Acta Cryst. (1980). B**36**, 708–710

Tertiary Phosphine Complex of Mercury(II) Chloride with Unusual Stoichiometry: $(Me_2EtP)_3(HgCl_2)_2$*

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(*Received* 27 *October* 1979; *accepted* 19 *November* 1979)

Abstract. $C_{12}H_{33}Cl_4Hg_2P_3$, $M_r = 813{\cdot}31$, orthorhombic, $P2_12_12_1$, $a = 18{\cdot}755\ (3)$, $b = 13{\cdot}749\ (3)$, $c = 9{\cdot}740\ (2)$ Å, $U = 2511{\cdot}57$ Å^3, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $Z = 4$, $D_m = 2{\cdot}19\ (2)$, $D_c = 2{\cdot}15$ Mg m^{-3}, μ(Mo $K\alpha$) = $12{\cdot}34$ mm^{-1}, $F(000) = 1512$. The structure was refined to $R = 0{\cdot}058$ for 2219 observed reflections. The complex consists of $[Hg\{(CH_3)_2(C_2H_5)P\}_2Cl]^+$ cations and $[Hg\{(CH_3)_2(C_2H_5)P\}Cl_3]^-$ anions linked by Cl bridges to give chains running parallel to c. The cation contains an almost linear P—Hg—P arrangement and there is considerable tetrahedral distortion about Hg in the anion, with angles at the metal varying from 98·2 to 132·9°.

Introduction. Hg^{II} halides are known to react with tertiary phosphines to form complexes having a variety of $R_3P:HgX_2$ ratios (Evans, Mann, Peiser & Purdie, 1940; Schmidbaur & Rathlein, 1973; Moers & Langhout, 1973). However, crystallographic data for these systems are limited and in particular, although the existence of 3:2 complexes has been reported [*e.g.* $(R_3P)_3(HgI_2)_2$, R = Pr, Bu; Evans *et al.*, 1940], no structures are available for complexes having this stoichiometry. We now report an analysis of a 3:2 type complex $(Me_2EtP)_3(HgCl_2)_2$ (preliminary report, Bell, Goldstein, Jones & Nowell, 1978). Crystals were selected from a sample thought to be $(Me_2EtP)_2HgCl_2$, but subsequent chemical and X-ray analyses showed that, while the bulk of the sample had 2:1 stoichiometry, the larger crystals had the composition $(Me_2EtP)_3(HgCl_2)_2$.

A colourless crystal 0·46 × 0·31 × 0·31 mm was selected. Cell dimensions were calculated from the centred settings of 25 reflections with $11 < \theta < 15°$, on an Enraf–Nonius CAD-4 diffractometer with monochromated Mo $K\alpha$ radiation. Intensities for reflections having θ in the range 1·1–20° were measured on the same instrument with a variable scan speed and an ω–$\frac{4}{3}\theta$ (goniometer-counter) scanning ratio, as optimized by peak-analysis routines. A scan interval of $\Delta\omega = (1{\cdot}5 + 0{\cdot}525 \tan \theta)°$ was employed. Of the 2324 reflections measured, 2219 had $I > 2\sigma(I)$ and were considered to be observed. [The net intensity $I = T - 2B$, where T = measured intensity, B = sum of background counts measured during the first and last sixth of the $\Delta\omega$ scan; $\sigma(I) = (T + 4B + 0{\cdot}0009I^2)^{1/2}$.] Corrections were made for Lorentz and polarization effects. The intensities of two central reflections were monitored and showed negligible deterioration.

The positions of the two independent Hg atoms were determined from the Patterson function and the remaining non-hydrogen atoms from successive electron density syntheses. Scattering factors were calculated with an analytical approximation (*International Tables for X-ray Crystallography*, 1974) and the weighting scheme was $w = 3{\cdot}9785/[\sigma^2(F_o) + 0{\cdot}0004(F_o)^2]$. Full-matrix refinement with anisotropic temperature factors for Hg, Cl, P and isotropic for C gave the final $R = 0{\cdot}058$ and $R' = 0{\cdot}066$. The final atomic parameters are given in Table 1.†

Table 1. *Fractional positional parameters* (×10^4) *with e.s.d.'s in parentheses*

	x	y	z
Hg(1)	4175 (0)	7439 (1)	−206 (1)
Hg(2)	3849 (1)	7642 (1)	4477 (1)
Cl(1)	3082 (4)	6242 (5)	377 (10)
Cl(2)	4592 (3)	7552 (5)	6747 (6)
Cl(3)	3242 (4)	9254 (5)	4901 (7)
Cl(4)	4727 (4)	8180 (6)	2780 (8)
P(1)	3361 (4)	8783 (5)	−383 (8)
P(2)	5109 (4)	6251 (5)	−112 (7)
P(3)	3132 (4)	6204 (6)	4676 (9)
C(11)	2903 (15)	8974 (21)	1248 (31)
C(12)	2653 (14)	8483 (18)	−1530 (28)
C(13)	3703 (16)	9923 (20)	−1054 (31)
C(14)	4386 (21)	10301 (27)	−249 (40)
C(21)	4864 (14)	5243 (19)	−1007 (29)
C(22)	5361 (15)	5877 (22)	1602 (33)
C(23)	5910 (13)	6662 (19)	−927 (29)
C(24)	6101 (18)	7718 (23)	−442 (34)
C(31)	3492 (13)	5183 (19)	3733 (30)
C(32)	3090 (19)	5902 (27)	6481 (38)
C(33)	2260 (19)	6344 (25)	3901 (41)
C(34)	1836 (23)	7116 (30)	4788 (44)

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* Systematic name: chlorobis(ethyldimethylphosphine)mercury(II) trichloro(ethyldimethylphosphine)mercurate(II).

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34910 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/80/030708-03$01.00

Discussion. Bond lengths and angles are given in Table 2. The complex has a chain-like structure in which Hg has alternating coordination numbers of four and five (Fig. 1). Although the Hg(1)–Cl(2″) and Hg(1)–Cl(4) distances of 3·07 (1) and 3·25 (1) Å lie within the sum of the van der Waals radii (3·53 Å; Grdenić, 1965; Pauling, 1960), they are considerably larger than the other Hg–Cl distances (2·45–2·69 Å) and the structure is thus best considered as consisting essentially of a polymeric arrangement of $[(Me_2EtP)_2HgCl]^+$ cations and $[(Me_2EtP)HgCl_3]^-$ anions. The ions are joined by Cl bridges to give chains running parallel to *c* which are stacked in sheets along *a* (Fig. 2).

Within the cationic species there is an unusual T-shaped arrangement about Hg of a Cl and two P atoms, such that the P(1)–Hg(1)–P(2) grouping is almost linear (172·3°) and the P–Hg–Cl(1) angles lie close to 90° (90·1, 97·6°). The Me_2EtP ligands appear to be sufficiently strong donors not only to displace a Cl atom from $HgCl_2$, but also to take up a diagonal P–Hg–P arrangement, a geometry which is commonly found in the structural chemistry of Hg^{II} (Grdenić, 1965). The Hg–P distances within the resulting $[(Me_2EtP)_2HgCl]^+$ ion are comparable to values found in other tertiary phosphine complexes [*e.g.* $(R_3P)HgCl_2$ (*R* = Ph, Bu, Et or Me); P–Hg, 2·34–2·41 Å (Bell, Goldstein, Jones & Nowell, 1976, 1978)]. In contrast, Hg(1)–Cl(1) is unusually long: it is considerably longer than that in $HgCl_2$ itself (2·36 Å; Grdenić, 1965), and also the Hg–Cl (non-bridging) distances in $(R_3P)HgCl_2$ complexes (*R* = Ph, Bu, Et or Me; Cl–Hg, 2·27–2·42 Å; Bell *et al.*, 1976, 1978). The tendency of small phosphines such as Et_3P and Me_2EtP to displace halogen from Hg^{II} halides and take up a diagonal arrangement has also been found for the 2:1 complexes $(Et_3P)_2HgCl_2$ and $(Me_2EtP)_2HgBr_2$ (Bell, Goldstein, Jones & Nowell, 1979). These latter complexes are both monomeric, but there is considerable tetrahedral distortion about Hg such that the P–Hg–P and *X*–Hg–*X* angles (*X* = Cl or Br) are 158·5 (5), 149° (mean) and 105·5 (5), 104·3° (mean) respec-

Table 2. *Bond distances* (Å) *and angles* (°)

Symmetry code: none *x*,*y*,*z*; (′) *x*, *y*, 1·0 + *z*; (″) *x*, *y*, −1·0 + *z*.

(*a*) Coordination about Hg atoms

E.s.d.'s are ~0·01 Å, ~0·5°.

Hg(1)–Cl(1)	2·69	Hg(2)–Cl(2)	2·62
Hg(1)–Cl(2″)	3·07	Hg(2)–Cl(3)	2·52
Hg(1)–Cl(4)	3·25	Hg(2)–Cl(4)	2·45
Hg(1)–P(1)	2·40	Hg(2)–P(3)	2·40
Hg(1)–P(2)	2·40		
Cl(1)–Hg(1)–Cl(2″)	115·4	P(1)–Hg(1)–P(2)	172·3
Cl(1)–Hg(1)–Cl(4)	104·2	Cl(2)–Hg(2)–Cl(3)	98·2
Cl(1)–Hg(1)–P(1)	90·1	Cl(2)–Hg(2)–Cl(4)	103·1
Cl(1)–Hg(1)–P(2)	97·6	Cl(2)–Hg(2)–P(3)	101·0
Cl(2″)–Hg(1)–Cl(4)	140·1	Cl(3)–Hg(2)–Cl(4)	98·5
Cl(2″)–Hg(1)–P(1)	93·1	Cl(3)–Hg(2)–P(3)	117·2
Cl(2″)–Hg(1)–P(2)	83·4	Cl(4)–Hg(2)–P(3)	132·9
Cl(4)–Hg(1)–P(1)	91·4	Hg(1′)–Cl(2)–Hg(2)	133·1
Cl(4)–Hg(1)–P(2)	86·9	Hg(1)–Cl(4)–Hg(2)	107·1

(*b*) The ligand molecules

E.s.d.'s are ~0·06 Å, ~2°.

P(1)–C(11)	1·83	P(3)–C(31)	1·81
P(1)–C(12)	1·79	P(3)–C(32)	1·81
P(1)–C(13)	1·82	P(3)–C(33)	1·81
P(2)–C(21)	1·70	C(13)–C(14)	1·59
P(2)–C(22)	1·81	C(23)–C(24)	1·57
P(2)–C(23)	1·79	C(33)–C(34)	1·58
Hg(1)–P(1)–C(11)	110	C(22)–P(2)–C(23)	106
Hg(1)–P(1)–C(12)	110	Hg(2)–P(3)–C(31)	113
Hg(1)–P(1)–C(13)	118	Hg(2)–P(3)–C(32)	107
C(11)–P(1)–C(12)	103	Hg(2)–P(3)–C(33)	113
C(11)–P(1)–C(13)	111	C(31)–P(3)–C(32)	109
C(12)–P(1)–C(13)	104	C(31)–P(3)–C(33)	102
Hg(1)–P(2)–C(21)	110	C(32)–P(3)–C(33)	113
Hg(1)–P(2)–C(22)	115	P(1)–C(13)–C(14)	113
Hg(1)–P(2)–C(23)	112	P(2)–C(23)–C(24)	111
C(21)–P(2)–C(22)	108	P(3)–C(33)–C(34)	107
C(21)–P(2)–C(23)	105		

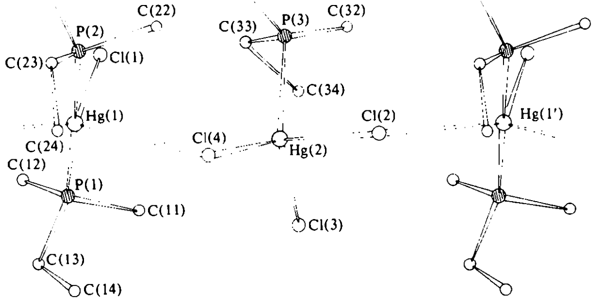

Fig. 1. Atom numbering and part of the chain running parallel to *c*.

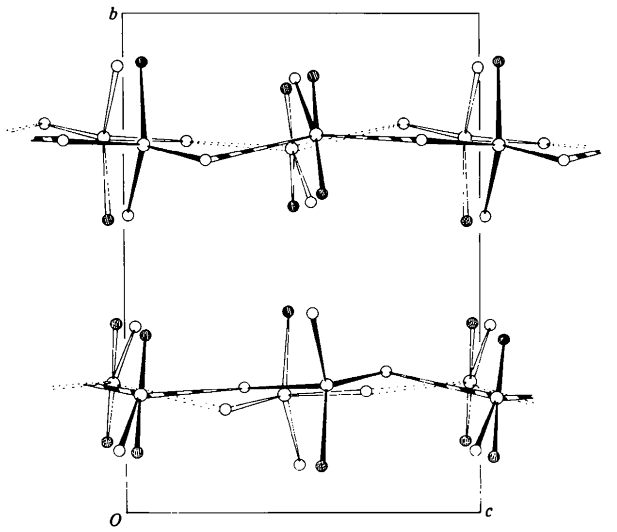

Fig. 2. Projection of the unit cell along *a*. Carbon atoms have been omitted for clarity.

tively. If Cl(2″) and Cl(4) are considered to be within the coordination sphere of Hg(1), the resulting polyhedron about the metal resembles that of an elongated trigonal bipyramid with the equatorial Cl(1), Cl(2″), Hg(1), Cl(4) unit almost planar.

Within the $[(Me_2EtP)HgCl_3]^-$ anion, Hg(2) is surrounded by a distorted tetrahedral arrangement with the angles at Hg ranging from 98·2 to 132·9°. This angular distortion may again reflect the donor ability of the phosphine and certainly the largest deviation from a regular tetrahedral angle involves P and Cl(4), the two atoms closest to Hg.

We thank the SRC for a Research Studentship (to TJ), an equipment grant and computing facilities, Dr P. L. Goggin for the sample, and Professor M. R. Truter for data-collection facilities.

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Acta Cryst. (1980). B**36**, 710–712

Polymeric Dibromo(2,4-dimethylpyridine)mercury(II)

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(*Received* 7 *November* 1979; *accepted* 26 *November* 1979)

Abstract. $[HgBr_2(C_7H_9N)]$, $C_7H_9Br_2HgN$, M_r = 467·55, monoclinic, *Cc*, a = 12·750 (11), b = 10·804 (11), c = 7·780 (8) Å, β = 94·00 (5)°, U = 1069·11 Å^3, Mo $K\alpha$, λ = 0·71069 Å, Z = 4, D_m = 2·91 (3), D_c = 2·90 Mg m^{-3}, μ(Mo $K\alpha$) = 21·16 mm^{-1}, $F(000)$ = 832. The final R = 0·053 for 684 observed reflections. The structure is polymeric, Hg being pentacoordinate within a distorted coordination polyhedron of a N and four Br atoms. Units of (2,4-dimethylpyridine)$HgBr_2$ are linked together by Br bridges to give single chains running parallel to **c**. Preliminary photographic evidence suggests that the analogous (2,4-dimethylpyridine)$HgCl_2$ has a similar structure.

Introduction. Hg^{II} halides are known to form 1:1 complexes with a wide range of neutral unidentate ligands (Dean, 1978). The types of structure adopted by these complexes in the solid state are numerous and contain Hg in a variety of coordination polyhedra. The coordination number of Hg ranges from four [*e.g.* $(Ph_3PSe)HgCl_2$, Cl-bridged dimer (Glasser, Ingram, King & McQuillan, 1969); (guanosine)$HgCl_2$, zigzag chain structure (Authier-Martin, Hubert, Rivest & Beauchamp, 1978)] to five [*e.g.* (tetrahydrothiophene)$HgCl_2$, polymeric Cl-bridged structure (Brändén, 1964)] and to six [*e.g.* (tetrahydrofuran)$HgBr_2$, Br-bridged double-chain structure (Frey, 1970)]. However, few crystallographic studies of $LHgX_2$ complexes in which L functions as a unidentate N-donor ligand have been reported, and the available data appear to be limited to (guanosine)$HgCl_2$ (Authier-Martin *et al.*, 1978) and (2,4,6-trimethylpyridine)$HgCl_2$ (Kulpe, 1967). To broaden the crystallographic base and hence facilitate establishment of vibrational spectra–structure correlations for such N-donor systems, we now report the X-ray study of (2,4-dimethylpyridine)HgX_2 (X = Cl, Br).

Addition of an ethanolic solution of 2,4-dimethylpyridine (0·005 mol) to a solution of either Hg^{II} chloride or bromide (0·005 mol) in ethanol gave complexes of composition $(C_7H_9N)HgX_2$ (X = Cl or Br). Great difficulty was encountered in obtaining crystals of a quality suitable for single-crystal X-ray analysis. Despite repeated recrystallization from a variety of solvents, the quality of the colourless crystals for both complexes was poor. Thus while unit-cell parameters were obtained from Weissenberg and precession photographs for both compounds (Table 1), only crystals of the Br complex were at all suitable for data collection.

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0567-7408/80/030710-03$01.00