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cis-Dichlorido(dimethyl sulfoxide-κS)-(*N*,*N*,*N*′,*N*′-tetramethylguanidine-$\kappa N''$)-platinum(II)

Ivan I. Eliseev,[a] Nadezhda A. Bokach,[a] Matti Haukka[b] and Irina A. Golenya[c]*

[a]Department of Chemistry, St Petersburg State University, 198504 Petrodvorets, Russian Federation, [b]University of Joensuu, Department of Chemistry, PO Box, 111, FI-80101 Joensuu, Finland, and [c]Kiev National Taras Shevchenko University, Department of Chemistry, Volodymyrska Str. 64, 01601 Kiev, Ukraine
Correspondence e-mail: igolenya@ua.fm

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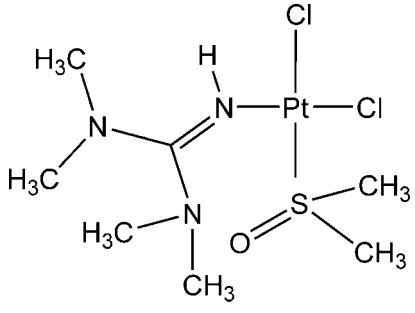
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(N–C) = 0.007 Å; R factor = 0.023; wR factor = 0.045; data-to-parameter ratio = 23.1.

In the title compound, *cis*-[$PtCl_2(C_5H_{13}N_3)(C_2H_6OS)$], the four-coordinate Pt^{II} atom is bonded to one N atom of the *N*,*N*,*N*′,*N*′-tetramethylguanidine ligand, one dimethyl sulfoxide S atom and two chloride ligands, forming a *cis*-square-planar geometry. The bond lengths and angles of the N—Pt—Cl functionality are typical for imine dichloridoplatinum(II) complexes. The H atom of the imino group is oriented towards the O atom of the sulfoxide group of a neighboring molecule and forms an N—H···O hydrogen bond.

Related literature

For guanidines serving as nucleophiles towards metal-activated nitriles at Pt^{II} and Pt^{IV} atoms, see: Gushchin *et al.* (2007, 2008); Tyan *et al.* (2008). For related structures, see: Bokach *et al.* (2003); Fairlie *et al.* (1997); Gonzalez *et al.* (2002); Makarycheva-Mikhailova *et al.* (2003). For a description of the Cambridge Structural Database, see: Allen (2002). For standard bond lengths, see: Allen *et al.* (1987).



Experimental

Crystal data

$[PtCl_2(C_5H_{13}N_3)(C_2H_6OS)]$
M_r = 459.30
Monoclinic, *Cc*
a = 10.1577 (5) Å
b = 19.1711 (8) Å
c = 8.6536 (3) Å
β = 119.304 (2)°
V = 1469.51 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 10.04 mm^{-1}
T = 120 K
0.24 × 0.13 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.151, T_{max} = 0.299
12560 measured reflections
3280 independent reflections
3044 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.045
S = 1.03
3280 reflections
142 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.49 e Å^{-3}
$\Delta\rho_{min}$ = −1.64 e Å^{-3}
Absolute structure: Flack (1983), 1598 Friedel pairs
Flack parameter: 0.008 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O1^{i}	0.86	2.21	3.021 (5)	159

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2007); 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: HG5281).

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supplementary materials

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cis-Dichlorido(dimethyl sulfoxide-κ*S*)(*N*,*N*,*N*′,*N*′-tetramethylguanidine-κ*N*′′)platinum(II)

Ivan I. Eliseev, Nadezhda A. Bokach, Matti Haukka and Irina A. Golenya

Comment

As a part of our ongoing investigations on structural features of platinum complexes with guanidines (Gushchin *et al.*, 2007; Gushchin *et al.*, 2008) a new compound, (I), having PtII-bound N,N,N′,N′-tetramethylguanidine, has been prepared and herein we report its X-ray crystal and molecular structures.

In the compound, the four-coordinate Pt atom has a distorted cis-square planar geometry where the Pt atom is bonded by one N atom of the N,N,N′,N′-tetramethylguanidine ligand and one S atom of the dimethyl sulfoxide and two chlorides in the *cis*-position (Fig. 1 and Table 1). The values of the Pt–Cl bond distances (2.3214 (13) and 2.327 (2) Å) agree well with those of previously characterized platinum(II) chloride compounds (Makarycheva-Mikhailova *et al.*, 2003; Gonzalez *et al.*, 2002). The Pt–N bonds [2.013 (4) Å for Pt–N_{imine}] are in accord with those found in *cis-/trans*-[$Pt(NH_3)_2${NH=C(NH_2)NMe_2}] (2.031 (9)/2.020 (3) Å), (Tyan *et al.*, 2008), [Pt{NH=C(NH_2)NMe_2}(dien)] $[SO_3CF_3]_2$ (2.018 (7) Å), (Fairlie *et al.*, 1997) and [$PtCl_4${NH=C(NMe_2)OC(NMe_2)=NH}] (2.015 (5) Å) (Bokach *et al.*, 2003).

The C=N bond length (C(1)–N(1) 1.316 (6) Å) is equal, within 3σ, to the average C=N double bond distance (1.31 Å) obtained from the Cambridge Crystal Structural Database (Version 5.27; Allen, 2002). The bond lengths C(1)–N(2) and C(1)–N(3) [1.342 (7) and 1.352 (6) Å, respectively] have values closer to a typical C–N single bond [Nsp^2–Csp^2 in amides 1.346 (11) Å] (Allen, 1987). In addition, the C=N bond length (1.316 (6) Å) and the C–N bonds lengths (C(1)–N(2) 1.342 (7), C(1)–N(3) 1.352 (6) Å) exhibit values typical, within 3σ, for the $(amidine)_2Pt^{II}$ complexes, viz. [Pt{NH=C(NH_2)NMe_2}(dien)]$^{2+}$, (1.31 (1), 1.394 (8) and 1.33 (1) Å) (Fairlie *et al.*, 1997), and *cis-/trans*-[$Pt(NH_3)_2${NH=C(NH_2)NMe_2}] (1.284 (14)/1.288 (5), 1.364 (14)/1.352 (5) and 1.364 (14)/1.341 (5) Å), (Tyan *et al.*, 2008). The H atom of the imino function is oriented towards the O atom of the sulfoxide group of the neighboring molecule forming the intermolecular hydrogen bond (Figure 2, Table 2).

Experimental

N,N,N′,N′-Tetramethylguanidine (13.8 g, 0.12 mmol) was added to K[$PtCl_3$(DMSO)] (50.0 mg, 0.12 mmol) in water (1 mL) and the reaction mixture was kept at room temperature for 2 h. The yellow crystalline precipitate were mechanically separated and subjected to the X-ray study. IR (KBr, selected bands, cm–1): 3008 (m, N–H), 1616 (s, C=N), 1134 (s, S=O); 1H NMR (CDCl3, δ, p.p.m.): 4.40 (s, br, 1H, =NH), 3,40 (s, 6H, Me2SO), 3.00 (s, br, 12H, Me2N–); Analyses calculated for $C_7H_{19}N_3Cl_2OPtS$: C 18.31, H 4.17, N 9.15%; found: C 18.05, H 4.15, N 8.59%.

Refinement

The NH hydrogen atoms was located from the difference Fourier map but constrained to ride on it's parent atom, with U_{iso} = 1.5 U_{eq}(parent atom). Other hydrogen atoms were positioned geometrically and were also constrained to ride on their

parent atoms, with C—H = 0.98 Å, and U_{iso} = 1.5 U_{eq}(parent atom). The highest peak is located 1.49 Å from atom H4B and the deepest hole is located 0.87 Å from atom Pt1.

Computing details

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

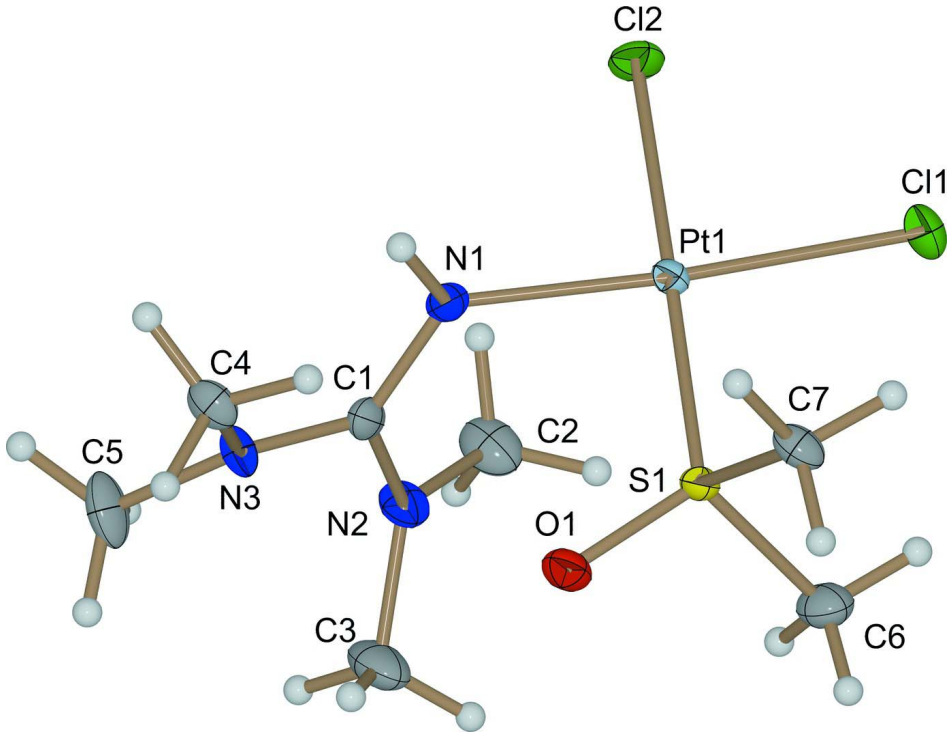

Figure 1

Molecular structure of (I), showing the atom-numbering scheme with displacement ellipsoids drawn at the 50% probability level.

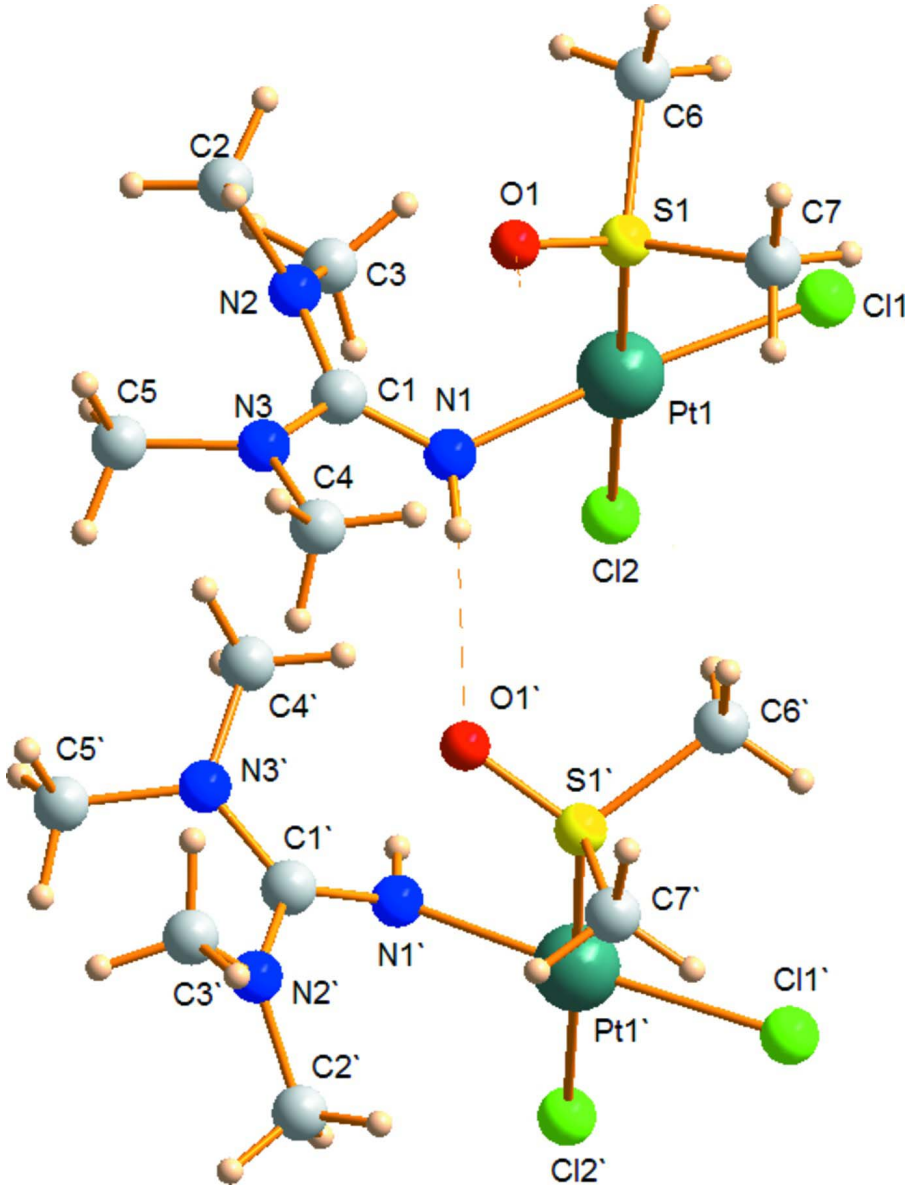

Figure 2

Molecular structure of (I), showing the intermolecular hydrogen bond.

cis-Dichlorido(dimethyl sulfoxide-_κS_)(_N_,_N_,_N′_,_N′_- tetramethylguanidine)platinum(II)

Crystal data

$[PtCl_2(C_5H_{13}N_3)(C_2H_6OS)]$
$M_r = 459.30$
Monoclinic, *Cc*
Hall symbol: C -2yc
$a = 10.1577\ (5)$ Å
$b = 19.1711\ (8)$ Å
$c = 8.6536\ (3)$ Å
$\beta = 119.304\ (2)°$
$V = 1469.51\ (11)$ Å^3
$Z = 4$
$F(000) = 872$
$D_x = 2.076$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6239 reflections
$\theta = 1.0–27.5°$
$\mu = 10.04$ mm^{-1}
$T = 120$ K
Block, pale yellow
0.24 × 0.13 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Horizontally mounted graphite crystal monochromator
Detector resolution: 9 pixels mm^{-1}
φ scans and ω scans with κ offset
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.151, T_{max} = 0.299
12560 measured reflections
3280 independent reflections
3044 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 27.5°, θ_{min} = 3.4°
h = −13→13
k = −24→24
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.045
S = 1.03
3280 reflections
142 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.49 e Å^{-3}
$\Delta\rho_{min}$ = −1.64 e Å^{-3}
Absolute structure: Flack (1983), 1598 Friedel pairs
Flack parameter: 0.008 (6)

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.

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 $F^2 > 2\text{sigma}(F^2)$ 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	0.96648 (6)	0.110788 (7)	1.03671 (6)	0.01299 (6)
Cl1	1.20421 (15)	0.15985 (7)	1.14273 (16)	0.0221 (3)
Cl2	0.9945 (3)	0.11372 (8)	1.3201 (3)	0.0229 (6)
S1	0.9352 (2)	0.10943 (7)	0.7678 (3)	0.0133 (5)
O1	0.7956 (4)	0.07948 (18)	0.6268 (4)	0.0197 (7)
N1	0.7691 (5)	0.0608 (2)	0.9550 (5)	0.0172 (9)
H1N	0.7766	0.0172	0.9792	0.026*
N2	0.5880 (5)	0.1425 (2)	0.7857 (6)	0.0201 (9)
N3	0.5363 (5)	0.0249 (2)	0.7283 (5)	0.0170 (9)
C1	0.6341 (6)	0.0760 (3)	0.8237 (6)	0.0162 (10)
C2	0.6478 (7)	0.1974 (3)	0.9182 (7)	0.0281 (12)
H2A	0.6875	0.1769	1.0365	0.042*
H2B	0.5671	0.2305	0.8972	0.042*
H2C	0.7291	0.2218	0.9105	0.042*

C3	0.4915 (7)	0.1652 (3)	0.6032 (7)	0.0329 (13)
H3A	0.4858	0.1281	0.5220	0.049*
H3B	0.5340	0.2074	0.5807	0.049*
H3C	0.3901	0.1752	0.5843	0.049*
C4	0.5856 (6)	−0.0446 (2)	0.7127 (6)	0.0201 (11)
H4A	0.6924	−0.0432	0.7446	0.030*
H4B	0.5253	−0.0610	0.5904	0.030*
H4C	0.5723	−0.0764	0.7926	0.030*
C5	0.3737 (6)	0.0318 (3)	0.6638 (8)	0.0300 (13)
H5A	0.3546	0.0749	0.7105	0.045*
H5B	0.3384	−0.0082	0.7039	0.045*
H5C	0.3197	0.0334	0.5340	0.045*
C6	0.9526 (7)	0.1948 (3)	0.7012 (7)	0.0250 (12)
H6A	0.9526	0.1926	0.5880	0.038*
H6B	1.0473	0.2157	0.7914	0.038*
H6C	0.8674	0.2234	0.6872	0.038*
C7	1.0888 (6)	0.0668 (3)	0.7656 (6)	0.0189 (11)
H7A	1.0886	0.0174	0.7943	0.028*
H7B	1.1836	0.0884	0.8537	0.028*
H7C	1.0791	0.0711	0.6477	0.028*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.01236 (9)	0.01404 (8)	0.01011 (8)	−0.00112 (17)	0.00359 (6)	−0.00035 (14)
Cl1	0.0163 (6)	0.0239 (6)	0.0214 (6)	−0.0052 (5)	0.0056 (5)	−0.0047 (5)
Cl2	0.0297 (13)	0.0281 (12)	0.0108 (10)	−0.0039 (8)	0.0099 (9)	−0.0004 (6)
S1	0.0130 (10)	0.0138 (10)	0.0105 (9)	0.0002 (6)	0.0037 (8)	0.0016 (6)
O1	0.018 (2)	0.0257 (19)	0.0129 (17)	0.0000 (15)	0.0058 (15)	−0.0009 (14)
N1	0.021 (2)	0.016 (2)	0.013 (2)	−0.0045 (17)	0.0072 (18)	0.0003 (16)
N2	0.016 (2)	0.018 (2)	0.022 (2)	0.0048 (18)	0.0057 (19)	0.0029 (18)
N3	0.010 (2)	0.019 (2)	0.020 (2)	−0.0008 (17)	0.0053 (18)	−0.0029 (17)
C1	0.013 (3)	0.022 (3)	0.016 (2)	−0.001 (2)	0.009 (2)	0.002 (2)
C2	0.027 (3)	0.021 (3)	0.030 (3)	0.005 (2)	0.008 (3)	−0.002 (2)
C3	0.026 (3)	0.029 (3)	0.026 (3)	0.002 (3)	−0.001 (3)	0.006 (2)
C4	0.019 (3)	0.019 (3)	0.017 (2)	0.000 (2)	0.006 (2)	−0.006 (2)
C5	0.014 (3)	0.032 (3)	0.044 (4)	−0.003 (2)	0.014 (3)	−0.010 (3)
C6	0.029 (3)	0.021 (3)	0.021 (3)	0.001 (2)	0.009 (2)	0.005 (2)
C7	0.016 (3)	0.019 (3)	0.017 (2)	0.004 (2)	0.004 (2)	−0.002 (2)

Geometric parameters (Å, º)

Pt1—N1	2.013 (4)	C2—H2C	0.9800
Pt1—S1	2.189 (2)	C3—H3A	0.9800
Pt1—Cl1	2.3214 (13)	C3—H3B	0.9800
Pt1—Cl2	2.327 (2)	C3—H3C	0.9800
S1—O1	1.462 (4)	C4—H4A	0.9800
S1—C7	1.769 (5)	C4—H4B	0.9800
S1—C6	1.773 (5)	C4—H4C	0.9800
N1—C1	1.316 (6)	C5—H5A	0.9800

N1—H1N	0.8556	C5—H5B	0.9800
N2—C1	1.342 (7)	C5—H5C	0.9800
N2—C2	1.452 (7)	C6—H6A	0.9800
N2—C3	1.459 (7)	C6—H6B	0.9800
N3—C1	1.352 (6)	C6—H6C	0.9800
N3—C4	1.451 (6)	C7—H7A	0.9800
N3—C5	1.467 (6)	C7—H7B	0.9800
C2—H2A	0.9800	C7—H7C	0.9800
C2—H2B	0.9800		

N1—Pt1—S1	91.13 (12)	N2—C3—H3A	109.5
N1—Pt1—Cl1	175.21 (12)	N2—C3—H3B	109.5
S1—Pt1—Cl1	90.38 (7)	H3A—C3—H3B	109.5
N1—Pt1—Cl2	88.20 (12)	N2—C3—H3C	109.5
S1—Pt1—Cl2	178.66 (11)	H3A—C3—H3C	109.5
Cl1—Pt1—Cl2	90.38 (7)	H3B—C3—H3C	109.5
O1—S1—C7	108.1 (2)	N3—C4—H4A	109.5
O1—S1—C6	107.6 (3)	N3—C4—H4B	109.5
C7—S1—C6	101.2 (3)	H4A—C4—H4B	109.5
O1—S1—Pt1	117.94 (19)	N3—C4—H4C	109.5
C7—S1—Pt1	110.29 (19)	H4A—C4—H4C	109.5
C6—S1—Pt1	110.4 (2)	H4B—C4—H4C	109.5
C1—N1—Pt1	129.5 (3)	N3—C5—H5A	109.5
C1—N1—H1N	111.0	N3—C5—H5B	109.5
Pt1—N1—H1N	115.1	H5A—C5—H5B	109.5
C1—N2—C2	122.2 (4)	N3—C5—H5C	109.5
C1—N2—C3	121.1 (4)	H5A—C5—H5C	109.5
C2—N2—C3	116.1 (4)	H5B—C5—H5C	109.5
C1—N3—C4	122.5 (4)	S1—C6—H6A	109.5
C1—N3—C5	121.4 (4)	S1—C6—H6B	109.5
C4—N3—C5	115.0 (4)	H6A—C6—H6B	109.5
N1—C1—N2	120.9 (5)	S1—C6—H6C	109.5
N1—C1—N3	120.7 (4)	H6A—C6—H6C	109.5
N2—C1—N3	118.4 (4)	H6B—C6—H6C	109.5
N2—C2—H2A	109.5	S1—C7—H7A	109.5
N2—C2—H2B	109.5	S1—C7—H7B	109.5
H2A—C2—H2B	109.5	H7A—C7—H7B	109.5
N2—C2—H2C	109.5	S1—C7—H7C	109.5
H2A—C2—H2C	109.5	H7A—C7—H7C	109.5
H2B—C2—H2C	109.5	H7B—C7—H7C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1^{i}	0.86	2.21	3.021 (5)	159

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