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(Di-2-pyridylamine- κ^2N^2, N^2')diiodido-palladium(II)

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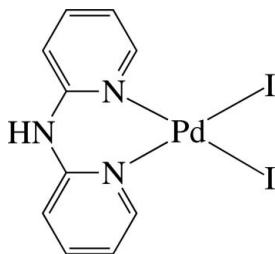
Received 28 July 2012; accepted 30 July 2012

Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(C-C) = 0.007$ Å; R factor = 0.028; wR factor = 0.065; data-to-parameter ratio = 21.7.

The Pd^{II} ion in the title complex, [PdI₂(C₁₀H₉N₃)], is four-coordinated in a distorted square-planar environment defined by the two pyridine N atoms of the chelating di-2-pyridylamine (dpa) ligand and two I⁻ anions. The dpa ligand is not planar, the dihedral angle between the pyridine rings being 51.2 (2)°. In the crystal, pairs of complex molecules are assembled through intermolecular N—H...I hydrogen bonds into dimeric species. The complexes are stacked in columns along the b axis and display several intermolecular π – π interactions between the pyridine rings, with a shortest ring centroid–centroid distance of 3.957 (3) Å.

Related literature

For the crystal structure of the related Pt^{II} complex [PtI₂(dpa)], see: Ha (2012).



Experimental

Crystal data

[PdI₂(C₁₀H₉N₃)]
 $M_r = 531.40$
Monoclinic, $P2_1/n$

$a = 8.2846$ (8) Å
 $b = 9.7782$ (9) Å
 $c = 16.5355$ (14) Å

$\beta = 102.344$ (2)°
 $V = 1308.5$ (2) Å³
 $Z = 4$
Mo $K\alpha$ radiation

$\mu = 6.11$ mm⁻¹
 $T = 200$ K
 $0.18 \times 0.14 \times 0.08$ mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.797$, $T_{\max} = 1.000$

9135 measured reflections
3152 independent reflections
2304 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.065$
 $S = 1.01$
3152 reflections

145 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.78$ e Å⁻³

Table 1
Selected bond lengths (Å).

Pd1—N1	2.068 (4)	Pd1—I1	2.5780 (5)
Pd1—N3	2.067 (4)	Pd1—I2	2.5957 (5)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2N\cdots I2^i$	0.92	2.80	3.656 (4)	155

Symmetry code: (i) $-x, -y + 2, -z$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0030747).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK5137).

References

- Bruker (2000). *SADABS*, *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Ha, K. (2012). *Acta Cryst.* **E68**, m479.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

supporting information

Acta Cryst. (2012). E68, m1144 [doi:10.1107/S1600536812033946]

(Di-2-pyridylamine- $\kappa^2N^2,N^{2'}$)diiodidopalladium(II)**Kwang Ha****S1. Comment**

The title complex, [PdI₂(dpa)] (dpa = di-2-pyridylamine, C₁₀H₉N₃), is isomorphous with the previously reported Pt^{II} complex [PtI₂(dpa)] (Ha, 2012).

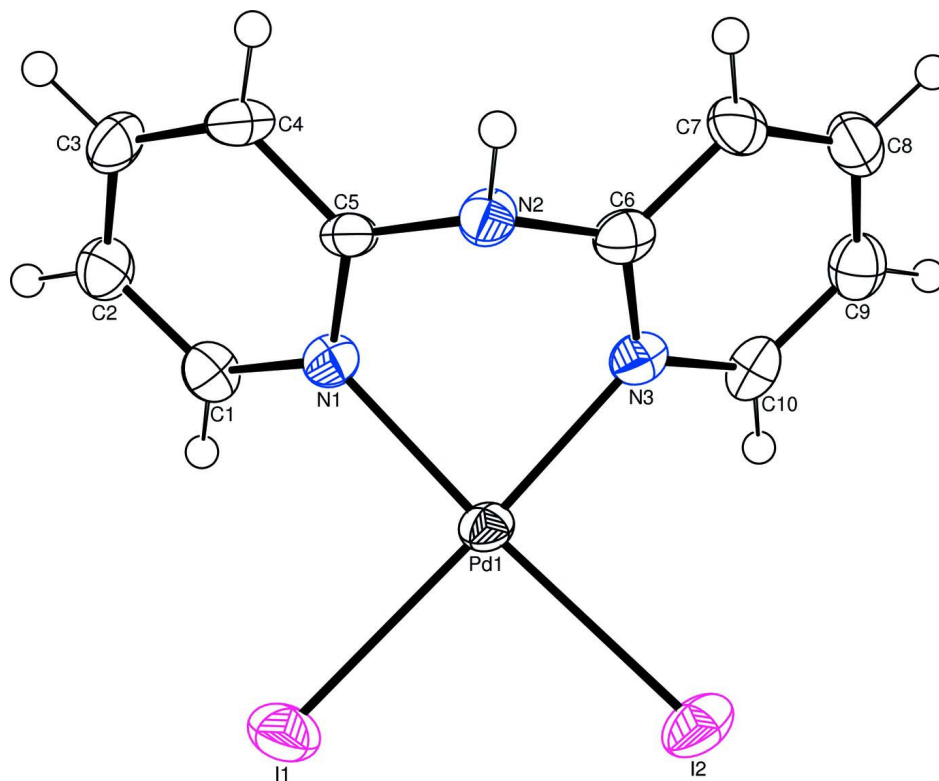
The Pd^{II} ion is four-coordinated in a distorted square-planar environment defined by the two pyridine N atoms of the chelating dpa ligand and two I⁻ anions (Fig. 1). In the crystal, the dpa ligand is not planar. The dihedral angle between the least-squares planes of the pyridine rings is 51.2 (2)°. The nearly planar pyridine rings [maximum deviation = 0.031 (3) Å] are considerably inclined to the least-squares plane of the PdI₂N₂ unit [maximum deviation = 0.081 (1) Å], making dihedral angles of 46.5 (1)° and 51.6 (1)°. The Pd—N and Pd—I bond lengths are nearly equivalent, respectively (Table 1). Pairs of complex molecules are assembled through intermolecular N—H⋯I hydrogen bonds into dimeric species. (Fig. 2 and Table 2). The complexes are stacked in columns along the *b* axis and display several intermolecular π - π interactions between the pyridine rings, with a shortest ring centroid-centroid distance of 3.957 (3) Å.

S2. Experimental

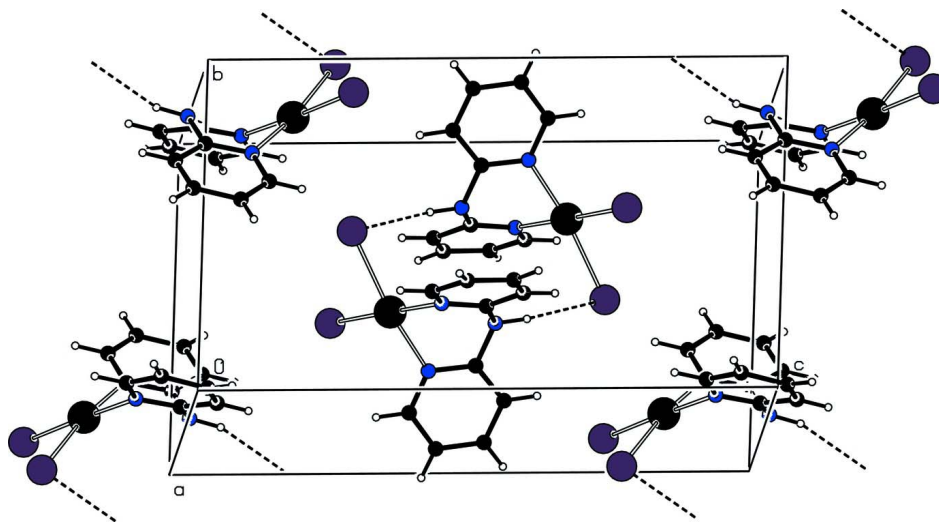
To a solution of Na₂PdCl₄ (0.1461 g, 0.497 mmol) and KI (0.7811 g, 4.705 mmol) in MeOH (30 ml) was added di-2-pyridylamine (0.0862 g, 0.519 mmol) followed by stirring at room temperature for 5 h. The formed precipitate was separated by filtration and washed with H₂O and acetone, and dried at 50 °C, to give a dark-orange powder (0.2322 g). Crystals suitable for X-ray analysis were obtained by slow evaporation from a CH₃NO₂ solution held at room temperature.

S3. Refinement

Carbon-bound H atoms were positioned geometrically and allowed to ride on their respective parent atoms: C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The nitrogen-bound H atom was located from a Fourier difference map and then allowed to ride on its parent atom in the final cycles of refinement with N—H = 0.92 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$. The highest peak (1.17 e Å⁻³) and the deepest hole (-0.78 e Å⁻³) in the difference Fourier map are located 1.99 Å and 0.82 Å, respectively, from the atoms H4 and I2. A number of reflections were omitted from the final cycles of refinement owing to poor agreement.

**Figure 1**

A structure detail of the title complex, with displacement ellipsoids drawn at the 50% probability level for non-H atoms.

**Figure 2**

A view of the unit-cell contents of the title complex. Intermolecular N—H...I hydrogen-bond interactions are drawn with dashed lines.

(Di-2-pyridylamine- κ^2N^2,N^2)diiiodidopalladium(II)*Crystal data*

[PdI₂(C₁₀H₉N₃)]
 $M_r = 531.40$
 Monoclinic, $P2_1/n$
 Hall symbol: -P 2yn
 $a = 8.2846$ (8) Å
 $b = 9.7782$ (9) Å
 $c = 16.5355$ (14) Å
 $\beta = 102.344$ (2)°
 $V = 1308.5$ (2) Å³
 $Z = 4$

$F(000) = 968$
 $D_x = 2.697$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 4274 reflections
 $\theta = 2.4$ – 28.3 °
 $\mu = 6.11$ mm⁻¹
 $T = 200$ K
 Block, red
 $0.18 \times 0.14 \times 0.08$ mm

Data collection

Bruker SMART 1000 CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2000)
 $T_{\min} = 0.797$, $T_{\max} = 1.000$

9135 measured reflections
 3152 independent reflections
 2304 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 28.3$ °, $\theta_{\text{min}} = 2.4$ °
 $h = -10 \rightarrow 11$
 $k = -13 \rightarrow 11$
 $l = -22 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.065$
 $S = 1.01$
 3152 reflections
 145 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
 $w = 1/[\sigma^2(F_o^2) + (0.0239P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.78$ e Å⁻³

Special details

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

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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Pd1	0.07287 (4)	0.84262 (4)	0.15317 (2)	0.02380 (10)
I1	-0.13829 (4)	0.86318 (4)	0.24664 (2)	0.03867 (11)
I2	0.24276 (4)	1.04417 (4)	0.230708 (19)	0.03719 (11)
N1	-0.0699 (5)	0.6997 (4)	0.0777 (2)	0.0248 (9)

N2	-0.0086 (5)	0.8273 (4)	-0.0325 (2)	0.0273 (9)
H2N	-0.0376	0.8473	-0.0881	0.041*
N3	0.2299 (5)	0.8278 (4)	0.0718 (2)	0.0269 (9)
C1	-0.1482 (6)	0.5937 (5)	0.1053 (3)	0.0288 (11)
H1	-0.1266	0.5751	0.1630	0.035*
C2	-0.2578 (6)	0.5121 (5)	0.0525 (3)	0.0340 (12)
H2	-0.3109	0.4381	0.0735	0.041*
C3	-0.2900 (6)	0.5389 (5)	-0.0318 (3)	0.0336 (12)
H3	-0.3679	0.4853	-0.0692	0.040*
C4	-0.2078 (6)	0.6437 (5)	-0.0604 (3)	0.0299 (11)
H4	-0.2266	0.6625	-0.1180	0.036*
C5	-0.0973 (5)	0.7219 (5)	-0.0047 (3)	0.0227 (10)
C6	0.1623 (6)	0.8357 (5)	-0.0085 (3)	0.0267 (11)
C7	0.2600 (6)	0.8499 (5)	-0.0670 (3)	0.0301 (12)
H7	0.2097	0.8615	-0.1238	0.036*
C8	0.4280 (6)	0.8469 (5)	-0.0424 (3)	0.0352 (13)
H8	0.4961	0.8574	-0.0815	0.042*
C9	0.4975 (6)	0.8284 (5)	0.0412 (3)	0.0343 (12)
H9	0.6138	0.8203	0.0597	0.041*
C10	0.3965 (6)	0.8219 (5)	0.0962 (3)	0.0293 (11)
H10	0.4446	0.8130	0.1535	0.035*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.0271 (2)	0.0261 (2)	0.01677 (18)	-0.00202 (16)	0.00160 (15)	0.00029 (15)
I1	0.0427 (2)	0.0497 (3)	0.02587 (19)	0.00181 (17)	0.01239 (16)	-0.00231 (16)
I2	0.0485 (2)	0.0335 (2)	0.02414 (18)	-0.00877 (16)	-0.00439 (15)	-0.00119 (14)
N1	0.027 (2)	0.023 (2)	0.023 (2)	0.0005 (17)	0.0030 (17)	0.0009 (17)
N2	0.030 (2)	0.031 (3)	0.018 (2)	-0.0062 (18)	0.0007 (17)	0.0053 (17)
N3	0.030 (2)	0.026 (2)	0.023 (2)	-0.0013 (18)	0.0020 (18)	-0.0016 (17)
C1	0.032 (3)	0.024 (3)	0.032 (3)	0.002 (2)	0.010 (2)	0.005 (2)
C2	0.036 (3)	0.028 (3)	0.039 (3)	-0.007 (2)	0.011 (2)	-0.002 (2)
C3	0.032 (3)	0.029 (3)	0.039 (3)	-0.009 (2)	0.006 (2)	-0.011 (2)
C4	0.042 (3)	0.028 (3)	0.019 (2)	-0.001 (2)	0.006 (2)	-0.004 (2)
C5	0.024 (2)	0.026 (3)	0.018 (2)	0.002 (2)	0.0038 (19)	-0.0044 (19)
C6	0.036 (3)	0.019 (3)	0.025 (3)	0.000 (2)	0.005 (2)	0.000 (2)
C7	0.043 (3)	0.023 (3)	0.028 (3)	-0.004 (2)	0.015 (2)	0.003 (2)
C8	0.040 (3)	0.029 (3)	0.043 (3)	-0.004 (2)	0.022 (3)	-0.003 (2)
C9	0.031 (3)	0.029 (3)	0.043 (3)	0.000 (2)	0.008 (2)	0.001 (2)
C10	0.024 (2)	0.022 (3)	0.038 (3)	0.000 (2)	-0.001 (2)	-0.001 (2)

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

Pd1—N1	2.068 (4)	C2—H2	0.9500
Pd1—N3	2.067 (4)	C3—C4	1.370 (7)
Pd1—I1	2.5780 (5)	C3—H3	0.9500
Pd1—I2	2.5957 (5)	C4—C5	1.382 (6)

N1—C5	1.351 (5)	C4—H4	0.9500
N1—C1	1.353 (6)	C6—C7	1.394 (6)
N2—C6	1.389 (6)	C7—C8	1.365 (7)
N2—C5	1.399 (6)	C7—H7	0.9500
N2—H2N	0.9200	C8—C9	1.390 (7)
N3—C6	1.329 (6)	C8—H8	0.9500
N3—C10	1.354 (6)	C9—C10	1.362 (7)
C1—C2	1.372 (7)	C9—H9	0.9500
C1—H1	0.9500	C10—H10	0.9500
C2—C3	1.388 (7)		
N3—Pd1—N1	85.31 (15)	C2—C3—H3	120.5
N3—Pd1—I1	176.37 (11)	C3—C4—C5	119.4 (4)
N1—Pd1—I1	92.33 (10)	C3—C4—H4	120.3
N3—Pd1—I2	91.40 (11)	C5—C4—H4	120.3
N1—Pd1—I2	172.21 (11)	N1—C5—C4	121.9 (4)
I1—Pd1—I2	90.598 (16)	N1—C5—N2	117.5 (4)
C5—N1—C1	118.3 (4)	C4—C5—N2	120.6 (4)
C5—N1—Pd1	116.8 (3)	N3—C6—N2	117.9 (4)
C1—N1—Pd1	124.6 (3)	N3—C6—C7	121.1 (4)
C6—N2—C5	121.6 (4)	N2—C6—C7	121.0 (4)
C6—N2—H2N	107.8	C8—C7—C6	119.8 (5)
C5—N2—H2N	116.2	C8—C7—H7	120.1
C6—N3—C10	119.0 (4)	C6—C7—H7	120.1
C6—N3—Pd1	117.2 (3)	C7—C8—C9	118.6 (5)
C10—N3—Pd1	123.6 (3)	C7—C8—H8	120.7
N1—C1—C2	122.1 (4)	C9—C8—H8	120.7
N1—C1—H1	118.9	C10—C9—C8	119.1 (5)
C2—C1—H1	118.9	C10—C9—H9	120.4
C1—C2—C3	119.2 (5)	C8—C9—H9	120.4
C1—C2—H2	120.4	N3—C10—C9	122.1 (5)
C3—C2—H2	120.4	N3—C10—H10	118.9
C4—C3—C2	119.1 (5)	C9—C10—H10	118.9
C4—C3—H3	120.5		
N3—Pd1—N1—C5	-46.2 (3)	C3—C4—C5—N1	-1.3 (7)
I1—Pd1—N1—C5	131.0 (3)	C3—C4—C5—N2	178.3 (4)
N3—Pd1—N1—C1	139.7 (4)	C6—N2—C5—N1	52.2 (6)
I1—Pd1—N1—C1	-43.0 (4)	C6—N2—C5—C4	-127.4 (5)
N1—Pd1—N3—C6	48.2 (4)	C10—N3—C6—N2	173.5 (4)
I2—Pd1—N3—C6	-124.7 (3)	Pd1—N3—C6—N2	-11.9 (6)
N1—Pd1—N3—C10	-137.4 (4)	C10—N3—C6—C7	-5.6 (7)
I2—Pd1—N3—C10	49.7 (4)	Pd1—N3—C6—C7	169.1 (4)
C5—N1—C1—C2	-2.3 (7)	C5—N2—C6—N3	-50.6 (6)
Pd1—N1—C1—C2	171.7 (4)	C5—N2—C6—C7	128.5 (5)
N1—C1—C2—C3	-0.1 (8)	N3—C6—C7—C8	4.2 (7)
C1—C2—C3—C4	1.9 (8)	N2—C6—C7—C8	-174.8 (5)
C2—C3—C4—C5	-1.2 (8)	C6—C7—C8—C9	0.6 (8)

C1—N1—C5—C4	3.0 (7)	C7—C8—C9—C10	-3.9 (8)
Pd1—N1—C5—C4	-171.4 (4)	C6—N3—C10—C9	2.2 (7)
C1—N1—C5—N2	-176.6 (4)	Pd1—N3—C10—C9	-172.1 (4)
Pd1—N1—C5—N2	9.0 (5)	C8—C9—C10—N3	2.6 (8)

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N2—H2N...I2 ⁱ	0.92	2.80	3.656 (4)	155

Symmetry code: (i) $-x, -y+2, -z$.