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[Ethylene-1,2-bis(diphenylphosphine)-*P*,*P*′]dinitratoplatinum(II) and *cis*-bis[(diphenylphosphinomethyl)-diphenylphosphine oxide-*O*,*P*]-platinum(II) dinitrate dihydrate

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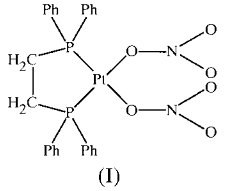
In [Pt(dppe)$(NO_3)_2$], where dppe is ethylene-1,2-bis(diphenylphosphine) ($C_{26}H_{24}P_2$), the Pt atom is coordinated by the two P atoms and by two O atoms of the two nitrate ions. The molecule has a distorted square-planar geometry, with one of the nitrate groups directed on each side of the plane. The cation in *cis*-[Pt(dppmO-*O*,*P*)$_2$]$(NO_3)_2\cdot 2H_2O$, where dppmO is bis(diphenylphosphinomethyl)diphenylphosphine oxide ($C_{25}H_{22}OP_2$), comprises two five-membered chelate rings, each dppmO ligand being coordinated to platinum through one P atom and the O atom. The larger P—Pt—P angle of 102.25 (4)° is due to steric interactions between the two phenyl groups on each P atom.

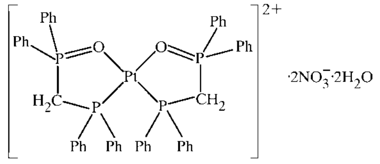
Comment

The dinitratoplatinum(II) complexes [Pt$(NO_3)_2$(P–P)] [P–P is dppm, $Ph_2PCH_2PPh_2$, or dppe, $Ph_2P(CH_2)_2PPh_2$] are useful intermediates in the synthesis of a wide variety of diphosphine–platinum complexes, since the weakly coordinated nitrates can be easily replaced by other ligands. They can be isolated or they may be generated *in situ* and used in further reactions without isolation (De Priest *et al.*, 1997). We prepared [ethylene-1,2-bis(diphenylphosphine)-*P*,*P*′]dinitratoplatinum(II), [Pt$(NO_3)_2$(dppe)], (I), as a precursor to the corresponding ascorbate complex by the reaction of [$PtCl_2$(dppe)] with silver nitrate in acetone solution (Arendse *et al.*, 1999). The only structure of a related platinum complex in the literature is that of *cis*-[Pt$(NO_3)_2(PMe_3)_2$] (Suzuki *et al.*, 1993).

Mixed phosphine–phosphine oxide ligands have been prepared by the reaction of $Ph_2P(CH_2)_nPPh_2$ with benzyl bromide, followed by aqueous NaOH (Abatjoglou & Kapicek, 1981). Palladium and platinum complexes of the type [M{$Ph_2P(CH_2)_nP(O)Ph_2$-*O*,*P*}$_2$]$^{2+}$ have been reported (Higgins *et al.*, 1987), although the dppmO ligand was reported to be formed in only low yield by the above method. The solid-state structure of [Pd(dppeO-*O*,*P*)$_2$]$(BF_4)_2$ has been reported recently by Coyle *et al.* (1998). We obtained *cis*-[bis(diphenylphosphinomethyl)diphenylphosphine oxide-*O*,*P*]platinum(II) dinitrate dihydrate, *cis*-[Pt{$Ph_2PCH_2P(O)PPh_2$}$_2$]$(NO_3)_2\cdot 2H_2O$, (II), as an unexpected by-product of the reaction between [$PtCl_2$(dppm)] and silver nitrate in air.



(I)



(II)

The molecular structure of (I) is shown in Fig. 1. The coordination geometry around the Pt atom is distorted square planar, with P1—Pt—P2, O1—Pt—P1, O4—Pt—P2 and O1—Pt—O4 angles of 85.85 (8), 90.82 (17), 98.15 (17) and 85.4 (2)°, respectively. The Pt—O—N angles are 113.5 (5) and 116.2 (5)°, and the NO_2 groups lie on opposite sides of the PtO_2P_2 plane. This feature was also observed in the structure of *cis*-[Pt$(NO_3)_2(PMe_3)_2$] (Suzuki *et al.*, 1993). The Pt—P distances of 2.215 (2) and 2.220 (2) Å, and the Pt—O distances of 2.111 (5) and 2.115 (5) Å, are similar to the corresponding distances in *cis*-[Pt$(NO_3)_2(PMe_3)_2$].

The molecular structure of the cation in (II) is bidentate (Fig. 2), coordinating through one P atom and the O atom of the phosphine oxide to form two five-membered chelate rings. The Pt—O distances are 2.089 (2) and 2.094 (2) Å, and the Pt—P distances are 2.2168 (10) and 2.2178 (10) Å. These Pt—O and Pt—P bond lengths are similar to the values of 2.108 (10) Å and 2.213 (4) Å, respectively, found in *cis*-[Pt{$Ph_2PNHP(O)Ph_2$-*O*,*P*}$_2$]$(BF_4)_2$ (Bhattacharyya *et al.*, 1996). The cation in the latter complex is analogous to that in (II), since it is also composed of two five-membered chelate

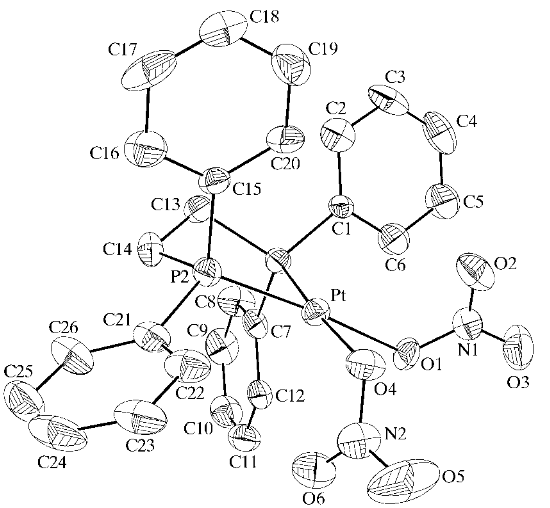


Figure 1
A view of (I) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

rings. The $Ph_2PNHP(O)Ph_2$ ligand is also isoelectronic with dppmO. In the present case, the coordination geometry about the Pt atom is distorted square planar. The O1—Pt—O2, O2—Pt—P3, O1—Pt—P2 and P2—Pt—P3 angles are 87.54 (10), 86.10 (7), 84.09 (7) and 102.25 (4)°, respectively, giving an angle sum of 359.98° around the metal. The larger P—Pt—P angle is due to the greater steric requirements of the phenyl groups on the two P atoms that lie *cis* to each other. The P—Pt—P angle in (II) is larger than that of 98.5 (2)° found in *cis*-$[Pt\{Ph_2PNHP(O)Ph_2\text{-}O,P\}_2]^{2+}$ (Bhattacharyya *et al.*, 1996); it is closer to the values of 103.2 (1) and 103.72 (9)° in the neutral complexes *cis*-$[Pt\{Ph_2PNP(O)Ph_2\text{-}O,P\}_2]$ (Bhattacharyya *et al.*, 1996) and *cis*-$[Pt\{Ph_2PCH_2C(O)(CF_3)_2\text{-}O,P\}_2]$ (Montgomery *et al.*, 1987).

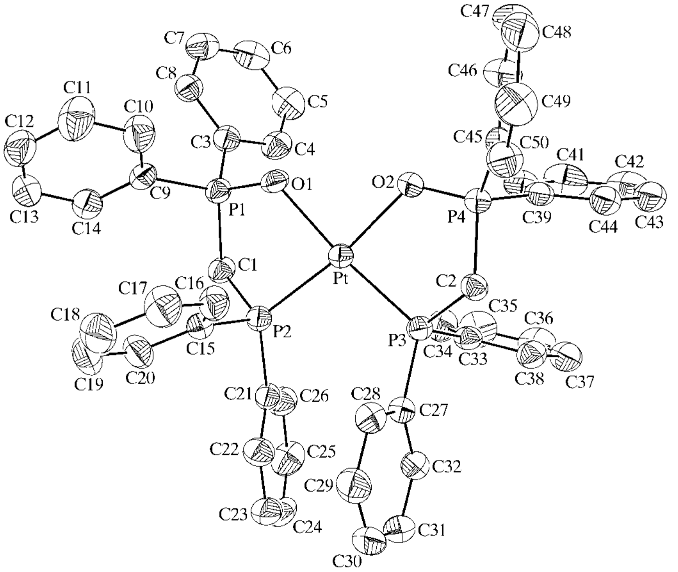


Figure 2
A view of the cation of (II) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

Experimental

Compound (I) was synthesized from $[PtCl_2(dppe)]$ (Anderson *et al.*, 1983) by halide abstraction with silver nitrate. Silver nitrate (0.34 g, 2.0 mmol) in water (5 ml) was added to an acetone solution (40 ml) of $[PtCl_2(dppe)]$ (0.66 g, 1.0 mmol). The mixture was stirred for 24 h in the dark at room temperature, and the precipitate of AgCl was collected by filtration through Celite. The filtrate was evaporated under reduced pressure and the products were obtained as a yellow powder (yield 0.40 g, 56%). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation from a $CDCl_3$ solution. Analysis calculated for $C_{26}H_{24}N_2O_6P_2Pt$: C 43.51, H 3.35, N 3.91%; found: C 43.64, H 3.31, N 3.81%; ^{31}P NMR ($CDCl_3$): δP 33.0 ($^1J_{Pt,P}$ = 3940 Hz). Compound (II) was prepared as follows: the reaction of $[PtCl_2(dppm)]$ (1.30 g, 2 mmol) with 2 equivalents of silver nitrate (0.68 g, 4.0 mmol) in acetone (100 ml) in the presence of air produced a 4:1 mixture of $[Pt(NO_3)_2(dppm)]$ and *cis*-$[Pt(dppmO\text{-}O,P)_2]^{2+}$, as determined by ^{31}P NMR spectroscopy [δ 4.6 (*s*, $^1J_{Pt,P}$ = 3810 Hz), 67.0 (*br*)]. On standing, crystals of (II) suitable for X-ray diffraction analysis were obtained.

Compound (I)

Crystal data

$[Pt(C_{26}H_{24}P_2)(NO_3)_2]$
$M_r = 717.50$
Monoclinic, *Cc*
$a = 10.4971$ (1) Å
$b = 15.5281$ (2) Å
$c = 16.3930$ (2) Å
$\beta = 101.51$ (1)°
$V = 2618.36$ (5) Å^3
$Z = 4$

$D_x = 1.820$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2$–26°
$\mu = 5.53$ mm^{-1}
$T = 223$ (2) K
Plate, colourless
0.30 × 0.20 × 0.04 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Blessing, 1995)
$T_{min} = 0.28$, $T_{max} = 0.80$
25 459 measured reflections
2576 independent reflections (plus 2561 Friedel-related reflections)

4304 reflections with $I > 2\sigma(I)$
$R_{int} = 0.10$
$\theta_{max} = 26°$
$h = -12 \rightarrow 12$
$k = -19 \rightarrow 19$
$l = -20 \rightarrow 20$
Intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.069$
$S = 1.03$
5137 reflections
334 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0148P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.31$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.024 (8)

Table 1
Selected geometric parameters (Å, °) for (I).

Pt—O4	2.111 (5)	O2—N1	1.227 (8)
Pt—O1	2.115 (5)	O3—N1	1.236 (8)
Pt—P1	2.215 (2)	O4—N2	1.277 (9)
Pt—P2	2.220 (2)	O5—N2	1.222 (9)
O1—N1	1.261 (8)	O6—N2	1.194 (9)
O4—Pt—O1	85.4 (2)	O2—N1—O3	122.2 (8)
O1—Pt—P1	90.82 (17)	O2—N1—O1	120.9 (7)
O4—Pt—P2	98.15 (17)	O3—N1—O1	116.8 (7)
P1—Pt—P2	85.85 (8)	O6—N2—O5	121.6 (9)
N1—O1—Pt	116.2 (5)	O6—N2—O4	121.2 (8)
N2—O4—Pt	113.5 (5)	O5—N2—O4	117.3 (8)

Compound (II)

Crystal data

$[Pt(C_{25}H_{22}OP_2)_2](NO_3)_2\cdot 2H_2O$
$M_r = 1155.87$
Monoclinic, $P2_1/n$
$a = 12.9843$ (2) Å
$b = 16.3998$ (2) Å
$c = 22.6979$ (3) Å
$\beta = 92.81$ (1)°
$V = 4827.47$ (11) Å^3
$Z = 4$

$D_x = 1.590$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.2$–26.4°
$\mu = 3.10$ mm^{-1}
$T = 213$ (2) K
Irregular, light yellow
0.36 × 0.28 × 0.22 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Blessing, 1995)
$T_{min} = 0.37$, $T_{max} = 0.51$
80 352 measured reflections
9898 independent reflections

7985 reflections with $I > 2\sigma(I)$
$R_{int} = 0.06$
$\theta_{max} = 26.46°$
$h = -16 \rightarrow 16$
$k = -20 \rightarrow 20$
$l = -28 \rightarrow 28$
Intensity decay: <2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 8.7121P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.069$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.09$	$\Delta\rho_{\max} = 0.75$ e Å^{-3}
9898 reflections	$\Delta\rho_{\min} = -0.59$ e Å^{-3}
604 parameters	
H-atom parameters constrained	

Table 2
Selected geometric parameters (Å, °) for (II).

Pt—O2	2.089 (2)	P1—C1	1.804 (4)
Pt—O1	2.094 (2)	P2—C1	1.837 (4)
Pt—P3	2.2168 (10)	P4—O2	1.520 (3)
Pt—P2	2.2178 (10)	P4—C2	1.806 (4)
P1—O1	1.525 (3)	P3—C2	1.844 (4)
O2—Pt—O1	87.54 (10)	P3—Pt—P2	102.25 (4)
O2—Pt—P3	86.10 (7)	O1—P1—C1	106.89 (16)
O1—Pt—P3	173.52 (7)	C1—P2—Pt	101.45 (13)
O2—Pt—P2	171.61 (7)	P1—O1—Pt	121.61 (14)
O1—Pt—P2	84.09 (7)	P1—C1—P2	106.00 (19)

H atoms were treated using appropriate riding models (*AFIX* = *m*3 in *SHELXTL-Plus*; Sheldrick, 1999). For both compounds, C—H distances of 0.98 and 0.94 Å were used for CH_2 and C_6H_5 groups, respectively. In the case of the solvent water molecules in (II), the H-atom positions were located from difference Fourier maps and were refined riding on their O atoms. For all H atoms, $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C,O})$. In (I), the largest peak in the final difference map is 0.88 Å from C19 and the deepest trough is 0.64 Å from the Pt atom. In (II), the largest peak is 1.67 Å from O6′.

For compounds (I) and (II), data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*. For compound (I), data reduction: *SHELXTL-Plus* (Sheldrick, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). For compound (II), data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1999); program(s) used to refine structure: *SHELXTL-Plus*. For compounds (I) and (II), molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1556). Services for accessing these data are described at the back of the journal.

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