Crystal Structure of Hexakis(triphenylphosphine oxide)dimercury(I) Bisperchlorate

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The title compound has been prepared and its crystal structure determined by single-crystal *X*-ray diffraction methods. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares methods to *R* 0·12 for 1696 independent visually estimated reflections. Crystals are triclinic, space group $P\bar{1}$, a = 12·55(1), b = 14·47(2), c = 16·05(2) Å, α = 120·0(1), β = 82·3(1), γ = 95·2(1)°. There is one dimeric unit in the cell, the best formulation being $[(Ph_3PO)_3Hg{-}Hg(Ph_3PO)_3][ClO_4]_2$. Hg–Hg is 2·522(2) Å. The centrosymmetric cationic species is discrete and the mercury environment approximately tetrahedral (Hg–O 2·29—2·43 Å); there is an inverse correlation between the Hg–O distance and the Hg–Hg–O angle. The perchlorate ion is subject to high thermal motion and is ill-defined; the Ph_3PO geometries are as expected.

COMPLEXES of mercury(I) perchlorate with oxygen or nitrogen donor ligands, L, have been well established both preparatively and structurally for the stoicheiometry $Hg_2(ClO_4)_2L_2$, the mercury dimer being axially co-ordinated by the ligands.[1] We have recently described the first structure determination of a complex with stoicheiometry $Hg_2(ClO_4)_2L_4$ (L = pyridine 1-oxide).[2] We now describe the preparation and structure determination of a complex of stoicheiometry $Hg_2(ClO_4)_2L_6$ (L = triphenylphosphine oxide).

EXPERIMENTAL

Preparation.—[A preparation has been previously described for the complex $Hg_2(ClO_4)_2(Ph_3PO)_4$.[3]] The present complex was prepared by the addition of a filtered solution of $Ph_3PO,\frac{1}{2}H_2O$ (5·15 g) in dry absolute methanol (20 ml) to a filtered solution of $Hg_2(ClO_4)_2,4H_2O$ (3·0 g) in absolute methanol–triethyl orthoformate (15 ml, 1 : 2 v/v), the latter acting as a dehydrating agent.[2] After being set aside overnight, the solution deposited small, colourless crystals, m.p. 171—172 °C (Found: C, 56·85; H, 4·3; Cl, 2·8; Hg,

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[1] D. L. Kepert, D. Taylor, and A. H. White, *Inorg. Chem.*, 1972, **11**, 1639, and references therein.

[2] D. L. Kepert, D. Taylor, and A. H. White, *J.C.S. Dalton*, 1973, 392.

[3] R. A. Potts and A. L. Allred, *Inorg. Chem.*, 1966, **5**, 1066.

17·5; O (difference), 10·2; P, 8·4. $C_{108}H_{90}Cl_2Hg_2O_{14}P_6$ requires C, 57·15; H, 4·0; Cl, 3·1; Hg, 17·7; P, 8·2; O, 9·9%).

Crystallography.—The crystals were prisms with the crystallographic axes coincident with the crystal edges. A single crystal 0·14 × 0·14 × 0·06 mm was used throughout.

Non-integrated X-ray intensity data were collected by the multiple-film equi-inclination Weissenberg method, with the crystal mounted about a and c respectively for the layers 0—3kl, hk0—1. Unit-cell calibration was effected by superimposing aluminium powder lines ($a_{298\ \mathrm{K}}$ 4·0494 Å)[4] on zero-layer photographs about the three axes. Nickel-filtered copper radiation was used throughout [$\lambda(K_{\bar{\alpha}}) = 1{\cdot}5418$ Å].[5] There was no evidence for crystal decomposition during data collection.

Crystal Data.—$C_{54}H_{45}ClHgO_7P_3$, $M = 1134{\cdot}9$, Triclinic, $a = 12{\cdot}55 \pm 0{\cdot}01$, $b = 14{\cdot}47 \pm 0{\cdot}02$, $c = 16{\cdot}05 \pm 0{\cdot}02$ Å, $\alpha = 120{\cdot}0 \pm 0{\cdot}1$, $\beta = 82{\cdot}3 \pm 0{\cdot}1$, $\gamma = 95{\cdot}2 \pm 0{\cdot}1°$, $U = 2499$ Å^3, $D_m = 1{\cdot}50 \pm 0{\cdot}02$ (by flotation), $Z = 2$, $D_c = 1{\cdot}51$, $F(000) = 1134$. Space group $P\bar{1}$ (No. 2, C_i^1)[6]. μ(Cu-K_α) = 78 cm^{-1}; transmission coefficient range 0·379—0·731.

The intensities of 1696 independent observed reflections were visually estimated by use of a graded calibrated intensity strip; only these non-zero reflections were used in the subsequent structure determination. The raw data were corrected for absorption,[7] and Lorentz and polarization factors and then scaled by internal correlation,[8] all reflections being assigned unit weights. Independent scale-factors were used for sets of reflections from the upper and lower halves of the non-zero layer photographs to offset the effects of spot-shape distortion.

Structure Determination.—The assumption of a dimeric mercury(I) species was justified by the computation of a three-dimensional unsharpened Patterson function computed on all data. (The centrosymmetric positioning of the Hg_2 entity suggested that solution should proceed on the assumption of $P\bar{1}$ symmetry rather than $P1$; this was subsequently vindicated by the successful solution of the structure.) A structure-factor calculation on the basis of the Hg atom alone with an arbitrary isotropic thermal parameter B 3·0 Å^2 gave a residual R 0·41. Phosphorus and chlorine atoms were located in a subsequent three-dimensional difference-Fourier synthesis; a structure-factor calculation with arbitrary B 5·0 Å^2 for these atoms gave R 0·28. Marked anisotropy of the mercury atom thermal motion, together with a comparatively small contribution to the scattering vitiated any attempt to locate the remaining non-hydrogen atoms by Fourier methods. After the introduction of thermal anisotropy components of the form: $\exp[-(\beta_{11}h^2 + \beta_{12}hk + \beta_{13}hl + \beta_{22}k^2 + \beta_{23}kl + \beta_{33}l^2)]$ for the mercury atom and refinement by block-diagonal (3 × 3, 6 × 6) least-squares procedures (local versions of programs SFLS 1, 2, by A. I. M. Rae), the data were selected according to the criteria $|F_c|/|F_o| > 0{\cdot}7$, $\sin^2\theta/\lambda^2 < 0{\cdot}3$;[9] the remaining non-hydrogen atoms were then located in successive difference-Fourier syntheses. The parameters of all atoms were then refined by further cycles of least-squares refinement assuming an isotropic model for the vibrations of all except the mercury atom. In the final stages, a weighting scheme of the form $w = (a + |F_o| + b|F_o|^2)^{-1}$ was introduced and found appropriate,[10] a and b being redetermined during refinement and $\Sigma w(|F_o| - |F_c|)^2$ being minimized. Refinement was terminated at R 0·116, [$R' = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{\frac{1}{2}} = 0{\cdot}144$] parameter shifts all being $<0{\cdot}3\sigma$ for the light atom parameters, and $<0{\cdot}1\sigma$ for those of the mercury. At this point R was still falling by *ca.* 0·001 per cycle; refinement was terminated at this point because of the scale of computational times and costs (271 parameters). A final difference-Fourier was substantially flat, the largest peaks being of the order of $<0{\cdot}6$ carbon atom near the mercury site. Final weighting-scheme constants were $a = 1{\cdot}72$, $b = 0{\cdot}145$. Although the perchlorate thermal parameters were high, they were stable during refinement and there was no evidence for positional disorder.

Scattering factors[11,12] employed were for monovalent mercury (corrected for anomalous dispersion; $\Delta f'$ only, because of the consideration of computing time)[13] and for the neutral atoms for the remainder. The final set of $|F_o|$ and $|F_c|$ are given in Supplementary Publication No. SUP 20725 (2 pp.).* Final atomic thermal and positional parameters are in Table 1, together with

TABLE 1

Final atomic fractional cell parameters of the asymmetric unit, $Hg(Ph_3PO)_3(ClO_4)$, and thermal parameters. Block-diagonal least-squares estimated standard deviations are in parentheses

Atom	x	y	z	B/Å^2
Hg	0·01925(12)	0·02045(7)	0·08276(7)	*
Cl	0·5250(10)	0·6227(7)	0·3345(8)	9·2(3)
O(1)	0·486(4)	0·556(3)	0·248(3)	19·3(15)
O(2)	0·547(4)	0·565(3)	0·365(3)	18·6(14)
O(3)	0·506(4)	0·719(3)	0·394(3)	17·9(13)
O(4)	0·631(5)	0·643(4)	0·276(4)	23·6(19)
Ligand (1):				
O(11)	0·071(2)	−0·065(1)	0·160(1)	6·2(4)
P(1)	0·1117(8)	−0·1749(5)	0·1204(6)	5·3(2)
C(11)	0·192(3)	−0·219(2)	0·006(2)	5·9(7)
C(12)	0·251(3)	−0·142(2)	−0·005(3)	8·5(9)
C(13)	0·338(4)	−0·177(3)	−0·083(3)	10·4(11)
C(14)	0·345(3)	−0·287(2)	−0·155(3)	8·5(9)
C(15)	0·278(3)	−0·358(2)	−0·139(2)	7·9(8)
C(16)	0·205(3)	−0·329(2)	−0·060(3)	8·4(9)
C(21)	0·007(3)	−0·269(2)	0·103(2)	7·9(8)
C(22)	−0·077(4)	−0·279(3)	0·048(3)	10·2(11)
C(23)	−0·164(4)	−0·350(3)	0·031(3)	10·3(11)
C(24)	−0·192(3)	−0·393(2)	0·090(3)	9·2(9)
C(25)	−0·123(4)	−0·377(3)	0·160(3)	11·1(12)
C(26)	−0·026(4)	−0·313(3)	0·169(3)	10·6(11)
C(31)	0·195(2)	−0·174(2)	0·206(2)	5·0(6)
C(32)	0·257(3)	−0·257(2)	0·178(2)	7·3(8)
C(33)	0·325(4)	−0·259(3)	0·236(3)	9·3(10)
C(34)	0·328(3)	−0·166(2)	0·331(3)	9·0(9)
C(35)	0·263(3)	−0·082(2)	0·363(3)	8·9(9)
C(36)	0·190(3)	−0·079(2)	0·298(2)	6·4(7)

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. Items less than 10 pp. are sent as full-sized copies.

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[13] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

TABLE 1 (*Continued*)

Atom	*x*	*y*	*z*	*B*/Å^2
Ligand (2)				
O(21)	−0·063(2)	0·123(1)	0·235(1)	6·2(4)
P(2)	−0·1059(8)	0·1597(5)	0·3405(5)	4·9(2)
C(41)	−0·149(3)	0·292(2)	0·396(2)	6·1(7)
C(42)	−0·227(3)	0·312(2)	0·350(2)	6·7(7)
C(43)	−0·262(3)	0·415(2)	0·380(2)	7·0(7)
C(44)	−0·226(3)	0·499(2)	0·472(2)	8·0(9)
C(45)	−0·140(4)	0·479(3)	0·517(3)	10·5(11)
C(46)	−0·108(3)	0·372(2)	0·479(3)	8·5(9)
C(51)	−0·004(3)	0·167(2)	0·410(2)	5·5(6)
C(52)	0·111(3)	0·191(2)	0·387(2)	6·2(7)
C(53)	0·193(4)	0·213(3)	0·456(3)	10·4(11)
C(54)	0·162(3)	0·189(2)	0·530(2)	7·6(8)
C(55)	0·035(4)	0·157(3)	0·535(3)	10·1(11)
C(56)	−0·063(5)	0·145(3)	0·483(3)	12·4(13)
C(61)	−0·208(3)	0·071(2)	0·351(2)	5·7(6)
C(62)	−0·191(3)	−0·031(2)	0·302(2)	5·7(6)
C(63)	−0·270(3)	−0·108(2)	0·307(3)	8·2(9)
C(64)	−0·366(3)	−0·069(2)	0·368(3)	8·6(9)
C(65)	−0·382(3)	0·036(2)	0·418(2)	8·5(9)
C(66)	−0·307(3)	0·113(2)	0·407(2)	8·4(9)
Ligand (3)				
O(31)	0·180(2)	0·128(1)	0·142(1)	6·0(4)
P(1)	0·2559(8)	0·2211(6)	0·1578(6)	5·9(2)
C(71)	0·346(2)	0·240(2)	0·247(2)	4·7(5)
C(72)	0·383(3)	0·150(2)	0·228(3)	8·7(9)
C(73)	0·444(4)	0·155(3)	0·298(3)	10·1(11)
C(74)	0·474(3)	0·255(3)	0·376(3)	9·0(9)
C(75)	0·445(3)	0·340(2)	0·373(2)	8·9(9)
C(76)	0·374(3)	0·341(2)	0·315(2)	6·2(7)
C(81)	0·329(3)	0·192(2)	0·044(2)	6·5(7)
C(82)	0·310(3)	0·111(2)	−0·039(2)	7·9(8)
C(83)	0·374(4)	0·078(3)	−0·135(3)	10·1(10)
C(84)	0·456(4)	0·142(3)	−0·129(3)	10·5(11)
C(85)	0·484(4)	0·229(3)	−0·039(3)	12·1(13)
C(86)	0·429(4)	0·264(3)	0·053(3)	10·9(11)
C(91)	0·182(3)	0·341(2)	0·203(2)	6·3(7)
C(92)	0·061(3)	0·337(2)	0·224(2)	7·4(8)
C(93)	0·006(3)	0·423(2)	0·260(2)	6·9(7)
C(94)	0·056(4)	0·519(3)	0·271(3)	11·2(12)
C(95)	0·165(4)	0·527(3)	0·253(3)	11·2(12)
C(96)	0·235(4)	0·435(2)	0·220(3)	9·4(10)

* Anisotropic thermal parameters (×10^4) for the mercury atom

β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
127(2)	−20(3)	−22(4)	96(1)	66(1)	47(1)

TABLE 2

Interatomic distance (Å) and angles (deg.), with estimated standard deviations in parentheses. Interspecies contacts have been calculated up to a distance of 3·5 Å. For the perchlorate and parts of the ligand groups where the accuracy is low, mean distances and angles only are listed with mean σ

(*a*) Perchlorate geometry

⟨Cl–O(*i*)⟩	1·35(5)	⟨O(*i*)–Cl–O(*j*)⟩	109(3)

No contacts <3·5 Å to Hg, P, or O

(*b*) Mercury environment

Hg–Hg$^{\mathrm{II}}$	2·522(2)	Hg$^{\mathrm{II}}$–Hg–O(11)	140·0(5)
Hg–O(11)	2·31(2)	Hg$^{\mathrm{II}}$–Hg–O(21)	133·5(5)
Hg–O(21)	2·29(2)	Hg$^{\mathrm{II}}$–Hg–O(31)	116·0(5)
Hg–O(31)	2·43(2)	Hg–O(11)–P(1)	131(1)
		Hg–O(21)–P(2)	160(1)
O(11) · · · O(21)	2·95(2)	Hg–O(31)–P(3)	152(1)
O(11) · · · O(31)	3·13(2)		
O(21) · · · O(31)	3·22(2)	O(11)–Hg–O(21)	79·4(7)
		O(11)–Hg–O(31)	82·6(7)
		O(21)–Hg–O(31)	86·4(7)

No other contacts to Hg <3·5 Å

TABLE 2 (*Continued*)

(*c*) Ligand (1)

(i) Phosphorus environment

P(1)–O(11)	1·50(2)	O(11)–P(1)–C(11)	111(1)
P(1)–C(11)	1·80(3)	O(11)–P(1)–C(21)	112(1)
P(1)–C(21)	1·74(4)	O(11)–P(1)–C(31)	109(1)
P(1)–C(31)	1·83(3)		

(ii) Phenyl ring (1)

⟨C(1 *i*)–C(1 *i* + 1)⟩	1·40(5)
⟨C(1 *i*)–C(1 *i* + 1)–C(1 *i* + 2)⟩	120(3)
⟨P(1)–C(11)–C(12,16)⟩	118(2)

(iii) Phenyl ring (2)

⟨C(2 *i*)–C(2 *i* + 1)⟩	1·43(6)
⟨C(2 *i*)–C(2 *i* + 1)–C(2 *i* + 2)⟩	120(4)
⟨P(1)–C(21)–C(22,26)⟩	122(3)

(iv) Phenyl ring (3)

⟨C(3 *i*)–C(3 *i* + 1)⟩	1·41(5)
⟨C(3 *i*)–C(3 *i* + 1)–C(3 *i* + 2)⟩	120(3)
⟨P(1)–C(31)–C(32,36)⟩	118(2)

(v) Interphenyl contacts (<3·5 Å)

C(11) · · · C(21)	2·86(5)	C(21) · · · C(16)	3·18(5)
C(11) · · · C(22)	3·48(6)	C(21) · · · C(31)	2·89(5)
C(11) · · · C(31)	2·94(4)	C(21) · · · C(32)	3·46(5)
C(11) · · · C(32)	3·28(4)	C(31) · · · C(26)	3·22(6)

(*d*) Ligand (2)

(i) Phosphorus environment

P(2)–O(21)	1·52(2)	O(21)–P(2)–C(41)	110(1)
P(2)–C(41)	1·77(3)	O(21)–P(2)–C(51)	112(1)
P(2)–C(51)	1·77(3)	O(21)–P(2)–C(61)	112(1)
P(2)–C(61)	1·79(3)		

(ii) Phenyl ring (4)

⟨C(4 *i*)–C(4 *i* + 1)⟩	1·44(5)
⟨C(4 *i*)–C(4 *i* + 1)–C(4 *i* + 2)⟩	120(3)
⟨P(2)–C(41)–C(42,46)⟩	118(2)

(ii) Phenyl ring (5)

⟨C(5 *i*)–C(5 *i* + 1)⟩	1·50(6)
⟨C(5 *i*)–C(5 *i* + 1)–C(5 *i* + 2)⟩	120(4)
⟨P(2)–C(51)–C(52,56)⟩	112(3)

(iv) Phenyl ring (6)

⟨C(6 *i*)–C(6 *i* + 1)⟩	1·40(5)
⟨C(6 *i*)–C(6 *i* + 1)–C(6 *i* + 2)⟩	120(4)
⟨P(2)–C(61)–C(62,66)⟩	119(2)

(v) Interphenyl contacts (<3·5 Å)

C(41) · · · C(51)	2·79(5)	C(51) · · · C(46)	2·96(5)
C(41) · · · C(56)	3·38(6)	C(51) · · · C(61)	2·85(5)
C(41) · · · C(61)	2·96(4)	C(51) · · · C(62)	3·42(4)
C(41) · · · C(62)	3·18(5)	C(61) · · · C(56)	2·71(6)

(*e*) Ligand (3)

(i) Phosphorus environment

P(3)–O(31)	1·50(2)	O(31)–P(3)–C(71)	108(1)
P(3)–C(71)	1·84(3)	O(31)–P(3)–C(81)	108(1)
P(3)–C(81)	1·79(3)	O(31)–P(3)–C(91)	110(1)
P(3)–C(91)	1·80(3)		

(ii) Phenyl ring (7)

⟨C(7 *i*)–C(7 *i* + 1)⟩	1·37(5)
⟨C(7 *i*)–C(7 *i* + 1)–C(7 *i* + 2)⟩	120(3)
⟨P(3)–C(71)–C(72,76)⟩	115(2)

(iii) Phenyl ring (8)

⟨C(8 *i*)–C(8 *i* + 1)⟩	1·41(6)
⟨C(8 *i*)–C(8 *i* + 1)–C(8 *i* + 2)⟩	120(3)
⟨P(3)–C(81)–C(82,86)⟩	119(3)

(iv) Phenyl ring (9)

⟨C(9 *i*)–C(9 *i* + 1)⟩	1·41(4)
⟨C(9 *i*)–C(9 *i* + 1)–C(9 *i* + 2)⟩	120(3)
⟨P(3)–C(91)–C(92,96)⟩	120(3)

TABLE 2 (*Continued*)

(v) Interphenyl contacts (<3·5 Å)

C(71) · · · C(81)	3·01(4)	C(81) · · · C(72)	3·46(5)
C(71) · · · C(86)	3·32(5)	C(81) · · · C(91)	2·92(5)
C(71) · · · C(91)	2·97(4)	C(81) · · · C(96)	3·41(5)
C(71) · · · C(96)	3·49(5)	C(91) · · · C(76)	3·20(5)

(*f*) Interligand contacts (other than O · · · O) within the asymmetric unit (<3·5 Å)

O(21) · · · C(92)	3·41(5)

(*g*) Perchlorate–phenyl contacts (<3·5 Å)

O(1) · · · C(96)	3·43(7)	O(3) · · · C(34^{IV})	3·42(6)
O(2) · · · C(43^{III})	3·49(6)	O(4) · · · C(24^{V})	3·32(7)
O(2) · · · C(75)	3·45(6)	O(4) · · · C(25^{V})	3·34(7)

(*h*) Interligand contacts between different asymmetric units

C(14) · · · C(42^{II})	3·48(5)	C(14) · · · C(86^{VII})	3·37(5)
C(14) · · · C(43^{II})	3·40(5)	C(13) · · · C(86^{VII})	3·47(5)
C(63) · · · C(83^{II})	3·43(5)	C(44) · · · C(76^{VIII})	3·42(5)

Roman numeral superscripts denote the following equivalent positions:

I	x, y, z	V	$1 + x, 1 + y, z$
II	$\bar{x}, \bar{y}, \bar{z}$	VI	$x - 1, y - 1, z$
III	$1 + x, y, z$	VII	$1 - x, \bar{y}, \bar{z}$
IV	$x, 1 + y, z$	VIII	$\bar{x}, 1 - y, 1 - z$

least-squares estimated standard deviations derived by a block-diagonal routine and therefore probably underestimates. Interatomic distances and angles are in Table 2; [14] least-squares planes for the phenyl rings are in Table 3. The unit-cell contents are depicted in Figure 1; Figure 2 gives the atomic numbering system used. Computing was carried out on the DEC PDP 10 machine at the University of Western Australia.

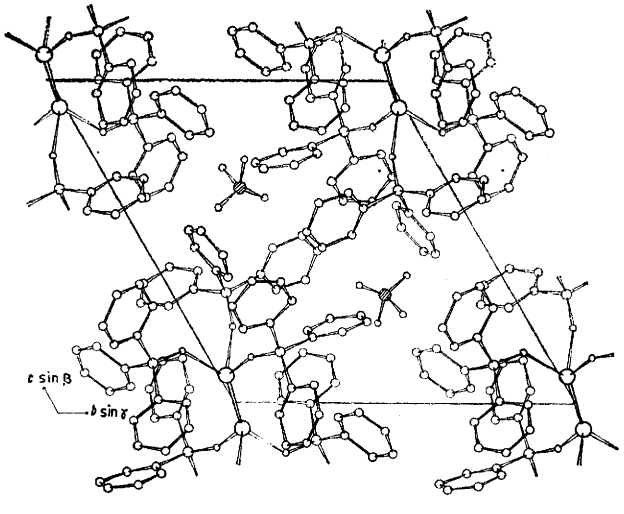

FIGURE 1 Unit cell contents projected on [100]

DISCUSSION

The essential structural features of the complex are summarized in Tables 1 and 2 and depicted in Figures 1 and 2. The structure consists of discrete dimeric $[Hg_2(Ph_3PO)_6]^{2+}$ cations and ClO_4^- anions. The cation is centrosymmetric about the origin, the Hg–Hg axis lying at angles of 72, 72, and 16° to the *a*, *b*, and *c* crystal axes. Although the mercury–mercury distance [2·522(2) Å] is in agreement with distances found in other mercury(I) compounds, it may be that mercury(I)

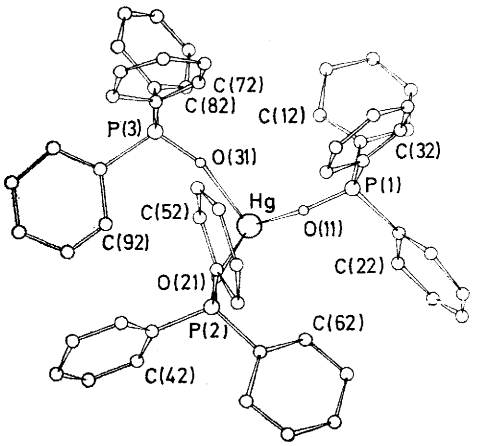

FIGURE 2 The co-ordination of the mercury atom viewed down the Hg–Hg bond, with the cation numbering system. (For clarity only one carbon atom of each phenyl ring is numbered; the remainder follow sequentially)

TABLE 3

Least-squares planes through phenyl rings, in the form * $lX + mY + nZ = p$, with standard deviations (σ Å); atomic deviations (Å) are listed in square brackets

	l	*m*	*n*	*p*	σ
Phenyl (1)	0·760	−0·372	0·533	3·291	0·04
[C(11) 0·01, C(12) −0·05, C(13) 0·07, C(14) −0·03, C(15) −0·02, C(16) 0·03, P(1) 0·32, O(11) −0·30]					
Phenyl (2)	−0·475	0·545	0·691	−1·803	0·06
[C(21) −0·08, C(22) 0·10, C(23) −0·06, C(24) −0·01, C(25) 0·02, C(26) 0·02, P(1) 0·17, O(11) 1·51]					
Phenyl (3)	0·634	0·690	−0·349	−1·867	0·01
[C(31) 0·00, C(32) −0·01, C(33) 0·00, C(34) 0·01, C(35) −0·02, C(36) 0·01, P(1) 0·09, O(11) 0·42]					
Phenyl (4)	0·648	0·512	−0·563	−3·433	0·04
[C(41) 0·00, C(42) −0·02, C(43) 0·05, C(44) −0·06, C(45) 0·04, C(46) −0·01, P(2) 0·07, O(21) 1·27]					
Phenyl (5)	−0·222	0·781	0·584	2·518	0·04
[C(51) 0·01, C(52) 0·06, C(53) −0·06, C(54) −0·02, C(55) −0·03, C(56) 0·03, P(2) 0·11, O(21) −0·58]					
Phenyl (6)	0·534	−0·339	0·774	3·276	0·03
[C(61) 0·03, C(62) 0·00, C(63) −0·02, C(64) −0·01, C(65) 0·04, C(66) −0·05, P(2) 0·07, O(21) −0·97]					
Phenyl (7)	0·720	0·361	−0·593	1·864	0·05
[C(71) −0·06, C(72) 0·07, C(73) −0·02, C(74) −0·05, C(75) 0·07, C(76) −0·01, P(3) −0·11, O(31) −1·04]					
Phenyl (8)	−0·634	0·762	−0·136	−0·780	0·02
[C(81) 0·02, C(82) −0·01, C(83) −0·01, C(84) 0·02, C(85) −0·01, C(86) −0·01, P(3) −0·10, O(31) −0·45]					
Phenyl (9)	0·231	−0·249	0·941	2·354	0·03
[C(91) −0·01, C(92) −0·03, C(93) 0·04, C(94) −0·02, C(95) −0·02, C(96) 0·03, P(3) −0·03, O(31) −0·13]					

* Orthogonal (Å) axes (X,Y,Z) are derived from the triclinic cell by the transformation:

$$[X,Y,Z] = \begin{bmatrix} a & b\,.\cos\gamma & c\,.\cos\beta \\ 0 & b\,.\sin\gamma & c\,.(\cos\alpha - \cos\beta\,.\cos\gamma)/\sin\gamma \\ 0 & 0 & U/(a\,.\,b\,.\sin\gamma) \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

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[14] M. E. Pippy and F. R. Ahmed, Div. Pure and App. Physics, NRC, Ottawa, Canada, Program NRC 12, BONDSCAN.

cations in which the mercury atoms exhibit multiple co-ordination have slightly longer Hg–Hg bonds than do cations with simple digonal co-ordination. (Table 4).[1,2,15-17] This may be rationalized in terms of an increase in electron density on the mercury atoms with more co-ordinated ligands resulting in a weakening of the mercury–mercury bond. The available bond-length data for the mercury(I) halides [18] and oxyanion salts however do not agree with the observed trend for the cationic species.[19-21]

TABLE 4

Cationic mercury–mercury distances (Å)

Compound	Hg–Hg
(*a*) Multiple mercury co-ordination	
$[Hg_2(Ph_3PO)_6](ClO_4)_2$	2·522(2) [a]
$[Hg_2(pyO)_4](ClO_4)_2$	2·523(2) [b]
$Hg_2(o\text{-phen})(NO_3)_2$	2·516(7) [c]
(*b*) Linear mercury co-ordination	
$[Hg_2(4\text{-CNpy})_2](ClO_4)_2$	2·498(2) [d]
$[Hg_2(3\text{-Clpy})_2](ClO_4)_2$	2·487(2) [e]
$[Hg_2(H_2O)_2]SiF_6$	2·495(3) [f]

[a] This work. [b] Ref. 2. [c] Ref. 15. [d] Ref. 1. [e] Ref. 16. [f] Ref. 17.

The co-ordination of each mercury atom in the $[Hg_2(Ph_3PO)_6]^{2+}$ cation is clearly a distorted tetrahedron consisting of the other mercury atom and the three oxygen atoms of the neighbouring Ph_3PO ligands at distances of 2·29, 2·31, and 2·43 Å. The associated Hg–Hg–O angles (134, 140, and 116°) indicate that no individual ligand occupies the usually strong axial co-ordination site of the mercury(I) ion. The mercury–oxygen distances are longer than observed for axial donor ligands (2·08—2·24 Å) and are consistent with a lengthening of the Hg–O bond as the Hg–Hg–O angle is decreased from 180°. Comparable Hg–O distances were found in the distorted tetrahedral configuration of $[HgCl_2(Ph_3AsO)_2]$ (2·32 and 2·37 Å).[22]

Because of the steric bulk of the Ph_3PO ligands, there is no mercury–perchlorate contact (see Figure 1); there are also few contacts of the perchlorate ion with the phenyl rings. As a consequence, the ion exhibits high thermal motion, limiting the amount of reflection data available and resulting in large standard deviations in the light atom parameters. For the perchlorate ion, the average Cl–O bond length and O–Cl–O angle are 1·35 Å and 109° respectively.

The mean P–O bond length [1·51(1) Å] in the Ph_3PO ligands is slightly longer than that found in the free ligand (1·46 Å),[23] consistent with a decrease in the electron density at the oxygen atom and a reduction of the σ and/or π bond orders of the phosphorus–oxygen bond. Other mean bond lengths (P–C 1·79, C–C 1·42 Å) and angles (O–P–C 110, P–C–C 118, and C–C–C, 120°) in the ligands are in general agreement with previously observed values.[23] The Hg–O–P system is bent, the angle ranging from 131 to 160°. It has been suggested that the size of the angle is dependent on steric factors.[24] The oxygen–oxygen contacts between adjacent ligands are all greater than the van der Waals' distance (2·8 Å).[25] There are no intercationic C · · · C distances significantly $<3·4$ Å and only six $<3·5$ Å. In view of the lack of any substantial number of short interspecies contacts, it is difficult to assess the role of steric or packing effects and it is not obvious what part they play, if any, in determining the variations observed in the Hg–O–P angles.

Mercury(I) compounds of the type $Hg_2L_2X_2$ have been shown to contain discrete dimeric cations, each mercury atom exhibiting digonal co-ordination (typically Hg–O 2·20 Å) [17] with long perpendicular contacts to the anions. In the present complex of the type $Hg_2L_6X_2$, each mercury atom in the discrete cation has a distorted tetrahedral co-ordination, the anion being outside the co-ordination sphere. For the only compound of stoicheiometry $Hg_2L_4X_2$ (L = pyridine 1-oxide),[2] the mercury atoms achieve a co-ordination configuration which is intermediate between digonal and tetrahedral, the stoicheiometry being maintained by the bridging nature of three of the four pyridine 1-oxide ligands.

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