compare favourably in the two compounds. The Ni—N distance for the pyridine ligands varies from 2·09 (2) to 2·16 (2) Å against 2·094 (8) and 2·145 (7) Å, average distances for the 5,7-dichloro complex and for the *trans*-5-chloro compound (García-Granda & Gómez-Beltrán, 1986), respectively. The Ni—N distances for the 5,7-dibromo-8-quinolinol ligand are in the range 2·03 (2)–2·09 (2) Å, Ni—O are between 2·01 (1) and 2·06 (1) Å, and the average N—Ni—O quinolinol bite angle is 80·5 (6)°. Recently a crystallographic study on a couple of 8-quinolinol derivatives (Banerjee & Saha, 1986) has been reported.

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References

BANERJEE, T. & SAHA, N. N. (1986). *Acta Cryst.* C**42**, 1408–1411.

BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., VAN DEN HARK, TH.E.M., PRICK, P. A. J., NOORDIK, J. H., BEURSKENS, G., GOULD, R. O. & PARTHASARATHI, V. (1983). *Conformation in Biology*, edited by R. SRINIVASAN & R. H. SARMA, pp. 389–406. New York: Adenine Press.

BEURSKENS, P. T., GOULD, R. O., BRUINS SLOT, H. J. & BOSMAN, W. P. (1987). *Z. Kristallogr.* Submitted.

GARCÍA-GRANDA, S., BEURSKENS, P. T., BEHM, H. J. J. & GÓMEZ-BELTRÁN, F. (1987). *Acta Cryst.* C**43**, 39–41.

GARCÍA-GRANDA, S. & GÓMEZ-BELTRÁN, F. (1986). *Acta Cryst.* C**42**, 33–35.

GRANT, D. F. & GABE, E. J. (1978). *J. Appl. Cryst.* **11**, 114–120.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination, Univ. of Cambridge, England.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 158–166.

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Orthorhombic Modification of Dichlorobis(triphenylphosphine)mercury(II)

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Abstract. $[HgCl_2(C_{18}H_{15}P)_2]$, $M_r = 796{\cdot}0$, orthorhombic, $Pna2_1$, $a = 17{\cdot}782\,(8)$, $b = 9{\cdot}9678\,(9)$, $c = 18{\cdot}283\,(7)$ Å, $U = 3241\,(4)$ Å^3, $Z = 4$, D_m (flotation) $= 1{\cdot}64\,(1)$, $D_x = 1{\cdot}631$ Mg m^{-3}, Mo $K\bar{\alpha}$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 4{\cdot}993$ mm^{-1}, $F(000) = 1560$, $T = 295\,(2)$ K, $R = 0{\cdot}058$ for 2541 observed reflections. The Hg atom in the orthorhombic polymorph of $[HgCl_2\{P(C_6H_5)_3\}_2]$ exists in a distorted tetrahedral arrangement of two Cl atoms [Hg—Cl(1) 2·504 (4), Hg—Cl(2) 2·491 (7) Å and Cl(1)—Hg—Cl(2) 106·6 (2)°], which define an approximate mirror plane, and two P atoms [Hg—P(1) 2·503 (6), Hg—P(2) 2·532 (4) Å and P(1)—Hg—P(2) 113·5 (1)°].

Experimental. Well formed crystals were obtained from the symmetrization (Coates & Lauder, 1965) reaction of $(C_6H_5)HgCl.P(C_6H_5)_3$ in acetonitrile solution held at 278–283 K. Enraf–Nonius CAD-4F diffractometer controlled by a PDP8/A computer, graphite-monochromated Mo $K\bar{\alpha}$ radiation; ω:2θ scan technique. Cell parameters on crystal 0·60 × 0·38 × 0·38 mm from least-squares procedure on 25 reflections ($9 \le \theta \le 13°$). Analytical absorption correction applied (Sheldrick, 1976); max./min. transmission factors 0·2419 and 0·0588. Space group from analysis. Total of 4286 reflections ($1 \le \theta \le 27{\cdot}5°$) measured in the range $-23 \le h \le 0$, $-12 \le k \le 0$, $-23 \le l \le 1$; in addition a number of high-angle Friedel pairs were measured. No significant variation in the net intensities of three reference reflections ($4\bar{7}\bar{4}$, $4\bar{5}\bar{3}$, $2\bar{6}\bar{1}$) measured every 3600 s. 3936 unique reflections; 2541 satisfied $I \ge 2{\cdot}5\sigma(I)$. Structure solved from interpretation of Patterson map; full-matrix least-squares refinement of 118 parameters based on F (Sheldrick, 1976). Anisotropic thermal parameters for Hg, Cl and P; phenyl rings refined as hexagonal rigid groups (Sheldrick, 1976); H atoms included in the model at their calculated positions. At convergence $R = 0{\cdot}058$, wR

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Table 1. *Fractional atomic coordinates and B_{eq} values* (Å²)

$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	B_{eq}
Hg	−0·11014 (3)	−0·06395 (5)	0·0	2·98
Cl(1)	0·0081 (2)	0·0722 (4)	−0·0043 (5)	3·87
Cl(2)	−0·1051 (3)	−0·1976 (6)	0·1150 (4)	3·93
P(1)	−0·1284 (3)	−0·2060 (5)	−0·1115 (3)	2·43
P(2)	−0·2145 (2)	0·1050 (4)	0·0199 (2)	2·70
C(1)	−0·0792 (5)	−0·3638 (9)	−0·1133 (5)	2·48
C(2)	−0·0623 (5)	−0·4238 (9)	−0·1803 (5)	3·81
C(3)	−0·0305 (5)	−0·5517 (9)	−0·1822 (5)	4·67
C(4)	−0·0155 (5)	−0·6196 (9)	−0·1171 (5)	3·80
C(5)	−0·0324 (5)	−0·5596 (9)	−0·0501 (5)	4·15
C(6)	−0·0642 (5)	−0·4318 (9)	−0·0482 (5)	3·14
C(7)	−0·1038 (5)	−0·1125 (9)	−0·1927 (6)	2·87
C(8)	−0·1445 (5)	−0·1233 (9)	−0·2577 (6)	3·72
C(9)	−0·1196 (5)	−0·0574 (9)	−0·3205 (6)	4·52
C(10)	−0·0540 (5)	0·0194 (9)	−0·3183 (6)	4·17
C(11)	−0·0133 (5)	0·0301 (9)	−0·2534 (6)	4·15
C(12)	−0·0382 (5)	−0·0358 (9)	−0·1906 (6)	3·50
C(13)	−0·2277 (5)	−0·2422 (8)	−0·1154 (6)	3·30
C(14)	−0·2784 (5)	−0·1384 (8)	−0·1291 (6)	3·82
C(15)	−0·3553 (5)	−0·1593 (8)	−0·1192 (6)	4·33
C(16)	−0·3815 (5)	−0·2839 (8)	−0·0956 (6)	5·67
C(17)	−0·3308 (5)	−0·3877 (8)	−0·0819 (6)	4·98
C(18)	−0·2539 (5)	−0·3668 (8)	−0·0918 (6)	4·12
C(19)	−0·2989 (6)	0·0380 (9)	0·0593 (7)	3·78
C(20)	−0·3559 (6)	0·1211 (9)	0·0859 (7)	4·65
C(21)	−0·4215 (6)	0·0651 (9)	0·1144 (7)	6·09
C(22)	−0·4303 (6)	−0·0739 (9)	0·1163 (7)	6·21
C(23)	−0·3733 (6)	−0·1570 (9)	0·0898 (7)	6·51
C(24)	−0·3077 (6)	−0·1010 (9)	0·0613 (7)	4·63
C(25)	−0·1846 (6)	0·2385 (10)	0·0804 (7)	3·09
C(26)	−0·2045 (6)	0·3719 (10)	0·0678 (7)	4·95
C(27)	−0·1816 (6)	0·4717 (10)	0·1163 (7)	6·27
C(28)	−0·1386 (6)	0·4382 (10)	0·1775 (7)	6·58
C(29)	−0·1187 (6)	0·3049 (10)	0·1901 (7)	7·67
C(30)	−0·1416 (6)	0·2050 (10)	0·1416 (7)	4·90
C(31)	−0·2396 (5)	0·1802 (10)	−0·0671 (6)	2·73
C(32)	−0·3138 (5)	0·2083 (10)	−0·0866 (6)	4·84
C(33)	−0·3302 (5)	0·2568 (10)	−0·1563 (6)	5·72
C(34)	−0·2723 (5)	0·2773 (10)	−0·2067 (6)	6·06
C(35)	−0·1981 (5)	0·2492 (10)	−0·1873 (6)	4·89
C(36)	−0·1817 (5)	0·2007 (10)	−0·1175 (6)	3·66

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

Hg—Cl(1)	2·504 (4)	Hg—Cl(2)	2·491 (7)
Hg—P(1)	2·503 (6)	Hg—P(2)	2·532 (4)
P(1)—C(1)	1·80 (1)	P(2)—C(19)	1·79 (1)
P(1)—C(7)	1·81 (1)	P(2)—C(25)	1·81 (1)
P(1)—C(13)	1·80 (1)	P(2)—C(31)	1·82 (1)

Cl(1)—Hg—Cl(2)	106·6 (2)	Cl(1)—Hg—P(1)	112·9 (2)
Cl(1)—Hg—P(2)	105·1 (1)	Cl(2)—Hg—P(1)	112·9 (1)
Cl(2)—Hg—P(2)	105·1 (2)	P(1)—Hg—P(2)	113·5 (1)
Hg—P(1)—C(1)	116·5 (4)	Hg—P(2)—C(19)	115·1 (4)
Hg—P(1)—C(7)	110·3 (4)	Hg—P(2)—C(25)	111·2 (4)
Hg—P(1)—C(13)	105·8 (4)	Hg—P(2)—C(31)	109·2 (4)
C(1)—P(1)—C(7)	108·5 (5)	C(19)—P(2)—C(25)	105·9 (5)
C(1)—P(1)—C(13)	107·5 (5)	C(19)—P(2)—C(31)	107·5 (5)
C(7)—P(1)—C(13)	107·9 (5)	C(25)—P(2)—C(31)	107·7 (5)

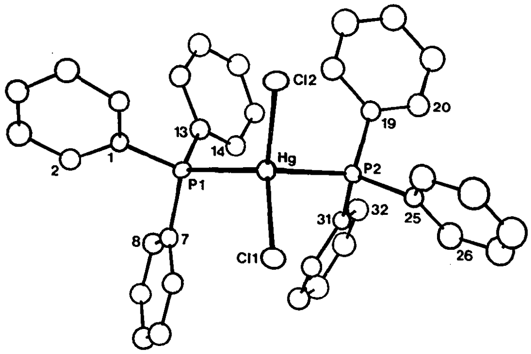

Fig. 1. Molecular structure and numbering scheme for [Hg-$Cl_2\{P(C_6H_5)_3\}_2$]. Atoms otherwise not indicated are C atoms (Johnson, 1971).

$= 0{\cdot}063$, $w = [\sigma^2(F) + 0{\cdot}0085F^2]^{-1}$, $S = 0{\cdot}80$, $(\Delta/\sigma)_{\max} < 0{\cdot}001$, $(\Delta\rho)_{\max} = 2{\cdot}60$ (near Hg), $(\Delta\rho)_{\min} = -3{\cdot}21$ e Å^{-3}; no extinction correction. Scattering factors for H, C, Cl and P given in *SHELX76* (Sheldrick, 1976) and those for neutral Hg corrected for f' and f'' (Hamilton & Ibers, 1974). Absolute structure determined from differences in Friedel pairs. All calculations on a VAX 11/785 computer system. Atomic parameters are given in Table 1, bond distances and angles in Table 2.* The numbering scheme used is shown in Fig. 1.

Related literature. There are significant differences in the Hg-atom environments found in the orthorhombic and monoclinic, $P2_1/c$ (Bell, Dee, Goldstein, McKenna & Nowell, 1983), polymorphs of $[HgCl_2\{P(C_6H_5)_3\}_2]$. In the monoclinic form, which was recrystallized from ethanol, the Hg—Cl [2·559 (2) and 2·545 (3) Å] and Hg—P [2·462 (2) and 2·478 (2) Å] bond distances are respectively longer and shorter than the corresponding bonds in the orthorhombic phase. Further, the Cl—Hg—Cl [110·7 (1)°] and P—Hg—P [134·1 (1)°] angles are *ca* 4 and 20° greater, respectively, than the equivalent bonds in the orthorhombic polymorph. The polymorphs probably arise as a result of two competing factors: (i) the requirement to minimize steric repulsion between the phosphine groups and (ii) to attain regular tetrahedral geometry about the Hg atom. The monoclinic polymorph of $[HgCl_2\{P(C_6H_5)_3\}_2]$ is a manifestation of the domination of criterion (i) over (ii) and in the orthorhombic phase criterion (ii) dominates over (i). In this context it is noteworthy that the [Hg-$Br_2\{P(C_6H_5)_3\}_2$] structure, for which preliminary details are available (Bell, Dee, Goldstein, McKenna & Nowell, 1983), is isomorphous with the orthorhombic Cl analogue and, further, the I derivative (Fälth, 1976) adopts a stereochemistry similar to those observed for the orthorhombic polymorphs.

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References

Bell, N. A., Dee, T. D., Goldstein, M., McKenna, P. J. & Nowell, I. W. (1983). *Inorg. Chim. Acta*, **71**, 135–140.
Coates, G. E. & Lauder, A. (1965). *J. Chem. Soc.* pp. 1857–1864.
Fälth, L. (1976). *Chem. Scr.* **9**, 71–73.

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* Lists of structure factors, thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44352 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

HAMILTON, W. C. & IBERS, J. A. (1974). Editors. *International Tables for X-ray Crystallography*, Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1971). *ORTEP*II. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

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Structure of (1α,3β,5α)-5-Chloro-1,3-diphenyl-5-bis(trimethylsilyl)methyl-1λ^6,3λ^6,2,4,6,5λ^5-dithiatriazaphosphorine 1,3-Dioxide

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Abstract. $C_{19}H_{29}ClN_3O_2PS_2Si_2$, $M_r = 518{\cdot}17$, monoclinic, $P2_1/n$, $a = 10{\cdot}751$ (3), $b = 22{\cdot}48$ (1), $c = 10{\cdot}942$ (3) Å, $\beta = 108{\cdot}58$ (2)°, $V = 2507$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}373$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71073$ Å, $\mu = 4{\cdot}9$ cm^{-1}, $F(000) = 1088$, $T = 130$ K, $R = 0{\cdot}069$ for 2831 observed reflections with $I > 2{\cdot}5\sigma(I)$. The inorganic ring skeleton has an envelope conformation. The S—N and P—N bond lengths (mean values) are 1·562 (6) and 1·590 (8) Å, respectively. One of the phenyl rings exhibits a disordered behaviour.

Experimental. Colourless crystals obtained by recrystallization from diethyl ether/pentane (1:1). Crystal (0·13 × 0·20 × 0·35 mm) was glued on top of a glass fibre and transferred into the cold nitrogen stream of the low-temperature unit on an Enraf–Nonius CAD-4F diffractometer interfaced to a PDP-11/23. Graphite-monochromated Mo $K\bar{\alpha}$ radiation. Cell dimensions from setting angles of 22 reflections ($7{\cdot}02 < \theta < 13{\cdot}94°$). Intensity data of 4390 reflections were collected; h −13→11, k 0→24, l 0→13; $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}6379$ Å^{-1}; $\omega/2\theta$ scan mode with $\Delta\omega = (0{\cdot}90 + 0{\cdot}35\tan\theta)°$. Three reference reflections measured every 167 min ($43\bar{6}$: r.m.s.d. 2·9%; $\bar{4}36$: r.m.s.d. 2·4%; $45\bar{4}$: r.m.s.d. 1·7%) showed no indication of crystal decomposition during the 160 h of X-ray exposure time. Intensities corrected for scale variation and for Lorentz and polarization effects. No absorption correction applied. Variance $\sigma^2(I)$ calculated on the basis of counting statistics plus the term $(PI)^2$, where P (= 0·040) is the instability constant as derived from the excess variance in the reference reflections (McCandlish, Stout & Andrews, 1975). Data set averaged in a set of 4046 unique reflections ($R_{\rm int} = 0{\cdot}070$). Structure solved by direct methods using *SHELXS* (Sheldrick, 1986) and refined on F by block-diagonal least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms ($R = 0{\cdot}079$, $wR = 0{\cdot}092$). The parameters of one of the phenyl rings [C(7)—C(12)] show unrealistic values; bond lengths (varying from 1·24 to 1·54 Å), bond angles (varying from 114 to 124°) and high temperature factors suggest some degree of disorder. Constrained group refinement introduced for [C(7)—C(12)] (C—C = 1·38, C—H = 1·0 Å and C—C—C = 120°). H atoms located on a difference Fourier map and included in the final refinement with one overall isotropic temperature factor. Convergence with 332 parameters was reached at $R = 0{\cdot}069$, $wR = 0{\cdot}076$, $w = 1$, $S = 3{\cdot}163$; 2831 observed reflections with $I > 2{\cdot}5\sigma(I)$; average $\Delta/\sigma = 0{\cdot}028$, maximum $\Delta/\sigma = 0{\cdot}197$. Minimum and maximum residual densities in final Fourier map −0·63 and 0·79 e Å^{-3}. In the vicinity of the disordered phenyl ring the densities are −1·35 and 1·75 e Å^{-3}, respectively. The observed conformation of the PNS ring approaches that of an envelope (Boeyens, 1978) with torsion angles ranging from −27·3 (6) to 29·4 (6)° and lowest asymmetry parameter value $\Delta C_s[\mathrm{P}(1)] = 3{\cdot}1$ (5)° (Duax, Weeks & Rohrer, 1976). Puckering parameters are $Q = 0{\cdot}243$ (5) Å, $\theta = 128$ (1)°, $\varphi = 309$ (2)° [(Cremer & Pople, 1975) e.s.d. following Norrestam (1981)]. Scattering factors from Cromer & Mann (1968). Anomalous-dispersion factors were taken from Cromer & Liberman (1970). All calculations carried

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