Preparation and Properties of Some Mercury Halide–Platinum Compounds and Crystal Structure of Di-μ-chloro-(dichloromercurio)bis(dimethylphenylphosphine)platinum(II)

By **Roy W. Baker,* Martin J. Braithwaite,** and (the late) **R. S. Nyholm,** William Ramsay, Ralph Forster, and Christopher Ingold Laboratories, University College London, Gower Street, London WC1

The compounds (I)—(VI) $(PPhMe_2)_2PtX_2(HgY_2)$ (X = Cl, Br, or I; Y = Cl or Br) have been prepared by the action of mercury(II) halide on *cis*-$(PPhMe_2)_2PtX_2$. The crystal structure of (I; X = Y = Cl) has been determined from diffractometer data. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: $a = 909{\cdot}2(3)$, $b = 1043{\cdot}8(4)$, $c = 2428{\cdot}6(8)$ pm, $\beta = 105{\cdot}12(2)°$. The structure was solved by Patterson and Fourier methods and refined by least-squares to R 0·057 for 2184 independent reflections. The complex contains two bridging chlorine atoms between Pt and Hg, the co-ordination being essentially square planar about Pt and distorted tetrahedral about Hg. Bond lengths suggest that $HgCl_2$ is only weakly co-ordinated.

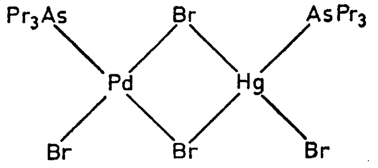
MANY reactions between transition-metal complexes and mercury(II) halides have been reported. In almost all cases it has been suggested that the product contains a metal–mercury bond. The formation of such products has been described as an oxidative addition reaction[1] [equation (1)], or Lewis acid–base adduct formation[2]

$$(Ph_3P)_2(CO)ClIr + HgCl_2 \longrightarrow (Ph_3P)_2(CO)Cl_2Ir(HgCl) \quad (1)$$

[equation (2)]. Many compounds of the latter variety

$$(\pi\text{-}C_5H_5)(CO)_2Co + HgCl_2 \longrightarrow (\pi\text{-}C_5H_5)(CO)_2Co(HgCl_2) \quad (2)$$

have been prepared but crystallographic evidence has only been reported in the case of the compound $(\pi\text{-}C_5H_5)(CO)_2Co(HgCl_2)$.[3] A related compound prepared from $(AsPr_3)_2PdBr_2$ and mercury(II) bromide[4] has also been reported and was considered, though without crystallographic evidence, to have a third type of structure, *i.e.*



We have found that the interaction of *cis*-$(PPhMe_2)_2PtX_2$ (X = Cl, Br, or I) with HgY_2 (Y = Cl or Br) in benzene, generally results in the immediate precipitation of a series of complexes of stoicheiometry $(PPhMe_2)_2PtX_2(HgY_2)$ (see Table 1). In some cases the addition of light petroleum is required for precipitation. Some of these and similar compounds have been previously prepared and their chemistry briefly described.[5]

TABLE 1

Physical and analytical data

		Colour	M.p./°C	C	H	X	P	Λ_M ‡
(I)	$(PPhMe_2)_2PtCl_2(HgCl_2)$ *	White	173	24·1(23·6) †	2·7(2·7)	17·4(17·5)	7·6(7·6)	44·6
(II)	$(PPhMe_2)_2PtCl_2(HgBr_2)$	White	135	21·5(21·3)	2·5(2·4)		6·8(6·9)	50·6
(III)	$(PPhMe_2)_2PtBr_2(HgCl_2)$	White	138	21·4(21·3)	2·4(2·4)		6·9(6·9)	50·4
(IV)	$(PPhMe_2)_2PtBr_2(HgBr_2)$	White	125	19·6(19·4)	2·2(2·2)	31·9(32·3)	6·2(6·3)	53·8
(V)	$(PPhMe_2)_2PtI_2(HgCl_2)$	Cream	122	19·5(19·3)	2·3(2·2)		6·0(6·2)	48·9
(VI)	$(PPhMe_2)_2PtI_2(HgBr_2)$	Yellow	127	17·8(17·7)	2·0(2·1)		5·9(5·7)	55·5

* Found: Pt, 23·6; Hg, 24·7. Calc. Pt, 24·0; Hg, 24·6%. † Calc. values in parentheses. ‡ Ohm^{-1} at 20 °C for $MeNO_2$ soln.

The complexes (I)—(VI) (Table 1) are air stable and can be recrystallised from benzene–light petroleum and acetone–light petroleum, but dissociate on attempted recrystallisation from ethanol–light petroleum to give the starting materials. They are all of a colour consistent with their containing platinum(II). For example, the complex $(PPhMe_2)_2PtCl_2(HgCl_2)$ is white, but would be expected to be yellow if a platinum(IV) species were present.

The ^1H n.m.r. spectrum of $(PPhMe_2)_2PtCl_2(HgCl_2)$ in methylene dichloride, which shows three doublets centred at τ 8·23 due to methyl resonance, is almost identical to that of the starting material *cis*-$(PPhMe_2)_2PtCl_2$. This could be due to the phosphine ligands of the product being in a mutually *cis*-position[6] and/or the presence of *cis*-$(PPhMe_2)_2PtCl_2$ produced upon dissociation of the complex in solution. In fact, molecular-weight measurements in chloroform indicate considerable dissociation (calc. 814; obs. 550).

Conductivity measurements on compounds (I)—(VI) gave values in the region 44—56 mhos at 20 °C (nitromethane). These values, which are low for 1 : 1 electrolytes,[7] may be a result of a dissociation of the type shown in equation (3) which would be expected to depress the

$$(PPhMe_2)_2PtCl_2HgCl_2 \rightleftharpoons (PPhMe_2)_2PtCl_2 + HgCl_2 \quad (3)$$

---

[1] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 1965, 5337.

[2] D. J. Cook, J. L. Dawes, and R. D. Kemmitt, *J. Chem. Soc.* (*A*), 1967, 1547.

[3] I. N. Nowell and R. D. Russell, *Chem. Comm.*, 1967, 658.

[4] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1940, 1230.

[5] P. R. Brookes, Ph.D. Thesis, University of Leeds, 1968.

[6] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 1966, 770.

[7] D. J. Phillips, Ph.D. Thesis, University of London, 1958.

conductivity. Alternatively they may be neutral compounds which ionise in solution. Attempts to isolate a cationic species by the addition of BF_4^- or BPh_4^- were unsuccessful and it would appear that the dissociation reaction (3) dominates the solution chemistry. When a nitromethane solution of mercury(II) chloride was titrated conductometrically against a nitromethane solution of *cis*-$(PPhMe_2)_2PtCl_2$ the maximum specific conductivity corresponded to the formation of a 1 : 1 addition complex. The product can be isolated from the nitromethane solution.

Several structures are possible for such a 1 : 1 addition complex, the two most important being those which contain a platinum–mercury bond and those in which the mercury(II) halide is linked by a halogen bridge to the platinum species. No relevant conclusion could be drawn from i.r. spectra or other data for solutions. To resolve the ambiguity the crystal structure of $(PPhMe_2)_2PtCl_2(HgCl_2)$ was determined and shown to contain a halogen bridge (Figure 1; see later).

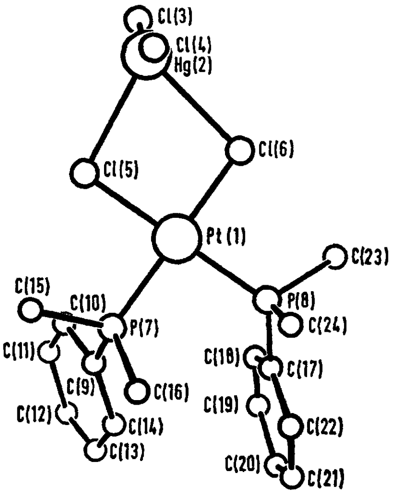


FIGURE 1 The molecule projected on the least-squares plane (Table 6)

TABLE 2

I.r. data (cm^{-1}) in the range 450—200 cm^{-1} (Nujol mulls)

(I)	435m, 364m, 360m, 343vs,[b] 315w, 295s,[a] 275m [a]
(II)	434m, 363s, 360s, 339w,[b] 323s, 315m, 298vs,[a] 278m,[a] 243vs [c]
(III)	434m, 363s, 360s, 339w,[b] 323s, 315m, 298vs,[a] 278m,[a] 243vs [c]
(IV)	433m, 363s, 358s, 320sh, 312m, 237vs [c]
(V)	438m, 363s, 357s, 318w, 294vs,[a] 268s,[a] 240m
(VI)	434m, 361m, 353s, 317w, 304m

vs = Very strong, s = strong, m = medium, w = weak, sh = shoulder.

[a] ν(Pt–Cl–Hg) bridge. [b] ν(HgCl). [c] ν(HgBr).

In the light of this structure the i.r. spectra of the other compounds (Table 2) can be explained. Compounds (I)—(III), and V which contain chlorine atoms show two bands in the region 294—298 and 268—278 cm^{-1} respectively, which can be assigned to two bridging chlorine atoms. The starting material *cis*-$(PPhMe_2)_2PtCl_2$ exhibits two bands due to ν(Pt–Cl) stretching at 309vs and 288vs cm^{-1}. On co-ordination to $HgCl_2$ these values are both lowered by approximately the same amount (14 and 13 cm^{-1}). In the case of $(PPhMe_2)_2PtCl_2(HgCl_2)$ the very strong band at 343 cm^{-1} may be assigned to the terminal chlorine atoms attached to the mercury. Though two bands are expected for such terminal chlorine atoms, that observed at 343 cm^{-1} is fairly broad and could conceal a second unresolved band. It was found possible to replace each of the four chlorine atoms of complex (I) in turn with iodine and bromine atoms, by reaction in acetone with NaI and LiBr respectively. The metal–halogen stretching frequencies for the complexes formed by reaction with NaI are shown in Table 3, together with analyses. As expected the terminal chlorine atoms attached to the mercury are replaced first, followed by replacement of the two bridging chlorine atoms. Of course there is a strong possibility of coupling of the various vibrations and deformations occurring and it is likely that none of the metal–halogen bands is associated with a pure mode.

The ready dissociation of these addition complexes in solution and the small change in ν(HgX) observed as compared with the parent mercury(II) halide[8] (374 vs, 331s, and 311 cm^{-1} for $HgCl_2$; 251vs for $HgBr_2$) shows that the mercury(II) halide is very weakly held.

The i.r. spectra of the complexes (II), (III), (V), and (VI) are complicated owing to the rapid halogen exchange which takes place between the mercury and platinum starting materials. This is evident from the fact that the i.r. spectrum (450—200 cm^{-1}) of the complex (II), is identical with that of the complex (III). The conductivities and melting points are also very similar; thus, presumably, the two complexes are either identical single compounds or a near identical mixture of isomers.

As the compound is neutral in the solid state the high conductivity values must be due to an ionisation process in solution.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 225 (450—200 cm^{-1}) for Nujol mulls. ^1H n.m.r. spectra were measured for dichloromethane solutions on a Varian T 60 spectrometer. Molecular weights were determined by vapour-pressure osmometry in chloroform solution. Melting points were taken on a Gallenkamp melting point apparatus. Light petroleum has b.p. 40—60 °C.

Preparation of Materials.—*cis*-$(PPhMe_2)_2PtX_2$ (X = Cl, Br, or I)[9] was prepared by a similar method to that described in the literature for *cis*-$(PEt_3)_2PtCl_2$. All other chemicals were reagent grade. All reactions were carried out under nitrogen.

Di-μ-chloro-(dichloromercurio)bis(dimethylphenylphosphine)platinum(II), *Complex* (I).—Mercury(II) chloride (0·05 g) in hot benzene (10 ml) was added to *cis*-$(PPhMe_2)_2PtCl_2$ (0·1 g) in benzene (10 ml), and heated under reflux until all solids had dissolved. The filtrate was cooled and a white crystalline compound precipitated. On careful addition of light petroleum to the mother liquor a further

---

[8] D. M. Adams, M. Goldstein, and E. F. Mooney, *Trans. Faraday Soc.*, 1963, **59**, 2228.

[9] K. A. Jensen, *Z. anorg. Chem.*, 1936, **229**, 225.

crop of product was precipitated. The crude product was recrystallised from hot benzene by careful addition of light petroleum (0·13 g, 86·5%). Complexes (II)—(VI) were prepared similarly.

Crystals of (I) become light yellow after prolonged exposure to air and light. The crystals were very badly developed, dagger shaped, and readily formed clusters.

Crystal Data.—$C_{16}H_{22}Cl_4HgP_2Pt$, $M = 814$, Monoclinic, $a = 909{\cdot}2(3)$, $b = 1043{\cdot}8(4)$, $c = 2428{\cdot}6(8)$ pm, $\beta = 105{\cdot}12(2)^\circ$, $U = 2225 \times 10^6$ pm^3, $D_m = 2{\cdot}40(3)$, $Z = 4$, $D_c = 2{\cdot}43 \times 10^3$ kg m^{-3}. Space group $P2_1/c$ (C^5_{2h}) from absences: $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. Mo-K_α radiation, $\lambda = 71{\cdot}07$ pm; μ(Mo-K_α) = 143 cm^{-1}.

TABLE 3

Metathetical reactions with NaI: metal–halogen stretching frequencies (cm^{-1} for Nujol mulls)

Equiv. NaI added			C	H
0	$(PPhMe_2)_2PtCl_2(HgCl_2)$	343vs, 295s, 275m		
1	$(PPhMe_2)_2PtCl_2(HgClI)$	335w, 296vs, 266vs	21·4(21·2)	2·5(2·4)
2	$(PPhMe_2)_2PtCl_2(HgI_2)$	294vs, 267vs	19·2(19·3)	2·3(2·2)
3	$(PPhMe_2)_2PtClI(HgI_2)$	293vs	17·8(17·6)	2·1(2·0)
4	$(PPhMe_2)_2PtI_2(HgI_2)$	*a*	16·3(16·3)	1·8(1·9)

[a] None in region 450—200 cm^{-1}.

TABLE 4

Fractional co-ordinates and thermal motion parameters * (all × 10^4) derived from the least-squares refinement, with estimated standard deviations in parentheses

Atom	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	4403(1)	1531(1)	0850(0·4)	195(4)	436(6)	251(0)	46(5)	42(5)	25(6)
Hg(2)	1933(1)	4298(1)	−0134(0·5)	461(8)	557(6)	362(0)	137(7)	104(5)	−12(6)
Cl(3)	1750(9)	5910(9)	0503(4)	480(47)	784(61)	724(56)	26(44)	136(42)	−298(50)
Cl(4)	1704(9)	3355(9)	−1014(3)	644(51)	806(61)	418(28)	244(49)	162(36)	−74(43)
Cl(5)	1795(8)	2165(8)	0585(3)	285(39)	706(55)	613(56)	146(37)	146(37)	310(43)
Cl(6)	4913(7)	3373(8)	0368(3)	297(35)	569(50)	557(56)	51(35)	94(31)	298(43)
P(7)	3786(7)	−0283(7)	1243(3)	242(35)	364(39)	334(28)	14(30)	99(26)	0(31)
P(8)	6923(7)	1120(8)	1091(3)	246(35)	635(50)	223(28)	67(35)	10(26)	81(31)
C(9)	3935(30)	−0174(26)	2007(11)	413(66)					
C(10)	3046(32)	0774(29)	2182(12)	488(72)					
C(11)	3135(36)	0815(32)	2771(13)	586(84)					
C(12)	4152(38)	0053(34)	3179(14)	667(92)					
C(13)	5013(35)	−0845(32)	2984(13)	580(82)					
C(14)	4966(34)	−0950(30)	2393(12)	532(77)					
C(15)	1787(29)	−0759(26)	0939(11)	398(64)					
C(16)	4771(32)	−1746(28)	1119(12)	483(73)					
C(17)	7752(29)	0536(26)	1811(11)	384(64)					
C(18)	7500(30)	1275(27)	2261(11)	431(67)					
C(19)	8155(34)	0924(31)	2822(12)	539(78)					
C(20)	9026(38)	−0248(34)	2916(15)	683(95)					
C(21)	9290(38)	−0933(35)	2475(15)	691(95)					
C(22)	8648(31)	−0563(27)	1913(11)	441(68)					
C(23)	8141(34)	2567(31)	1101(13)	559(80)					
C(24)	7398(33)	0022(29)	0563(12)	508(76)					

* The Debye–Waller factor is defined as $T = \exp[-2\pi^2\sum_i\sum_j a^*_i a^*_j h_i h_j U_{ij}]$ for non carbon atoms and $T = \exp[-8\pi^2 U \sin^2\theta/\lambda^2]$ for carbon atoms.

Intensity Measurements.—Three-dimensional *X*-ray diffraction data for a small single-crystal *ca.* 0·14 × 0·10 × 0·30 mm were collected on a computer-controlled [10] Stoe four-circle diffractometer by use of Mo-K_α radiation with graphite monochromator (002). A coupled θ—2θ step scan with $\Delta 2\theta = 0{\cdot}04^\circ$, a counting time of 5 s per step, and a peak width of 1·6° were used. In the range 2θ 6—45°, 3308 observations, covering two octants of reciprocal space ($\pm h$, $+k$, $+l$) were measured, of which 2184 were regarded as observed [$I \geqslant 3\sigma$ (I)], and were corrected for Lorentz and polarisation effects. No corrections for absorption were made.

Structure Solution and Refinement.—The positions of platinum and mercury were found from an unsharpened Patterson synthesis. A Fourier synthesis using observed data phased with the two metal atoms produced a satisfactory trial structure. Successive cycles of full-matrix least-squares refinement with anisotropic thermal parameters for platinum, mercury, chlorine, and phosphorus and isotropic thermal parameters for carbon were carried out until all parameter shifts were $<0{\cdot}1\sigma$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1$ for all diffraction data. Atomic scattering factors for neutral platinum, mercury, chlorine, and carbon were taken from ref. 11. The final was R 0·057. A further refinement using scattering factors for Pt^{2+}, Hg^{2+}, and Cl^- produced parameter shifts which were $<0{\cdot}1$ of the standard deviations of the refinement with neutral atoms.

Since it is difficult to distinguish between platinum and mercury by use of *X*-ray diffraction, a second structure which differs from the first by having the Pt and Hg atoms interchanged was subjected to least-squares refinement. The residual was also 0·057 and all the refined parameters differed from those of the first structure by $<0{\cdot}2\sigma$ for the corresponding parameters. The structure with square

---

[10] W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and R. T. Roseberry, 'The Oak Ridge Computer Controlled *X*-ray Diffractometer,' U.S. Atomic Energy Commission.

[11] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

planar Pt and distorted tetrahedral Hg co-ordination is more acceptable simply on chemical arguments.

All computational work was carried out on the University of London ATLAS computer and the University College IBM 360 computer with programs described in refs. 12 and 13.

TABLE 5

Interatomic distances (pm) and angles (°) derived from the atom positions in Table 4, with estimated standard deviations in parentheses

(*a*) Distances

Pt(1)–Cl(5)	238·2(7)
Pt(1)–Cl(6)	236·0(8)
Pt(1)–P(7)	225·6(7)
Pt(1)–P(8)	225·3(7)
Hg(2)–Cl(3)	232·1(9)
Hg(2)–Cl(4)	231·2(8)
Hg(2)–Cl(5)	285·1(8)
Hg(2)–Cl(6)	283·4(7)
Hg(2)–Cl(3′)	324·0(9)
Hg(2)–Cl(6′)	391·3(7)
P(7)–C(9)	183(3)
P(7)–C(15)	184(3)
P(7)–C(16)	183(3)
P(8)–C(17)	182(3)
P(8)–C(23)	187(3)
P(8)–C(24)	185(3)
C(9)–C(10)	141(4)
C(9)–C(14)	140(4)
C(10)–C(11)	141(4)
C(11)–C(12)	141(5)
C(12)–C(13)	138(5)
C(13)–C(14)	143(4)
C(17)–C(18)	140(4)
C(17)–C(22)	139(4)
C(18)–C(19)	139(4)
C(19)–C(20)	144(5)
C(20)–C(21)	136(5)
C(21)–C(22)	139(4)
Pt(1)–Hg(2)	403·7(2)
Hg(2)–Hg(2′)	401·4(2)

(*b*) Angles

Cl(5)–Pt(1)–Cl(6)	87·1(3)
Cl(5)–Pt(1)–P(7)	90·5(3)
Cl(5)–Pt(1)–P(8)	174·8(3)
Cl(6)–Pt(1)–P(7)	175·3(3)
Cl(6)–Pt(1)–P(8)	88·1(3)
P(7)–Pt(1)–P(8)	94·5(3)
Cl(3)–Hg(2)–Cl(4)	156·9(3)
Cl(3)–Hg(2)–Cl(5)	97·8(3)
Cl(3)–Hg(2)–Cl(6)	100·8(3)
Cl(4)–Hg(2)–Cl(5)	103·0(3)
Cl(4)–Hg(2)–Cl(6)	95·6(3)
Cl(5)–Hg(2)–Cl(6)	70·2(3)
Cl(3′)–Hg(2)–Cl(3)	89·1(3)
Cl(3′)–Hg(2)–Cl(4)	83·0(3)
Cl(3′)–Hg(2)–Cl(5)	84·8(3)
Cl(3′)–Hg(2)–Cl(6)	154·1(3)
Pt(1)–P(7)–C(9)	115(1)
Pt(1)–P(7)–C(15)	113(1)
Pt(1)–P(7)–C(16)	116(1)
C(9)–P(7)–C(15)	103(1)
C(9)–P(7)–C(16)	108(1)
C(15)–P(7)–C(16)	101(1)
P(7)–C(9)–C(10)	117(2)
P(7)–C(9)–C(14)	120(2)
C(10)–C(9)–C(14)	123(3)
C(9)–C(10)–C(11)	116(3)
C(10)–C(11)–C(12)	123(3)
C(11)–C(12)–C(13)	118(3)
C(12)–C(13)–C(14)	122(3)
C(13)–C(14)–C(9)	118(3)
Pt(1)–P(8)–C(17)	117(1)
Pt(1)–P(8)–C(23)	114(1)
Pt(1)–P(8)–C(24)	110(1)
C(17)–P(8)–C(23)	99(1)
C(17)–P(8)–C(24)	110(1)
C(23)–P(8)–C(24)	105(1)
P(8)–C(17)–C(18)	117(2)
P(8)–C(17)–C(22)	122(2)
C(18)–C(17)–C(22)	121(3)
C(17)–C(18)–C(19)	120(3)
C(18)–C(19)–C(20)	117(3)
C(19)–C(20)–C(21)	122(3)
C(20)–C(21)–C(22)	121(3)
C(21)–C(22)–C(17)	119(3)

Hg(2′) and Cl(3′) are symmetry related to Hg(2) and Cl(3) by the centre of symmetry at 0, ½, 0; Cl(6′) is related to Cl(6) by the centre of symmetry at ½, ½, 0.

The results obtained from this analysis are summarised in Tables 4 and 5 and Figures 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20448 (13 pp., 1 microfiche).*

DISCUSSION

Description of the Structure.—The co-ordination about the platinum is essentially square planar. The least-squares plane through Pt(1), Cl(5), Cl(6), P(7), and P(8) is given in Table 6. The bond lengths and angles in this square planar arrangement compare well with those found in $(\mathrm{Me_3P})_2\mathrm{PtCl_2}$.[14] The chlorine atoms Cl(5) and Cl(6) are also co-ordinated to the mercury atom, thus forming chlorine bridges between the two metal atoms. The distances Cl(5)–Hg(2) and Cl(6)–Hg(2) are considerably longer than the distances Cl(3)–Hg(2) and Cl(4)–Hg(2) which suggests that the $\mathrm{HgCl_2}$ group is only weakly co-ordinated. Evidence for the weak bonding comes also from the angles about the mercury atom formed by the four chlorine atoms Cl(3)—(6) *viz.* Cl(3)–Hg(2)–Cl(4) 157 and Cl(5)–Hg(2)–Cl(6) 70°. This distorted tetrahedral co-ordination is common in mercury structures.[15-17] Another chlorine atom is situated 324 pm from the mercury atom. According to the definition of bonding distances in mercury compounds given by Grdenic[18] this chlorine atom may be considered to be co-ordinated to the mercury atom also. Hence the mercury atom is surrounded by five chlorine atoms (forming a distorted trigonal bipyramid) in much the

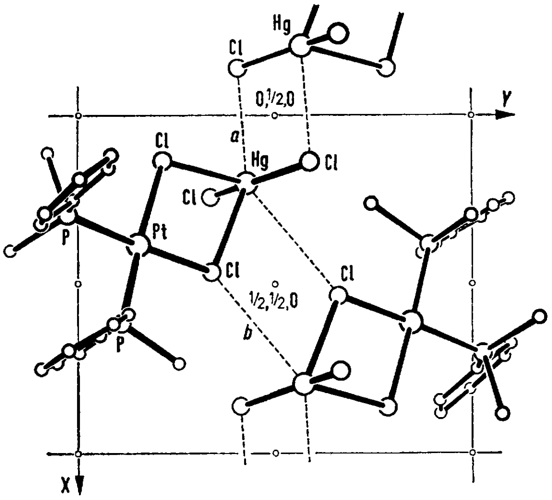


FIGURE 2 Part of the molecular packing projected on (001); $a = 324$, $b = 391$ pm

TABLE 6

Equation of least-squares plane for the platinum co-ordinated ligands, in the form $AX + BY + CZ = D$.† Deviations (pm) from the plane are given in square brackets

Equation of plane:

$$-0{\cdot}108X + 0{\cdot}505Y + 0{\cdot}857Z = 4{\cdot}283$$

[Pt(1) 1·7, Cl(5) 5·4, Cl(6) −6·4, P(7) −6·2, P(8) 5·5, Hg(2) −32·6]

† Based on orthonormalised co-ordinates, X, Y, Z where X is parallel to crystallographic axis a; Y is perpendicular to X in the crystallographic plane ab, and Z is perpendicular to the plane ab.

---

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[12] SFLS Program in AA, G. Shearing, University of Manchester, 1965.

[13] Fourier Program for LUNA Circular No. 1·1, 1964; Distance Angle Program for LUNA, Circular No. 4, 1965, J. Dollimore, University of London Institute of Computer Science.

[14] G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 725.

[15] C.-I. Branden, *Acta Chem. Scand.*, 1963, **17**, 1363.

[16] C.-I. Branden, *Arkiv Kemi*, 1964, **22**, 485.

[17] A. Cooper, E. M. Gopalakrishna, and D. A. Norton, *Acta Cryst.*, 1968, **B24**, 935.

[18] D. Grdenic, *Quart. Rev.*, 1965, XIX(3), 303.

same way as the mercury atom in the tetrahydrothiophene–mercury chloride complex [19] which is bonded to four chlorine atoms and one sulphur atom. The chlorine atom at **324** pm is related to Cl(**3**) by a crystallographic centre of symmetry (0, $\frac{1}{2}$, 0) and thus creates chlorine bridges between two mercury atoms. The Hg–Hg distance is **401** pm.

We thank Monsanto Company for financial support (to M. J. B.), the S.R.C. and M.R.C. for support, Margaret Dellow for computer programs, Barbara Munday for the drawings, Patricia Brennan for technical assistance, and Drs. M. D. Johnson and P. Pauling for helpful discussion.

[2/275 *Received, 7th February,* 1972]

---

[19] C.-I. Branden, *Arkiv Kemi*, 1964, **22**, 495.