

| | | | |
|-----------|------------|--------------|------------|
| O3—Cu—O5' | 88.13 (5) | O3'—Cu'—O5' | 90.84 (6) |
| O3—Cu—O6 | 84.81 (5) | O3'—Cu'—O6'' | 84.81 (5) |
| O3—Cu—N1 | 95.84 (6) | O3'—Cu'—N1' | 93.36 (5) |
| O5'—Cu—O6 | 170.18 (4) | O5'—Cu'—O6'' | 175.63 (5) |
| O5'—Cu—N1 | 96.46 (5) | O5'—Cu'—N1' | 85.42 (5) |
| O6—Cu—N1 | 91.05 (5) | O6''—Cu'—N1' | 94.31 (6) |

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

Table 2. Hydrogen-bonding geometry (Å, °)

| D—H...A | D—H | H...A | D...A | D—H...A |
|------------------------------|----------|----------|-----------|---------|
| N2—H21...O1 ⁱ | 0.78 (3) | 2.18 (3) | 2.882 (2) | 151 (3) |
| N2—H22...O4 ⁱⁱ | 0.88 (3) | 2.04 (3) | 2.883 (2) | 161 (2) |
| O2—H23...O7 | 0.79 (3) | 1.97 (3) | 2.755 (2) | 172 (3) |
| O2—H24...O5 ⁱⁱⁱ | 0.73 (3) | 1.94 (3) | 2.666 (2) | 172 (3) |
| O3—H31...O4 ^{iv} | 0.76 (3) | 1.93 (3) | 2.693 (2) | 174 (3) |
| O3—H32...O7 ⁱⁱⁱ | 0.80 (3) | 1.89 (3) | 2.687 (2) | 175 (2) |
| O4—H42...O4 ^v | 0.77 (3) | 1.90 (3) | 2.669 (2) | 177 (3) |
| O4—H41...O6 ^v | 0.72 (3) | 2.04 (3) | 2.754 (2) | 170 (3) |
| N2'—H21'...O7 ⁱⁱⁱ | 0.83 (3) | 2.06 (3) | 2.887 (2) | 170 (3) |
| N2'—H22'...O8 ^v | 0.82 (3) | 1.99 (3) | 2.763 (2) | 158 (3) |
| O2'—H24'...O7 ^v | 0.79 (3) | 1.91 (3) | 2.695 (2) | 172 (3) |
| O2'—H23'...O8 ^{vi} | 0.78 (3) | 1.91 (3) | 2.683 (2) | 173 (3) |
| O3'—H31'...O7 ^{vi} | 0.73 (3) | 1.95 (3) | 2.670 (2) | 168 (3) |
| O3'—H32'...O8 ^{vi} | 0.86 (3) | 1.77 (3) | 2.627 (2) | 178 (3) |
| O4'—H41'...O1 ^v | 0.88 (3) | 2.11 (3) | 2.903 (2) | 149 (3) |
| O4'—H42'...O6 | 0.67 (3) | 2.09 (4) | 2.762 (2) | 174 (4) |

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $x - 1, y - 1, z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $x - 1, y, z$; (v) $x, 1 + y, z$; (vi) $1 - x, 1 - y, -z$.

The title structure was solved by direct methods and refined by full-matrix least-squares calculations. All non-H atoms were refined anisotropically. All H atoms were located from a difference synthesis and refined isotropically.

Data collection: Siemens P3 software. Cell refinement: Siemens P3 software. Data reduction: XDISK in SHELXTLIPC (Sheldrick, 1990). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997b). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a). Molecular graphics: XP in SHELXTLIPC. Software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1250). Services for accessing these data are described at the back of the journal.

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[Bis(diphenylphosphino)methane]dinitrato-palladium(II) tris(deuteriochloroform) solvate

NIGAM P. RATH,* ROBERT A. STOCKLAND JR AND GORDON K. ANDERSON*

Department of Chemistry, University of Missouri–St Louis, 8001 Natural Bridge Road, St Louis, MO 63121, USA.
E-mail: nigam_rath@umsl.edu

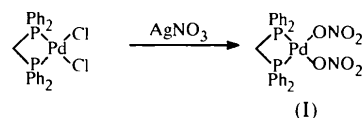
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Abstract

In the title compound, [methylenebis(diphenylphosphine-*P*)]bis(nitrato-*O*)palladium(II) tris(deuteriochloroform) solvate, [Pd(NO₃)₂(C₂₅H₂₂P₂)]·3CDCl₃ or [Pd(NO₃)₂(dppm)]·3CDCl₃ [where dppm is bis(diphenylphosphino)methane], the PdO₂P₂ unit is planar, but the molecule is significantly distorted from ideal square-planar geometry. Principal dimensions include: Pd—P 2.2240(8) and 2.2345(7), Pd—O 2.103(2) and 2.130(2) Å, P—Pd—P 72.52(3), O—Pd—O 85.23(9), and P—Pd—O 97.55(7) and 104.73(6)°. The CDCl₃ molecules associate with the complex via C—D...O hydrogen bonds.

Comment

In the course of our investigations of palladium and platinum complexes containing weakly coordinating anionic ligands (Fallis *et al.*, 1991; Oliver & Anderson, 1992), we have investigated the role of nitrate ligands. Reactions of palladium or platinum complexes of the type [MCl₂(P—P)] with AgNO₃ (2 mole equivalents) produce the corresponding dinitrate derivatives in good yields. The nitrate groups are displaced readily, so these complexes serve as good sources of the M(P—P)²⁺ fragment. During our studies, we obtained crystals of the palladium species [Pd(NO₃)₂(dppm)] [where dppm is bis(diphenylphosphino)methane], (I), as its tris(deuteriochloroform) solvate.



The structure analysis of [Pd(NO₃)₂(dppm)] reveals that the nitrate anions are coordinated through oxygen, and the PdO₂P₂ unit is perfectly planar (the sum of the angles around palladium is 360.03°), although the molecule is distorted significantly from square-planar geometry (Fig. 1). The P—Pd—P angle of 72.52(3)°

is a consequence of the presence of the four-membered ring involving the chelated dppm ligand. The O—Pd—O angle is also less than 90°, whereas the two P—Pd—O angles are greater [97.54 (7) and 104.73 (6)°]. The Pd—P distances (Table 1) are comparable to reported short Pd—P distances [2.217 (3) and 2.233 (2) Å; Wink, 1990] due to the poor *trans* influence of the ONO₂ ligand. The N—O distances involving the coordinated O atoms are approximately 0.07 Å longer than those to the free O atoms. This is as expected since the terminal N—O bonds should exhibit some multiple-bond character.

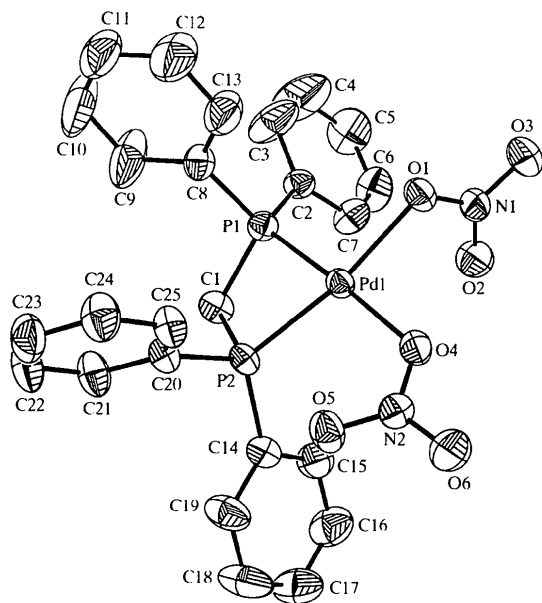


Fig. 1. View of the title complex showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

The molecular structures of five palladium–nitrate complexes have been reported previously (Table 2). The [Pd(NO₃)₂(PPh₃)(OPPh₃)] complex adopts a *trans* geometry, whereas [Pd(NO₃)₂(Me₂SO)₂] is *cis*. The other three examples contain bidentate ligands and are therefore forced to have *cis* geometry. The Pd—O distances in the present complex, (I), are longer than those reported for *cis*-[Pd(NO₃)₂(Me₂SO)₂], [Pd(NO₃)₂-(diphenylphenanthroline)], [Pd(NO₃)₂(1,10-dithia-18-crown-6)] or [Pd(NO₃)₂{(tPrO)₂P(O)CH₂C(O)NEt₂}]. The longer Pd—O distances are a consequence of the greater *trans* influence of the phosphine groups in the present case. The small P—Pd—P angle in [Pd(NO₃)₂-(dppm)] is typical of complexes containing chelating dppm. The O—Pd—O angle is smaller than those found in [Pd(NO₃)₂(diphenylphenanthroline)] or [Pd(NO₃)₂{(tPrO)₂P(O)CH₂C(O)NEt₂}], which may be a consequence of the presence of relatively bulky phenyl groups on the P atoms, although in *cis*-[Pd(NO₃)₂-(Me₂SO)₂], the angle is only 83.0°.

The asymmetric unit of the title compound contains three CDCl₃ molecules. The D atoms (referred to as H1S, H2S and H3S) of the solvent molecules and some aromatic H atoms from the phenyl groups, as well as the methylene H atom from the dppm ligand, form intermolecular hydrogen bonds (details are given in Table 3). A search of the Cambridge Structural Database (Allen & Kennard, 1993) for systems of the type [PdX₂(dppm)] resulted in five structures where X = Cl, Br, I, SCN and CF₃C(O)O. Out of these five compounds, only two [X = Cl (Steffen & Palenik, 1976) and CF₃C(O)O (Wink, 1990)] form hydrogen bonds involving a methylene H atom [distances: C—H...Cl 2.47 and C—H...O 2.41 Å; angles around hydrogen are 162.9 and 163.3°, respectively]. The ONO₂ compound seems to have the strongest hydrogen bond but deviates most from linearity. The CH₂ resonances in the ¹H NMR spectra of [PdX₂(dppm)] (X = NO₃, Cl) are not shifted significantly from those where X = CH₂SiMe₃ or 2,4,6-Me₃C₆H₂ (Stockland *et al.*, 1997), suggesting that the hydrogen bonding is not maintained in solution.

Experimental

The title compound was prepared by treatment of a dichloromethane solution of [PdCl₂(dppm)] (0.10 g, 0.18 mmol) with AgNO₃ (0.091 g, 0.53 mmol). The solution was stirred for 48 h, then filtered and the solvents removed. The resulting solid was washed with ether and dried *in vacuo*, leaving the product as a pale yellow solid (0.068 g, 62%). Analysis calculated for C₂₅H₂₂N₂O₆P₂Pd: C 48.80, H 3.58%; found: C 49.60, H 3.68%; ¹H NMR (CDCl₃): δH 4.02 (t, ²J_{PH} = 11.0 Hz, 2H, PCH₂P), 7.2–7.8 (m, 20H, PPh); ³¹P{¹H} NMR (CDCl₃): δP –50.6. Crystals suitable for X-ray diffraction analysis were grown from CDCl₃ solution by slow evaporation.

Crystal data

[Pd(NO₃)₂(C₂₅H₂₂P₂)]·
3CDCl₃
M_r = 975.80
Monoclinic
P2₁/c
a = 13.9841 (2) Å
b = 16.8118 (2) Å
c = 16.8033 (2) Å
β = 93.858 (1)°
V = 3941.47 (9) Å³
Z = 4
D_x = 1.645 Mg m⁻³
D_m not measured

Mo Kα radiation
λ = 0.71073 Å
Cell parameters from 8192
reflections
θ = 2–25°
μ = 1.203 mm⁻¹
T = 203 (2) K
Cubic
0.42 × 0.42 × 0.40 mm
Colorless

Data collection

Bruker CCD area-detector
diffractometer
φ and ω scans
Absorption correction:
empirical (SADABS;
Blessing, 1995)
T_{min} = 0.54, T_{max} = 0.62

7938 reflections with
I > 2σ(I)
R_{int} = 0.04
θ_{max} = 27.5°
h = –18 → 18
k = 0 → 21
l = 0 → 21

109 227 measured reflections
9037 independent reflections

Intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.109$
 $S = 1.034$
9037 reflections
471 parameters
H atoms not refined
 $w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 7.3285P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.020$
 $\Delta\rho_{\max} = 1.353 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.079 \text{ e } \text{Å}^{-3}$
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

| | | | |
|-----------|------------|-----------|------------|
| Pd1—O4 | 2.103 (2) | Pd1—P1 | 2.2241 (8) |
| Pd1—O1 | 2.130 (2) | Pd1—P2 | 2.2345 (7) |
| O1—Pd1—P1 | 97.54 (7) | P1—Pd1—P2 | 72.52 (3) |
| O4—Pd1—P2 | 104.72 (6) | | |

Table 2. Selected bond distances and angles (Å, °) for palladium–nitrate complexes

| Complex | Pd—O1 | Pd—O2 | O1—Pd—O2 |
|--|------------|-----------|-----------|
| [Pd(NO ₃) ₂ (dppm)] ^a | 2.103 (2) | 2.130 (2) | 85.26 (9) |
| <i>trans</i> -[Pd(NO ₃) ₂ (PPh ₃)(OPPh ₃)] ^b | 2.031 (7) | 2.031 (8) | 179.0 (3) |
| <i>cis</i> -[Pd(NO ₃) ₂ (Me ₂ SO) ₂] ^c | 2.066 | — | 83.0 |
| [Pd(NO ₃) ₂ (diphenylphenanthroline)] ^d | 2.028 (3) | — | 91.3 (1) |
| [Pd(NO ₃) ₂ (1,10-dithia-18-crown-6)] ^e | 2.039 (10) | 2.052 (8) | 88.8 (5) |
| [Pd(NO ₃) ₂ {(^t PrO) ₂ P(O)-CH ₂ C(O)NEt ₂ }] ^f | 1.995 (5) | 1.989 (6) | 89.0 (2) |

Notes: (a) this work; (b) Jones *et al.* (1986); (c) Langs *et al.* (1967); (d) Tomroos (1995); (e) Izatt *et al.* (1990); (f) Jessup *et al.* (1983).

Table 3. Hydrogen-bonding geometry (Å, °)

| D—H...A | D—H | H...A | D...A | D—H...A |
|----------------------------|------|-------|-----------|---------|
| C1—H1B...O6 ⁱ | 0.98 | 2.38 | 3.257 (4) | 149 |
| C1S—H1S...O1 | 0.99 | 2.44 | 3.318 (5) | 148 |
| C1S—H1S...O3 | 0.99 | 2.37 | 3.103 (5) | 131 |
| C2S—H2S...O3 ⁱⁱ | 0.99 | 2.42 | 3.310 (6) | 149 |
| C3S—H3S...O6 ⁱ | 0.99 | 2.51 | 3.232 (5) | 129 |
| C6—H6...O4 ⁱⁱⁱ | 0.94 | 2.59 | 3.477 (4) | 157 |
| C7—H7...O2 ⁱⁱⁱ | 0.94 | 2.48 | 3.148 (5) | 128 |
| C9—H9...O6 ⁱ | 0.94 | 2.52 | 3.455 (6) | 178 |

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $1 - x, 1 - y, 1 - z$.

Data were collected by the double-pass method using the CCD area-detector system. The first 50 frames of data were recollected at the end of data collection to monitor crystal decay. H atoms were treated using appropriate riding models ($AFIX = m3$). Two of the three CDCl₃ molecules show disorder. The disordered Cl atoms were refined with distance constraints ($DFIX, C—Cl = 1.700 \pm 0.005 \text{ Å}$) and their occupancy factors were refined as free variables (Sheldrick, 1998).

Data collection: *SMART* (Bruker, 1998). Cell refinement: *SMART*. Data reduction: *SAINT* (Bruker, 1998). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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[N(CH₃)₄]₄H₁₂Ge₉O₂₆·14H₂O

AKHILESH TRIPATHI,^a VICTOR G. YOUNG JR,^b
GEOFFREY M. JOHNSON,^c CHRISTOPHER L. CAHILL^a AND
JOHN B. PARISE^{a,c}

^aDepartment of Chemistry, SUNY, Stony Brook, NY 11794-3400, USA, ^bDepartment of Chemistry, The University of Minnesota, MN 55455, USA, and ^cDepartment of Geosciences, SUNY, Stony Brook, NY 11794-2100, USA.
E-mail: jparise@notes.cc.sunysb.edu

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Abstract

The title compound, tetrakis(tetramethylammonium) dodecahydroxotetradecaaxononagermanate tetradecahydrate, (C₄H₁₂N)₄[Ge₉O₁₄(OH)₁₂]·14H₂O, was synthe-