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Key indicators

Single-crystal X-ray study
T = 200 K
Mean $\sigma(C-C)$ = 0.009 Å
R factor = 0.047
wR factor = 0.115
Data-to-parameter ratio = 18.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis(diphenylphosphinato- κO)bis(diphenylphosphinic acid- κO)bis(pyridine- κN)mercury(II)

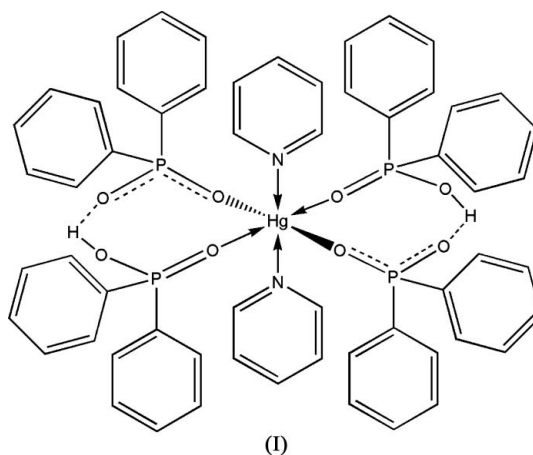
In the centrosymmetric molecule of the title compound, $[\text{Hg}(\text{C}_{12}\text{H}_{10}\text{O}_2\text{P})_2(\text{C}_5\text{H}_5\text{N})_2(\text{C}_{12}\text{H}_{11}\text{O}_2\text{P})_2]$, the approximately octahedral Hg atom is coordinated by two each of phenylphosphinate, phosphinic acid and pyridine ligands. Each pair of phosphinic acid and phosphinate ligands features an intramolecular hydrogen bond, so forming an eight-membered ring.

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Comment

The ability of phosphinate ligands to promote the formation of bridged coordination polymers (Vioux *et al.*, 2004) prompted us to study its mercury compounds (Siqueira *et al.*, 2006). In the course of crystallization, one sample had crystals in the form of blocks, instead of the usual needle morphology characteristic of the coordination polymer *catena*- $[\text{Hg}(\mu\text{-O}_2\text{PPh}_2)_2(\text{NC}_5\text{H}_5)_2]$. A single-crystal X-ray study of the crystals revealed that the title compound, (I), had formed. This phenomenon has been reported for the Mn^{II} complex of phenylphosphinic acid (Betz & Bino, 1988).



One half-molecule of (I) is found in the asymmetric unit; the complete molecule is generated by the crystallographic centre of inversion coincident with the Hg atom (Fig. 1). The approximately octahedral coordination around the Hg atom is formed by four equatorial O atoms from the mono-coordinate diphenylphosphinate and diphenylphosphinic acid ligands and two axial N atoms of the pyridine ligands. The Hg–O and Hg–N distances are similar to those of the previously reported polymeric species, in which they are 2.529 (3) and 2.190 (3) Å, respectively. The much longer Hg–O bond can be attributed to the coordinating anion nature of the diphenylphosphinate ligand, where the Hg–O bonds are

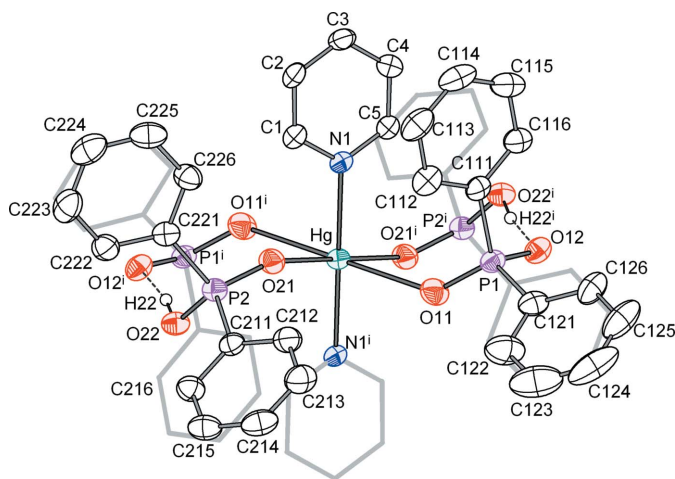


Figure 1

The structure of (I), showing the atom-numbering scheme and with displacement ellipsoids drawn at the 50% probability level. The symmetry-equivalent C atoms are shown as grey lines. Hydrogen bonds are shown as dashed lines, and H atoms not involved in hydrogen bonding have been omitted. [Symmetry code: (i) $-x, -y, -z + 1$.]

formed largely by electrostatic attraction. The angles around the Hg centre show a variation from ideal, due to the tilt of $78.68(9)^\circ$ between the equatorial plane of the Hg and O atoms and the line formed by the two axial N atoms.

An intramolecular hydrogen bond between the diphenylphosphinate and the diphenylphosphinic acid ligands presumably stabilizes the formation of the molecular compound by the formation of an eight-membered ring. For both diphenylphosphinate and diphenylphosphinic acid ligands, the P–O distance for the O atom bound to the metal center is shorter than that to the free O atom. This indicates that both ligands have the predominant character $\text{O}=\text{P}-\text{O}$ where, contrary to expectations, the doubly bonded O atom of the diphenylphosphinate ligand binds to the Hg centre. The localization of the formal negative charge on the free O atom can be attributed to the strong hydrogen bonding in which the atom participates. The previously reported compound $[\text{Mn}(\text{O}_2\text{PPh}_2)_2(\text{HO}_2\text{PPh}_2)_2(\text{OCN}(\text{CH}_3)_2)_2]$ (Betz & Bino, 1988) has a very similar geometry.

Experimental

Crystals of (I) formed by the slow evaporation of a solution of $[\text{Hg}(\text{O}_2\text{PPh}_2)_2]$ in a mixture of dimethylformamide–pyridine–methanol (1:1:1 v/v/v).

Crystal data

$[\text{Hg}(\text{C}_{12}\text{H}_{10}\text{O}_2\text{P})_2(\text{C}_5\text{H}_5\text{N})_2(\text{C}_{12}\text{H}_{11}\text{O}_2\text{P})_2]$
 $M_r = 1229.49$
 Triclinic, $P1$
 $a = 9.4511(3) \text{ \AA}$
 $b = 12.3528(5) \text{ \AA}$
 $c = 12.6391(4) \text{ \AA}$
 $\alpha = 101.853(2)^\circ$
 $\beta = 109.278(2)^\circ$
 $\gamma = 95.797(2)^\circ$
 $V = 1340.19(8) \text{ \AA}^3$

$Z = 1$
 $D_x = 1.523 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 27102 reflections
 $\theta = 2.9\text{--}27.5^\circ$
 $\mu = 3.05 \text{ mm}^{-1}$
 $T = 200(2) \text{ K}$
 Prism, colourless
 $0.30 \times 0.12 \times 0.08 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ scans
 Absorption correction: multi-scan (SADABS; Bruker, 2004)
 $T_{\text{min}} = 0.630, T_{\text{max}} = 0.784$
 25466 measured reflections
 6145 independent reflections

5482 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.078$
 $\theta_{\text{max}} = 27.7^\circ$
 $h = -12 \rightarrow 11$
 $k = -16 \rightarrow 15$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.1115$
 $S = 1.02$
 6145 reflections
 332 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 1.7278P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 3.14 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.51 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0051 (10)

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Hg–N1	2.168 (4)	P1–O12	1.534 (4)
Hg–O11	2.549 (4)	P2–O21	1.493 (4)
Hg–O21	2.561 (3)	P2–O22	1.527 (4)
P1–O11	1.487 (4)	O22–H22	0.84
N1–Hg–O11 ⁱ	79.77 (13)	O11–P1–O12	118.1 (2)
N1–Hg–O21 ⁱ	95.71 (13)	O21–P2–O22	117.7 (2)
O11 ⁱ –Hg–O21 ⁱ	95.02 (12)	P1–O11–Hg	133.7 (2)
O11–Hg–O21 ⁱ	84.98 (12)	P2–O21–Hg	139.8 (2)
O11–Hg–O21	95.02 (12)	P2–O22–H22	109.5
O12–P1–O11–Hg	−73.5 (4)	O22–P2–O21–Hg	−10.1 (4)
N1–Hg–O11–P1	−26.9 (3)	N1–Hg–O21–P2	136.2 (3)
N1 ⁱ –Hg–O11–P1	153.1 (3)	N1 ⁱ –Hg–O21–P2	−43.8 (3)
O21 ⁱ –Hg–O11–P1	68.0 (3)	O11 ⁱ –Hg–O21–P2	56.1 (3)
O21–Hg–O11–P1	−112.0 (3)	O11–Hg–O21–P2	−123.9 (3)

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

Table 2

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O22–H22 \cdots O12 ⁱ	0.84	1.62	2.447 (5)	167

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

All H atoms were found in a difference Fourier map before being repositioned geometrically and refined using a riding model, with $C\text{--}H = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the H atoms of the pyridine and phenyl rings, and $O\text{--}H = 0.84 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ for the H atom on the diphenylphosphinic acid ligand. The highest residual electron-density peak is 1.27 \AA from Hg and the deepest hole is 0.88 \AA from the Hg atom. None of the largest peaks is chemically sensible and they are likely to be absorption artifacts.

Data collection: COLLECT (Nonius, 2000); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Crystal Impact, 2005); software used to prepare material for publication: WinGX (Farrugia, 1999).

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