

Tetrachlorido(4,4'-dimethyl-2,2'-bipyridine- κ^2N,N')platinum(IV)

Leila Hojjat Kashani,^a Vahid Amani,^a Mohammad Yousefi^{a*} and Hamid Reza Khavasi^b

^aIslamic Azad University, Shahr-e-Rey Branch, Tehran, Iran, and ^bDepartment of Chemistry, Shahid Beheshti University, Tehran 1983963113, Iran

Correspondence e-mail: myousefi50@yahoo.com

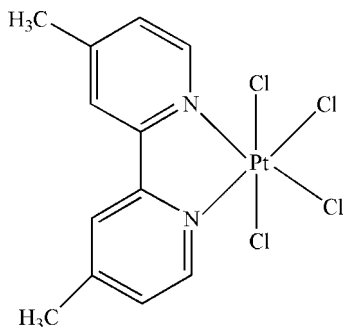
Received 1 June 2008; accepted 2 June 2008

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(C-C) = 0.008$ Å; R factor = 0.038; wR factor = 0.097; data-to-parameter ratio = 24.8.

The asymmetric unit of the title compound, $[PtCl_4(C_{12}H_{12}N_2)]$, contains one half-molecule; a twofold rotation axis passes through the Pt atom and the mid-point of the C—C bond linking the two rings. The Pt^{IV} atom is six-coordinated in an octahedral configuration by two N atoms of the 4,4'-dimethyl-2,2'-bipyridine ligand and four terminal Cl atoms. In the crystal structure, there are weak π – π interactions between pyridine rings, with a centroid–centroid distance of 4.365 (3) Å.

Related literature

For related literature, see: Hedin (1886); Joergensen (1900); Bajusz *et al.* (1989); Vorobevdesyatovskii *et al.* (1991); Gaballa *et al.* (2003); Casas *et al.* (2005); Hambley (1986); Hafizovic *et al.* (2006); Delir Kheirollahi Nezhad *et al.* (2008); Crowder *et al.* (2004); Junicke *et al.* (1997); Khripun *et al.* (2006); Witkowski *et al.* (1997); Kuduk-Jaworska *et al.* (1988, 1990); Bokach *et al.* (2003); Kukushkin *et al.* (1998); Garnovskii *et al.* (2001); Luzyanin, Kukushkin *et al.* (2002); Gonzalez *et al.* (2002); Luzyanin, Haukka *et al.* (2002); Yousefi *et al.* (2007).



Experimental

Crystal data

$[PtCl_4(C_{12}H_{12}N_2)]$	$V = 1610.2$ (3) Å ³
$M_r = 521.12$	$Z = 4$
Orthorhombic, $Pccn$	Mo $K\alpha$ radiation
$a = 6.9497$ (7) Å	$\mu = 9.36$ mm ⁻¹
$b = 13.3774$ (13) Å	$T = 298$ (2) K
$c = 17.3195$ (16) Å	$0.25 \times 0.23 \times 0.21$ mm

Data collection

Stoe IPDS II diffractometer	5803 measured reflections
Absorption correction: numerical [shape of crystal determined optically (<i>X-SHAPE</i> and <i>X-RED</i> ; Stoe & Cie, 2005)]	2157 independent reflections
$T_{\min} = 0.172$, $T_{\max} = 0.275$	1779 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	87 parameters
$wR(F^2) = 0.097$	H-atom parameters constrained
$S = 1.16$	$\Delta\rho_{\text{max}} = 0.95$ e Å ⁻³
2157 reflections	$\Delta\rho_{\text{min}} = -0.81$ e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Pt1—N1	2.031 (4)	Pt1—Cl1	2.3146 (16)
Pt1—Cl2	2.3038 (13)		
N1—Pt1—N1 ⁱ	80.4 (2)	Cl2—Pt1—Cl1 ⁱ	90.96 (6)
N1—Pt1—Cl2	175.58 (12)	N1—Pt1—Cl1	89.81 (14)
N1—Pt1—Cl2 ⁱ	95.40 (13)	Cl2—Pt1—Cl1	91.34 (6)
Cl2—Pt1—Cl2 ⁱ	88.85 (8)	Cl1 ⁱ —Pt1—Cl1	176.78 (8)
N1—Pt1—Cl1 ⁱ	87.72 (14)		

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

Data collection: *X-Area* (Stoe & Cie, 2005); cell refinement: *X-Area*; data reduction: *X-Red* (Stoe & Cie, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We are grateful to the Islamic Azad University, Shahr-e-Rey Branch, for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2470).

References

- Bajusz, S., Janaky, T., Csernus, V. J., Bokser, L., Fedeke, M., Srkalovic, G., Redding, T. W. & Schally, A. V. (1989). *Proc. Natl Acad. Sci. USA*, **86**, 6313–6317.
- Bokach, N. A., Pakhomova, T. B., Kukushkin, V. Y., Haukka, M. & Pombeiro, A. J. L. (2003). *Inorg. Chem.* **42**, 7560–7568.
- Casas, J. S., Castineiras, A., Parajo, Y., Sanchez, A., Gonzalez, A. S. & Sordo, J. (2005). *Polyhedron*, **24**, 1196–1202.
- Crowder, K. N., Garcia, S. J., Burr, R. L., North, J. M., Wilson, M. H., Conley, B. L., Fanwick, P. E., White, P. S., Sienerth, K. D. & Granger, R. M. (2004). *Inorg. Chem.* **43**, 72–78.
- Delir Kheirollahi Nezhad, P., Azadbakht, F., Amani, V. & Khavasi, H. R. (2008). *Acta Cryst.* **E64**, m575–m576.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Gaballa, A., Wagner, C., Schmidt, H. & Steinborn, D. (2003). *Z. Anorg. Allg. Chem.* **629**, 703–710.

- Garnovskii, D. A., Kukushkin, V. Y., Haukka, M., Wagner, G. & Pombeiro, A. J. L. (2001). *J. Chem. Soc. Dalton Trans*, pp. 560–566.
- Gonzalez, A. M., Cini, R., Intini, F. P., Pacifico, C. & Natile, G. (2002). *Inorg. Chem.* **41**, 470–478.
- Hafizovic, J., Olsbye, U. & Lillerud, K. P. (2006). *Acta Cryst.* **E62**, m414–m416.
- Hambley, T. W. (1986). *Acta Cryst.* **C42**, 49–51.
- Hedin, S. G. (1886). *Acta Univ. Lund.* **22**, 1–6.
- Kuduk-Jaworska, J., Kubiak, M. & Głowiak, T. (1988). *Acta Cryst.* **C44**, 437–439.
- Kuduk-Jaworska, J., Kubiak, M., Głowiak, T. & Jeżowska-Trzebiatowska, B. (1990). *Acta Cryst.* **C46**, 2046–2049.
- Joergensen, S. M. (1900). *Z. Anorg. Chem.* **25**, 353–377.
- Junicke, H., Schenzel, K., Heinemann, F. W., Pelz, K., Bogel, H. & Steinborn, D. (1997). *Z. Anorg. Allg. Chem.* **623**, 603–607.
- Khripun, A. V., Selivanov, S. I., Kukushkin, V. Y. & Haukka, M. (2006). *Inorg. Chim. Acta*, **359**, 320–326.
- Kukushkin, V. Y., Pakhomova, T. B., Kukushkin, Y. N., Herrmann, R., Wagner, G. & Pombeiro, A. J. L. (1998). *Inorg. Chem.* **37**, 6511–6517.
- Luzyanin, K. V., Haukka, M., Bokach, N. A., Kuznetsov, M. L., Kukushkin, V. Y. & Pombeiro, A. J. L. (2002). *J. Chem. Soc. Dalton Trans*, pp. 1882–1887.
- Luzyanin, K. V., Kukushkin, V. Y., Kuznetsov, M. L., Garnovskii, D. A., Haukka, M. & Pombeiro, A. J. L. (2002). *Inorg. Chem.* **41**, 2981–2986.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Stoe & Cie (2005). *X-AREA, X-SHAPE and X-RED*. Stoe & Cie, Darmstadt, Germany.
- Vorobevdesyatovskii, N. V., Barinov, A. A., Lukin, Y. N., Sokolov, V. V., Demidov, V. N. & Kuptsov, A. Y. (1991). *Zh. Obshch. Khim.* **61**, 709–716.
- Witkowski, H., Freisinger, E. & Lippert, B. (1997). *Chem. Commun.* pp. 1315–1316.
- Yousefi, M., Teimouri, S., Amani, V. & Khavasi, H. R. (2007). *Acta Cryst.* **E63**, m2869–m2870.

supporting information

Acta Cryst. (2008). E64, m905–m906 [doi:10.1107/S1600536808016796]

Tetrachlorido(4,4'-dimethyl-2,2'-bipyridine- κ^2 N,N')platinum(IV)

Leila Hojjat Kashani, Vahid Amani, Mohammad Yousefi and Hamid Reza Khavasi

S1. Comment

Amine platinum(IV) complexes have been known since the end of the last century (Hedin, 1886; Joergensen, 1900). Some of them have cancerostatic properties from which new interest aroused in these complexes (Bajusz *et al.*, 1989; Vorobevdesyatovskii *et al.*, 1991). Due to the kinetic inertness of hexachloro -platinato(IV), *cis*- and *trans*-[PtCl₄L₂] complexes (L=N, O, P, S donor ligand) were mainly prepared by oxidation reactions of the corresponding platinum(II) complexes [PtCl₂L₂] (Hedin, 1886; Joergensen, 1900).

Several Pt^{IV} complexes, with formula, [PtCl₄(N-N)], such as [PtCl₄(bipy)], (II), (Gaballa *et al.*, 2003), [PtCl₄(Me₂bim)], (III), (Casas *et al.*, 2005), [PtCl₄(bipy)], (IV), (Hambley, 1986), [PtCl₄(dcbipy)].H₂O, (V), (Hafizovic *et al.*, 2006), [PtCl₄{pz(py)₂}], (VI), (Delir Kheirollahi Nezhad *et al.*, 2008) and [PtCl₄(dpk)], (VII), (Crowder *et al.*, 2004) [where bipy is 2,2'-bi-pyrimidinyl, Me₂bim is 1,1'-dimethyl-2,2'-bi-imidazolyl, bipy is 2,2'-bipyridine, dcbipy is 2,2'-bipyridine-5,5'-dicarboxylic acid, pz(py)₂ is 2,3-bis(2-pyridyl)pyrazine and dpk is bis(2-pyridyl)ketone] have been synthesized and characterized by single-crystal X-ray diffraction methods.

There are also several Pt^{IV} complexes, with formula, [PtCl₄L₂], such as *cis*- and *trans*-[PtCl₄(py)₂], (VIII), (Junicke *et al.*, 1997), *cis*- and *trans*-[PtCl₄(PzH)₂], (IX), (Khripun *et al.*, 2006), *trans*-[PtCl₄(NH₃)₂](1-Mu), (X), (Witkowski *et al.*, 1997), *trans*-[PtCl₄(1-Prim)₂], (XI), (Kuduk-Jaworska *et al.*, 1988), *cis*-[PtCl₄(1-Etim)₂], (XII), (Kuduk-Jaworska *et al.*, 1990), *trans*-[PtCl₄{NH=C(NMe₂)OH}₂], (XIII), (Bokach *et al.*, 2003), *trans*-[PtCl₄{NH=C(Me)ON=CMe₂}₂], (XIV), (Kukushkin *et al.*, 1998), *cis*-[PtCl₄{NH=C(Et)N=CPh₂}₂], (XV), (Garnovskii *et al.*, 2001), *trans*-[PtCl₄{NH=C(Et)ON=C(OH)Ph}₂].2DMSO, (XVI), (Luzyanin, Kukushkin *et al.*, 2002), *trans*-[PtCl₄{NH=C(OMe)Bu}₂], (XVII), (Gonzalez *et al.*, 2002), *trans*-[PtCl₄{NH=C(OH)Et}₂], (XVIII), (Luzyanin, Haukka *et al.*, 2002) and *trans*-[PtCl₄(pz)₂], (XIX), (Yousefi *et al.*, 2007) [where PzH is pyrazole, 1-Mu is 1-methyluracil, 1-Prim is 1-propylimidazole, 1-Etim is 1-ethylimidazolyl and Pz is pyrazine] have been synthesized and characterized by single-crystal X-ray diffraction methods. We report herein the synthesis and crystal structure of the title compound, (I).

The asymmetric unit of (I) (Fig. 1) contains one-half molecule. The Pt^{IV} atom is six-coordinated in octahedral configuration (Table 1) by two N atoms of 4,4'-dimethyl-2,2'-bipyridine ligand and four terminal Cl atoms. The Pt-Cl and Pt-N bond lengths and angles (Table 1) are in good agreement with the corresponding values in (II), (III), (V) and (VI).

In the crystal structure, weak π — π interactions between pyridine rings [symmetry code: 3/2 - x, 1/2 - y, z] may be effective in the stabilization of the structure, with a centroid-centroid distance of 4.365 (3) Å.

S2. Experimental

For the preparation of the title compound, a solution of 4,4'-dimethyl-2,2'-bipyridine (0.11 g, 0.58 mmol) in methanol (10 ml) was added to a solution of H₂PtCl₆.6H₂O, (0.30 g, 0.58 mmol) in methanol (10 ml) at room temperature. Crystals suitable for X-ray analysis were obtained by methanol diffusion in a solution of yellow precipitate in DMSO after one

week (yield; 0.25 g, 82.8%).

S3. Refinement

H atoms were positioned geometrically, with C-H = 0.93 and 0.96 Å for aromatic and methyl H and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

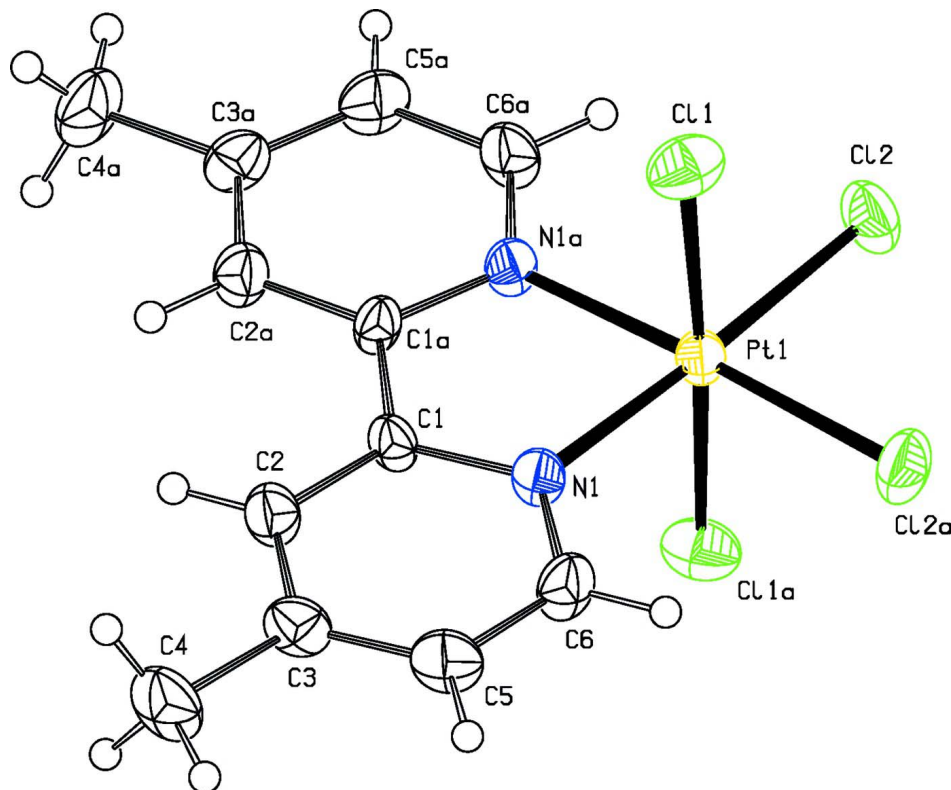


Figure 1

The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level [symmetry code: (a) $1/2 - x, 1/2 - y, z$].

Tetrachlorido(4,4'-dimethyl-2,2'-bipyridine- κ^2N,N')platinum(IV)

Crystal data

$[\text{PtCl}_4(\text{C}_{12}\text{H}_{12}\text{N}_2)]$

$M_r = 521.12$

Orthorhombic, *Pccn*

Hall symbol: -P 2ab 2ac

$a = 6.9497$ (7) Å

$b = 13.3774$ (13) Å

$c = 17.3195$ (16) Å

$V = 1610.2$ (3) Å³

$Z = 4$

$F(000) = 976$

$D_x = 2.150$ Mg m⁻³

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

Cell parameters from 1510 reflections

$\theta = 2.8\text{--}29.2^\circ$

$\mu = 9.36$ mm⁻¹

$T = 298$ K

Prism, yellow

$0.25 \times 0.23 \times 0.21$ mm

Data collection

Stoe IPDS II

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 0.15 mm pixels mm⁻¹

rotation method scans

Absorption correction: numerical

shape of crystal determined optically

$T_{\min} = 0.172$, $T_{\max} = 0.275$
 5803 measured reflections
 2157 independent reflections
 1779 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

$\theta_{\max} = 29.2^\circ$, $\theta_{\min} = 2.8^\circ$
 $h = -6 \rightarrow 9$
 $k = -18 \rightarrow 17$
 $l = -23 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.097$
 $S = 1.16$
 2157 reflections
 87 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
 $w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 3.1448P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.007$
 $\Delta\rho_{\max} = 0.96 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.81 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. (X-SHAPE and X-RED; Stoe & Cie, 2005)

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 $F^2 > 2\sigma(F^2)$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Pt1	0.2500	0.2500	0.451996 (14)	0.02949 (11)
Cl1	0.0431 (2)	0.38548 (12)	0.45575 (10)	0.0500 (4)
Cl2	0.0689 (2)	0.17462 (12)	0.35700 (8)	0.0481 (3)
N1	0.4010 (6)	0.3087 (3)	0.5416 (2)	0.0316 (9)
C1	0.3349 (8)	0.2829 (4)	0.6127 (3)	0.0304 (10)
C2	0.4230 (8)	0.3185 (4)	0.6782 (3)	0.0381 (11)
H2	0.3744	0.3015	0.7265	0.046*
C3	0.5850 (8)	0.3801 (4)	0.6728 (3)	0.0399 (12)
C4	0.6800 (11)	0.4197 (6)	0.7439 (4)	0.0578 (18)
H4A	0.7228	0.3649	0.7753	0.069*
H4B	0.5898	0.4595	0.7725	0.069*
H4C	0.7884	0.4601	0.7296	0.069*
C5	0.6513 (9)	0.4028 (5)	0.5998 (4)	0.0472 (14)
H5	0.7597	0.4429	0.5942	0.057*
C6	0.5593 (9)	0.3668 (5)	0.5349 (3)	0.0424 (13)
H6	0.6065	0.3827	0.4862	0.051*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.03027 (15)	0.03300 (16)	0.02522 (16)	-0.00577 (10)	0.000	0.000
Cl1	0.0429 (7)	0.0431 (8)	0.0638 (10)	0.0050 (6)	0.0091 (7)	0.0049 (6)
Cl2	0.0523 (8)	0.0592 (8)	0.0327 (6)	-0.0138 (7)	-0.0124 (6)	-0.0019 (6)
N1	0.031 (2)	0.035 (2)	0.0283 (19)	-0.0121 (18)	-0.0011 (16)	-0.0041 (16)
C1	0.031 (2)	0.036 (2)	0.024 (2)	-0.011 (2)	-0.0050 (19)	0.0000 (18)
C2	0.040 (3)	0.044 (3)	0.031 (2)	-0.007 (2)	-0.002 (2)	0.004 (2)
C3	0.035 (3)	0.039 (3)	0.046 (3)	-0.011 (2)	-0.007 (2)	-0.001 (2)
C4	0.054 (4)	0.070 (4)	0.049 (4)	-0.021 (4)	-0.018 (3)	-0.005 (3)
C5	0.036 (3)	0.053 (4)	0.053 (3)	-0.020 (3)	-0.006 (3)	-0.003 (3)
C6	0.040 (3)	0.052 (3)	0.035 (2)	-0.020 (3)	0.007 (2)	-0.001 (2)

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

Pt1—N1	2.031 (4)	C2—H2	0.9300
Pt1—N1 ⁱ	2.031 (4)	C3—C5	1.380 (9)
Pt1—Cl2	2.3038 (13)	C3—C4	1.494 (8)
Pt1—Cl2 ⁱ	2.3038 (13)	C4—H4A	0.9600
Pt1—Cl1 ⁱ	2.3146 (16)	C4—H4B	0.9600
Pt1—Cl1	2.3146 (16)	C4—H4C	0.9600
C1—N1	1.359 (6)	C5—C6	1.379 (8)
C1—C2	1.374 (7)	C5—H5	0.9300
C1—C1 ⁱ	1.472 (10)	C6—N1	1.352 (7)
C2—C3	1.398 (7)	C6—H6	0.9300
N1—Pt1—N1 ⁱ	80.4 (2)	C3—C2—H2	119.7
N1—Pt1—Cl2	175.58 (12)	C5—C3—C2	117.4 (5)
N1 ⁱ —Pt1—Cl2	95.40 (13)	C5—C3—C4	122.0 (5)
N1—Pt1—Cl2 ⁱ	95.40 (13)	C2—C3—C4	120.6 (6)
N1 ⁱ —Pt1—Cl2 ⁱ	175.58 (12)	C3—C4—H4A	109.5
Cl2—Pt1—Cl2 ⁱ	88.85 (8)	C3—C4—H4B	109.5
N1—Pt1—Cl1 ⁱ	87.72 (14)	H4A—C4—H4B	109.5
N1 ⁱ —Pt1—Cl1 ⁱ	89.81 (14)	C3—C4—H4C	109.5
Cl2—Pt1—Cl1 ⁱ	90.96 (6)	H4A—C4—H4C	109.5
Cl2 ⁱ —Pt1—Cl1 ⁱ	91.34 (6)	H4B—C4—H4C	109.5
N1—Pt1—Cl1	89.81 (14)	C6—C5—C3	121.0 (5)
N1 ⁱ —Pt1—Cl1	87.72 (14)	C6—C5—H5	119.5
Cl2—Pt1—Cl1	91.34 (6)	C3—C5—H5	119.5
Cl2 ⁱ —Pt1—Cl1	90.96 (6)	N1—C6—C5	120.6 (5)
Cl1 ⁱ —Pt1—Cl1	176.78 (8)	N1—C6—H6	119.7
N1—C1—C2	120.6 (5)	C5—C6—H6	119.7
N1—C1—C1 ⁱ	115.0 (3)	C6—N1—C1	119.9 (4)
C2—C1—C1 ⁱ	124.4 (3)	C6—N1—Pt1	125.3 (3)
C1—C2—C3	120.5 (5)	C1—N1—Pt1	114.8 (3)
C1—C2—H2	119.7		

N1—C1—C2—C3	-1.5 (9)	C1 ⁱ —C1—N1—C6	-178.3 (6)
C1 ⁱ —C1—C2—C3	179.4 (7)	C2—C1—N1—Pt1	-179.3 (4)
C1—C2—C3—C5	-0.1 (9)	C1 ⁱ —C1—N1—Pt1	-0.1 (8)
C1—C2—C3—C4	179.4 (6)	N1 ⁱ —Pt1—N1—C6	178.1 (6)
C2—C3—C5—C6	0.7 (10)	C11 ⁱ —Pt1—N1—C6	87.9 (5)
C4—C3—C5—C6	-178.8 (7)	C11—Pt1—N1—C6	-94.2 (5)
C3—C5—C6—N1	0.3 (10)	N1 ⁱ —Pt1—N1—C1	0.0 (3)
C5—C6—N1—C1	-2.0 (9)	C12 ⁱ —Pt1—N1—C1	178.7 (4)
C5—C6—N1—Pt1	-179.9 (5)	C11 ⁱ —Pt1—N1—C1	-90.2 (4)
C2—C1—N1—C6	2.6 (9)	C11—Pt1—N1—C1	87.8 (4)

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