

Bis(di-2-pyridylamine- $\kappa^2N^2,N^{2'}$)-palladium(II) bis(thiocyanate)

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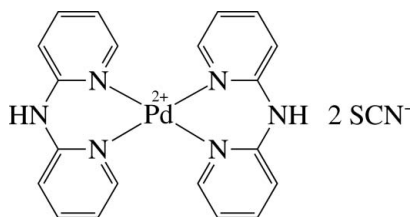
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.034; wR factor = 0.088; data-to-parameter ratio = 14.4.

The Pd^{II} atom of the title salt, [Pd(C₁₀H₉N₃)₂](NCS)₂, lies on a center of inversion and exists in a square-planar environment defined by the four pyridine N atoms derived from the two chelating di-2-pyridylamine (dpa) ligands. The chelate ring displays a boat conformation with a dihedral angle between the pyridine rings of 43.0 (1)°. Adjacent thiocyanate ions are linked to the cations by N—H···N hydrogen bonds.

Related literature

For the crystal structures of the related cationic Pd^{II} and Pt^{II} complexes, [Pd(dpa)₂](X)₂ ($X = Cl, PF_6$ or NO_3) and [Pt(dpa)₂](Br)₂·H₂O, see: Živković *et al.* (2007); Antonioli *et al.* (2008); Ha (2012a,b).



Experimental

Crystal data

[Pd(C ₁₀ H ₉ N ₃) ₂](NCS) ₂	$V = 1107.9$ (2) Å ³
$M_r = 564.96$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.7353$ (9) Å	$\mu = 1.06$ mm ⁻¹
$b = 17.478$ (2) Å	$T = 200$ K
$c = 8.3822$ (10) Å	$0.16 \times 0.09 \times 0.09$ mm
$\beta = 102.137$ (2)°	

Data collection

Bruker SMART 1000 CCD diffractometer	6810 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	2172 independent reflections
$T_{\min} = 0.876$, $T_{\max} = 1.000$	1552 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	151 parameters
$wR(F^2) = 0.088$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 1.10$ e Å ⁻³
2172 reflections	$\Delta\rho_{\text{min}} = -0.61$ e Å ⁻³

Table 1

Selected bond lengths (Å).

Pd1—N3	2.021 (3)	Pd1—N1	2.032 (3)
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Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2N\cdots N4^i$	0.92	1.94	2.846 (5)	170

 Symmetry code: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5285).

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supporting information

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Bis(di-2-pyridylamine- $\kappa^2N^2,N^{2'}$)palladium(II) bis(thiocyanate)**Kwang Ha****S1. Comment**

Crystal structures of the related cationic Pd^{II} and Pt^{II} complexes, such as [Pd(dpa)₂](X)₂ (dpa = di-2-pyridylamine, C₁₀H₉N₃; X = Cl, PF₆ or NO₃) (Živković *et al.*, 2007; Antonioli *et al.*, 2008; Ha, 2012*a*) and [Pt(dpa)₂]Br₂·H₂O (Ha, 2012*b*), have been investigated previously.

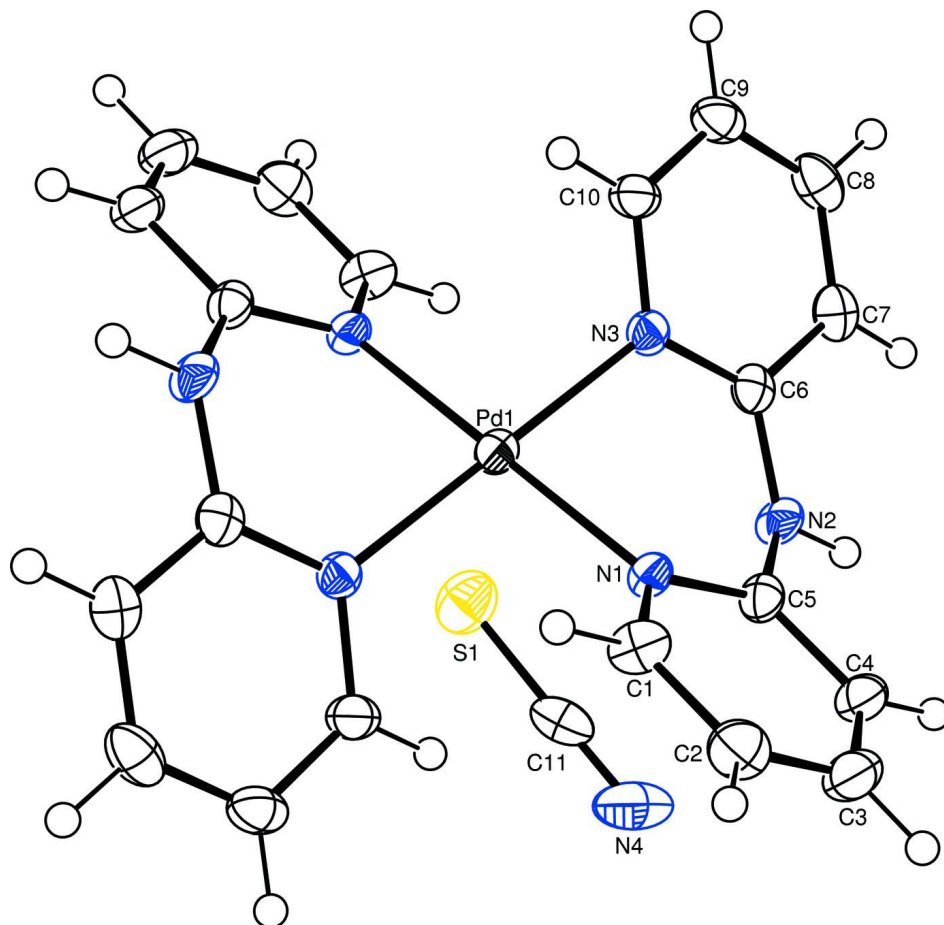
The asymmetric unit of the title compound, [Pd(dpa)₂](SCN)₂, contains one half of a cationic Pd^{II} complex and one SCN⁻ anion (Fig. 1). In the complex, the Pd^{II} ion is four-coordinated in a distorted square-planar environment by the four pyridine N atoms derived from the two chelating dpa ligands. The Pd^{II} ion is located on an inversion centre, and thus the PdN₄ unit is exactly planar. The dpa ligands display a boat conformation with a dihedral angle between the least-squares planes of the two pyridine rings of 43.0 (1)°. The nearly planar pyridine rings [maximum deviation = 0.039 (2) Å] are considerably inclined to the PdN₄ unit, making dihedral angles of 40.1 (2)° and 42.5 (1)°. The two Pd—N bond lengths are nearly equivalent [Pd—N: 2.021 (3) and 2.032 (3) Å] (Table 1). The SCN⁻ anion is almost linear (Table 1), and two anions are linked to the cationic complex by intermolecular N—H···N hydrogen bonds between the N atom of the anions and the N—H group of the cation (Fig. 2 and Table 2). The complex molecules are stacked into columns along the *a* axis. In the columns, several intermolecular π - π interactions between the pyridine rings are present, the shortest ring centroid-centroid distance being 3.436 (2) Å.

S2. Experimental

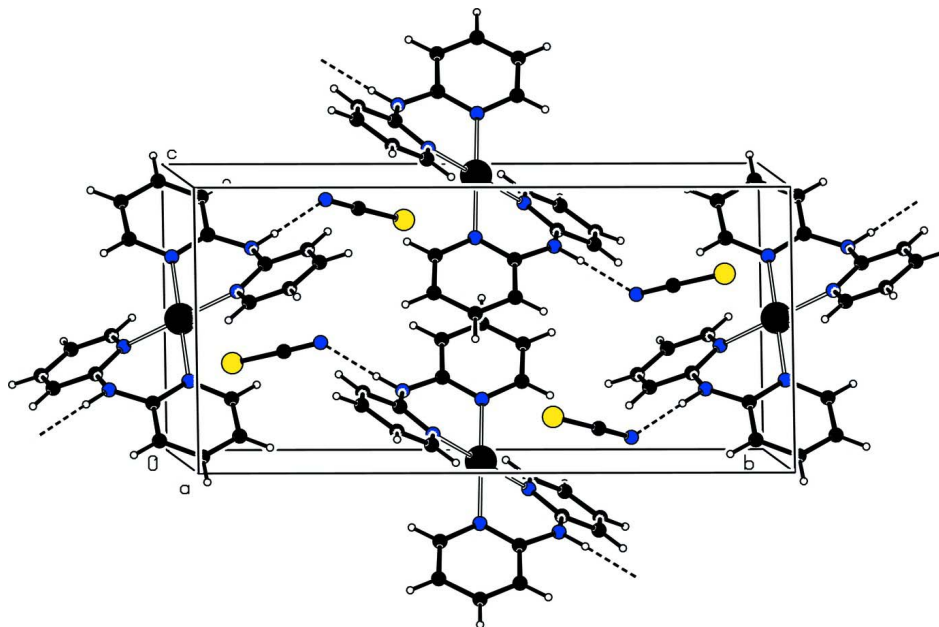
The title complex was obtained as a byproduct from the reaction of Na₂PdCl₄ (0.1462 g, 0.497 mmol) with KSCN (0.4688 g, 4.824 mmol) and di-2-pyridylamine (0.0877 g, 0.512 mmol) in MeOH (30 ml)/acetone (30 ml). After stirring of the reaction mixture for 24 h at room temperature, the formed precipitate was separated by filtration, washed with H₂O and acetone, to give the main product as a pale red powder (0.1562 g). A small amount of the yellow byproduct was obtained from the mixture of filtrate and washing solution. Yellow crystals were obtained by slow evaporation from a CH₃CN solution of the byproduct 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Nitrogen-bound H atom was located from the difference Fourier map 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 (1.10 e Å⁻³) and the deepest hole (-0.61 e Å⁻³) in the difference Fourier map are located 0.85 Å and 1.48 Å, respectively, from the atoms C1 and H1.

**Figure 1**

A structure detail of the title compound, with displacement ellipsoids drawn at the 50% probability level for non-H atoms. Unlabelled atoms are generated by the application of the inversion centre.

**Figure 2**

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

Bis(di-2-pyridylamine- κ^2N^2, N^2)palladium(II) bis(thiocyanate)

Crystal data

[Pd(C₁₀H₉N₃)₂](NCS)₂

$M_r = 564.96$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.7353$ (9) Å

$b = 17.478$ (2) Å

$c = 8.3822$ (10) Å

$\beta = 102.137$ (2)°

$V = 1107.9$ (2) Å³

$Z = 2$

$F(000) = 568$

$D_x = 1.694$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2711 reflections

$\theta = 2.3$ – 25.9 °

$\mu = 1.06$ mm⁻¹

$T = 200$ K

Block, yellow

$0.16 \times 0.09 \times 0.09$ 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)

$T_{\min} = 0.876$, $T_{\max} = 1.000$

6810 measured reflections

2172 independent reflections

1552 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$

$\theta_{\max} = 26.0$ °, $\theta_{\min} = 2.3$ °

$h = -9 \rightarrow 6$

$k = -21 \rightarrow 20$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.088$

$S = 1.07$

2172 reflections

151 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
 $w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 0.3195P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.10 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.61 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Pd1	0.5000	0.0000	0.5000	0.02072 (15)
N1	0.6536 (4)	0.08760 (17)	0.6087 (4)	0.0216 (7)
N2	0.4264 (4)	0.12533 (17)	0.7419 (4)	0.0240 (8)
H2N	0.3803	0.1669	0.7859	0.036*
N3	0.4123 (4)	-0.00805 (17)	0.7101 (4)	0.0199 (7)
C1	0.8191 (5)	0.0992 (2)	0.5843 (5)	0.0274 (9)
H1	0.8688	0.0616	0.5253	0.033*
C2	0.9181 (5)	0.1620 (2)	0.6399 (5)	0.0319 (10)
H2	1.0339	0.1681	0.6204	0.038*
C3	0.8453 (6)	0.2168 (2)	0.7258 (5)	0.0329 (11)
H3	0.9097	0.2619	0.7633	0.039*
C4	0.6808 (5)	0.2056 (2)	0.7562 (5)	0.0283 (10)
H4	0.6303	0.2427	0.8155	0.034*
C5	0.5868 (5)	0.1392 (2)	0.6995 (4)	0.0223 (9)
C6	0.3700 (5)	0.0553 (2)	0.7841 (4)	0.0207 (9)
C7	0.2737 (5)	0.0502 (2)	0.9079 (5)	0.0283 (10)
H7	0.2371	0.0954	0.9545	0.034*
C8	0.2331 (5)	-0.0194 (2)	0.9605 (5)	0.0303 (11)
H8	0.1663	-0.0234	1.0432	0.036*
C9	0.2900 (5)	-0.0854 (2)	0.8927 (5)	0.0293 (10)
H9	0.2673	-0.1346	0.9315	0.035*
C10	0.3784 (5)	-0.0773 (2)	0.7701 (5)	0.0247 (9)
H10	0.4184	-0.1220	0.7244	0.030*
S1	0.15609 (16)	0.10410 (7)	0.31675 (16)	0.0421 (3)
N4	0.3250 (5)	0.2438 (2)	0.4024 (5)	0.0511 (11)
C11	0.2561 (6)	0.1855 (3)	0.3654 (5)	0.0326 (10)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.0234 (3)	0.0179 (2)	0.0213 (2)	-0.00227 (18)	0.00572 (16)	-0.00236 (19)
N1	0.0248 (19)	0.0182 (18)	0.0214 (18)	-0.0019 (13)	0.0037 (14)	-0.0016 (14)
N2	0.0285 (19)	0.0178 (18)	0.0275 (19)	0.0043 (14)	0.0099 (15)	-0.0034 (14)
N3	0.0189 (17)	0.0213 (18)	0.0186 (16)	-0.0031 (13)	0.0023 (13)	-0.0019 (14)
C1	0.019 (2)	0.025 (2)	0.040 (3)	0.0017 (17)	0.0094 (18)	0.0015 (19)
C2	0.024 (2)	0.040 (3)	0.031 (2)	-0.0078 (19)	0.0037 (19)	0.003 (2)
C3	0.038 (3)	0.023 (2)	0.034 (3)	-0.0071 (19)	-0.001 (2)	0.0007 (19)
C4	0.035 (3)	0.019 (2)	0.029 (2)	-0.0023 (17)	0.0043 (19)	-0.0002 (18)
C5	0.024 (2)	0.021 (2)	0.019 (2)	0.0034 (16)	-0.0014 (16)	0.0011 (17)
C6	0.019 (2)	0.024 (2)	0.017 (2)	0.0009 (16)	0.0000 (16)	-0.0010 (17)
C7	0.025 (2)	0.034 (3)	0.026 (2)	0.0012 (18)	0.0031 (18)	-0.0058 (19)
C8	0.021 (2)	0.049 (3)	0.022 (2)	-0.0057 (18)	0.0057 (17)	0.0035 (19)
C9	0.028 (2)	0.030 (2)	0.026 (2)	-0.0100 (18)	-0.0002 (18)	0.0047 (19)
C10	0.025 (2)	0.024 (2)	0.024 (2)	-0.0045 (17)	0.0036 (18)	0.0033 (18)
S1	0.0391 (7)	0.0371 (7)	0.0512 (8)	0.0015 (5)	0.0122 (6)	-0.0057 (6)
N4	0.053 (3)	0.041 (3)	0.060 (3)	-0.011 (2)	0.013 (2)	0.018 (2)
C11	0.029 (3)	0.039 (3)	0.031 (3)	0.008 (2)	0.010 (2)	0.013 (2)

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

Pd1—N3	2.021 (3)	C3—C4	1.363 (5)
Pd1—N3 ⁱ	2.021 (3)	C3—H3	0.9500
Pd1—N1	2.032 (3)	C4—C5	1.399 (5)
Pd1—N1 ⁱ	2.032 (3)	C4—H4	0.9500
N1—C5	1.350 (5)	C6—C7	1.402 (5)
N1—C1	1.354 (5)	C7—C8	1.355 (6)
N2—C6	1.371 (5)	C7—H7	0.9500
N2—C5	1.382 (5)	C8—C9	1.396 (6)
N2—H2N	0.9200	C8—H8	0.9500
N3—C6	1.342 (5)	C9—C10	1.356 (5)
N3—C10	1.358 (5)	C9—H9	0.9500
C1—C2	1.364 (5)	C10—H10	0.9500
C1—H1	0.9500	S1—C11	1.630 (5)
C2—C3	1.387 (6)	N4—C11	1.161 (5)
C2—H2	0.9500		
N3—Pd1—N3 ⁱ	180.0	C2—C3—H3	120.2
N3—Pd1—N1	86.18 (12)	C3—C4—C5	119.6 (4)
N3 ⁱ —Pd1—N1	93.82 (12)	C3—C4—H4	120.2
N3—Pd1—N1 ⁱ	93.82 (12)	C5—C4—H4	120.2
N3 ⁱ —Pd1—N1 ⁱ	86.18 (12)	N1—C5—N2	119.9 (3)
N1—Pd1—N1 ⁱ	180.00 (11)	N1—C5—C4	120.8 (4)
C5—N1—C1	118.1 (3)	N2—C5—C4	119.2 (3)
C5—N1—Pd1	119.9 (3)	N3—C6—N2	119.7 (3)
C1—N1—Pd1	121.8 (3)	N3—C6—C7	120.6 (4)

C6—N2—C5	125.0 (3)	N2—C6—C7	119.6 (4)
C6—N2—H2N	115.5	C8—C7—C6	119.6 (4)
C5—N2—H2N	114.2	C8—C7—H7	120.2
C6—N3—C10	118.6 (3)	C6—C7—H7	120.2
C6—N3—Pd1	120.3 (2)	C7—C8—C9	119.6 (4)
C10—N3—Pd1	120.8 (3)	C7—C8—H8	120.2
N1—C1—C2	123.3 (4)	C9—C8—H8	120.2
N1—C1—H1	118.3	C10—C9—C8	118.4 (4)
C2—C1—H1	118.3	C10—C9—H9	120.8
C1—C2—C3	118.2 (4)	C8—C9—H9	120.8
C1—C2—H2	120.9	C9—C10—N3	122.7 (4)
C3—C2—H2	120.9	C9—C10—H10	118.6
C4—C3—C2	119.7 (4)	N3—C10—H10	118.6
C4—C3—H3	120.2	N4—C11—S1	178.6 (4)
N3—Pd1—N1—C5	-41.3 (3)	C6—N2—C5—N1	38.3 (5)
N3 ⁱ —Pd1—N1—C5	138.7 (3)	C6—N2—C5—C4	-139.6 (4)
N3—Pd1—N1—C1	143.2 (3)	C3—C4—C5—N1	-3.0 (6)
N3 ⁱ —Pd1—N1—C1	-36.8 (3)	C3—C4—C5—N2	174.9 (3)
N1—Pd1—N3—C6	44.1 (3)	C10—N3—C6—N2	170.2 (3)
N1 ⁱ —Pd1—N3—C6	-135.9 (3)	Pd1—N3—C6—N2	-16.2 (4)
N1—Pd1—N3—C10	-142.4 (3)	C10—N3—C6—C7	-7.7 (5)
N1 ⁱ —Pd1—N3—C10	37.6 (3)	Pd1—N3—C6—C7	165.9 (3)
C5—N1—C1—C2	-3.3 (6)	C5—N2—C6—N3	-35.6 (5)
Pd1—N1—C1—C2	172.3 (3)	C5—N2—C6—C7	142.3 (4)
N1—C1—C2—C3	0.0 (6)	N3—C6—C7—C8	4.4 (5)
C1—C2—C3—C4	1.9 (6)	N2—C6—C7—C8	-173.5 (3)
C2—C3—C4—C5	-0.4 (6)	C6—C7—C8—C9	1.0 (6)
C1—N1—C5—N2	-173.1 (3)	C7—C8—C9—C10	-2.8 (6)
Pd1—N1—C5—N2	11.2 (5)	C8—C9—C10—N3	-0.6 (6)
C1—N1—C5—C4	4.7 (5)	C6—N3—C10—C9	5.9 (5)
Pd1—N1—C5—C4	-170.9 (3)	Pd1—N3—C10—C9	-167.7 (3)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2N ⁱⁱ —N4 ⁱⁱ	0.92	1.94	2.846 (5)	170

Symmetry code: (ii) $x, -y+1/2, z+1/2$.