ligand. The conformations of the complex cations for (1) and (2) are shown in Figs. 2 and 3, respectively. In the case of (1), Fig. 2 shows one of the two enantiomorphs present in the unit cell, *i.e.* the ferrocene groups have the *S,S* conformer. For (2) (Fig. 3) the conformation is *S,R*. Bond parameters associated with the biphosphine ligands are not unusual and compare favourably with those found for these ligands in [(*L L*)RhNBD]ClO_4 complexes (Cullen, Kim, Einstein & Jones, 1984), *viz* P—C distances show a similar trend, *i.e.* P—C(Cp) < P—C(Ph) < P—C(Bu^t); the deviations of P atoms out of their associated Cp ring planes are in agreement with the equivalent deviations in the [(*L L*)RhNBD]ClO_4 series (Cullen, Kim, Einstein & Jones, 1984) and can be explained in the same way. The closest contact between the 'disordered' perchlorate anions and their respective cations is 2·62 Å between O(1)* and H(135) in (1) and 2·43 Å between O(5) and H(111*C*) in (2). Intramolecular distances are not unusual.

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* O(1) denotes the ordered oxygen atom of the perchlorate group while O(2)–O(7) denote the disordered oxygen atoms (see *Experimental*). The hydrogen-atom numbering schemes are such that their serial numbers are the same as the parent carbon, with additional letters *A*, *B* or *C* in the case of methyl hydrogens.

The authors would like to thank Dr W. R. Cullen for his gift of the crystals, Professor K. Prout and Dr D. Watkin for the use of the *CRYSTALS* crystallographic suite, Dr E. J. Gabe for use of the *NRC* crystal structure system, and NSERC for financial support.

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Structure of Tetraphenylphosphonium Triiodomercurate(II), $[P(C_6H_5)_4][HgI_3]$

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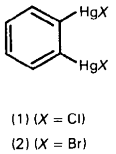
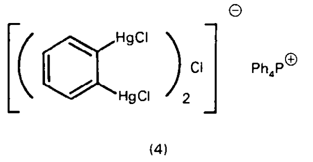
(*Received* 23 *August* 1984; *accepted* 30 *October* 1984)

Abstract. $M_r = 920·70$, triclinic, $P\bar{1}$, $a = 9·163\,(7)$, $b = 10·921\,(3)$, $c = 13·300\,(7)$ Å, $\alpha = 85·04\,(3)$, $\beta = 76·57\,(5)$, $\gamma = 85·84\,(4)$°, $V = 1287·9$ Å^3, $Z = 2$, $D_x = 2·374$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\bar{\alpha}) = 1·54178$ Å (graphite-monochromated), $\mu = 40·74$ mm^{-1}, $F(000) = 836$, $T = 293$ K. Final $R = 0·043$ for 3754 unique non-zero reflections. The unit cell contains two $[P(C_6H_5)_4]^+$ cations and one centrosymmetric $[Hg_2I_6]^{2-}$ anion. In the anion, two iodines bridge two HgI_2 units, and the coordination about mercury is approximately tetrahedral. The main distances are: Hg—I(terminal) = 2·707 (1) and 2·690 (1) Å, Hg—I(bridge) = 2·864 (1) and 2·962 (1) Å, mean P—C = 1·789 (8) Å.

Introduction. Treatment of μ-*o*-phenylene-bis[chloromercury(II)] (1) and μ-*o*-phenylene-bis[bromomercury(II)] (2) with a variety of phosphonium and ammonium halides produces salts of anionic complexes like structure (4) (Wuest & Zacharie, 1985). We were surprised to find that analogous reactions of μ-*o*-phenylene-bis[iodomercury(II)] (3) do not yield similar complexes, but give instead the products of redistribution reactions. For example, X-ray crystallographic study has shown that the salt formed from equimolar amounts of compound (3) and tetraphenylphosphonium iodide is in fact tetraphenylphosphonium triiodomercurate(II). The structure of this salt is described below.



(1) (*X* = Cl)
(2) (*X* = Br)
(3) (*X* = I)



(4)

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Table 1. *Refined atomic coordinates* ($\times 10^4$, Hg, I $\times 10^5$) *and equivalent isotropic thermal parameters* ($\times 10^3$)

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}(Å^2)
Hg	62468 (5)	−128 (4)	35677 (3)	61
I(1)	52849 (10)	−9020 (6)	20106 (5)	64
I(2)	91711 (8)	4815 (5)	30824 (5)	53
I(3)	42191 (8)	18324 (5)	46173 (4)	58
P	517 (2)	5573 (1)	2185 (1)	28
C(11)*	−1386 (8)	5125 (6)	2370 (5)	30
C(12)	−2555 (10)	5914 (7)	2793 (7)	46
C(13)	−4053 (11)	5605 (9)	2873 (9)	60
C(14)	−4328 (10)	4509 (9)	2522 (7)	52
C(15)	−3135 (11)	3724 (8)	2086 (8)	53
C(16)	−1666 (10)	4042 (7)	1999 (7)	43
C(21)	1780 (8)	4341 (6)	1675 (5)	29
C(22)	2793 (9)	4487 (7)	705 (6)	38
C(23)	3716 (11)	3517 (9)	332 (7)	56
C(24)	3678 (11)	2408 (9)	881 (8)	56
C(25)	2742 (10)	2235 (7)	1851 (7)	46
C(26)	1795 (10)	3173 (6)	2216 (6)	40
C(31)	929 (9)	5977 (6)	3359 (5)	34
C(32)	1809 (10)	5192 (8)	3905 (5)	41
C(33)	2181 (12)	5614 (11)	4768 (6)	58
C(34)	1685 (13)	6751 (9)	5091 (6)	59
C(35)	769 (16)	7501 (9)	4587 (8)	68
C(36)	367 (14)	7124 (8)	3712 (7)	59
C(41)	782 (8)	6890 (6)	1279 (5)	31
C(42)	−182 (10)	7160 (7)	611 (6)	39
C(43)	93 (11)	8163 (7)	−119 (6)	46
C(44)	1328 (10)	8852 (7)	−187 (6)	44
C(45)	2251 (11)	8589 (7)	457 (7)	49
C(46)	2039 (10)	7595 (7)	1220 (6)	44

* The C atoms are assigned two-digit symbols. The first digit indicates the ring number (1 to 4); the second corresponds to sequential numbering in the ring, with atom 1 being bonded to P.

Experimental. Equimolar amounts of *μ*-*o*-phenylene-[bis(iodomercury(II)] (3) and tetraphenylphosphonium iodide were stirred in dichloromethane at 298 K until a homogeneous solution was formed. Addition of hexane followed by filtration yielded a solution from which yellow prisms of tetraphenylphosphonium triiodomercurate(II) crystallized [m.p. 473–474 K; lit. (Deacon, Jones & Rogasch, 1963) m.p. 473–473·5 K]. This material was identical by IR, melting point, and mixed melting point with a sample prepared by treating mercuric iodide in dichloromethane with an equimolar amount of tetraphenylphosphonium iodide. A crystal of dimensions 0·075 (001–00$\bar{1}$) × 0·075 (010–0$\bar{1}$0) × 0·150 mm (110–$\bar{1}\bar{1}$0) was used for the X-ray analysis.

Unit-cell parameters were determined with an Enraf–Nonius CAD-4 diffractometer. A set of 25 Cu $K\alpha$ reflections randomly distributed in the Laue sphere ($10 < \theta < 25°$) was created by the automatic search procedure of the CAD-4 software. These reflections were centered four times and the automatic indexing routine yielded the reduced triclinic cell given in the *Abstract*. This cell was checked by means of oscillation photographs about the three axes, which showed the expected layer line spacings. The Niggli parameters clearly indicated that no higher symmetry was present.

Data collected as described elsewhere (Bélanger-Gariépy & Beauchamp, 1980). $2\theta_{max} = 140°$. Range of hkl: $0 \leq h \leq 12$, $-13 \leq k \leq 13$, $-16 \leq l \leq 16$. Standards (e.s.d.): 020 (1·7%), $\bar{1}\bar{1}\bar{2}$ (1·7%) $\bar{1}0\bar{1}$ (1·0%). Set of 4884 unique reflections measured, 3754 observed, 1130 unobserved [$I < 3{\cdot}0\sigma(I)$]. Corrected for Lorentz effect, polarization and absorption (Gaussian integration, grid 8 × 8 × 8, transmission range: 0·011–0·114).

Hg, I and P atoms located by direct methods (*MULTAN*74, Main, Woolfson, Lessinger, Germain & Declercq, 1974). C atoms found from standard Fourier techniques. $\sum w(|F_o| - |F_c|)^2$ minimized by full-matrix least squares (isotropic), then by block-diagonal least squares (anisotropic). Parameters refined: scale factor, coordinates and anisotropic temperature factors of non-H atoms. Phenyl H atoms fixed at calculated positions (C—H = 0·95 Å, sp^2 hybridization, isotropic $B = 6{\cdot}0$ Å^2). Coordinates of H atoms recalculated after each least-squares cycle. Final $R = 0{\cdot}043$, $wR = 0{\cdot}050$, $S = 1{\cdot}72$; $w = 1/\sigma^2(F)$. Δ/σ in last cycle: max. 0·20, av. 0·07. Residuals in last difference Fourier map: max. 1·2, min. −2·6 (both near Hg and I), general background $\leq \pm 0{\cdot}6$ e Å^{-3}.

Scattering curves from Cromer & Waber (1965), except for H (Stewart, Davidson & Simpson, 1965). Anomalous-dispersion terms for Hg, I and P from Cromer (1965). Programs used listed elsewhere (Authier-Martin & Beauchamp, 1977).

Discussion. Refined coordinates and U_{eq} values are listed in Table 1.*

The unit cell contains two $[P(C_6H_5)_4]^+$ cations and one $[Hg_2I_6]^{2-}$ anion (Fig. 1). The bond distances and angles are listed in Table 2 according to the numbering scheme of Fig. 1.

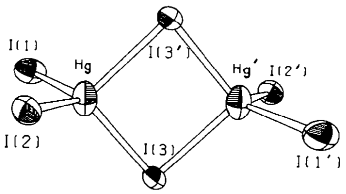

Fig. 1. *ORTEP* drawing (Johnson, 1976) of the $[Hg_2I_6]^{2-}$ anion. Primed and unprimed atoms are related by the crystallographic inversion center at ($\frac{1}{2}$,0,$\frac{1}{2}$). The ellipsoids correspond to 50% probability.

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* Lists of structure factors, anisotropic thermal parameters, fixed H-atom coordinates, interatomic distances and bond angles in the phenyl rings, and weighted least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39876 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°)

Hg–I(1)	2·707 (1)	P–C(11)	1·801 (8)
Hg–I(2)	2·690 (1)	P–C(21)	1·782 (7)
Hg–I(3)	2·864 (1)	P–C(31)	1·787 (7)
Hg–I(3ⁱ)	2·962 (1)	P–C(41)	1·787 (7)
I(1)–Hg–I(2)	114·09 (3)	Hg–I(3)–Hg′	85·70 (2)
I(1)–Hg–I(3)	113·40 (3)	C(11)–P–C(21)	109·2 (3)
I(1)–Hg–I(3′)	109·46 (3)	C(11)–P–C(31)	112·4 (3)
I(2)–Hg–I(3)	115·97 (2)	C(11)–P–C(41)	108·7 (3)
I(2)–Hg–I(3′)	107·44 (2)	C(21)–P–C(31)	109·5 (3)
I(3)–Hg–I(3′)	94·30 (2)	C(21)–P–C(41)	109·2 (3)
		C(31)–P–C(41)	107·8 (3)

Symmetry code: (′) $1 - x, -y, 1 - z$.

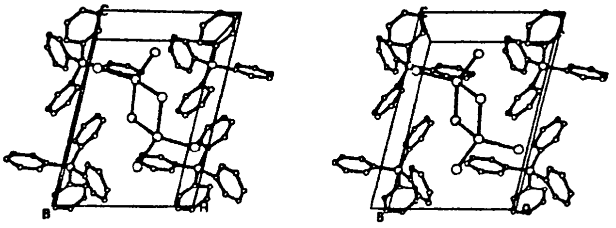

Fig. 2. Stereoview of the unit cell down the *c* axis. The atoms are represented by spheres of arbitrary sizes and the H atoms are omitted for simplicity.

The $[Hg_2I_6]^{2-}$ anion occupies an inversion center of the unit cell. Each mercury is surrounded by four iodines in a distorted tetrahedral arrangement, and the structure can be envisioned as a pair of HgI_4 tetrahedra sharing an edge. This dimeric arrangement has been reported for two other triiodomercurates (Contreras, Seguel & Honle, 1980; Beurskens, Bosman & Cras, 1972) as well as for various bromo- and chloromercurates (Goggin, King, McEwan, Taylor, Woodward & Sandstrom, 1982; Gal, Beurskens, Cras, Beurskens & Willemse, 1976; Kistenmacher, Rossi, Chiang, Van Duyne & Siedle, 1980; Spek, 1979). The difference between the Hg—I(bridge) distances [2·864 (1) and 2·962 (1) Å] is significant, and both bonds are much longer than the Hg—I(terminal) bonds [2·707 (1) and 2·690 (1) Å]. In other structures, these distances range from 2·669 to 2·711 Å (terminal) and from 2·873 to 3·044 Å (bridge). The central Hg_2I_2 bridging unit is planar by symmetry, and the internal angles [Hg—I(3)—Hg′ = 85·70 (2) and I(3)—Hg—I(3′) = 94·30 (2)°] are similar to those found in other $[Hg_2I_6]^{2-}$ units (ranges 85·7–86·4° and 93·6–94·3° respectively). The plane of the bridging Hg_2I_2 unit makes an angle of 91·7° with the plane of the terminal HgI_2 unit, which in turn makes an angle of 3·4° with the plane of the other terminal HgI_2 unit.

The $[P(C_6H_5)_4]^+$ cation has the usual tetrahedral distribution of bonds around P. The P—C distances average 1·789 Å (Table 2) as found elsewhere (Bogaard & Rae, 1982). The C—C bond lengths average 1·39 Å, and the internal angles average 120·0°.* The rings are planar within 2·2 σ (0·020 Å), but the P atom is significantly distant from these planes: 0·113 (2), 0·029 (2), 0·138 (2) and 0·090 (2) Å for rings 1 to 4, respectively.

The packing diagram (Fig. 2) shows that independent $[Hg_2I_6]^{2-}$ anions occupy the inversion center at $(\frac{1}{2},0,\frac{1}{2})$ in the unit cell. The smallest interionic I···I distance (5·58 Å) is much greater than the sum of the van der Waals radii (4·24 Å, Huheey, 1975). Fig. 2 shows that four $[P(C_6H_5)_4]^+$ cations form a layer parallel to the unit-cell *ac* plane at $y \sim \frac{1}{2}$. A similar set of four cations is found above the upper face, thereby creating a cavity filled by the $[Hg_2I_6]^{2-}$ anion.

We wish to thank the Natural Sciences and Engineering Research Council of Canada and the Ministère de l'Education du Québec for financial support.

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* See previous footnote.