

La cohésion de la structure est due essentiellement aux attractions électrostatiques entre les ions. Elle fait aussi intervenir la liaison hydrogène $N(1) \cdots H(N1) \cdots Cl(1^i) [(i): 1 + x, y, z]$ longue de 3,326 (7) Å et dont l'angle est voisin de 166°.

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Structure of Dibromo(diphenylphosphinoacetic acid)mercury(II), $HgBr_2 \cdot (C_6H_5)_2PCH_2COOH$

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Abstract. $[HgBr_2(C_{14}H_{13}O_2P)]$, $M_r = 604.65$, monoclinic, $P2_1/c$, $a = 11.052$ (2), $b = 11.149$ (2), $c = 15.810$ (3) Å, $\beta = 122.28$ (1)°, $V = 1647.0$ (6) Å³, $Z = 4$, $D_m = 2.417$ (2), $D_x = 2.439$ (1) Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 13.85$ mm⁻¹, $F(000) = 1112$, $T = 296$ K, $R = 0.039$ for 1745 unique observed reflections. The structure consists of centrosymmetric, doubly halogen-bridged dimers with Hg atoms in a distorted tetrahedral environment. The carboxyl group of the ligand is not coordinated but participates in hydrogen bridges resulting in infinite chains. No other contacts except those at normal van der Waals distances appear in the structure.

Introduction. Tertiary phosphine complexes of mercury(II) halides with the composition $HgX_2(R_3P)$ possess a wide variety of structural types (Bell, Goldstein, Jones & Nowell, 1983). Unlike simple tertiary phosphines, diphenylphosphinoacetic acid as a functionalized phosphine ligand can, and frequently does, introduce novel structural features resulting from the presence of the carboxyl group. Therefore, it seemed interesting to investigate the crystal structure of the title complex which was synthesized (Podlahová & Gracias, 1985) as a member of an extensive series of mercury(II) complexes with diphenylphosphinoacetic acid.

Experimental. The crystals were obtained by vapor diffusion of dichloromethane into a saturated solution of the complex in acetone. The investigated prismatic crystal with a size of 0.21 × 0.20 × 0.11 mm has well developed {011} and {102} faces. Density measured pycnometrically under xylene. A Stoe four-circle diffractometer with graphite monochromator, 63 reflections with 2θ range 30–36° used for lattice-parameter refinement, absorption-correction values 0.1383 to 0.2944, maximum $\sin\theta/\lambda$ value 0.5378 Å⁻¹, h, k, l range: -11, 10; 0, 11; 0, 16. Three standard reflections monitored after every 120 without any significant intensity fluctuation; 2745 measured reflections, 2131 unique reflections, 386 unobserved reflections according to criterion $F_o < 3\sigma(F_o)$, $R_{int} = 0.0256$. Direct methods, F_o magnitudes used, full-matrix least-squares refinement of positional parameters and anisotropic thermal parameters of non-H atoms in two blocks; H atoms except one located from difference map, isotropic thermal parameters of H atoms were not refined and were equal to the isotropic thermal parameters of their bonding partners, multiplied by 1.1. $R = 0.0386$, $wR = 0.0261$, $GOF = 2.02$, $w = 1.656/\sigma^2(F_o)$, ratio of maximum least-squares shift to e.s.d. in last refinement cycle 0.07, maximum and minimum height in final difference map 0.75 and -0.73 e Å⁻³, secondary-

extinction coefficient $g = 4.968 \times 10^{-6}$, source of atomic scattering factors and f', f'' : *MULTAN80* (Main *et al.*, 1980); programs used: *MULTAN80*, *ORTEP* (Johnson, 1965).*

* Lists of structure factors, anisotropic thermal parameters and positional parameters of H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42668 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

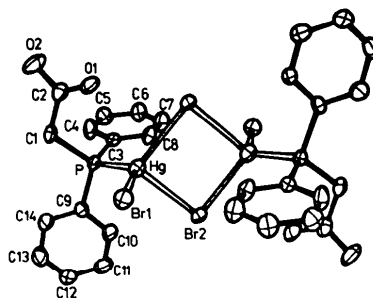


Fig. 1. *ORTEP* drawing (36% probability) of the structure of the $\text{HgBr}_2 \cdot (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{COOH}$ dimer. H atoms (omitted for clarity) are given the numbers of their bonding partners.

Table 1. Final coordinates ($\times 10^4$, for Hg $\times 10^5$) and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Hg	53191 (4)	10652 (4)	41388 (13)	0.0346 (1)
Br(1)	7816 (1)	856 (1)	4489 (1)	0.0389 (4)
Br(2)	5453 (1)	1346 (1)	5900 (1)	0.0316 (4)
P	3253 (2)	2032 (2)	2735 (2)	0.0262 (9)
C(1)	3746 (9)	3585 (7)	2676 (6)	0.032 (4)
C(2)	4292 (10)	4231 (8)	3669 (7)	0.036 (4)
O(1)	4934 (8)	3732 (5)	4464 (5)	0.050 (3)
O(2)	4012 (8)	5359 (6)	3570 (5)	0.061 (3)
C(3)	1670 (8)	2080 (8)	2784 (6)	0.027 (3)
C(4)	543 (9)	2822 (9)	2127 (6)	0.044 (4)
C(5)	-718 (10)	2816 (9)	2110 (7)	0.047 (4)
C(6)	-892 (10)	2060 (9)	2735 (7)	0.044 (4)
C(7)	212 (10)	1311 (9)	3374 (7)	0.047 (4)
C(8)	1487 (9)	1330 (8)	3402 (6)	0.036 (4)
C(9)	2703 (9)	1265 (8)	1579 (6)	0.029 (3)
C(10)	2399 (11)	70 (8)	1552 (6)	0.044 (5)
C(11)	1927 (11)	-589 (9)	692 (7)	0.049 (5)
C(12)	1732 (11)	-45 (10)	-159 (7)	0.046 (5)
C(13)	2051 (12)	1118 (10)	-132 (7)	0.059 (5)
C(14)	2512 (10)	1800 (9)	732 (6)	0.043 (4)

Discussion. The atomic coordinates are given in Table 1 and important bond lengths and angles are summarized in Table 2. The structure consists of centrosymmetrical dimers (Fig. 1) with double halogen bridges of approximately equal length, which is the most frequent arrangement for this type of complex. In accordance with the steric requirements of the bromide and phosphine ligands, mercury adopts a distorted tetrahedral coordination. The distances and angles in the diphenylphosphinoacetic acid molecule are all normal and comparable to those in related complexes with the P-bonded ligand (Podlahová, Loub & Ječný, 1979; Hazell, Hazell, Kratochvíl & Podlahová, 1981; Jegorov, Kratochvíl, Langer & Podlahová, 1984). Although mercury is formally coordinatively unsaturated, the carboxyl group does not participate in coordination to the metal. It forms the usual centrosymmetric twofold hydrogen bridge (the appropriate H atom of the bridge could not be located but the remaining atoms are coplanar), through which the dimers are arranged into infinite chains. Further contacts between the chains are at the usual van der Waals distances and do not appear to contribute significantly to stabilization of the structure.

Table 2. Bond lengths (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

Hg—Br(1)	2.519 (1)	Br(1)—Hg—Br(2)	109.3 (1)
Hg—Br(2)	2.726 (1)	Br(1)—Hg—P	128.9 (1)
Hg—P	2.426 (2)	Br(1)—Hg—Br(2) ^a	101.6 (1)
Hg—Br(2) ^b	2.811 (1)	Br(2)—Hg—P	113.2 (1)
		Br(2)—Hg—Br(2) ^b	89.0 (1)
		Br(2) ^b —Hg—P	106.2 (1)
P—C(1)	1.832 (8)	Hg—P—C(1)	107.9 (4)
P—C(3)	1.792 (8)	Hg—P—C(3)	116.0 (4)
P—C(9)	1.805 (8)	Hg—P—C(9)	111.1 (4)
		C(1)—P—C(3)	107.3 (6)
		C(1)—P—C(9)	110.1 (6)
		C(3)—P—C(9)	104.5 (6)
		P—C(1)—C(2)	111.0 (6)
C(2)—O(1)	1.201 (11)	O(1)—C(2)—O(2)	123.3 (9)
C(2)—O(2)	1.285 (12)		
O(1)—O(2) ^b	2.858 (9)		

Symmetry code: (i) $1-x, -y, 1-z$; (ii) $1-x, 1-y, 1-z$.

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