



# Synthesis, crystal structure and Hirshfeld surface analysis of bis(caffeinium) hexachlorido-platinum(IV) in comparison with some related compounds

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Received 14 April 2023

Accepted 8 June 2023

Edited by A. S. Batsanov, University of Durham, United Kingdom

**Keywords:** crystal structure; platinum; Pt; caffeine; Hirshfeld surface analysis; hexahalide;  $\pi$ -stacking.

**CCDC reference:** 2268577

**Supporting information:** this article has supporting information at journals.iucr.org/e

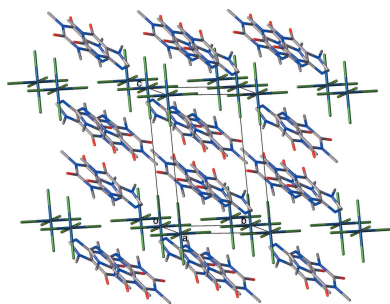
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The molecular and crystal structure of the title compound, (C<sub>8</sub>H<sub>11</sub>N<sub>4</sub>O<sub>2</sub>)<sub>2</sub>[PtCl<sub>6</sub>], synthesized from hexachloroplatinic acid and caffeine in methanol, was studied by single-crystal X-ray diffraction. The caffeinium cations form a double layer *via* hydrogen bonds and  $\pi$ -stacking interactions. The Hirshfeld surface analysis showed that the largest contribution to the crystal packing is made by H $\cdots$ H (31.2%), H $\cdots$ Cl/Cl $\cdots$ H (22.6%), O $\cdots$ H/H $\cdots$ O (21.9%) contacts for the cation and H $\cdots$ Cl/Cl $\cdots$ H (79.3%) contacts for the anion.

## 1. Chemical context

Caffeine is a biologically active compound involved in a number of biochemical processes (Costa *et al.*, 2010; Santos *et al.*, 2010; Herman & Herman, 2012). Some sources consider it the most common medicine in the world, constantly used by the population (Knapik *et al.*, 2022). It is known that caffeine compounds are able to exert a strong influence on the action of various pharmaceutical drugs (Traganos *et al.*, 1991). Currently, an active search is underway for platinum-based pharmaceutical drugs, primarily those with antitumor activity (Dilruba & Kalayda, 2016). In this regard, it seemed important to us to study the interaction of caffeine with the chemical forms of platinum used in the pharmaceutical industry. In addition, platinum is actively used as a catalyst in chemical reactions, including various fields of fine organic synthesis (Blaser & Studer, 2007; Zhang *et al.*, 2006; Seselj *et al.*, 2015). Study of interaction of Pt<sup>IV</sup> with various heterocyclic organic molecules is of great importance in the context of search for new catalytic reactions and synthetic routes. Studies on the interaction of hexachloroplatinates with various biological organic compounds have been performed before, for example by Novikov *et al.* (2021, 2022).

In this work, the title compound **I** containing [PtCl<sub>6</sub>]<sup>2-</sup> anions and caffeinium cations was synthesized by the reaction of caffeine with H<sub>2</sub>[PtCl<sub>6</sub>] in methanol and structurally characterized, using Hirshfeld surface analysis to estimate relative contribution of non-covalent intermolecular interactions in comparison with similar compounds, bis(3-carboxypyridinium) hexachloroplatinum RECJAO (**II**; Novikov *et al.*, 2022)



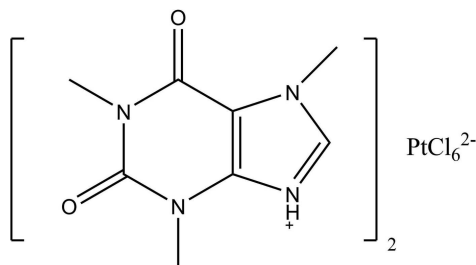
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**Table 1**  
 Selected geometric parameters (Å, °).

Pt1—Cl1	2.3153 (6)	Pt1—Cl3	2.3222 (6)
Pt1—Cl2	2.3161 (6)		
Cl1—Pt1—Cl2	89.97 (2)	Cl1 <sup>i</sup> —Pt1—Cl3	89.93 (2)
Cl1 <sup>i</sup> —Pt1—Cl2	90.03 (2)	Cl2 <sup>i</sup> —Pt1—Cl3 <sup>i</sup>	89.48 (3)
Cl1—Pt1—Cl3	90.07 (2)	Cl2—Pt1—Cl3 <sup>i</sup>	90.52 (3)

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

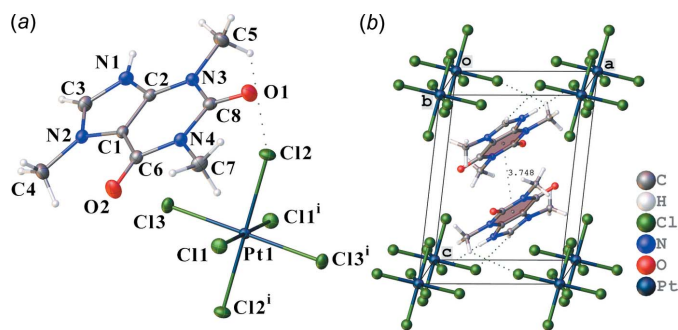
 and methylcaffeinium hexafluorophosphate AXUQIT (**III**); Kascatan-Nebioglu *et al.*, 2004).


## 2. Structural commentary

Compound **I** (Fig. 1a) crystallizes in the triclinic space group  $P\bar{1}$ . The unit cell (Fig. 1b) contains two caffeine cations and one centrosymmetric hexachloroplatinate anion with a platinum atom in a special position 1a. In the imidazole ring of the caffeine molecule, the nitrogen N1 atom is protonated. The cation, including the methyl groups, has a flat geometry (maximum deviation for non-hydrogen atoms 0.030 Å). The  $[\text{PtCl}_6]^{2-}$  anion has a slightly distorted octahedral geometry with similar Pt—Cl bond distances (Table 1).

## 3. Supramolecular features

Hydrogen bonds and  $\pi$ -stacking play a significant role in the formation of intermolecular interactions in the crystal structure of **I**.  $\pi$ -stacking is observed between the six-membered pyrimidine rings. Pairs of parallel cations related by an inversion centre, are stacked with interplanar separation of 3.404 (3) Å (Fig. 1b).


**Figure 1**  
 (a) Molecular structure of the title compound and (b) the unit cell with  $\pi$ -stacking interactions [symmetry code: (i)  $-x, -y, -z$ ].

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 <sup>i</sup> ···Cl3 <sup>ii</sup>	0.85 (2)	2.45 (2)	3.296 (2)	174 (3)
C3—H3···Cl2 <sup>ii</sup>	0.89 (3)	2.81 (3)	3.455 (3)	131 (3)
C5—H5C···Cl2	0.96	2.91	3.563 (3)	127
C7—H7B···O1 <sup>iii</sup>	0.96	2.44	3.346 (4)	157

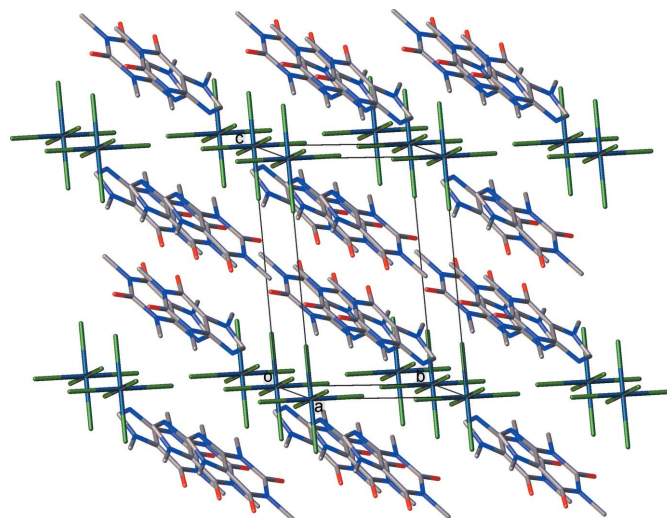
 Symmetry codes: (ii)  $-x + 1, -y + 1, -z$ ; (iii)  $-x + 1, -y, -z + 1$ .

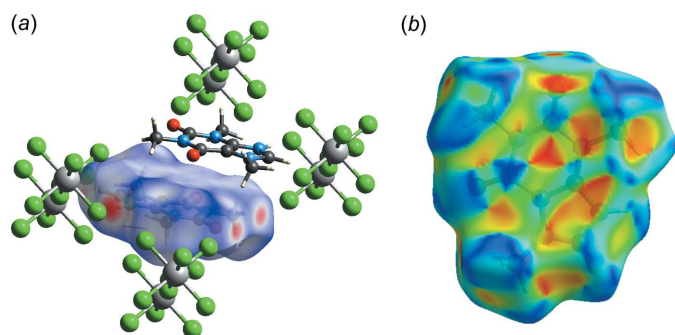
Similarly,  $\pi$ -halogen interactions (Lucas *et al.*, 2016; Savastano *et al.*, 2018; Frontera *et al.*, 2011; Novikov *et al.*, 2022) are found between the aromatic ring C6/N4/C8/N3/C2/C1 (centroid  $C_z$ ) and chlorine atoms Cl1 and Cl2, with  $C_z\cdots\text{Cl}$  distances of 3.8643 (11) and 3.7170 (11) Å, respectively, and  $\alpha$  angles between the ring plane and the  $C_z\cdots\text{Cl}$  vector of 61.82 (7) and 62.28 (7)°, respectively. It is uncertain whether such an interaction exists with Cl3 [ $C_z\cdots\text{Cl} = 4.1102$  (12) Å,  $\alpha = 58.68$  (8)°].

The crystal packing in **I** can be represented as cationic and anionic layers parallel to the (001) plane (Fig. 2). The caffeine cations are linked by  $\pi$ -stacking interactions and weak C—H···O hydrogen bonds into double layers, which are connected to the anionic layers by hydrogen bonds of the N—H···Cl and C—H···C types (Table 2), the N1—H1···Cl3<sup>ii</sup> [symmetry code: (ii)  $-x + 1, -y + 1, -z$ ] interaction being the strongest.

## 4. Hirshfeld surface analysis

*Crystal Explorer 21* was used to calculate the Hirshfeld surfaces (HS) and two-dimensional fingerprint plots (Figs. 3 and 4). The donor and acceptor groups are visualized using a standard (high) surface resolution and  $d_{\text{norm}}$  surfaces are mapped over a fixed colour scale of  $-0.401$  (red) to  $1.063$  (blue) for cation and  $-0.402$  to  $0.934$  a.u. for anion, as illus-

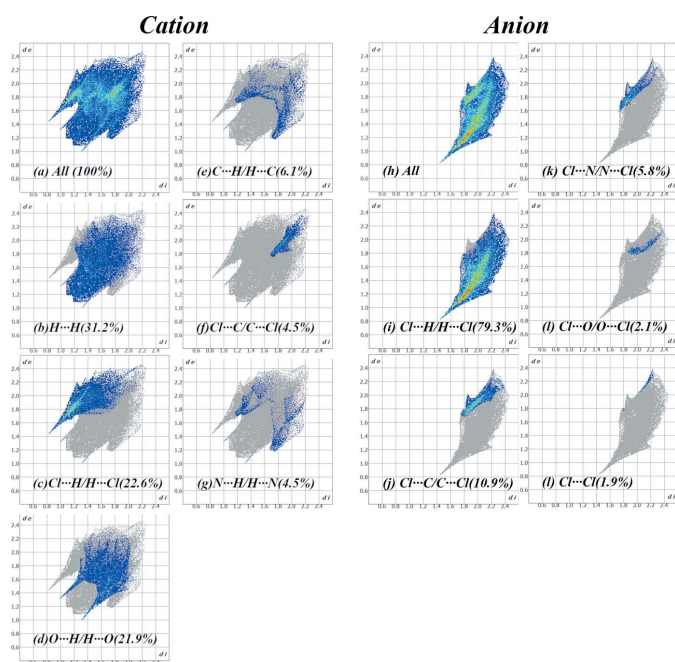

**Figure 2**  
 Crystal packing of **I**, showing the pseudo-layered character.



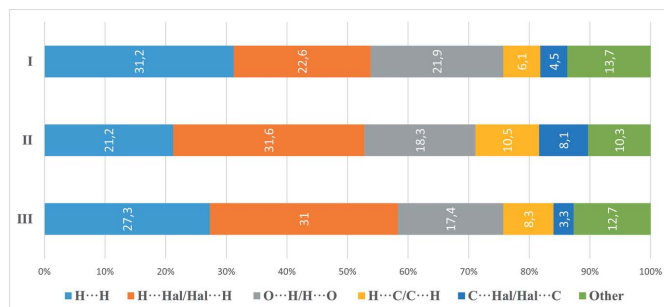
**Figure 3**  
Hirshfeld surface of the caffeinium cation mapped over (a)  $d_{\text{norm}}$  and (b) shape-index.

trated in Fig. 3. Additionally, characteristic red and blue triangles indicative of  $\pi$ -stacking interactions are observed on the shape-index surface (Fig. 3b).

Analysis of intermolecular contacts shows that for the caffeinium cation, the largest contributions are made by  $\text{H}\cdots\text{H}$ ,  $\text{Cl}\cdots\text{H}/\text{H}\cdots\text{Cl}$  and  $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$  contacts (Fig. 5), and for the anion, by  $\text{Cl}\cdots\text{H}/\text{H}\cdots\text{Cl}$  and  $\text{Cl}\cdots\text{C}/\text{C}\cdots\text{Cl}$  contacts (Fig. 6). Whereas  $\text{H}\cdots\text{H}$  contacts correspond to van der Waals interactions,  $\text{O}\cdots\text{H}$  and  $\text{Cl}\cdots\text{H}$  contacts can be described as weak hydrogen bonds. Typically, hydrogen bonds are revealed by characteristic discrete ‘spikes’ in the fingerprint plots – indeed, such features can be observed in Fig. 4c,d,i. The structures of **II** and **III** show distributions of contacts (Figs. 5 and 6) broadly similar to that of **I**, if corrected for the different cation–anion ratios (1:1 for **I** and **III**, 2:1 for **II**).



**Figure 4**  
Two-dimensional fingerprint plots for the cations and anions in **I**.



**Figure 5**  
Percentage contributions of intermolecular interactions for the cations in **I** and similar compounds.

## 5. Database survey

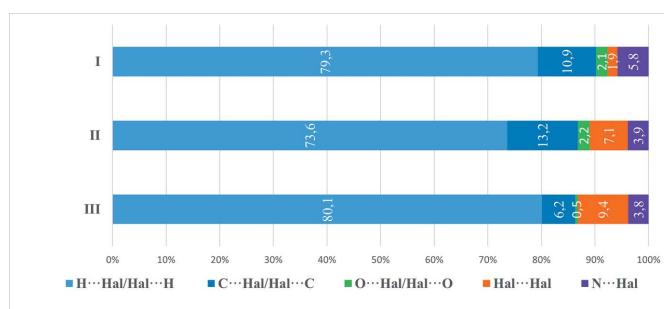
A search of the Cambridge Structural Database (CSD, Version 5.43, update of November 2022; Groom *et al.*, 2016) revealed 13 unique structures with caffeinium cations, but none of them contained anions of  $\text{MHal}_6$  type. The closest analogues of **I** found were **II** and **III** (see above), the former containing N-protonated 3-carboxypyridine (nicotinic acid) as the cation and  $[\text{PtCl}_6]^{2-}$  as the anion, the latter containing a caffeinium cation with a methylated (rather than protonated) N1 atom and a  $\text{PF}_6^-$  anion.

## 6. Synthesis and crystallization

A saturated solution of dried caffeine in 5 mL of methanol was prepared, to which a few drops of a concentrated solution of hexachloroplatinic acid in hydrochloric acid were added. After one week, the yellow crystals of **I** that formed were extracted from the solution.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Reflections with resolution  $> 5 \text{ \AA}$ , obscured by the beamstop (beam diameter 0.6 mm), were excluded from the refinement. The methyl groups  $\text{C5H}_3$  and  $\text{C7H}_3$  were refined as rigid bodies rotating around N–C



**Figure 6**  
Percentage contributions of intermolecular interactions for the anions in **I** and similar compounds.

Table 3

Experimental details.

Crystal data	
Chemical formula	(C <sub>8</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub> ) <sub>2</sub> [PtCl <sub>6</sub> ]
<i>M</i> <sub>r</sub>	798.20
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.8800 (2), 8.1542 (2), 10.5374 (3)
$\alpha$ , $\beta$ , $\gamma$ (°)	95.784 (2), 91.525 (2), 112.472 (1)
<i>V</i> (Å <sup>3</sup> )	620.92 (3)
<i>Z</i>	1
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	6.34
Crystal size (mm)	0.18 × 0.08 × 0.02
Data collection	
Diffractometer	Bruker Kappa APEXII area-detector
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.734, 1.000
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	9764, 3616, 3573
<i>R</i> <sub>int</sub>	0.035
(sin $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.703
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.022, 0.041, 1.04
No. of reflections	3616
No. of parameters	173
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.45, -0.89

Computer programs: *APEX3* (Bruker, 2018), *SAINT* (Bruker, 2013), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

bonds [*U*<sub>iso</sub>(H) refined], C4H<sub>3</sub> as rotationally disordered between two orientations with occupancies of 0.62 (4) and 0.38 (4) [*U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C)], with C–H 0.96 Å in each case. The H atoms at N1 and C3 were refined isotropically.

### Acknowledgements

The X-ray diffraction experiment was carried out at the Centre of Shared Use of Physical Methods of Investigation of IPCE RAS.

### Funding information

Funding for this research was provided by: Ministry of Science and Higher Education of the Russian Federation (award No. 122011300061-3). This work was supported by the RUDN University Strategic Academic Leadership Program.

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## supporting information

*Acta Cryst.* (2023). E79, 644-647 [https://doi.org/10.1107/S2056989023005157]

## Synthesis, crystal structure and Hirshfeld surface analysis of bis(caffeinium) hexachloridoplatinum(IV) in comparison with some related compounds

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### Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *S SAINT* v7.68A (Bruker, 2013); data reduction: *S SAINT* v7.68A (Bruker, 2013); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: Olex2 1.5 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 1.5 (Dolomanov *et al.*, 2009).

### Bis(1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-9-ium) hexachloridoplatinum(IV)

#### Crystal data

(C<sub>8</sub>H<sub>11</sub>N<sub>4</sub>O<sub>2</sub>)<sub>2</sub>[PtCl<sub>6</sub>]

*M<sub>r</sub>* = 798.20

Triclinic, *P* $\bar{1}$

*a* = 7.8800 (2) Å

*b* = 8.1542 (2) Å

*c* = 10.5374 (3) Å

$\alpha$  = 95.784 (2)°

$\beta$  = 91.525 (2)°

$\gamma$  = 112.472 (1)°

*V* = 620.92 (3) Å<sup>3</sup>

*Z* = 1

*F*(000) = 386

*D<sub>x</sub>* = 2.135 Mg m<sup>-3</sup>

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

Cell parameters from 4212 reflections

$\theta$  = 3.1–29.8°

$\mu$  = 6.34 mm<sup>-1</sup>

*T* = 296 K

Plate, orange

0.18 × 0.08 × 0.02 mm

#### Data collection

Bruker Kappa APEXII area-detector diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)

*T<sub>min</sub>* = 0.734, *T<sub>max</sub>* = 1.000

9764 measured reflections

3616 independent reflections

3573 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.035

$\theta_{\max}$  = 30.0°,  $\theta_{\min}$  = 3.5°

*h* = -11→11

*k* = -11→11

*l* = -14→14

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.022

*wR*(*F*<sup>2</sup>) = 0.041

*S* = 1.04

3616 reflections

173 parameters

1 restraint

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

*w* = 1/[ $\sigma^2(F_o^2) + (0.0171P)^2$ ]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.89 \text{ e } \text{\AA}^{-3}$$

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Pt1	0.000000	0.000000	0.000000	0.02050 (4)	
Cl1	-0.04784 (10)	0.01026 (9)	0.21599 (5)	0.03560 (15)	
Cl2	0.30304 (9)	0.03978 (10)	0.04685 (6)	0.03557 (14)	
Cl3	0.08989 (10)	0.30803 (8)	0.01376 (6)	0.03532 (14)	
O1	0.5394 (3)	0.1187 (3)	0.3683 (2)	0.0474 (5)	
O2	0.1510 (3)	0.4010 (3)	0.4685 (2)	0.0517 (6)	
N1	0.5642 (3)	0.6187 (3)	0.1713 (2)	0.0340 (5)	
H1	0.656 (3)	0.646 (4)	0.126 (3)	0.053 (10)*	
N2	0.3378 (3)	0.6487 (3)	0.2696 (2)	0.0317 (5)	
N3	0.5758 (3)	0.3628 (3)	0.2700 (2)	0.0296 (5)	
N4	0.3502 (3)	0.2641 (3)	0.42037 (19)	0.0289 (5)	
C1	0.3648 (4)	0.5055 (3)	0.3126 (2)	0.0271 (5)	
C2	0.5073 (4)	0.4880 (3)	0.2510 (2)	0.0269 (5)	
C3	0.4589 (4)	0.7135 (4)	0.1859 (3)	0.0378 (7)	
H3	0.475 (4)	0.812 (4)	0.150 (3)	0.046 (9)*	
C4	0.1984 (5)	0.7171 (4)	0.3115 (3)	0.0485 (8)	
H4A	0.127241	0.645910	0.373253	0.058*	0.38 (4)
H4B	0.258237	0.838989	0.349513	0.058*	0.38 (4)
H4C	0.118735	0.711220	0.239191	0.058*	0.38 (4)
H4D	0.208901	0.818169	0.268052	0.058*	0.62 (4)
H4E	0.077905	0.625090	0.291792	0.058*	0.62 (4)
H4F	0.217407	0.752859	0.402113	0.058*	0.62 (4)
C5	0.7299 (4)	0.3460 (4)	0.2023 (3)	0.0461 (8)	
H5A	0.817041	0.334293	0.262454	0.097 (9)*	
H5B	0.788825	0.450488	0.160388	0.097 (9)*	
H5C	0.684455	0.242150	0.139850	0.097 (9)*	
C6	0.2746 (4)	0.3915 (3)	0.4059 (2)	0.0306 (5)	
C7	0.2650 (4)	0.1360 (4)	0.5105 (3)	0.0387 (7)	
H7A	0.226895	0.194389	0.581227	0.051 (5)*	
H7B	0.352395	0.090814	0.541266	0.051 (5)*	
H7C	0.159753	0.038818	0.468151	0.051 (5)*	
C8	0.4901 (4)	0.2398 (4)	0.3536 (2)	0.0312 (6)	

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Pt1	0.02068 (7)	0.02260 (7)	0.01919 (6)	0.00823 (5)	0.00384 (4)	0.00678 (4)

C11	0.0415 (4)	0.0448 (4)	0.0214 (3)	0.0164 (3)	0.0078 (2)	0.0081 (2)
C12	0.0232 (3)	0.0458 (4)	0.0396 (3)	0.0136 (3)	0.0015 (2)	0.0125 (3)
C13	0.0420 (4)	0.0236 (3)	0.0410 (3)	0.0114 (3)	0.0123 (3)	0.0088 (2)
O1	0.0488 (13)	0.0419 (12)	0.0622 (14)	0.0242 (11)	0.0122 (10)	0.0258 (10)
O2	0.0584 (15)	0.0519 (14)	0.0569 (13)	0.0294 (12)	0.0344 (11)	0.0201 (11)
N1	0.0342 (13)	0.0317 (12)	0.0351 (12)	0.0088 (10)	0.0109 (10)	0.0131 (9)
N2	0.0337 (12)	0.0253 (11)	0.0357 (11)	0.0106 (10)	0.0019 (9)	0.0054 (9)
N3	0.0285 (12)	0.0289 (11)	0.0327 (11)	0.0110 (9)	0.0066 (9)	0.0085 (8)
N4	0.0331 (12)	0.0278 (11)	0.0258 (10)	0.0103 (9)	0.0052 (8)	0.0090 (8)
C1	0.0280 (13)	0.0218 (12)	0.0303 (12)	0.0079 (10)	0.0015 (10)	0.0040 (9)
C2	0.0288 (13)	0.0236 (12)	0.0251 (11)	0.0062 (10)	0.0009 (9)	0.0049 (9)
C3	0.0453 (18)	0.0281 (14)	0.0393 (15)	0.0110 (13)	0.0048 (12)	0.0129 (11)
C4	0.0430 (18)	0.0396 (18)	0.071 (2)	0.0243 (15)	0.0078 (16)	0.0092 (15)
C5	0.0368 (17)	0.0457 (18)	0.062 (2)	0.0201 (14)	0.0206 (14)	0.0134 (15)
C6	0.0328 (14)	0.0288 (13)	0.0283 (12)	0.0097 (11)	0.0043 (10)	0.0033 (10)
C7	0.0433 (17)	0.0378 (16)	0.0320 (13)	0.0087 (13)	0.0098 (12)	0.0172 (11)
C8	0.0290 (14)	0.0296 (14)	0.0329 (13)	0.0081 (11)	0.0001 (10)	0.0082 (10)

*Geometric parameters (Å, °)*

Pt1—C11 <sup>i</sup>	2.3153 (6)	N4—C7	1.464 (3)
Pt1—C11	2.3153 (6)	N4—C8	1.389 (3)
Pt1—C12 <sup>i</sup>	2.3161 (6)	C1—C2	1.358 (4)
Pt1—C12	2.3161 (6)	C1—C6	1.433 (3)
Pt1—C13	2.3222 (6)	C3—H3	0.89 (3)
Pt1—C13 <sup>i</sup>	2.3222 (6)	C4—H4A	0.9600
O1—C8	1.213 (3)	C4—H4B	0.9600
O2—C6	1.213 (3)	C4—H4C	0.9600
N1—H1	0.846 (18)	C4—H4D	0.9600
N1—C2	1.370 (3)	C4—H4E	0.9600
N1—C3	1.335 (4)	C4—H4F	0.9600
N2—C1	1.380 (3)	C5—H5A	0.9600
N2—C3	1.312 (4)	C5—H5B	0.9600
N2—C4	1.469 (4)	C5—H5C	0.9600
N3—C2	1.354 (3)	C7—H7A	0.9600
N3—C5	1.468 (3)	C7—H7B	0.9600
N3—C8	1.389 (3)	C7—H7C	0.9600
N4—C6	1.399 (3)		
C11 <sup>i</sup> —Pt1—C11	180.0	C1—C2—N1	107.3 (2)
C11—Pt1—C12	89.97 (2)	N1—C3—H3	125 (2)
C11—Pt1—C12 <sup>i</sup>	90.03 (2)	N2—C3—N1	109.9 (2)
C11 <sup>i</sup> —Pt1—C12	90.03 (2)	N2—C3—H3	125 (2)
C11 <sup>i</sup> —Pt1—C12 <sup>i</sup>	89.97 (2)	N2—C4—H4A	109.5
C11—Pt1—C13 <sup>i</sup>	89.93 (2)	N2—C4—H4B	109.5
C11—Pt1—C13	90.07 (2)	N2—C4—H4C	109.5
C11 <sup>i</sup> —Pt1—C13	89.93 (2)	H4A—C4—H4B	109.5
C11 <sup>i</sup> —Pt1—C13 <sup>i</sup>	90.07 (2)	H4A—C4—H4C	109.5

C12—Pt1—Cl2 <sup>i</sup>	180.0	H4B—C4—H4C	109.5
Cl2 <sup>i</sup> —Pt1—Cl3	90.52 (3)	H4D—C4—H4E	109.5
Cl2—Pt1—Cl3	89.48 (3)	H4D—C4—H4F	109.5
Cl2 <sup>i</sup> —Pt1—Cl3 <sup>i</sup>	89.48 (3)	H4E—C4—H4F	109.5
Cl2—Pt1—Cl3 <sup>i</sup>	90.52 (3)	N3—C5—H5A	109.5
Cl3 <sup>i</sup> —Pt1—Cl3	180.0	N3—C5—H5B	109.5
C2—N1—H1	128 (2)	N3—C5—H5C	109.5
C3—N1—H1	124 (2)	H5A—C5—H5B	109.5
C3—N1—C2	107.7 (2)	H5A—C5—H5C	109.5
C1—N2—C4	125.7 (2)	H5B—C5—H5C	109.5
C3—N2—C1	108.2 (2)	O2—C6—N4	122.2 (2)
C3—N2—C4	126.1 (2)	O2—C6—C1	126.5 (3)
C2—N3—C5	123.2 (2)	N4—C6—C1	111.2 (2)
C2—N3—C8	117.9 (2)	N4—C7—H7A	109.5
C8—N3—C5	118.8 (2)	N4—C7—H7B	109.5
C6—N4—C7	116.2 (2)	N4—C7—H7C	109.5
C8—N4—C6	127.2 (2)	H7A—C7—H7B	109.5
C8—N4—C7	116.5 (2)	H7A—C7—H7C	109.5
N2—C1—C6	131.1 (2)	H7B—C7—H7C	109.5
C2—C1—N2	106.9 (2)	O1—C8—N3	120.5 (3)
C2—C1—C6	122.0 (2)	O1—C8—N4	122.1 (2)
N3—C2—N1	128.6 (2)	N4—C8—N3	117.3 (2)
N3—C2—C1	124.1 (2)		
N2—C1—C2—N1	-0.4 (3)	C5—N3—C2—N1	-0.8 (4)
N2—C1—C2—N3	179.0 (2)	C5—N3—C2—C1	179.9 (3)
N2—C1—C6—O2	-0.4 (5)	C5—N3—C8—O1	-1.5 (4)
N2—C1—C6—N4	-179.0 (2)	C5—N3—C8—N4	177.2 (2)
C1—N2—C3—N1	0.3 (3)	C6—N4—C8—O1	-175.8 (3)
C2—N1—C3—N2	-0.6 (3)	C6—N4—C8—N3	5.4 (4)
C2—N3—C8—O1	175.7 (2)	C6—C1—C2—N1	-178.6 (2)
C2—N3—C8—N4	-5.5 (3)	C6—C1—C2—N3	0.7 (4)
C2—C1—C6—O2	177.4 (3)	C7—N4—C6—O2	3.3 (4)
C2—C1—C6—N4	-1.2 (3)	C7—N4—C6—C1	-178.1 (2)
C3—N1—C2—N3	-178.7 (3)	C7—N4—C8—O1	0.3 (4)
C3—N1—C2—C1	0.6 (3)	C7—N4—C8—N3	-178.4 (2)
C3—N2—C1—C2	0.0 (3)	C8—N3—C2—N1	-178.0 (3)
C3—N2—C1—C6	178.1 (3)	C8—N3—C2—C1	2.8 (4)
C4—N2—C1—C2	-179.4 (3)	C8—N4—C6—O2	179.4 (3)
C4—N2—C1—C6	-1.4 (4)	C8—N4—C6—C1	-2.0 (4)
C4—N2—C3—N1	179.8 (3)		

Symmetry code: (i)  $-x, -y, -z$ .*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ Cl3 <sup>ii</sup>	0.85 (2)	2.45 (2)	3.296 (2)	174 (3)



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C3—H3···Cl2 <sup>ii</sup>	0.89 (3)	2.81 (3)	3.455 (3)	131 (3)
C5—H5C···Cl2	0.96	2.91	3.563 (3)	127
C7—H7B···O1 <sup>iii</sup>	0.96	2.44	3.346 (4)	157

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