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trans-Bis[2-(aminomethyl)pyridine-κ^2N,N']-platinum(II)] bis(hexafluoridophosphate)

Hajime Nishimura[a] and Nobuyuki Matsushita[b]*

[a]Department of Chemistry, Graduate School of Arts and Sciences, The University of Tokyo, Komaba 3-8-1, Meguro-ku, Tokyo, 153-8902, Japan, and [b]Department of Chemistry & Research Center for Smart Molecules, Rikkyo University, Nishi-Ikebukuro 3-34-1, Toshima-ku, Tokyo, 171-8501, Japan. *Correspondence e-mail: cnmatsu@rikkyo.ac.jp

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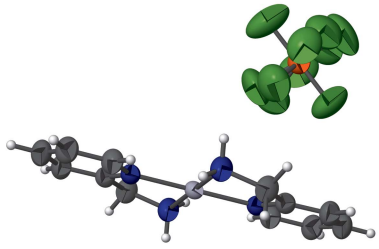
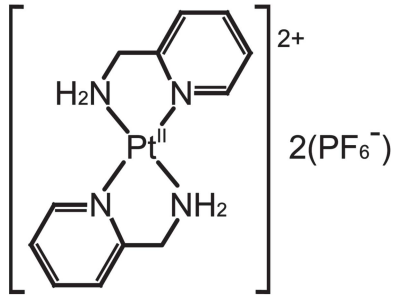
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $[Pt(amp)_2](PF_6)_2$ [amp = 2-(aminomethyl)pyridine, $C_6H_8N_2$], crystallizes in the space group $P\overline{1}$ with a half of one $[Pt(amp)_2]^{2+}$ cation and one hexafluoridophosphate ion in the asymmetric unit. The Pt^{II} atom lies on an inversion centre and has a square-planar coordination sphere defined by two amino groups and two pyridine moieties of two 2-(aminomethyl)pyridine chelate ligands. The crystal structure of the title salt is composed of alternating rows of $[Pt(amp)_2]^{2+}$ cations and PF_6^- anions. The crystal packing is stabilized by N—H···F hydrogen bonds between the amino groups and the hexafluoridophosphate anions. The PF_6 anion is disordered over two sets of sites with an occupancy ratio of 0.744 (6):0.256 (6).

3D view



Chemical scheme



Structure description

trans-Bis[(2-(aminomethyl)pyridine-κ^2N,N')platinum(II)] bis(hexafluoridophosphate), $[Pt(amp)_2](PF_6)_2$ (amp = 2-(aminomethyl)pyridine), was prepared in order to elucidate the single-crystalline photochromism of $[Pt(amp)_2]$ salts. One of them, $[Pt(amp)_2]Cl_2{\cdot}H_2O$, has been reported as the first single-crystalline photochromic metal-complex salt (Nishimura & Matsushita, 2002). The title salt is the hexafluoridophosphate of *trans*-bis(2-(aminomethyl)pyridine-κ^2N,N')platinum(II) complex and does not display single-crystalline photochromic behavior under the same photo-irradiation conditions as $[Pt(amp)_2]Cl_2{\cdot}H_2O$, *i.e.* under the visible light of a tungsten lamp.

The molecular components of the title salt are displayed in Fig. 1. The asymmetric unit comprises half of one $[Pt(amp)_2]^{2+}$ cation and one hexafluoridophosphate anion. The Pt^{II} atom of $[Pt(amp)_2]^{2+}$ cation lies on an inversion centre and is coordinated by four N atoms of two amino groups and two pyridine moieties of the two 2-(aminomethyl)-pyridine chelate ligands in a *trans* configuration. The methylpyridine part of the

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···F2^{i}	0.89	2.40	3.080 (8)	133
N1—H1A···F4	0.89	2.24	2.971 (9)	139
N1—H1B···F6^{ii}	0.89	2.46	3.233 (10)	146
N1—H1A···F2B	0.89	2.22	2.98 (2)	143
N1—H1B···F5B^{ii}	0.89	2.05	2.84 (2)	148

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

2-(aminomethyl)pyridine ligand forms a planar configuration with the r.m.s. deviation of the least-squares plane formed by atoms C1–C6 and N2 being 0.0066 Å. The dihedral angle between the methylpyridine plane and the [PtN_4] coordination plane is 10.4 (2)°. The $[Pt(amp)_2]^{2+}$ cation does not adapt a co-planar configuration and is slightly distorted.

The Pt—N_{amine} [2.044 (3) Å] and Pt—$N_{pyridine}$ [2.013 (3) Å] bond lengths, and N—Pt—N [80.67 (12)°] bond angle in the chelate ring are consistent with those values reported for $[Pt(amp)_2]Cl_2·H_2O$ [Pt—N_{amine} = 2.043 (5), 2.048 (4) Å, Pt—$N_{pyridine}$ = 2.011 (4), 2.018 (4) Å, N—Pt—N = 81.06 (17), 81.33 (18)°; Nishimura & Matsushita, 2002].

The crystal structure of the title salt is composed of alternating rows of $[Pt(amp)_2]^{2+}$ cations and PF_6^- anions (Fig. 2). The arrangement of the cations and anions in the crystal packing of the title salt is very similar to that of the chloride monohydrate, $[Pt(amp)_2]Cl_2·H_2O$ (Nishimura & Matsushita, 2002). The N—H···F hydrogen bonds between the amino groups of $[Pt(amp)_2]^{2+}$ cations and the fluorine atoms of the PF_6^- anions stabilize the crystal packing of the title salt (Fig. 3 and Table 1).

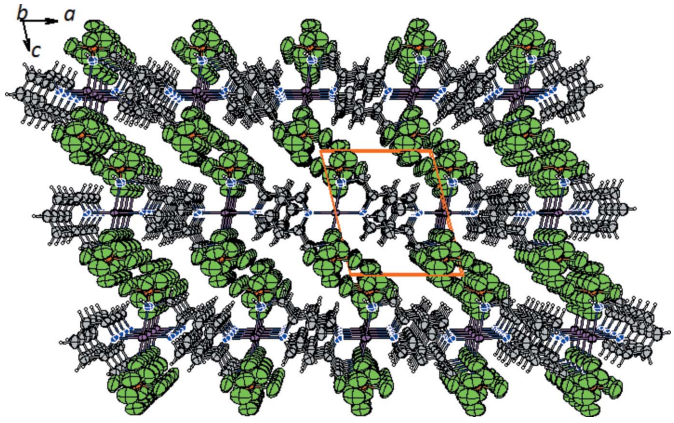


Figure 2
The crystal packing of the title salt, viewed along the b axis. Orange solid lines indicate the unit cell.

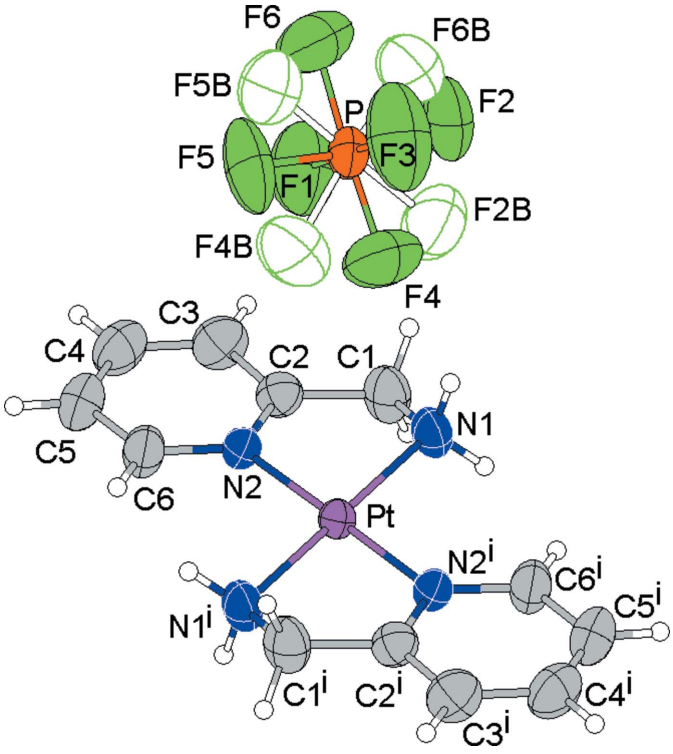


Figure 1
The structures of the molecular components of the title salt, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. The green hollow F ellipsoids and the black hollow lines between P and F atoms represent the minor disorder component of the PF_6 anion [symmetry code: (i) $-x, 1-y, 1-z$].

Synthesis and crystallization

To a solution of $[Pt(amp)_2]Cl_2·H_2O$ (216 mg) dissolved in water (60 ml) was slowly added a solution of NH_4PF_6 (150 mg)

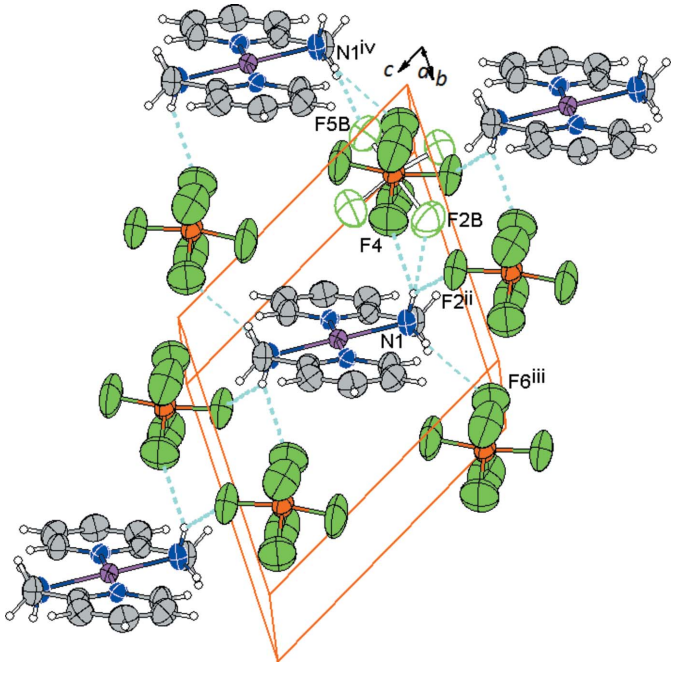


Figure 3
Hydrogen bonds between the amino groups of the 2-(aminomethyl)pyridine ligands of the platinum complex molecules and fluorine atoms of the hexafluoridophosphate anions, represented by light-blue dashed lines. Orange solid lines indicate the unit cell. The minor disordered parts of the PF_6 anions were omitted for clarify except for one site [symmetry codes: (ii) $-x, 1-y, -z$; (iii) $x, 1+y, z$; (iv) $x, -1+y, z$].

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Pt(C_6H_8N_2)_2](PF_6)_2$
M_r	701.32
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	7.3011 (3), 8.3055 (3), 9.2821 (3)
α, β, γ (°)	64.226 (4), 75.212 (5), 84.540 (6)
V (Å^3)	489.99 (4)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	7.44
Crystal size (mm)	0.41 × 0.29 × 0.12
Data collection	
Diffractometer	Rigaku R-AXIS RAPID imaging-plate
Absorption correction	Integration (*NUMABS*; Rigaku, 1999)
T_{min}, T_{max}	0.206, 0.508
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12933, 3484, 3484
R_{int}	0.059
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.757
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.067, 1.05
No. of reflections	3484
No. of parameters	180
No. of restraints	48
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.92, −1.55

Computer programs: *PROCESS-AUTO* (Rigaku, 1998), *RAPID-AUTO* (Rigaku, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 2018) and *publCIF* (Westrip, 2010).

dissolved in water (40 ml). A short time later, slightly yellowish colourless needle-like crystals precipitated. The crystals were collected by filtration and air-dried. Yield: 158 mg (52%). Elemental analysis: found: C, 20.51; H, 2.28; N, 7.99%, calculated for $C_{12}H_{16}F_{12}N_4P_2Pt$: C, 20.55; H, 2.30; N, 7.99%. The elemental analysis was carried out by the Laboratory of Organic Elemental Analysis, Department of Chemistry, Graduate School of Science, The University of Tokyo. A single-crystal suitable for X-ray crystallography was chosen from the crystals collected.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The structure was refined as a two-component disordered structure of the PF_6 anion, the minor fluorine atoms of which were based on the positions of residual peaks. The occupancy ratio of 0.744 (6):0.256 (6) for the two orientations was obtained by refinement with a free variable. The maximum and minimum electron density peaks are located 0.76 and 0.68 Å, respectively, from the Pt atom.

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full crystallographic data

IUCrData (2018). **3**, x181236 [https://doi.org/10.1107/S2414314618012361]

trans-Bis[2-(aminomethyl)pyridine-κ^2N,N']platinum(II) bis(hexafluoridophosphate)

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Crystal data

$[Pt(C_6H_8N_2)_2](PF_6)_2$
M_r = 701.32
Triclinic, $P\overline{1}$
a = 7.3011 (3) Å
b = 8.3055 (3) Å
c = 9.2821 (3) Å
α = 64.226 (4)°
β = 75.212 (5)°
γ = 84.540 (6)°
V = 489.99 (4) Å^3
Z = 1
$F(000)$ = 332
D_x = 2.377 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 13361 reflections
θ = 2.5–32.6°
μ = 7.44 mm^{-1}
T = 296 K
Needle, colourless
0.41 × 0.29 × 0.12 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: integration (NUMABS; Rigaku, 1999)
T_{min} = 0.206, T_{max} = 0.508
12933 measured reflections
3484 independent reflections
3484 reflections with $I > 2\sigma(I)$
R_{int} = 0.059
θ_{max} = 32.6°, θ_{min} = 2.5°
h = −11→10
k = −12→12
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.067
S = 1.05
3484 reflections
180 parameters
48 restraints
Primary atom site location: heavy-atom method
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.92 e Å^{-3}
$\Delta\rho_{min}$ = −1.55 e Å^{-3}
Extinction correction: (SHELXL2014; Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.038 (3)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Pt	0.0000	0.5000	0.5000	0.03263 (7)	
N1	0.1202 (5)	0.6204 (5)	0.2528 (4)	0.0488 (7)	
H1A	0.0691	0.5740	0.2015	0.059*	
H1B	0.0954	0.7367	0.2141	0.059*	
N2	0.2490 (4)	0.3730 (4)	0.4965 (3)	0.0375 (5)	
C1	0.3271 (6)	0.5969 (6)	0.2169 (5)	0.0525 (8)	
H1C	0.3901	0.7028	0.2015	0.063*	
H1D	0.3682	0.5818	0.1155	0.063*	
C2	0.3812 (5)	0.4376 (5)	0.3542 (4)	0.0416 (6)	
C3	0.5584 (6)	0.3611 (7)	0.3380 (6)	0.0555 (9)	
H3	0.6484	0.4074	0.2382	0.067*	
C4	0.5998 (6)	0.2157 (7)	0.4716 (7)	0.0608 (10)	
H4	0.7185	0.1640	0.4638	0.073*	
C5	0.4624 (7)	0.1487 (6)	0.6161 (7)	0.0582 (10)	
H5	0.4870	0.0500	0.7072	0.070*	
C6	0.2876 (6)	0.2284 (5)	0.6259 (5)	0.0489 (7)	
H6	0.1946	0.1814	0.7237	0.059*	
P	0.13393 (16)	0.17834 (14)	0.13320 (13)	0.04854 (19)	
F1	0.3338 (7)	0.2085 (8)	0.1472 (8)	0.1137 (18)	
F3	−0.0705 (8)	0.1541 (9)	0.1136 (8)	0.132 (3)	
F2	0.1733 (10)	0.3286 (9)	−0.0505 (7)	0.096 (2)	0.744 (6)
F4	0.0336 (12)	0.3072 (11)	0.2050 (11)	0.115 (2)	0.744 (6)
F5	0.0933 (13)	0.0057 (10)	0.2996 (9)	0.118 (3)	0.744 (6)
F6	0.2280 (17)	0.0422 (11)	0.0581 (12)	0.135 (3)	0.744 (6)
F2B	0.131 (3)	0.399 (3)	0.070 (3)	0.107 (4)	0.256 (6)
F4B	0.076 (4)	0.167 (4)	0.313 (3)	0.115 (4)	0.256 (6)
F5B	0.161 (4)	−0.014 (3)	0.182 (4)	0.114 (4)	0.256 (6)
F6B	0.199 (4)	0.222 (4)	−0.047 (3)	0.110 (4)	0.256 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt	0.03905 (9)	0.02788 (9)	0.02934 (8)	0.00042 (5)	−0.00823 (5)	−0.01065 (5)
N1	0.0496 (14)	0.0518 (17)	0.0335 (12)	0.0053 (13)	−0.0089 (11)	−0.0093 (11)
N2	0.0410 (11)	0.0324 (11)	0.0383 (12)	0.0031 (9)	−0.0117 (10)	−0.0137 (9)
C1	0.0476 (16)	0.053 (2)	0.0392 (16)	−0.0015 (15)	−0.0034 (13)	−0.0073 (14)
C2	0.0415 (13)	0.0400 (15)	0.0424 (15)	−0.0001 (11)	−0.0075 (12)	−0.0178 (12)
C3	0.0430 (16)	0.060 (2)	0.061 (2)	0.0034 (16)	−0.0062 (16)	−0.028 (2)
C4	0.0504 (18)	0.059 (2)	0.077 (3)	0.0162 (17)	−0.019 (2)	−0.033 (2)

C5	0.058 (2)	0.046 (2)	0.066 (3)	0.0142 (17)	−0.0238 (19)	−0.0179 (18)
C6	0.0517 (16)	0.0405 (16)	0.0461 (17)	0.0085 (14)	−0.0153 (14)	−0.0104 (13)
P	0.0556 (5)	0.0396 (4)	0.0434 (4)	0.0051 (4)	−0.0151 (4)	−0.0104 (3)
F1	0.081 (2)	0.114 (4)	0.137 (5)	−0.003 (2)	−0.057 (3)	−0.028 (3)
F3	0.102 (3)	0.126 (5)	0.136 (5)	−0.032 (3)	−0.067 (3)	0.001 (3)
F2	0.103 (4)	0.078 (3)	0.063 (3)	−0.004 (3)	−0.022 (3)	0.011 (3)
F4	0.131 (5)	0.106 (4)	0.117 (5)	0.030 (4)	−0.012 (4)	−0.072 (4)
F5	0.143 (5)	0.090 (4)	0.071 (3)	−0.021 (4)	−0.043 (3)	0.024 (3)
F6	0.197 (7)	0.089 (4)	0.118 (5)	0.038 (4)	−0.019 (5)	−0.060 (4)
F2B	0.125 (7)	0.072 (6)	0.108 (7)	0.012 (6)	−0.025 (6)	−0.027 (6)
F4B	0.146 (7)	0.117 (7)	0.074 (6)	0.001 (7)	−0.018 (6)	−0.038 (6)
F5B	0.165 (8)	0.067 (6)	0.099 (7)	0.009 (6)	−0.038 (7)	−0.022 (6)
F6B	0.154 (8)	0.099 (7)	0.071 (6)	0.005 (7)	−0.027 (6)	−0.032 (6)

Geometric parameters (Å, º)

Pt—N2^{i}	2.013 (3)	C4—C5	1.373 (8)
Pt—N2	2.013 (3)	C4—H4	0.9300
Pt—N1	2.044 (3)	C5—C6	1.382 (6)
Pt—N1^{i}	2.044 (3)	C5—H5	0.9300
N1—C1	1.475 (5)	C6—H6	0.9300
N1—H1A	0.8900	P—F5B	1.46 (2)
N1—H1B	0.8900	P—F6B	1.50 (2)
N2—C2	1.340 (4)	P—F4	1.532 (6)
N2—C6	1.349 (4)	P—F1	1.551 (4)
C1—C2	1.491 (5)	P—F5	1.565 (5)
C1—H1C	0.9700	P—F4B	1.58 (2)
C1—H1D	0.9700	P—F2	1.586 (5)
C2—C3	1.388 (5)	P—F3	1.590 (5)
C3—C4	1.381 (7)	P—F6	1.590 (7)
C3—H3	0.9300	P—F2B	1.66 (2)
N2^{i}—Pt—N2	180.0	N2—C6—C5	121.3 (4)
N2^{i}—Pt—N1	99.33 (12)	N2—C6—H6	119.3
N2—Pt—N1	80.67 (12)	C5—C6—H6	119.3
N2^{i}—Pt—N1^{i}	80.67 (12)	F5B—P—F6B	92.5 (15)
N2—Pt—N1^{i}	99.33 (12)	F5B—P—F1	93.4 (12)
N1—Pt—N1^{i}	180.0	F6B—P—F1	93.6 (11)
C1—N1—Pt	111.7 (2)	F4—P—F1	95.5 (5)
C1—N1—H1A	109.3	F4—P—F5	96.1 (5)
Pt—N1—H1A	109.3	F1—P—F5	93.4 (4)
C1—N1—H1B	109.3	F5B—P—F4B	96.4 (15)
Pt—N1—H1B	109.3	F6B—P—F4B	170.4 (15)
H1A—N1—H1B	107.9	F1—P—F4B	82.2 (10)
C2—N2—C6	119.3 (3)	F4—P—F2	93.1 (5)
C2—N2—Pt	116.6 (2)	F1—P—F2	91.2 (3)
C6—N2—Pt	124.2 (2)	F5—P—F2	169.3 (5)
N1—C1—C2	110.6 (3)	F5B—P—F3	88.2 (12)

N1—C1—H1C	109.5	F6B—P—F3	85.2 (11)
C2—C1—H1C	109.5	F4—P—F3	84.0 (5)
N1—C1—H1D	109.5	F1—P—F3	178.0 (3)
C2—C1—H1D	109.5	F5—P—F3	88.5 (4)
H1C—C1—H1D	108.1	F4B—P—F3	98.8 (11)
N2—C2—C3	121.5 (4)	F2—P—F3	87.0 (3)
N2—C2—C1	116.0 (3)	F4—P—F6	177.1 (6)
C3—C2—C1	122.5 (4)	F1—P—F6	87.4 (5)
C4—C3—C2	119.3 (4)	F5—P—F6	83.6 (5)
C4—C3—H3	120.3	F2—P—F6	86.9 (5)
C2—C3—H3	120.3	F3—P—F6	93.2 (6)
C5—C4—C3	118.8 (4)	F5B—P—F2B	173.1 (15)
C5—C4—H4	120.6	F6B—P—F2B	84.9 (13)
C3—C4—H4	120.6	F1—P—F2B	80.5 (9)
C4—C5—C6	119.8 (4)	F4B—P—F2B	85.9 (13)
C4—C5—H5	120.1	F3—P—F2B	97.8 (9)
C6—C5—H5	120.1		
Pt—N1—C1—C2	22.8 (5)	N2—C2—C3—C4	−0.3 (7)
C6—N2—C2—C3	−1.3 (5)	C1—C2—C3—C4	178.8 (4)
Pt—N2—C2—C3	179.6 (3)	C2—C3—C4—C5	1.2 (7)
C6—N2—C2—C1	179.6 (4)	C3—C4—C5—C6	−0.7 (8)
Pt—N2—C2—C1	0.5 (4)	C2—N2—C6—C5	1.9 (6)
N1—C1—C2—N2	−15.6 (5)	Pt—N2—C6—C5	−179.1 (3)
N1—C1—C2—C3	165.3 (4)	C4—C5—C6—N2	−0.9 (7)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···F2^{ii}	0.89	2.40	3.080 (8)	133
N1—H1*A*···F4	0.89	2.24	2.971 (9)	139
N1—H1*B*···F6^{iii}	0.89	2.46	3.233 (10)	146
N1—H1*A*···F2*B*	0.89	2.22	2.98 (2)	143
N1—H1*B*···F5*B*^{iii}	0.89	2.05	2.84 (2)	148

Symmetry codes: (ii) −*x*, −*y*+1, −*z*; (iii) *x*, *y*+1, *z*.