

Dichlorido(*o*-phenylenediamine)palladium(II)

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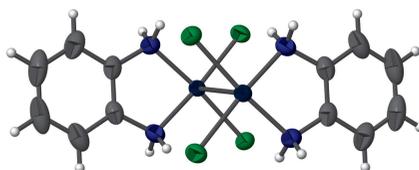
Keywords: crystal structure; columnar structure; infinite metal chain; palladium(II) complex; hydrogen bonding.

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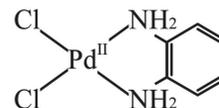
Structural data: full structural data are available from iucrdata.iucr.org

The Pd^{II} atom in the title compound, [PdCl₂{(C₆H₄)(NH₂)₂}], lies on a twofold rotation axis and has a square-planar coordination environment defined by two N atoms of an *o*-phenylenediamine ligand and two Cl[−] ions. In the crystal, the planar Pd complex molecules are stacked parallel to the *c* axis, resulting in a columnar structure. In the column, an infinite almost straight Pd chain is formed, suggesting weak metal–metal interactions. The crystal packing is stabilized by a three-dimensional N–H...Cl hydrogen-bonding network between the amino groups and the Cl ligands of adjacent molecules.

3D view



Chemical scheme



Structure description

The molecular structure of the title compound is displayed in Fig. 1. Its asymmetric unit comprises half of a [PdCl₂{(C₆H₄)(NH₂)₂}] molecule, the other half being completed by application of a twofold rotation operation. The Pd^{II} atom is coordinated by two N atoms of an *o*-phenylenediamine molecule and two Cl[−] ions in a slightly distorted square-planar configuration (Table 1). The r.m.s. deviation of the least-squares plane formed by atoms Pd1, N1, C1, C2 and C3 is 0.0176 Å. The Pd1–N1 [2.0297 (13) Å] and Pd1–Cl1 [2.3159 (4) Å] bond lengths are consistent with those reported for *cis*-[PdCl₂(NH₃)₂] [Pd–N = 1.99 (4) and 2.13 (4) Å, Pd–Cl = 2.26 (2) and 2.29 (2) Å; Kirik *et al.*, 1996], for [PdCl₂(en)] [en is ethylenediamine; Pd–N = 1.978 (12) Å, Pd–Cl = 2.309 (3) Å; Iball *et al.*, 1975] or for [PdCl₂(tn)] [tn is 1,3-diaminopropane; Pd–N = 2.036 (2) Å, Pd–Cl = 2.3296 (15) Å; Odoko & Okabe, 2006]. Bond lengths and angles of the *o*-phenylenediamine moiety (Table 1) are not significantly different from those of the bis(*o*-phenylenediamine)platinum(II) complex, [Pt(C₆H₈N₂)₂]Cl₂·2H₂O [N–C = 1.450 (2) Å, C–C = 1.365 (6)–1.389 (4) Å; Konno & Matsushita, 2006].

As shown in Fig. 2, the neutral planar molecules of the title compound stack parallel to the *c* axis, resulting in a columnar structure. The planar [PdCl₂{(C₆H₄)(NH₂)₂}] units are

Table 1

Selected geometric parameters (Å, °).

N1—C1	1.458 (2)	C2—C3	1.371 (3)
C1—C1 ⁱ	1.375 (3)	C3—C3 ⁱ	1.416 (8)
C1—C2	1.391 (2)		
N1—Pd1—N1 ⁱ	84.36 (8)	C1—N1—Pd1	110.22 (10)
N1—Pd1—Cl1	90.71 (4)	C1 ⁱ —C1—C2	120.62 (12)
Cl1 ⁱ —Pd1—Cl1	94.26 (2)	C1 ⁱ —C1—N1	117.58 (8)
N1—Pd1—Pd1 ⁱⁱ	95.75 (4)	C2—C1—N1	121.80 (16)
Cl1—Pd1—Pd1 ⁱⁱ	94.083 (12)	C3—C2—C1	119.3 (2)
N1—Pd1—Pd1 ⁱⁱⁱ	84.83 (4)	C2—C3—C3 ⁱ	120.13 (16)
Cl1—Pd1—Pd1 ⁱⁱⁱ	85.393 (12)		

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

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1A...Cl1 ^{iv}	0.90	2.54	3.3508 (15)	151
N1—H1B...Cl1 ^v	0.90	2.74	3.3860 (15)	129
N1—H1B...Cl1 ^{vi}	0.90	2.66	3.3278 (15)	132

Symmetry codes: (iv) $x, -y + 1, z + \frac{1}{2}$; (v) $x, -y + 1, z - \frac{1}{2}$; (vi) $-x, -y + 1, -z$.

arranged in parallel and the *o*-phenylenediamine moieties alternate with each other owing to the *c*-glide operation. In the column, an infinite almost straight [Pd...Pd...Pd = 179.232 (7)°] Pd chain is formed with a short interatomic distance [Pd...Pd = 3.3510 (6) Å], suggesting weak metal–metal interactions. The Pd...Pd distance of the title compound is slightly shorter than those of *cis*-[PdCl₂(NH₃)₂] [3.3886 (1) Å; Kirik *et al.*, 1996] or [PdCl₂(en)] [3.369 Å; Iball *et al.*, 1975], which have similar columnar structures.

The shorter intermolecular Pd...Pd distance of the title compound suggests that the columnar structure is stabilized by weak metal–metal interactions. The columnar structure of the title compound is further stabilized by intermolecular N—H...Cl hydrogen bonds between adjacent molecules in the column (Fig. 2 and Table 2). Intercolumnar hydrogen bonds also help to stabilize the crystal packing of the columns (Fig. 3 and Table 2).

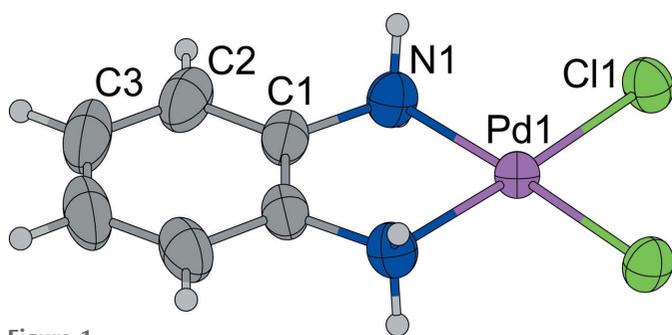


Figure 1

A view of the molecular structure of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. Non-labelled atoms are related to labelled atoms by $(-x + 1, y, -z + \frac{1}{2})$.

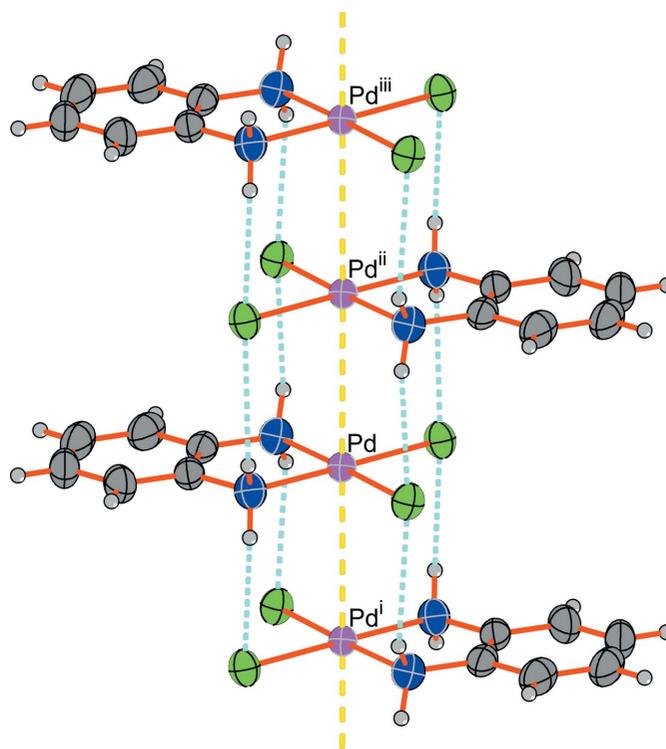


Figure 2

A view of the columnar structure of the title compound. Light-blue dashed lines represent hydrogen bonds between adjacent molecules in the column. Yellow dashed lines display the short contact between Pd atoms in the column. [Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x, y, z + 1$].

Synthesis and crystallization

To an aqueous HCl solution (1.0 M, 20 ml) of K₂[PdCl₄] (0.050 mmol, 16 mg) was slowly added an aqueous HCl solution (1.0 M, 20 ml) of *o*-phenylenediamine (0.050 mmol,

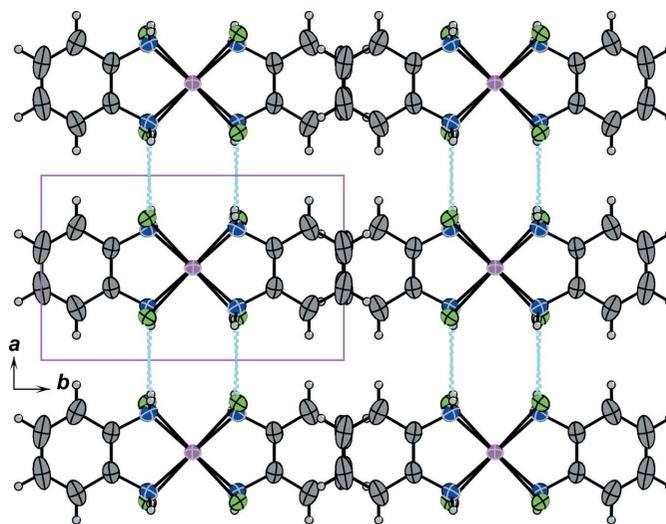


Figure 3

The crystal packing of the title compound, viewed along the *c* axis. Light-blue dashed lines represent the intercolumnar hydrogen bonds. Magenta solid lines indicate the unit cell.

Table 3
Experimental details.

Crystal data	
Chemical formula	[PdCl ₂ (C ₆ H ₈ N ₂)]
<i>M_r</i>	285.44
Crystal system, space group	Monoclinic, <i>P2/c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.0734 (8), 10.4076 (12), 6.7019 (12)
β (°)	116.683 (4)
<i>V</i> (Å ³)	440.83 (11)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.65
Crystal size (mm)	0.22 × 0.11 × 0.07
Data collection	
Diffraction	Rigaku R-AXIS RAPID imaging-plate
Absorption correction	Multi-scan (<i>ABSCOR</i> ; Higashi, 1995)
<i>T_{min}</i> , <i>T_{max}</i>	0.611, 0.824
No. of measured, independent and observed [<i>F</i> ² > 2σ(<i>F</i> ²)] reflections	11439, 1578, 1449
<i>R_{int}</i>	0.022
(sin θ/λ) _{max} (Å ⁻¹)	0.756
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.020, 0.053, 1.09
No. of reflections	1578
No. of parameters	52
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.07, -0.77

Computer programs: *RAPID-AUTO* (Rigaku, 1998), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 2017) and *pubCIF* (Westrip, 2010).

5 mg), and then the solution was sealed in a screw-cap vial and was kept at 323 K for 24 h in the dark. Pale-yellow needle-like crystals suitable for X-ray analysis were obtained (yield 28%).

Elemental analysis: found: C, 25.17; H, 2.93; N, 9.64%, calculated for C₆H₈Cl₂N₂Pd: C, 25.24; H, 2.82; N, 9.81%. Elemental analysis was carried out by Laboratory of Organic Elemental Analysis, Department of Chemistry, Graduate School of Science, The University of Tokyo.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The maximum and minimum electron density peaks are located 1.68 Å from atom Pd1 and 0.78 Å from atom Pd1, respectively.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x170144 [<https://doi.org/10.1107/S2414314617001444>]

Dichlorido(*o*-phenylenediamine)palladium(II)

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Dichlorido(*o*-phenylenediamine)palladium(II)*Crystal data*

[PdCl₂(C₆H₈N₂)]

M_r = 285.44

Monoclinic, *P2/c*

Hall symbol: -*P* 2yc

a = 7.0734 (8) Å

b = 10.4076 (12) Å

c = 6.7019 (12) Å

β = 116.683 (4)°

V = 440.83 (11) Å³

Z = 2

F(000) = 276

D_x = 2.150 Mg m⁻³

Mo *K*α radiation, λ = 0.71075 Å

Cell parameters from 6414 reflections

θ = 3.9–32.2°

μ = 2.65 mm⁻¹

T = 296 K

Needle, pale yellow

0.22 × 0.11 × 0.07 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate
diffractometer

Radiation source: X-ray sealed tube

Graphite monochromator

Detector resolution: 10.00 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

T_{min} = 0.611, *T_{max}* = 0.824

11439 measured reflections

1578 independent reflections

1449 reflections with $F^2 > 2\sigma(F^2)$

R_{int} = 0.022

θ_{\max} = 32.5°, θ_{\min} = 3.2°

h = -10→10

k = -15→15

l = -9→10

Refinement

Refinement on *F*²

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.020

$wR(F^2)$ = 0.053

S = 1.09

1578 reflections

52 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.032P)^2 + 0.0862P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.07 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.77 \text{ e \AA}^{-3}$

Extinction correction: SHELXL97 (Sheldrick,
2008), $F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.126 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

- 2.4031 (0.0035) x + 0.0000 (0.0000) y + 6.6544 (0.0013) z = 0.4621 (0.0016)

* 0.0000 (0.0000) Pd1 * -0.0263 (0.0008) C11 * 0.0315 (0.0013) N1 * 0.0022 (0.0014) C1 * -0.0016 (0.0015) C2 * 0.0034 (0.0028) C3 * 0.0263 (0.0008) C11_\$6 * -0.0315 (0.0013) N1_\$6 * -0.0022 (0.0014) C1_\$6 * 0.0016 (0.0015) C2_\$6 * -0.0034 (0.0028) C3_\$6

Rms deviation of fitted atoms = 0.0176

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Pd1	0.5000	0.498921 (11)	0.2500	0.03038 (8)
C11	0.23288 (6)	0.65031 (4)	0.14958 (7)	0.04182 (10)
N1	0.2865 (2)	0.35440 (13)	0.1776 (2)	0.0406 (3)
H1A	0.2218	0.3604	0.2662	0.049*
H1B	0.1874	0.3613	0.0349	0.049*
C1	0.3920 (2)	0.23028 (14)	0.2113 (2)	0.0412 (3)
C2	0.2807 (4)	0.11529 (17)	0.1706 (3)	0.0571 (4)
H2	0.1345	0.1157	0.1169	0.069*
C3	0.3889 (6)	0.00139 (14)	0.2104 (5)	0.0720 (10)
H3	0.3161	-0.0760	0.1853	0.086*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.02747 (9)	0.03112 (10)	0.02949 (10)	0.000	0.01007 (6)	0.000
C11	0.03435 (16)	0.03968 (17)	0.0480 (2)	0.00551 (12)	0.01543 (14)	0.00033 (14)
N1	0.0340 (6)	0.0396 (6)	0.0424 (6)	-0.0047 (5)	0.0120 (5)	-0.0018 (5)
C1	0.0559 (8)	0.0341 (6)	0.0324 (6)	-0.0043 (5)	0.0188 (6)	-0.0011 (5)
C2	0.0783 (12)	0.0449 (8)	0.0486 (9)	-0.0199 (8)	0.0288 (9)	-0.0076 (7)
C3	0.132 (3)	0.0362 (9)	0.0565 (15)	-0.0183 (8)	0.0496 (19)	-0.0068 (6)

Geometric parameters (\AA , $^\circ$)

Pd1—N1	2.0297 (13)	N1—H1B	0.9000
Pd1—N1 ⁱ	2.0297 (13)	C1—C1 ⁱ	1.375 (3)
Pd1—C11 ⁱ	2.3159 (4)	C1—C2	1.391 (2)
Pd1—C11	2.3159 (4)	C2—C3	1.371 (3)
Pd1—Pd1 ⁱⁱ	3.3510 (6)	C2—H2	0.9300
Pd1—Pd1 ⁱⁱⁱ	3.3510 (6)	C3—C3 ⁱ	1.416 (8)
N1—C1	1.458 (2)	C3—H3	0.9300
N1—H1A	0.9000		

N1—Pd1—N1 ⁱ	84.36 (8)	C1—N1—Pd1	110.22 (10)
N1—Pd1—Cl1 ⁱ	174.81 (4)	C1—N1—H1A	109.6
N1 ⁱ —Pd1—Cl1 ⁱ	90.71 (4)	Pd1—N1—H1A	109.6
N1—Pd1—Cl1	90.71 (4)	C1—N1—H1B	109.6
N1 ⁱ —Pd1—Cl1	174.81 (4)	Pd1—N1—H1B	109.6
Cl1 ⁱ —Pd1—Cl1	94.26 (2)	H1A—N1—H1B	108.1
N1—Pd1—Pd1 ⁱⁱ	95.75 (4)	C1 ⁱ —C1—C2	120.62 (12)
N1 ⁱ —Pd1—Pd1 ⁱⁱ	84.83 (4)	C1 ⁱ —C1—N1	117.58 (8)
Cl1 ⁱ —Pd1—Pd1 ⁱⁱ	85.393 (12)	C2—C1—N1	121.80 (16)
Cl1—Pd1—Pd1 ⁱⁱ	94.083 (12)	C3—C2—C1	119.3 (2)
N1—Pd1—Pd1 ⁱⁱⁱ	84.83 (4)	C3—C2—H2	120.4
N1 ⁱ —Pd1—Pd1 ⁱⁱⁱ	95.75 (4)	C1—C2—H2	120.4
Cl1 ⁱ —Pd1—Pd1 ⁱⁱⁱ	94.083 (12)	C2—C3—C3 ⁱ	120.13 (16)
Cl1—Pd1—Pd1 ⁱⁱⁱ	85.393 (12)	C2—C3—H3	119.9
Pd1 ⁱⁱ —Pd1—Pd1 ⁱⁱⁱ	179.232 (7)	C3 ⁱ —C3—H3	119.9
N1 ⁱ —Pd1—N1—C1	-0.57 (7)	Pd1—N1—C1—C1 ⁱ	1.8 (2)
Cl1 ⁱ —Pd1—N1—C1	-18.8 (5)	Pd1—N1—C1—C2	-179.16 (12)
Cl1—Pd1—N1—C1	177.81 (10)	C1 ⁱ —C1—C2—C3	0.6 (3)
Pd1 ⁱⁱ —Pd1—N1—C1	83.63 (10)	N1—C1—C2—C3	-178.4 (2)
Pd1 ⁱⁱⁱ —Pd1—N1—C1	-96.89 (10)	C1—C2—C3—C3 ⁱ	-0.7 (5)

Symmetry codes: (i) $-x+1, y, -z+1/2$; (ii) $-x+1, -y+1, -z$; (iii) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots Cl1 ^{iv}	0.90	2.54	3.3508 (15)	151
N1—H1B \cdots Cl1 ^v	0.90	2.74	3.3860 (15)	129
N1—H1B \cdots Cl1 ^{vi}	0.90	2.66	3.3278 (15)	132

Symmetry codes: (iv) $x, -y+1, z+1/2$; (v) $x, -y+1, z-1/2$; (vi) $-x, -y+1, -z$.