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 Dibromido(2,3-di-2-pyridylpyrazine- κ^2N^2,N^3)platinum(II)

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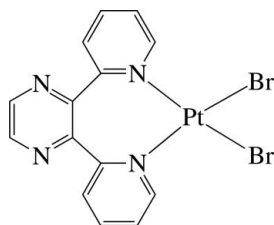
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 Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(C-C) = 0.010$ Å;
R factor = 0.032; wR factor = 0.067; data-to-parameter ratio = 17.5.

The Pt^{II} ion in the title complex, [PtBr₂(C₁₄H₁₀N₄)], has a slightly distorted square-planar environment defined by the two pyridyl N atoms of the chelating 2,3-di-2-pyridylpyrazine ligand and two bromide anions. In the crystal, the pyridyl rings are considerably inclined to the least-squares plane of the PtBr₂N₂ unit [maximum deviation = 0.064 (2) Å] with dihedral angles of 65.2 (2) and 66.0 (2)°. The nearly planar pyrazine ring [maximum deviation = 0.020 (5) Å] is almost perpendicular to the unit plane with a dihedral angle of 89.2 (2)°. Two independent weak intermolecular C—H···Br hydrogen bonds, both involving the same Br atom as a hydrogen-bond acceptor, give rise to chains running along the *a* and *b* axes, forming a layer structure extending parallel to (001). The complexes are stacked in columns along the *a* axis. When viewed down the *b* axis, the successive complexes stack in the opposite direction.

Related literature

For an isomer of the title complex, see: Ha (2011). For crystal structures of the related Pt^{II} complexes, see: Granifo *et al.* (2000); Cai *et al.* (2009).



Experimental

Crystal data

 [PtBr₂(C₁₄H₁₀N₄)]
 $M_r = 589.17$

 Monoclinic, $P2_1/n$
 $a = 8.4989$ (12) Å

 $b = 15.348$ (2) Å
 $c = 12.0277$ (16) Å
 $\beta = 101.403$ (3)°
 $V = 1538.0$ (4) Å³
 $Z = 4$

 Mo $K\alpha$ radiation
 $\mu = 14.32$ mm⁻¹
 $T = 200$ K
 $0.18 \times 0.18 \times 0.13$ mm

Data collection

 Bruker SMART 1000 CCD
diffractometer
Absorption correction: multi-scan
(SADABS; Bruker, 2000)
 $T_{\min} = 0.105$, $T_{\max} = 0.156$

 10118 measured reflections
3323 independent reflections
2484 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.067$
 $S = 0.99$
3323 reflections

 190 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 1.66$ e Å⁻³
 $\Delta\rho_{\min} = -0.84$ e Å⁻³

Table 1

Selected bond lengths (Å).

Pt1—N3	2.026 (5)	Pt1—Br1	2.4202 (8)
Pt1—N4	2.029 (5)	Pt1—Br2	2.4335 (8)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C6—H6···Br1 ⁱ	0.95	2.88	3.524 (6)	126
C11—H11···Br1 ⁱⁱ	0.95	2.88	3.688 (7)	143

 Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

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.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5295).

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supporting information

Acta Cryst. (2011). E67, m1307 [doi:10.1107/S160053681103412X]

Dibromido(2,3-di-2-pyridylpyrazine- κ^2N^2,N^3)platinum(II)**Kwang Ha****S1. Comment**

The title complex, [PtBr₂(dpp)] (dpp is 2,3-di-2-pyridylpyrazine, C₁₄H₁₀N₄), is a structural isomer of the previously reported Pt(II) complex (Ha, 2011). The Pt^{II} ion has a slightly distorted square-planar environment defined by the two pyridyl N atoms of the chelating dpp ligand and two bromide anions (Fig. 1). The coordination mode of the dpp ligand is similar to that found in the mononuclear Pt(II) complexes [PtCl₂(dpq)] (dpq = 2,3-di-2-pyridylquinoxaline) (Granifo *et al.*, 2000) and [PtCl₂(dcdpp)] (dcdpp = 2,3-dicyano-5,6-di-2-pyridylpyrazine) (Cai *et al.*, 2009).

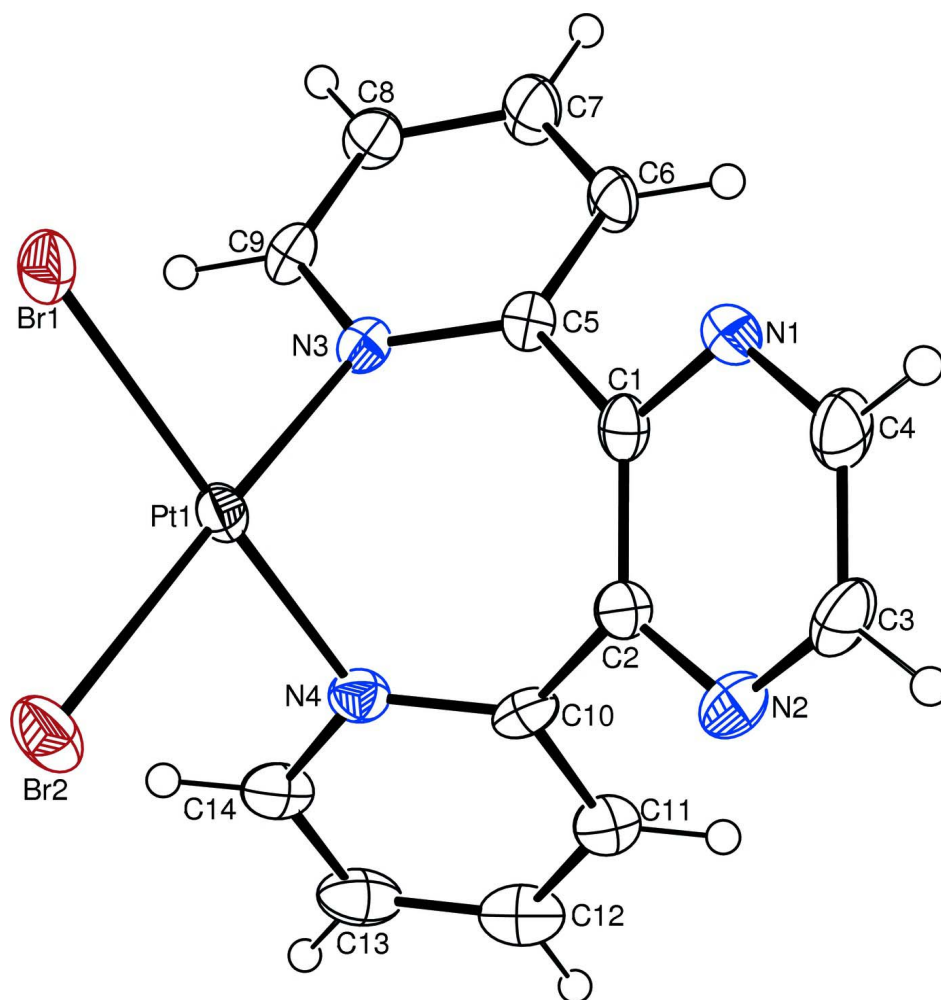
The N₃—Pt1—N₄ chelate angle of 87.7 (2)° and Br—Br repelling contribute the distortion of square, and therefore the *trans* axes are slightly bent [\angle Br1—Pt1—N₄ = 174.08 (15)° and \angle Br2—Pt1—N₃ = 178.19 (14)°]. The Pt—N and Pt—Br bond lengths are nearly equivalent, respectively (Table 1). In the crystal, the two pyridyl rings are considerably inclined to the least-squares plane of the PtBr₂N₂ unit [maximum deviation = 0.064 (2) Å] with dihedral angles of 65.2 (2)° and 66.0 (2)°, respectively. The nearly planar pyrazine ring [maximum deviation = 0.020 (5) Å] is almost perpendicular to the unit plane with a dihedral angle of 89.2 (2)°. The dihedral angle between the two pyridyl rings is 80.5 (2)°. Two independent intermolecular C—H \cdots Br hydrogen bonds, both involving the same Br atom as an H-bond acceptor, give rise to chains running along the *a* and *b* axes, forming a layer structure extending parallel to the *ab* plane (Fig. 2 and Table 2). The complexes are stacked in columns along the *a* axis. When viewed down the *b* axis, the successive complexes stack in the opposite direction. In the columns, numerous inter- and intramolecular π - π interactions between the six-membered rings are present, the shortest ring centroid-centroid distance being 3.833 (4) Å.

S2. Experimental

The title complex was obtained as a byproduct from the reaction of K₂PtBr₄ (0.2967 g, 0.500 mmol) with 2,3-di-2-pyridylpyrazine (0.1173 g, 0.501 mmol) in H₂O (20 ml). After stirring of the reaction mixture for 3 h at room temperature, the formed precipitate was separated by filtration, washed with H₂O and acetone, to give the main product as a red-brown powder (0.1326 g) (Ha, 2011). The yellow byproduct (0.0299 g) was obtained from the mixture of filtrate and washing solution. Crystals suitable for X-ray analysis were obtained by slow evaporation from a CH₃NO₂ solution of the byproduct.

S3. Refinement

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 highest peak (1.66 e Å⁻³) and the deepest hole (-0.84 e Å⁻³) in the difference Fourier map are located 1.95 Å and 0.89 Å from the atoms H12 and Pt1, respectively.

**Figure 1**

The structure of the title complex, with displacement ellipsoids drawn at the 50% probability level; H atoms are shown as small circles of arbitrary radius.

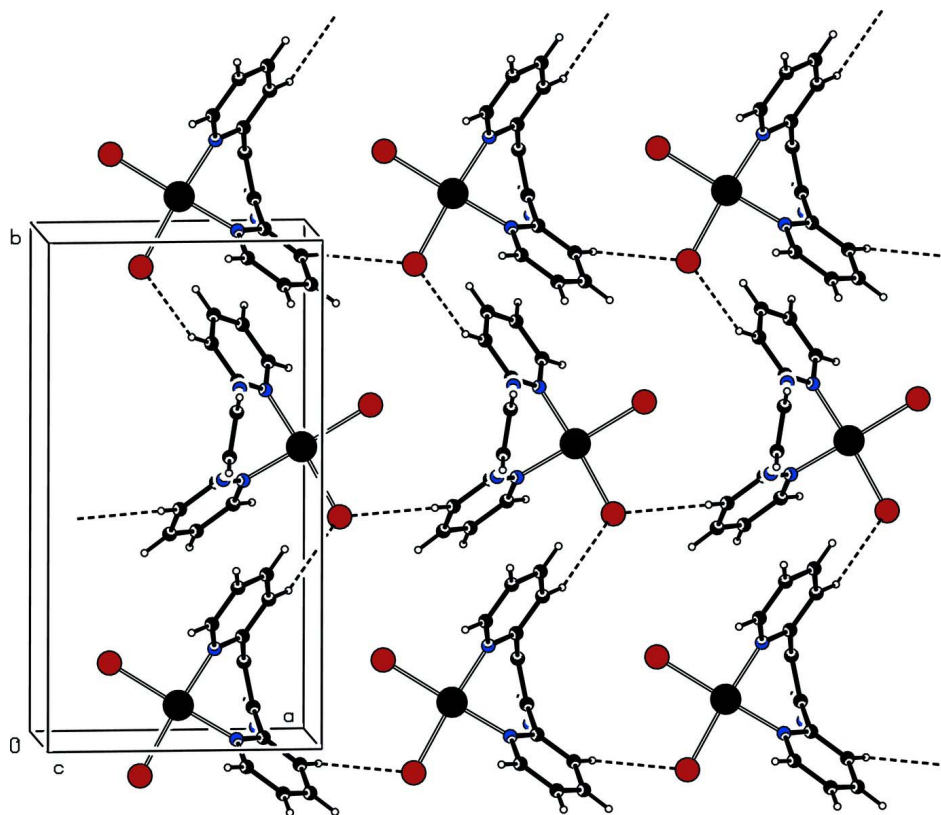


Figure 2

View of the hydrogen-bond interactions of the title complex. Hydrogen-bonds are drawn with dashed lines.

Dibromido(2,3-di-2-pyridylpyrazine- κ^2N^2,N^3)platinum(II)

Crystal data

[PtBr₂(C₁₄H₁₀N₄)]

$M_r = 589.17$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 8.4989$ (12) Å

$b = 15.348$ (2) Å

$c = 12.0277$ (16) Å

$\beta = 101.403$ (3)°

$V = 1538.0$ (4) Å³

$Z = 4$

$F(000) = 1080$

$D_x = 2.544$ Mg m⁻³

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

Cell parameters from 4242 reflections

$\theta = 2.7$ – 27.0 °

$\mu = 14.32$ mm⁻¹

$T = 200$ K

Block, yellow

$0.18 \times 0.18 \times 0.13$ 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)

$T_{\min} = 0.105$, $T_{\max} = 0.156$

10118 measured reflections

3323 independent reflections

2484 reflections with $I > 2\sigma(I)$

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

$\theta_{\max} = 27.0$ °, $\theta_{\min} = 2.2$ °

$h = -9 \rightarrow 10$

$k = -11 \rightarrow 19$

$l = -13 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.067$
 $S = 0.99$
 3323 reflections
 190 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
 $w = 1/[\sigma^2(F_o^2) + (0.0237P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.66 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.84 \text{ e } \text{Å}^{-3}$

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	$U_{\text{iso}}^*/U_{\text{eq}}$
Pt1	0.52128 (3)	0.060963 (16)	0.31708 (2)	0.02517 (9)
Br1	0.38241 (9)	-0.07734 (4)	0.30704 (6)	0.03471 (18)
Br2	0.27287 (9)	0.14353 (5)	0.26735 (6)	0.0413 (2)
N1	0.8219 (7)	0.0077 (3)	0.0833 (5)	0.0314 (14)
N2	0.7631 (7)	0.1861 (4)	0.0810 (5)	0.0368 (15)
N3	0.7311 (6)	-0.0055 (3)	0.3550 (4)	0.0238 (12)
N4	0.6520 (7)	0.1724 (3)	0.3406 (4)	0.0284 (13)
C1	0.8029 (8)	0.0499 (4)	0.1780 (5)	0.0265 (15)
C2	0.7701 (8)	0.1400 (4)	0.1755 (6)	0.0304 (16)
C3	0.7799 (10)	0.1437 (5)	-0.0117 (6)	0.042 (2)
H3	0.7738	0.1755	-0.0802	0.051*
C4	0.8060 (9)	0.0552 (5)	-0.0126 (6)	0.0394 (19)
H4	0.8128	0.0272	-0.0819	0.047*
C5	0.8339 (8)	-0.0057 (4)	0.2819 (5)	0.0231 (14)
C6	0.9675 (8)	-0.0587 (4)	0.3011 (6)	0.0305 (16)
H6	1.0386	-0.0590	0.2492	0.037*
C7	0.9973 (9)	-0.1111 (5)	0.3954 (6)	0.0392 (18)
H7	1.0881	-0.1485	0.4087	0.047*
C8	0.8944 (8)	-0.1088 (4)	0.4708 (6)	0.0333 (17)
H8	0.9149	-0.1436	0.5375	0.040*
C9	0.7622 (8)	-0.0557 (4)	0.4483 (5)	0.0266 (15)
H9	0.6909	-0.0544	0.4999	0.032*
C10	0.7583 (9)	0.1933 (4)	0.2760 (5)	0.0307 (16)
C11	0.8525 (9)	0.2669 (4)	0.3000 (6)	0.0397 (19)
H11	0.9274	0.2815	0.2540	0.048*

C12	0.8379 (10)	0.3187 (5)	0.3903 (6)	0.043 (2)
H12	0.9026	0.3693	0.4073	0.052*
C13	0.7293 (10)	0.2969 (5)	0.4557 (6)	0.044 (2)
H13	0.7186	0.3322	0.5187	0.053*
C14	0.6361 (9)	0.2243 (4)	0.4303 (5)	0.0352 (18)
H14	0.5598	0.2096	0.4753	0.042*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.02370 (16)	0.02954 (16)	0.02362 (14)	0.00465 (12)	0.00797 (11)	0.00200 (11)
Br1	0.0235 (4)	0.0404 (4)	0.0414 (4)	-0.0026 (3)	0.0092 (3)	-0.0002 (3)
Br2	0.0357 (5)	0.0529 (5)	0.0367 (4)	0.0204 (4)	0.0108 (3)	0.0100 (3)
N1	0.035 (4)	0.029 (3)	0.033 (3)	0.004 (3)	0.014 (3)	-0.002 (3)
N2	0.043 (4)	0.035 (4)	0.033 (3)	0.001 (3)	0.009 (3)	0.012 (3)
N3	0.026 (3)	0.024 (3)	0.021 (3)	-0.004 (2)	0.003 (2)	0.000 (2)
N4	0.032 (4)	0.025 (3)	0.028 (3)	0.004 (3)	0.005 (3)	0.003 (2)
C1	0.019 (4)	0.036 (4)	0.025 (4)	-0.003 (3)	0.005 (3)	0.001 (3)
C2	0.023 (4)	0.028 (4)	0.042 (4)	-0.001 (3)	0.009 (3)	0.004 (3)
C3	0.058 (6)	0.041 (5)	0.033 (4)	-0.002 (4)	0.021 (4)	0.013 (3)
C4	0.042 (5)	0.051 (5)	0.029 (4)	0.006 (4)	0.014 (3)	0.014 (3)
C5	0.023 (4)	0.027 (4)	0.018 (3)	-0.002 (3)	0.001 (3)	0.000 (3)
C6	0.017 (4)	0.035 (4)	0.042 (4)	0.003 (3)	0.012 (3)	0.006 (3)
C7	0.024 (4)	0.044 (5)	0.050 (5)	0.008 (3)	0.010 (4)	0.013 (4)
C8	0.030 (4)	0.031 (4)	0.038 (4)	0.004 (3)	0.005 (3)	0.006 (3)
C9	0.025 (4)	0.031 (4)	0.024 (3)	-0.006 (3)	0.004 (3)	0.004 (3)
C10	0.035 (4)	0.022 (4)	0.032 (4)	-0.001 (3)	0.001 (3)	0.008 (3)
C11	0.042 (5)	0.032 (4)	0.046 (5)	0.001 (4)	0.012 (4)	0.003 (4)
C12	0.045 (5)	0.029 (4)	0.048 (5)	0.000 (4)	-0.009 (4)	-0.004 (4)
C13	0.067 (6)	0.030 (5)	0.031 (4)	0.009 (4)	0.002 (4)	-0.005 (3)
C14	0.055 (5)	0.030 (4)	0.019 (4)	0.009 (4)	0.007 (3)	0.002 (3)

Geometric parameters (Å, °)

Pt1—N3	2.026 (5)	C4—H4	0.9500
Pt1—N4	2.029 (5)	C5—C6	1.380 (8)
Pt1—Br1	2.4202 (8)	C6—C7	1.373 (9)
Pt1—Br2	2.4335 (8)	C6—H6	0.9500
N1—C1	1.347 (8)	C7—C8	1.379 (9)
N1—C4	1.349 (8)	C7—H7	0.9500
N2—C3	1.323 (8)	C8—C9	1.371 (9)
N2—C2	1.329 (8)	C8—H8	0.9500
N3—C9	1.344 (7)	C9—H9	0.9500
N3—C5	1.357 (7)	C10—C11	1.381 (9)
N4—C10	1.341 (8)	C11—C12	1.372 (9)
N4—C14	1.368 (8)	C11—H11	0.9500
C1—C2	1.410 (9)	C12—C13	1.367 (10)
C1—C5	1.493 (8)	C12—H12	0.9500

C2—C10	1.479 (9)	C13—C14	1.366 (10)
C3—C4	1.376 (9)	C13—H13	0.9500
C3—H3	0.9500	C14—H14	0.9500
N3—Pt1—N4	87.7 (2)	C6—C5—C1	118.7 (6)
N3—Pt1—Br1	88.20 (14)	C7—C6—C5	119.7 (6)
N4—Pt1—Br1	174.08 (15)	C7—C6—H6	120.2
N3—Pt1—Br2	178.19 (14)	C5—C6—H6	120.2
N4—Pt1—Br2	91.13 (15)	C6—C7—C8	119.5 (7)
Br1—Pt1—Br2	93.08 (3)	C6—C7—H7	120.3
C1—N1—C4	117.0 (6)	C8—C7—H7	120.3
C3—N2—C2	117.7 (6)	C9—C8—C7	119.1 (6)
C9—N3—C5	119.6 (5)	C9—C8—H8	120.5
C9—N3—Pt1	119.7 (4)	C7—C8—H8	120.5
C5—N3—Pt1	120.4 (4)	N3—C9—C8	121.7 (6)
C10—N4—C14	120.0 (6)	N3—C9—H9	119.2
C10—N4—Pt1	122.2 (4)	C8—C9—H9	119.2
C14—N4—Pt1	117.6 (5)	N4—C10—C11	120.2 (6)
N1—C1—C2	120.7 (6)	N4—C10—C2	120.3 (6)
N1—C1—C5	113.7 (6)	C11—C10—C2	119.5 (6)
C2—C1—C5	125.4 (6)	C12—C11—C10	120.0 (7)
N2—C2—C1	121.0 (6)	C12—C11—H11	120.0
N2—C2—C10	113.9 (6)	C10—C11—H11	120.0
C1—C2—C10	124.7 (6)	C13—C12—C11	119.3 (7)
N2—C3—C4	122.4 (6)	C13—C12—H12	120.3
N2—C3—H3	118.8	C11—C12—H12	120.3
C4—C3—H3	118.8	C14—C13—C12	119.9 (7)
N1—C4—C3	121.1 (7)	C14—C13—H13	120.0
N1—C4—H4	119.4	C12—C13—H13	120.0
C3—C4—H4	119.4	C13—C14—N4	120.5 (7)
N3—C5—C6	120.5 (6)	C13—C14—H14	119.8
N3—C5—C1	120.8 (6)	N4—C14—H14	119.8
N4—Pt1—N3—C9	115.6 (5)	N1—C1—C5—C6	45.0 (8)
Br1—Pt1—N3—C9	-60.1 (4)	C2—C1—C5—C6	-129.7 (7)
N4—Pt1—N3—C5	-70.2 (5)	N3—C5—C6—C7	-0.6 (10)
Br1—Pt1—N3—C5	114.1 (4)	C1—C5—C6—C7	-179.3 (6)
N3—Pt1—N4—C10	62.4 (5)	C5—C6—C7—C8	-1.1 (11)
Br2—Pt1—N4—C10	-116.2 (5)	C6—C7—C8—C9	1.6 (11)
N3—Pt1—N4—C14	-113.5 (5)	C5—N3—C9—C8	-1.2 (9)
Br2—Pt1—N4—C14	67.8 (5)	Pt1—N3—C9—C8	173.0 (5)
C4—N1—C1—C2	-0.9 (9)	C7—C8—C9—N3	-0.4 (10)
C4—N1—C1—C5	-175.9 (6)	C14—N4—C10—C11	0.3 (10)
C3—N2—C2—C1	3.3 (10)	Pt1—N4—C10—C11	-175.6 (5)
C3—N2—C2—C10	177.1 (6)	C14—N4—C10—C2	-176.9 (6)
N1—C1—C2—N2	-2.5 (10)	Pt1—N4—C10—C2	7.3 (9)
C5—C1—C2—N2	171.9 (6)	N2—C2—C10—N4	128.9 (7)
N1—C1—C2—C10	-175.6 (6)	C1—C2—C10—N4	-57.6 (10)

C5—C1—C2—C10	-1.2 (11)	N2—C2—C10—C11	-48.3 (9)
C2—N2—C3—C4	-0.8 (11)	C1—C2—C10—C11	125.3 (7)
C1—N1—C4—C3	3.3 (10)	N4—C10—C11—C12	0.2 (11)
N2—C3—C4—N1	-2.6 (12)	C2—C10—C11—C12	177.4 (6)
C9—N3—C5—C6	1.7 (9)	C10—C11—C12—C13	-0.1 (11)
Pt1—N3—C5—C6	-172.5 (5)	C11—C12—C13—C14	-0.3 (11)
C9—N3—C5—C1	-179.6 (6)	C12—C13—C14—N4	0.8 (11)
Pt1—N3—C5—C1	6.2 (8)	C10—N4—C14—C13	-0.8 (10)
N1—C1—C5—N3	-133.7 (6)	Pt1—N4—C14—C13	175.3 (5)
C2—C1—C5—N3	51.5 (9)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C6—H6...Br1 ⁱ	0.95	2.88	3.524 (6)	126
C11—H11...Br1 ⁱⁱ	0.95	2.88	3.688 (7)	143

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+3/2, y+1/2, -z+1/2$.