d_{C-H} = 1.08$ Å), were included isotropically, gave an R value of 0.060. In the final refinement another 36 reflexions were omitted, the 23 with $I < 4\sigma(I)$ and 13 for which there was a large discrepancy between F_c and F_o , probably due to extinction. The final R value was 0.053.*

The atomic scattering factors were those of Cromer & Mann (1968) with corrections from Cromer & Liberman (1970) for anomalous scattering for the non-hydrogen atoms.

Discussion. The atomic coordinates with e.s.d.'s are given in Table 1. The Hg atoms are in the special positions 4(a) of the space group $C2/c$; thus the molecule is centrosymmetric, the C–Hg–C bond angle exactly 180° and the S atoms are necessarily in the

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34377 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional (fractional) parameters

Standard deviations in the units of the last significant digits are given in parentheses.

	x	y	z
Hg	0.000	0.0000	0.0000
C(1)	0.0812 (9)	0.1624 (34)	0.1494 (25)
C(2)	0.1435 (9)	0.0789 (38)	0.1682 (27)
C(3)	0.1865 (11)	0.2382 (48)	0.2748 (30)
C(4)	0.1615 (10)	0.4346 (39)	0.3369 (27)
S	0.0807 (2)	0.4294 (8)	0.2682 (7)
H(1)	0.1541	−0.0908	0.1100
H(2)	0.2342	0.2058	0.3111
H(3)	0.1859	0.5891	0.4175

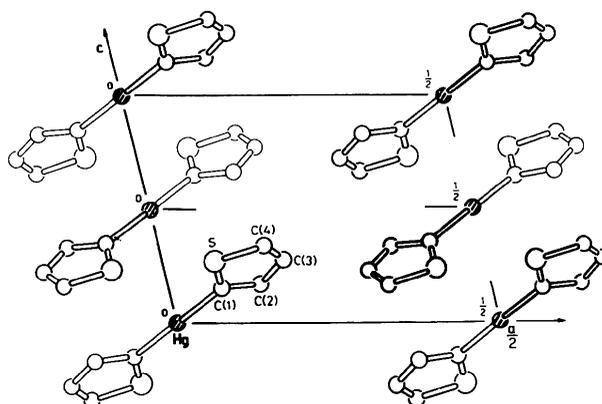


Fig. 1. The molecules of di(2-thienyl)mercury in the crystal structure viewed along the b axis with the Hg atoms at $y = 0, \frac{1}{2}$. The H atoms are not shown.

anti conformation (Fig. 1). The thienyl ring is planar; the deviations of the atom positions from the least-squares best plane through the S atom and the C atoms of the asymmetric unit (defined by the equation $-0.25835X - 0.53182Y + 0.80649Z + 0.06647 = 0$, with respect to the orthogonal axes a, b, c^*) are less than the e.s.d.'s of the atomic coordinates. Since the Hg atom is displaced from this plane by 0.07 Å the molecule is not strictly planar but bent at the C(1) atom like the molecule of diphenylmercury (Grdenić, Kamenar & Nagl, 1977). The angle between the Hg—C(1) bond and the line connecting C(1) with the middle of the C(3)—C(4) bond is 178.4°.

The interatomic distances and bond angles are given in Table 2. The Hg—C bond of 2.061 (18) Å is shorter than those of 2.09, 2.08 (2) and 2.085 (7) Å in the analogous bis(pentafluorophenyl)mercury (Kunchur & Mathew, 1966), di-*p*-tolylmercury (Mathew & Kunchur, 1970) and diphenylmercury (Grdenić, Kamenar & Nagl, 1977) as well as in other organomercury structures (Kuz'mina, Bokij & Struchkov, 1975). The difference, which is less than two standard deviations, is not significant. If it really exists it can be explained by the electron-donating character of the thienyl ring. Such a shortening of the carbon-to-metal bond was also observed in a thienyl derivative of cyclopentadienyl-iron (Andrianov, Sergeeva, Struchkov, Anisimov, Kolobova & Beschastnov, 1970). The analogy is also seen in the C—C bonds in the thienyl ring where the C(1)—C(2) bond is longer and the C(2)—C(3) bond shorter than the corresponding bonds in the thiophene molecule (Bak, Cristensen, Rastrup-Andersen & Tannenbaum, 1956). The intermolecular C...H and S...S contacts agree approximately with the sum of the van der Waals radii, if the values of 1.77, 1.17 and 1.80 Å, are taken for C, H and S, respectively (Bondi, 1964). However, the molecules are more closely packed through the S...S^{III} contacts of 3.451 (7) Å, but not through the Hg...S^{III} contacts of 3.619 (5) Å which are larger than the sum of the van der Waals radii, with 1.50 Å (Grdenić, 1965) or 1.55 Å (Bondi, 1964) as the radius for Hg. Consequently, there is no additional Hg...S non-valence bonding in the structure and the effective coordination of Hg is its characteristic digonal coordination (Grdenić, 1965).

Table 2. *Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses*

(a) Measured			
Hg—C(1)	2.061 (18)	C(4)—S	1.709 (21)
C(1)—C(2)	1.400 (27)	Hg...S ^{III}	3.619 (5)
C(2)—C(3)	1.387 (29)	S...S ^{III}	3.451 (7)
C(3)—C(4)	1.327 (34)	C(3)...C(3 ^{IV})	3.906 (34)
C(1)—S	1.704 (19)	C(3)...C(4)	3.744 (32)
Hg—C(1)—C(2)	126.9 (14)	C(2)—C(3)—C(4)	115.4 (20)
Hg—C(1)—S	123.1 (11)	C(3)—C(4)—S	110.6 (16)
C(2)—C(1)—S	110.0 (14)	C(4)—S—C(1)	92.6 (10)
C(1) C(2) C(3)	111.3 (19)		
(b) Calculated			
C(2)—H(1)	1.07	C(3)...H(3 ^b)	2.92
C(3)—H(2)	1.02	C(3)...H(1 ^b)	2.95
C(4)—H(3)	1.10	C(4)...H(1 ^b)	2.84
C(2)...H(3 ^b)	2.94	S...H(1 ^b)	3.30

Symmetry code

(i)	$x, 1-y, -\frac{1}{2}+z$	(iii)	$-x, y, \frac{1}{2}-z$
(ii)	$x, -y, \frac{1}{2}+z$	(iv)	$\frac{1}{2}-x, \frac{1}{2}-y, 1-z$

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