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Tetrakis(azido-κN)(di-2-pyridylamine-$\kappa^2N^2,N^{2'}$)platinum(IV)

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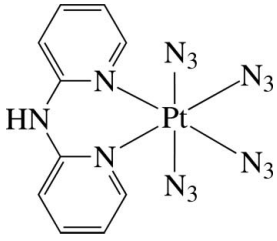
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.011 Å; R factor = 0.036; wR factor = 0.077; data-to-parameter ratio = 12.8.

In the title complex, $[Pt(N_3)_4(C_{10}H_9N_3)]$, the Pt^{IV} ion is six-coordinated in a slightly distorted octahedral environment by the two pyridine N atoms of the chelating di-2-pyridylamine (dpa) ligand and four N atoms from four azide anions. The dpa ligand is not planar, the dihedral angle between the pyridine rings being 20.0 (3)°. The azide ligands are slightly bent [N—N—N = 173.5 (8)–175.1 (8)°]. In the crystal, the complex molecules are connected by N—H···N hydrogen bonds, forming a chain along the b axis. An intermolecular π–π interaction between the chains is also present, the ring centroid–centroid distance being 3.713 (4) Å.

Related literature

For the crystal structure of the related chlorido Pt^{IV} complex $[PtCl_4(dpa)]$, see: Ha (2011).



Experimental

Crystal data

$[Pt(N_3)_4(C_{10}H_9N_3)]$
M_r = 534.41
Monoclinic, $P2_1/c$
a = 7.0057 (4) Å
b = 14.7685 (9) Å
c = 14.9633 (9) Å
β = 98.118 (1)°
V = 1532.64 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 9.19 mm^{-1}
T = 200 K
0.18 × 0.07 × 0.06 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.420, T_{max} = 0.576
9422 measured reflections
3004 independent reflections
2132 reflections with $I > 2\sigma(I)$
R_{int} = 0.063

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.077
S = 0.94
3004 reflections
235 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.86 e Å^{-3}

Table 1
Selected bond lengths (Å).

Pt1—N4	2.029 (7)	Pt1—N1	2.061 (6)
Pt1—N7	2.030 (7)	Pt1—N3	2.067 (6)
Pt1—N13	2.057 (6)	Pt1—N10	2.076 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*N*···N10^{i}	0.92	2.13	3.031 (9)	167
N2—H2*N*···N11^{i}	0.92	2.60	3.381 (9)	143

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

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*.

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: IS5092).

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Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2012). E**68**, m447 [https://doi.org/10.1107/S1600536812011178]

Tetrakis(azido-κN)(di-2-pyridylamine-$\kappa^2N^2,N^{2'}$)platinum(IV)

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S1. Comment

Crystal structure of the related chlorido Pt^{IV} complex, $[PtCl_4(dpa)]$ (dpa = di-2-pyridylamine, $C_{10}H_9N_3$), has been reported previously (Ha, 2011).

In the title complex, $[Pt(N_3)_4(dpa)]$, the Pt^{IV} ion is six-coordinated in a slightly distorted octahedral environment by the two pyridine N atoms of the chelating dpa ligand and four N atoms from four azide anions (Fig. 1). In the crystal structure, the dpa ligand is not planar. The dihedral angle between the least-squares planes of the pyridine rings is 20.0 (3)°. The Pt—N(dpa) and Pt—N(azide) bond lengths are nearly equivalent [Pt—N: 2.029 (7)–2.076 (6) Å] (Table 1). The azido ligands are slightly bent with the bond angles of <N4—N5—N6 = 174.1 (9)°, <N7—N8—N9 = 173.5 (8)°, <N10—N11—N12 = 174.3 (8)° and <N13—N14—N15 = 175.1 (8)°. But, the N—N bond lengths of the ligands are almost equal [N—N: 1.129 (9)–1.236 (9) Å]. The complex molecules are stacked in columns along the *a* axis and are connected by intermolecular N—H···N hydrogen bonds, forming chains along the *b* axis (Fig. 2 and Table 2). Along the *b* axis, successive chains stack in opposite directions. An intermolecular π–π interaction between the pyridine rings is also present, the ring centroid-centroid distance being 3.713 (4) Å.

S2. Experimental

To a solution of $Na_2PtCl_6.6H_2O$ (0.1684 g, 0.300 mmol) in MeOH (30 ml) were added NaN_3 (0.2129 g, 3.275 mmol) and di-2-pyridylamine (0.1046 g, 0.611 mmol), and the mixture was refluxed for 5 h. The formed precipitate was separated by filtration and washed with H_2O and MeOH, and dried at 50 °C, to give a yellow powder (0.0687 g). Crystals suitable for X-ray analysis were obtained by slow evaporation from an acetone solution.

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_{iso}(H) = 1.2U_{eq}(C)]. Nitrogen-bound H atom was located in a difference Fourier map and then allowed to ride on its parent atom in the final cycles of refinement with N—H = 0.92 Å and U_{iso}(H) = 1.5 U_{eq}(N). The highest peak (2.25 eÅ^{-3}) and the deepest hole (-0.86 eÅ^{-3}) in the difference Fourier map are located 1.25 Å and 1.09 Å from the atoms N4 and C10, respectively.

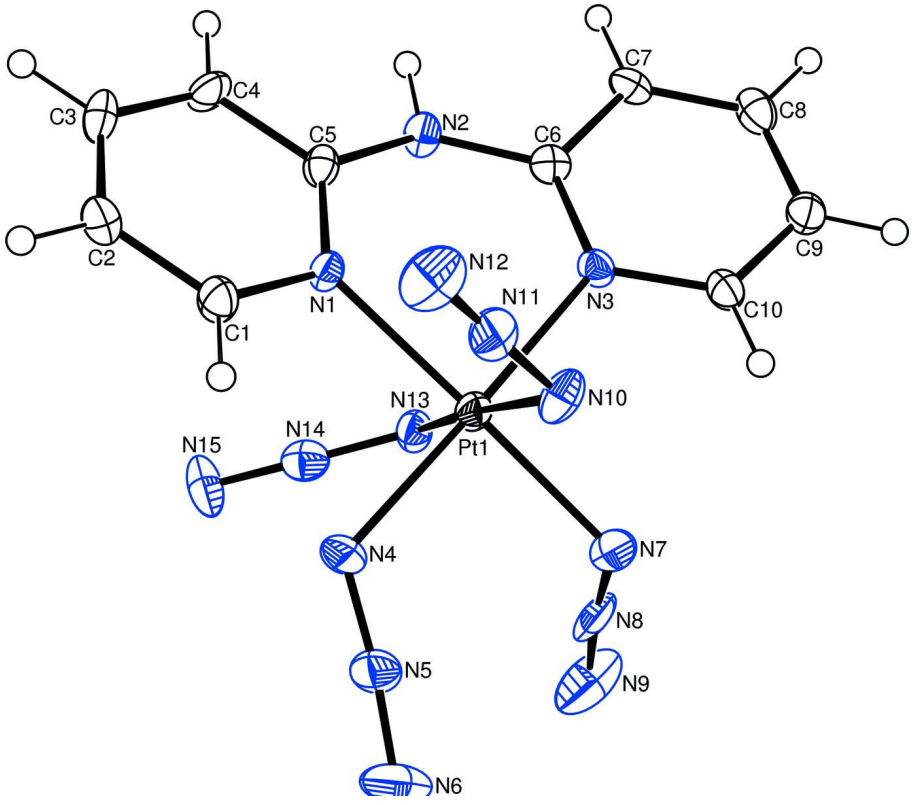

Figure 1

A structure detail of the title complex, with displacement ellipsoids drawn at the 40% probability level for non-H atoms.

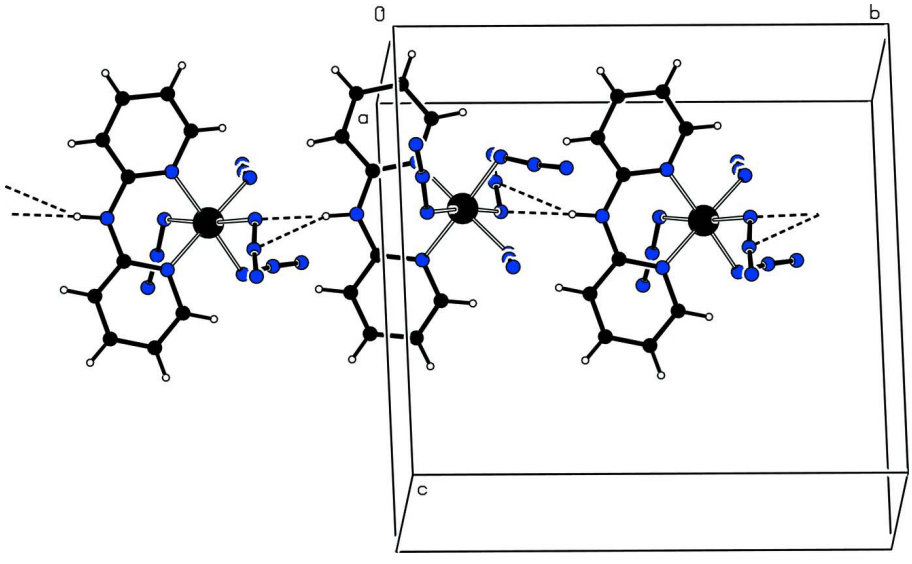

Figure 2

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

Tetrakis(azido-κN)(di-2-pyridylamine-$\kappa^2N^2,N^{2'}$)platinum(IV)

Crystal data

$[Pt(N_3)_4(C_{10}H_9N_3)]$
$M_r = 534.41$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.0057$ (4) Å
$b = 14.7685$ (9) Å
$c = 14.9633$ (9) Å
$\beta = 98.118$ (1)°
$V = 1532.64$ (16) Å^3
$Z = 4$
$F(000) = 1008$
$D_x = 2.316$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3131 reflections
$\theta = 2.8$–$25.9°$
$\mu = 9.19$ mm^{-1}
$T = 200$ K
Block, yellow
0.18 × 0.07 × 0.06 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)
$T_{min} = 0.420$, $T_{max} = 0.576$
9422 measured reflections
3004 independent reflections
2132 reflections with $I > 2\sigma(I)$
$R_{int} = 0.063$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.0°$
$h = -8 \rightarrow 8$
$k = -18 \rightarrow 17$
$l = -18 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.077$
$S = 0.94$
3004 reflections
235 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
$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.25$ e Å^{-3}
$\Delta\rho_{min} = -0.86$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Pt1	0.81972 (4)	0.15708 (2)	0.266198 (19)	0.02164 (11)
N1	0.8308 (9)	0.0693 (4)	0.1599 (4)	0.0190 (14)
N2	0.9443 (9)	−0.0523 (4)	0.2561 (4)	0.0229 (15)
H2N	0.9692	−0.1135	0.2562	0.034*

N3	1.0214 (9)	0.0791 (4)	0.3460 (4)	0.0200 (14)
C1	0.7670 (11)	0.0998 (5)	0.0743 (5)	0.0256 (19)
H1	0.7444	0.1627	0.0644	0.031*
C2	0.7353 (11)	0.0410 (6)	0.0027 (5)	0.0279 (19)
H2	0.6910	0.0628	−0.0563	0.033*
C3	0.7682 (12)	−0.0494 (6)	0.0174 (5)	0.032 (2)
H3	0.7438	−0.0911	−0.0313	0.038*
C4	0.8357 (12)	−0.0795 (5)	0.1014 (5)	0.0271 (19)
H4	0.8587	−0.1423	0.1115	0.033*
C5	0.8713 (11)	−0.0191 (5)	0.1725 (5)	0.0211 (17)
C6	1.0400 (11)	−0.0099 (5)	0.3320 (5)	0.0201 (17)
C7	1.1569 (11)	−0.0630 (5)	0.3944 (5)	0.0229 (18)
H7	1.1680	−0.1262	0.3847	0.028*
C8	1.2555 (11)	−0.0231 (6)	0.4697 (5)	0.0278 (19)
H8	1.3342	−0.0587	0.5132	0.033*
C9	1.2400 (11)	0.0690 (6)	0.4821 (5)	0.028 (2)
H9	1.3085	0.0978	0.5337	0.034*
C10	1.1251 (11)	0.1176 (6)	0.4191 (5)	0.0232 (18)
H10	1.1172	0.1813	0.4267	0.028*
N4	0.6200 (11)	0.2306 (5)	0.1855 (4)	0.0369 (19)
N5	0.5449 (10)	0.2945 (5)	0.2159 (4)	0.0302 (16)
N6	0.4660 (13)	0.3556 (6)	0.2374 (6)	0.063 (3)
N7	0.8045 (10)	0.2450 (5)	0.3692 (5)	0.0319 (17)
N8	0.6586 (12)	0.2401 (5)	0.4068 (4)	0.0353 (19)
N9	0.5310 (14)	0.2423 (6)	0.4464 (6)	0.059 (3)
N10	1.0370 (10)	0.2427 (4)	0.2364 (4)	0.0281 (17)
N11	1.0858 (10)	0.2358 (4)	0.1613 (5)	0.0306 (17)
N12	1.1381 (12)	0.2365 (5)	0.0918 (5)	0.041 (2)
N13	0.6117 (10)	0.0768 (4)	0.3100 (4)	0.0247 (15)
N14	0.4674 (10)	0.0646 (4)	0.2548 (4)	0.0281 (17)
N15	0.3276 (11)	0.0487 (5)	0.2071 (5)	0.043 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.02640 (18)	0.01631 (17)	0.02080 (17)	0.00107 (15)	−0.00153 (12)	−0.00106 (14)
N1	0.024 (4)	0.016 (4)	0.016 (4)	−0.002 (3)	0.001 (3)	−0.001 (3)
N2	0.035 (4)	0.013 (4)	0.019 (4)	−0.001 (3)	−0.003 (3)	0.005 (3)
N3	0.020 (4)	0.019 (4)	0.019 (4)	0.002 (3)	−0.001 (3)	0.003 (3)
C1	0.031 (5)	0.024 (5)	0.020 (5)	0.001 (4)	−0.001 (4)	0.002 (3)
C2	0.026 (5)	0.033 (5)	0.023 (5)	0.002 (4)	−0.003 (4)	0.001 (4)
C3	0.038 (5)	0.039 (6)	0.017 (4)	−0.001 (4)	−0.004 (4)	−0.007 (4)
C4	0.038 (5)	0.016 (5)	0.027 (5)	0.003 (4)	0.003 (4)	−0.006 (3)
C5	0.021 (4)	0.026 (5)	0.016 (4)	−0.004 (4)	0.004 (3)	−0.002 (3)
C6	0.018 (4)	0.020 (5)	0.024 (4)	−0.004 (3)	0.007 (3)	0.002 (3)
C7	0.018 (4)	0.021 (5)	0.030 (5)	0.003 (3)	0.003 (4)	0.005 (3)
C8	0.022 (4)	0.041 (6)	0.020 (4)	0.000 (4)	0.003 (4)	0.004 (4)
C9	0.020 (4)	0.038 (6)	0.027 (5)	0.000 (4)	0.004 (4)	−0.009 (4)

C10	0.021 (4)	0.024 (5)	0.023 (5)	0.002 (4)	−0.002 (4)	0.001 (3)
N4	0.044 (5)	0.033 (5)	0.029 (4)	0.022 (4)	−0.010 (4)	−0.002 (3)
N5	0.035 (4)	0.020 (4)	0.035 (4)	0.003 (4)	0.002 (3)	0.004 (3)
N6	0.070 (7)	0.049 (6)	0.067 (6)	0.038 (5)	0.000 (5)	−0.005 (5)
N7	0.029 (4)	0.029 (4)	0.037 (4)	0.002 (3)	0.004 (4)	−0.009 (3)
N8	0.059 (6)	0.024 (4)	0.022 (4)	−0.001 (4)	0.001 (4)	−0.013 (3)
N9	0.071 (7)	0.049 (6)	0.063 (6)	−0.022 (5)	0.038 (5)	−0.025 (4)
N10	0.039 (4)	0.018 (4)	0.027 (4)	−0.011 (3)	0.005 (3)	−0.005 (3)
N11	0.034 (4)	0.015 (4)	0.041 (5)	−0.006 (3)	−0.003 (4)	−0.002 (3)
N12	0.056 (6)	0.030 (5)	0.040 (5)	−0.007 (4)	0.014 (4)	0.001 (4)
N13	0.029 (4)	0.020 (4)	0.024 (4)	−0.002 (3)	−0.003 (3)	0.000 (3)
N14	0.031 (4)	0.028 (4)	0.027 (4)	0.003 (3)	0.011 (4)	0.003 (3)
N15	0.031 (5)	0.062 (6)	0.030 (5)	−0.005 (4)	−0.011 (4)	0.002 (4)

Geometric parameters (Å, º)

Pt1—N4	2.029 (7)	C4—C5	1.383 (10)
Pt1—N7	2.030 (7)	C4—H4	0.9500
Pt1—N13	2.057 (6)	C6—C7	1.393 (10)
Pt1—N1	2.061 (6)	C7—C8	1.369 (11)
Pt1—N3	2.067 (6)	C7—H7	0.9500
Pt1—N10	2.076 (6)	C8—C9	1.379 (11)
N1—C5	1.344 (9)	C8—H8	0.9500
N1—C1	1.372 (9)	C9—C10	1.356 (11)
N2—C5	1.373 (9)	C9—H9	0.9500
N2—C6	1.385 (9)	C10—H10	0.9500
N2—H2N	0.9200	N4—N5	1.200 (9)
N3—C6	1.340 (9)	N5—N6	1.129 (9)
N3—C10	1.350 (9)	N7—N8	1.236 (9)
C1—C2	1.373 (10)	N8—N9	1.141 (10)
C1—H1	0.9500	N10—N11	1.223 (9)
C2—C3	1.367 (11)	N11—N12	1.151 (9)
C2—H2	0.9500	N13—N14	1.225 (9)
C3—C4	1.353 (11)	N14—N15	1.152 (9)
C3—H3	0.9500		

N4—Pt1—N7	90.2 (3)	C4—C3—H3	120.1
N4—Pt1—N13	92.2 (3)	C2—C3—H3	120.1
N7—Pt1—N13	90.6 (3)	C3—C4—C5	120.3 (8)
N4—Pt1—N1	88.6 (3)	C3—C4—H4	119.9
N7—Pt1—N1	178.8 (3)	C5—C4—H4	119.9
N13—Pt1—N1	89.4 (2)	N1—C5—N2	121.2 (6)
N4—Pt1—N3	178.4 (3)	N1—C5—C4	120.5 (7)
N7—Pt1—N3	91.3 (3)	N2—C5—C4	118.3 (7)
N13—Pt1—N3	87.3 (2)	N3—C6—N2	121.7 (7)
N1—Pt1—N3	89.9 (2)	N3—C6—C7	120.5 (7)
N4—Pt1—N10	90.6 (3)	N2—C6—C7	117.8 (7)
N7—Pt1—N10	83.8 (3)	C8—C7—C6	119.4 (8)

N13—Pt1—N10	173.8 (2)	C8—C7—H7	120.3
N1—Pt1—N10	96.2 (2)	C6—C7—H7	120.3
N3—Pt1—N10	90.1 (3)	C7—C8—C9	119.7 (8)
C5—N1—C1	119.0 (6)	C7—C8—H8	120.2
C5—N1—Pt1	122.3 (5)	C9—C8—H8	120.2
C1—N1—Pt1	118.1 (5)	C10—C9—C8	118.6 (8)
C5—N2—C6	131.3 (6)	C10—C9—H9	120.7
C5—N2—H2N	113.5	C8—C9—H9	120.7
C6—N2—H2N	111.9	N3—C10—C9	122.6 (8)
C6—N3—C10	119.1 (6)	N3—C10—H10	118.7
C6—N3—Pt1	122.0 (5)	C9—C10—H10	118.7
C10—N3—Pt1	118.6 (5)	N5—N4—Pt1	119.8 (6)
N1—C1—C2	121.0 (8)	N6—N5—N4	174.1 (9)
N1—C1—H1	119.5	N8—N7—Pt1	116.3 (5)
C2—C1—H1	119.5	N9—N8—N7	173.5 (8)
C3—C2—C1	119.2 (8)	N11—N10—Pt1	117.1 (5)
C3—C2—H2	120.4	N12—N11—N10	174.3 (8)
C1—C2—H2	120.4	N14—N13—Pt1	115.1 (5)
C4—C3—C2	119.9 (8)	N15—N14—N13	175.1 (8)

N4—Pt1—N1—C5	−149.7 (6)	C10—N3—C6—N2	−176.9 (6)
N13—Pt1—N1—C5	−57.5 (6)	Pt1—N3—C6—N2	9.2 (9)
N3—Pt1—N1—C5	29.7 (6)	C10—N3—C6—C7	3.3 (10)
N10—Pt1—N1—C5	119.8 (6)	Pt1—N3—C6—C7	−170.6 (5)
N4—Pt1—N1—C1	20.5 (6)	C5—N2—C6—N3	23.2 (12)
N13—Pt1—N1—C1	112.7 (6)	C5—N2—C6—C7	−157.0 (7)
N3—Pt1—N1—C1	−160.1 (5)	N3—C6—C7—C8	−1.0 (11)
N10—Pt1—N1—C1	−70.0 (6)	N2—C6—C7—C8	179.2 (6)
N7—Pt1—N3—C6	152.3 (6)	C6—C7—C8—C9	−0.9 (11)
N13—Pt1—N3—C6	61.7 (6)	C7—C8—C9—C10	0.6 (11)
N1—Pt1—N3—C6	−27.7 (6)	C6—N3—C10—C9	−3.7 (11)
N10—Pt1—N3—C6	−123.9 (6)	Pt1—N3—C10—C9	170.4 (6)
N7—Pt1—N3—C10	−21.7 (6)	C8—C9—C10—N3	1.8 (12)
N13—Pt1—N3—C10	−112.2 (6)	N7—Pt1—N4—N5	−4.3 (7)
N1—Pt1—N3—C10	158.4 (5)	N13—Pt1—N4—N5	86.4 (7)
N10—Pt1—N3—C10	62.1 (5)	N1—Pt1—N4—N5	175.7 (7)
C5—N1—C1—C2	3.2 (11)	N10—Pt1—N4—N5	−88.1 (7)
Pt1—N1—C1—C2	−167.4 (6)	N4—Pt1—N7—N8	74.2 (6)
N1—C1—C2—C3	0.0 (12)	N13—Pt1—N7—N8	−18.0 (6)
C1—C2—C3—C4	−1.6 (12)	N3—Pt1—N7—N8	−105.3 (6)
C2—C3—C4—C5	0.1 (12)	N10—Pt1—N7—N8	164.8 (6)
C1—N1—C5—N2	176.9 (7)	N4—Pt1—N10—N11	−73.8 (6)
Pt1—N1—C5—N2	−13.0 (9)	N7—Pt1—N10—N11	−164.0 (6)
C1—N1—C5—C4	−4.7 (10)	N1—Pt1—N10—N11	14.8 (6)
Pt1—N1—C5—C4	165.4 (6)	N3—Pt1—N10—N11	104.7 (6)
C6—N2—C5—N1	−21.0 (12)	N4—Pt1—N13—N14	31.4 (6)
C6—N2—C5—C4	160.5 (7)	N7—Pt1—N13—N14	121.6 (6)
C3—C4—C5—N1	3.2 (12)	N1—Pt1—N13—N14	−57.2 (6)

C3—C4—C5—N2	−178.4 (7)	N3—Pt1—N13—N14	−147.1 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*N*···N10^{i}	0.92	2.13	3.031 (9)	167
N2—H2*N*···N11^{i}	0.92	2.60	3.381 (9)	143

Symmetry code: (i) −*x*+2, *y*−1/2, −*z*+1/2.