

(2,2'-Bipyrimidine- κ^2N^1, N^1')bis(thiocyanato- κN)platinum(II)

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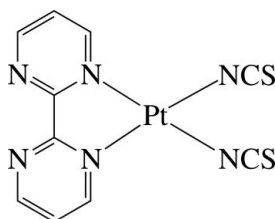
Received 19 April 2012; accepted 19 April 2012

Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(C-C) = 0.017$ Å; R factor = 0.043; wR factor = 0.105; data-to-parameter ratio = 14.3.

In the title complex, $[Pt(NCS)_2(C_8H_6N_4)]$, the Pt^{II} ion is four-coordinated in a distorted square-planar environment defined by two pyrimidine N atoms derived from a chelating 2,2'-bipyrimidine (bpym) ligand and two mutually *cis* N atoms from two SCN^- anions. The thiocyanate ligands are almost linear, displaying N—C—S bond angles of 178.6 (11) and 173.7 (11)°, and the N atoms are slightly bent coordinated to the Pt atom with Pt—N—C bond angles of 172.7 (9) and 160.4 (10)°. In the crystal, molecules are held together by C—H...S hydrogen bonds. Intramolecular C—H...N hydrogen bonds are also observed.

Related literature

For the crystal structures of related Pt^{II} complexes $[PtX_2(bpym)]$ ($X = Cl, I$ or Br), see: Kaim *et al.* (2002); Ha (2010, 2011).



Experimental

Crystal data

$[Pt(NCS)_2(C_8H_6N_4)]$
 $M_r = 469.42$
Monoclinic, $P2_1/n$
 $a = 11.0871$ (8) Å
 $b = 9.8779$ (7) Å
 $c = 12.8790$ (9) Å
 $\beta = 115.135$ (1)°

$V = 1276.91$ (16) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 11.31$ mm⁻¹
 $T = 200$ K
 $0.34 \times 0.28 \times 0.28$ mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{min} = 0.680$, $T_{max} = 1.000$

7611 measured reflections
2467 independent reflections
2179 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.105$
 $S = 1.09$
2467 reflections

172 parameters
H-atom parameters constrained
 $\Delta\rho_{max} = 4.86$ e Å⁻³
 $\Delta\rho_{min} = -1.72$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|--------|-----------|--------|------------|
| Pt1—N1 | 2.014 (9) | Pt1—N5 | 1.958 (9) |
| Pt1—N4 | 1.999 (8) | Pt1—N6 | 2.017 (11) |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------|-------|-------------|-------------|---------------|
| C1—H1...N5 | 0.95 | 2.55 | 3.053 (15) | 114 |
| C8—H8...N6 | 0.95 | 2.62 | 3.138 (15) | 115 |
| C8—H8...S2 ⁱ | 0.95 | 2.87 | 3.496 (11) | 124 |

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; 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*.

This work was supported by the Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0030747).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5882).

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supporting information

Acta Cryst. (2012). E68, m676 [doi:10.1107/S1600536812017552]

(2,2'-Bipyrimidine- κ^2N^1,N^1')bis(thiocyanato- κN)platinum(II)**Kwang Ha****S1. Comment**

Crystal structures of Pt^{II} complexes with 2,2'-bipyrimidine (bpym; C₈H₆N₄) and halogen ions, [PtX₂(bpym)] (X = Cl, I or Br), have been reported previously (Kaim *et al.*, 2002; Ha, 2010; Ha, 2011).

In the title complex, [Pt(NCS)₂(bpym)], the Pt^{II} ion is four-coordinated in a distorted square-planar environment defined by two pyrimidine N atoms derived from a chelating bpym ligand and two mutually *cis* N atoms from two SCN⁻ anions (Fig. 1). The main contribution to the distortion is the tight N1—Pt1—N4 chelate angle of 80.9 (3)°, which results in non-linear *trans* axes [\angle N1—Pt1—N6 = 176.2 (4)° and \angle N4—Pt1—N5 = 174.5 (4)°]. The Pt—N(bpym) and Pt—N(NCS) bond lengths are nearly equivalent [Pt—N: 1.958 (9)–2.017 (11) Å] (Table 1). The thiocyanato ligands are almost linear displaying N—C—S bond angles of 178.6 (11)° and 173.7 (11)°, and the N atoms are slightly bent coordinated to the Pt atom with the Pt—N—C bond angles of 172.7 (9)° and 160.4 (10)°, characteristic of an N-bonded conformation. The nearly planar bpym ligand [maximum deviation = 0.09 (1) Å] is slightly inclined to the least-squares plane of the PtN₄ unit [maximum deviation = 0.015 (5) Å], making a dihedral angle of 3.6 (5)°. In the crystal, two complex molecules are assembled by intermolecular C—H \cdots S hydrogen bonds with C \cdots S = 3.496 (11) Å, forming a dimer-type species (Fig. 2, Table 2). Intramolecular C—H \cdots N hydrogen bonds are also observed (Table 2).

S2. Experimental

To a solution of K₂PtCl₄ (0.2087 g, 0.503 mmol) in H₂O (15 ml) and acetone (15 ml) were added KSCN (0.5071 g, 5.218 mmol) and 2,2'-bipyrimidine (0.0809 g, 0.512 mmol), and refluxed for 3 h. After evaporation of the solvent, the residue was dissolved in CH₃CN (20 ml), then filtered through a plug of silica gel (2 cm x 7 cm). The solvent of the eluate was removed *in vacuo*, the residue was washed with ether, and dried at 323 K, to give an orange powder (0.0686 g). Orange block-like crystals, suitable for X-ray analysis, were obtained by slow evaporation of a CH₃CN solution at room temperature.

S3. Refinement

H atoms were included in calculated positions and treated as riding atoms: C—H = 0.95 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The highest peak (4.86 e Å⁻³) and the deepest hole (-1.72 e Å⁻³) in the difference Fourier map are located 0.91 Å and 0.79 Å, respectively, from the Pt1 atom.

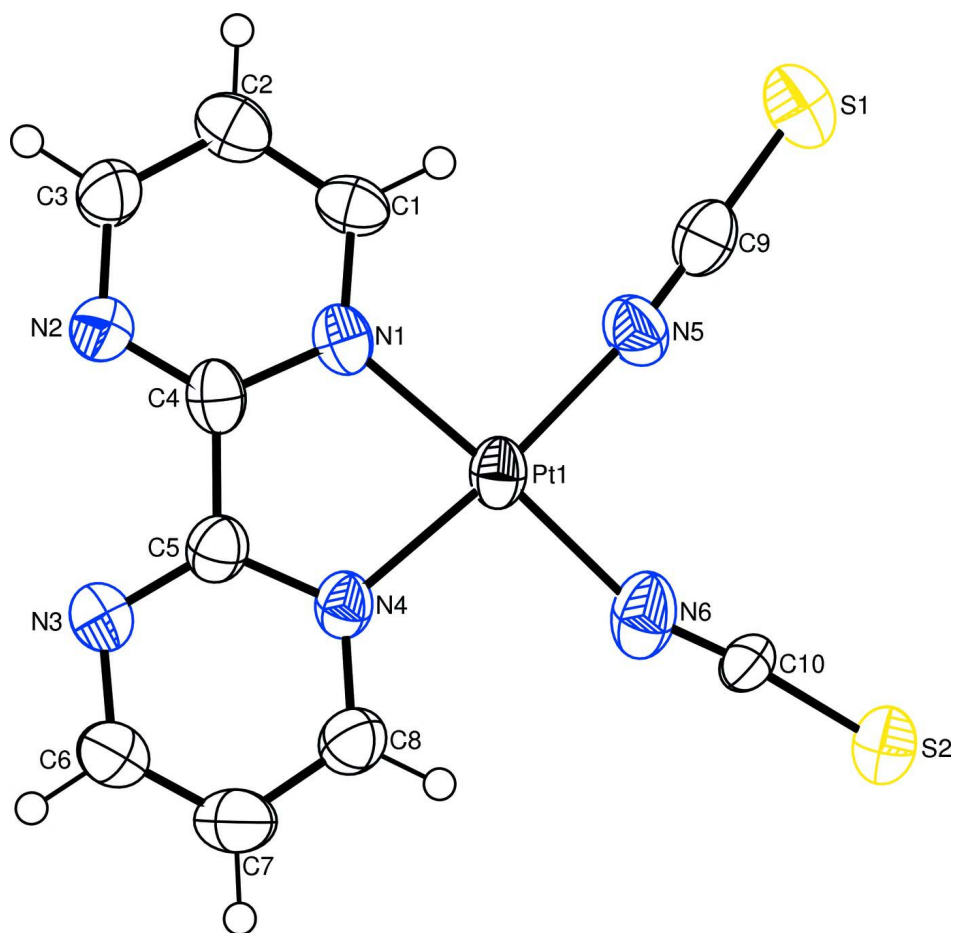


Figure 1

The molecular structure of the title complex, with atom numbering. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

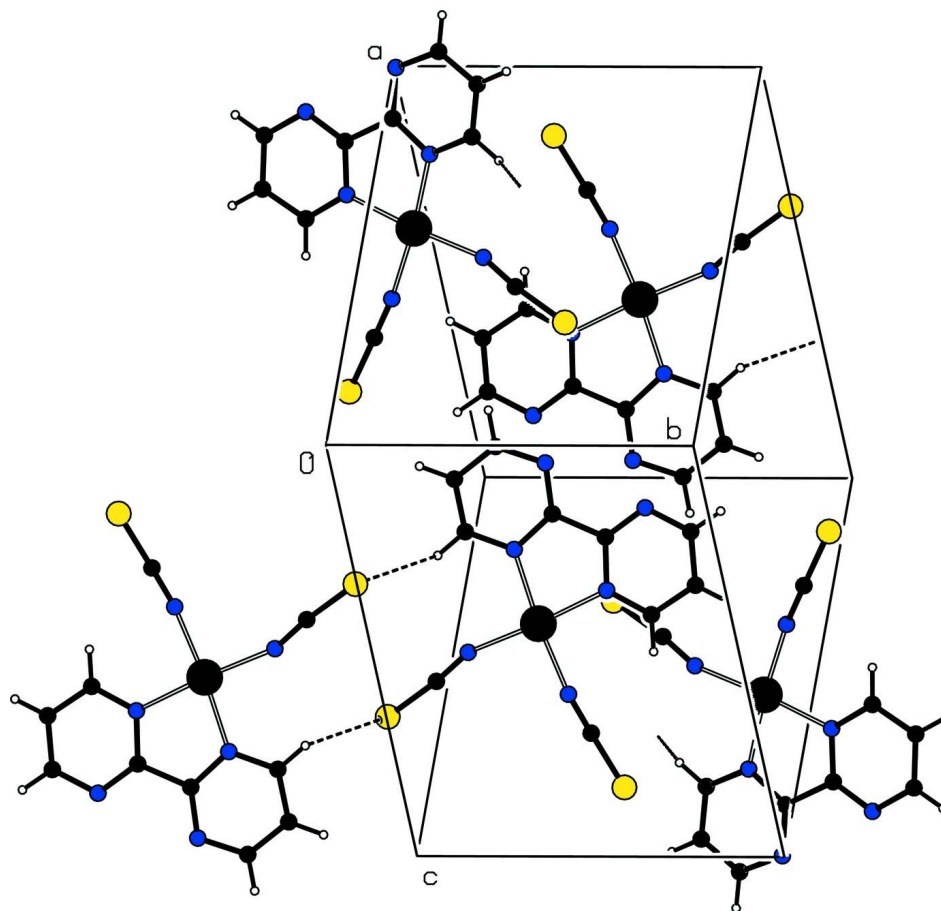


Figure 2

A view along the *a* axis of the crystal packing of the title complex. Intermolecular C—H...S hydrogen-bonds are shown as dashed lines (see Table 2 for details).

(2,2'-Bipyrimidine- κ^2N^1,N^1')bis(thiocyanato- κN)platinum(II)

Crystal data

[Pt(NCS)₂(C₈H₆N₄)]

M_r = 469.42

Monoclinic, *P*2₁/*n*

Hall symbol: -*P* 2₁/*n*

a = 11.0871 (8) Å

b = 9.8779 (7) Å

c = 12.8790 (9) Å

β = 115.135 (1)°

V = 1276.91 (16) Å³

Z = 4

F(000) = 872

D_x = 2.442 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 5056 reflections

θ = 2.7–26.0°

μ = 11.31 mm⁻¹

T = 200 K

Block, orange

0.34 × 0.28 × 0.28 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} = 0.680, *T_{max}* = 1.000

7611 measured reflections

2467 independent reflections

2179 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 2.0^\circ$

$h = -13 \rightarrow 13$
 $k = -12 \rightarrow 11$
 $l = -15 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.105$
 $S = 1.09$
 2467 reflections
 172 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
 $w = 1/[\sigma^2(F_o^2) + (0.030P)^2 + 21.4936P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 4.86 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.72 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|-------------|----------------------------------|
| Pt1 | 0.16191 (4) | 0.40380 (4) | 0.58301 (3) | 0.04005 (15) |
| S1 | -0.0058 (3) | 0.6087 (4) | 0.8261 (3) | 0.0601 (8) |
| S2 | 0.0260 (3) | -0.0068 (3) | 0.6854 (3) | 0.0519 (7) |
| N1 | 0.2144 (8) | 0.5882 (9) | 0.5497 (7) | 0.0382 (18) |
| N2 | 0.3270 (10) | 0.6962 (9) | 0.4524 (8) | 0.050 (2) |
| N3 | 0.3600 (10) | 0.4377 (10) | 0.3743 (8) | 0.049 (2) |
| N4 | 0.2425 (8) | 0.3496 (9) | 0.4767 (7) | 0.0385 (18) |
| N5 | 0.0853 (9) | 0.4748 (10) | 0.6838 (8) | 0.048 (2) |
| N6 | 0.1173 (10) | 0.2136 (11) | 0.6120 (8) | 0.058 (3) |
| C1 | 0.1920 (10) | 0.7047 (11) | 0.5879 (8) | 0.042 (2) |
| H1 | 0.1456 | 0.7078 | 0.6352 | 0.051* |
| C2 | 0.2375 (11) | 0.8237 (12) | 0.5579 (9) | 0.048 (3) |
| H2 | 0.2214 | 0.9091 | 0.5835 | 0.057* |
| C3 | 0.3061 (12) | 0.8148 (11) | 0.4906 (9) | 0.049 (3) |
| H3 | 0.3390 | 0.8950 | 0.4711 | 0.059* |
| C4 | 0.2822 (10) | 0.5887 (11) | 0.4827 (8) | 0.041 (2) |
| C5 | 0.2989 (10) | 0.4514 (11) | 0.4419 (9) | 0.041 (2) |
| C6 | 0.3601 (12) | 0.3115 (12) | 0.3349 (10) | 0.054 (3) |
| H6 | 0.4017 | 0.2973 | 0.2848 | 0.064* |
| C7 | 0.3040 (13) | 0.2034 (12) | 0.3627 (10) | 0.055 (3) |
| H7 | 0.3042 | 0.1161 | 0.3317 | 0.066* |
| C8 | 0.2465 (11) | 0.2250 (11) | 0.4376 (9) | 0.047 (2) |

| | | | | |
|-----|-------------|-------------|------------|-----------|
| H8 | 0.2097 | 0.1511 | 0.4615 | 0.056* |
| C9 | 0.0462 (10) | 0.5294 (12) | 0.7422 (9) | 0.046 (3) |
| C10 | 0.0757 (10) | 0.1268 (10) | 0.6445 (9) | 0.038 (2) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|---------------|--------------|--------------|
| Pt1 | 0.0392 (2) | 0.0493 (3) | 0.0308 (2) | −0.00470 (17) | 0.01392 (16) | 0.00473 (17) |
| S1 | 0.0539 (17) | 0.082 (2) | 0.0512 (17) | 0.0017 (16) | 0.0284 (14) | −0.0038 (16) |
| S2 | 0.0481 (15) | 0.0567 (17) | 0.0519 (16) | −0.0078 (13) | 0.0222 (13) | 0.0038 (13) |
| N1 | 0.035 (4) | 0.052 (5) | 0.025 (4) | 0.000 (4) | 0.010 (3) | 0.002 (4) |
| N2 | 0.068 (6) | 0.040 (5) | 0.051 (5) | −0.003 (4) | 0.034 (5) | 0.000 (4) |
| N3 | 0.059 (6) | 0.050 (6) | 0.047 (5) | −0.002 (4) | 0.030 (5) | −0.001 (4) |
| N4 | 0.041 (4) | 0.043 (5) | 0.030 (4) | −0.005 (4) | 0.014 (4) | 0.002 (4) |
| N5 | 0.052 (5) | 0.058 (6) | 0.040 (5) | −0.004 (5) | 0.025 (4) | −0.007 (4) |
| N6 | 0.062 (6) | 0.072 (7) | 0.039 (5) | −0.018 (5) | 0.020 (5) | 0.003 (5) |
| C1 | 0.046 (6) | 0.045 (6) | 0.032 (5) | 0.003 (5) | 0.013 (4) | −0.009 (4) |
| C2 | 0.049 (6) | 0.056 (7) | 0.032 (5) | 0.002 (5) | 0.012 (5) | −0.008 (5) |
| C3 | 0.062 (7) | 0.043 (6) | 0.047 (6) | −0.012 (5) | 0.028 (5) | −0.007 (5) |
| C4 | 0.036 (5) | 0.055 (6) | 0.029 (5) | −0.003 (5) | 0.011 (4) | 0.004 (4) |
| C5 | 0.040 (5) | 0.043 (6) | 0.040 (6) | −0.005 (4) | 0.016 (5) | 0.000 (4) |
| C6 | 0.066 (7) | 0.050 (7) | 0.052 (7) | 0.003 (6) | 0.032 (6) | −0.005 (5) |
| C7 | 0.072 (8) | 0.044 (6) | 0.047 (6) | 0.008 (6) | 0.021 (6) | −0.002 (5) |
| C8 | 0.053 (6) | 0.043 (6) | 0.043 (6) | −0.007 (5) | 0.019 (5) | −0.002 (5) |
| C9 | 0.043 (6) | 0.048 (6) | 0.041 (6) | −0.006 (5) | 0.011 (5) | 0.009 (5) |
| C10 | 0.048 (6) | 0.028 (5) | 0.041 (5) | −0.006 (4) | 0.023 (5) | 0.001 (4) |

Geometric parameters (Å, °)

| | | | |
|-----------|------------|----------|------------|
| Pt1—N1 | 2.014 (9) | N5—C9 | 1.151 (14) |
| Pt1—N4 | 1.999 (8) | N6—C10 | 1.135 (13) |
| Pt1—N5 | 1.958 (9) | C1—C2 | 1.397 (16) |
| Pt1—N6 | 2.017 (11) | C1—H1 | 0.9500 |
| S1—C9 | 1.625 (13) | C2—C3 | 1.378 (15) |
| S2—C10 | 1.602 (10) | C2—H2 | 0.9500 |
| N1—C1 | 1.316 (13) | C3—H3 | 0.9500 |
| N1—C4 | 1.363 (13) | C4—C5 | 1.494 (15) |
| N2—C4 | 1.301 (13) | C6—C7 | 1.359 (17) |
| N2—C3 | 1.328 (14) | C6—H6 | 0.9500 |
| N3—C5 | 1.318 (14) | C7—C8 | 1.380 (16) |
| N3—C6 | 1.346 (14) | C7—H7 | 0.9500 |
| N4—C8 | 1.338 (13) | C8—H8 | 0.9500 |
| N4—C5 | 1.357 (13) | | |
| N5—Pt1—N4 | 174.5 (4) | C1—C2—H2 | 120.6 |
| N5—Pt1—N1 | 93.6 (4) | N2—C3—C2 | 121.3 (11) |
| N4—Pt1—N1 | 80.9 (3) | N2—C3—H3 | 119.4 |
| N5—Pt1—N6 | 90.1 (4) | C2—C3—H3 | 119.4 |

| | | | |
|---------------|------------|--------------|-------------|
| N4—Pt1—N6 | 95.4 (4) | N2—C4—N1 | 125.1 (10) |
| N1—Pt1—N6 | 176.2 (4) | N2—C4—C5 | 121.0 (9) |
| C1—N1—C4 | 118.5 (9) | N1—C4—C5 | 113.8 (9) |
| C1—N1—Pt1 | 126.4 (7) | N3—C5—N4 | 125.5 (10) |
| C4—N1—Pt1 | 115.1 (7) | N3—C5—C4 | 120.1 (9) |
| C4—N2—C3 | 117.4 (9) | N4—C5—C4 | 114.4 (9) |
| C5—N3—C6 | 115.3 (10) | N3—C6—C7 | 123.7 (11) |
| C8—N4—C5 | 117.6 (9) | N3—C6—H6 | 118.1 |
| C8—N4—Pt1 | 126.9 (7) | C7—C6—H6 | 118.1 |
| C5—N4—Pt1 | 115.5 (7) | C6—C7—C8 | 117.5 (11) |
| C9—N5—Pt1 | 172.7 (9) | C6—C7—H7 | 121.3 |
| C10—N6—Pt1 | 160.4 (10) | C8—C7—H7 | 121.3 |
| N1—C1—C2 | 118.9 (10) | N4—C8—C7 | 120.3 (10) |
| N1—C1—H1 | 120.5 | N4—C8—H8 | 119.8 |
| C2—C1—H1 | 120.5 | C7—C8—H8 | 119.8 |
| C3—C2—C1 | 118.8 (10) | N5—C9—S1 | 178.6 (11) |
| C3—C2—H2 | 120.6 | N6—C10—S2 | 173.7 (11) |
| | | | |
| N5—Pt1—N1—C1 | -1.9 (8) | Pt1—N1—C4—N2 | -178.9 (8) |
| N4—Pt1—N1—C1 | 177.6 (9) | C1—N1—C4—C5 | -178.5 (8) |
| N5—Pt1—N1—C4 | 176.6 (7) | Pt1—N1—C4—C5 | 2.8 (10) |
| N4—Pt1—N1—C4 | -3.9 (7) | C6—N3—C5—N4 | 2.6 (16) |
| N1—Pt1—N4—C8 | -175.8 (9) | C6—N3—C5—C4 | -174.8 (10) |
| N6—Pt1—N4—C8 | 5.2 (9) | C8—N4—C5—N3 | -1.5 (16) |
| N1—Pt1—N4—C5 | 4.4 (7) | Pt1—N4—C5—N3 | 178.3 (9) |
| N6—Pt1—N4—C5 | -174.5 (7) | C8—N4—C5—C4 | 176.0 (9) |
| N5—Pt1—N6—C10 | 5 (3) | Pt1—N4—C5—C4 | -4.2 (11) |
| N4—Pt1—N6—C10 | -174 (3) | N2—C4—C5—N3 | 0.2 (16) |
| C4—N1—C1—C2 | 0.4 (14) | N1—C4—C5—N3 | 178.5 (9) |
| Pt1—N1—C1—C2 | 178.9 (7) | N2—C4—C5—N4 | -177.5 (9) |
| N1—C1—C2—C3 | -0.9 (15) | N1—C4—C5—N4 | 0.9 (13) |
| C4—N2—C3—C2 | -1.2 (17) | C5—N3—C6—C7 | -1.1 (18) |
| C1—C2—C3—N2 | 1.3 (17) | N3—C6—C7—C8 | -1.4 (19) |
| C3—N2—C4—N1 | 0.7 (16) | C5—N4—C8—C7 | -1.3 (15) |
| C3—N2—C4—C5 | 178.8 (10) | Pt1—N4—C8—C7 | 178.9 (8) |
| C1—N1—C4—N2 | -0.3 (15) | C6—C7—C8—N4 | 2.6 (17) |

Hydrogen-bond geometry (Å, °)

| <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> |
|--------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C1—H1 \cdots N5 | 0.95 | 2.55 | 3.053 (15) | 114 |
| C8—H8 \cdots N6 | 0.95 | 2.62 | 3.138 (15) | 115 |
| C8—H8 \cdots S2 ⁱ | 0.95 | 2.87 | 3.496 (11) | 124 |

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