metal-organic compounds

(2,2′-Bipyrimidine-$\kappa^2N^1,N^{1'}$)bis(thio-cyanato-κN)platinum(II)

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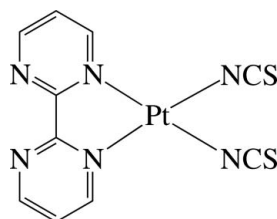Correspondence e-mail: hakwang@chonnam.ac.kr

In the title complex, [Pt(NCS)$_2$(C$_8$H$_6$N$_4$)], 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$_8$H$_6$N$_4$)]	V = 1276.91 (16) Å³
M_r = 469.42	Z = 4
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 11.0871 (8) Å	μ = 11.31 mm⁻¹
b = 9.8779 (7) Å	T = 200 K
c = 12.8790 (9) Å	0.34 × 0.28 × 0.28 mm
β = 115.135 (1)°	

Data collection

Bruker SMART 1000 CCD diffractometer	7611 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	2467 independent reflections
T_{min} = 0.680, T_{max} = 1.000	2179 reflections with $I > 2\sigma(I)$
	R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043	172 parameters
$wR(F^2)$ = 0.105	H-atom parameters constrained
S = 1.09	$\Delta\rho_{max}$ = 4.86 e Å⁻³
2467 reflections	$\Delta\rho_{min}$ = −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···A	D—H	H···A	D···A	D—H···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: *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*.

References

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supplementary materials

(2,2′-Bipyrimidine-*κ*²*N*¹,*N*¹′)bis(thiocyanato-*κN*)platinum(II)

Kwang Ha

Comment

Crystal structures of Pt^{II} complexes with 2,2′-bipyrimidine (bpym; $C_8H_6N_4$) and halogen ions, $[PtX_2(bpym)]$ (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 [<N1—Pt1—N6 = 176.2 (4)° and <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 PtN_4 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⋯S hydrogen bonds with C⋯S = 3.496 (11) Å, forming a dimer-type species (Fig. 2, Table 2). Intramolecular C—H⋯N hydrogen bonds are also observed (Table 2).

Experimental

To a solution of K_2PtCl_4 (0.2087 g, 0.503 mmol) in H_2O (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 CH_3CN (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 CH_3CN solution at room temperature.

Refinement

H atoms were included in calculated positions and treated as riding atoms: C—H = 0.95 Å with $U_{iso}(H) = 1.2U_{eq}(C)$. 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.

Computing details

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* (Bruker, 2000); 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* (Sheldrick, 2008).
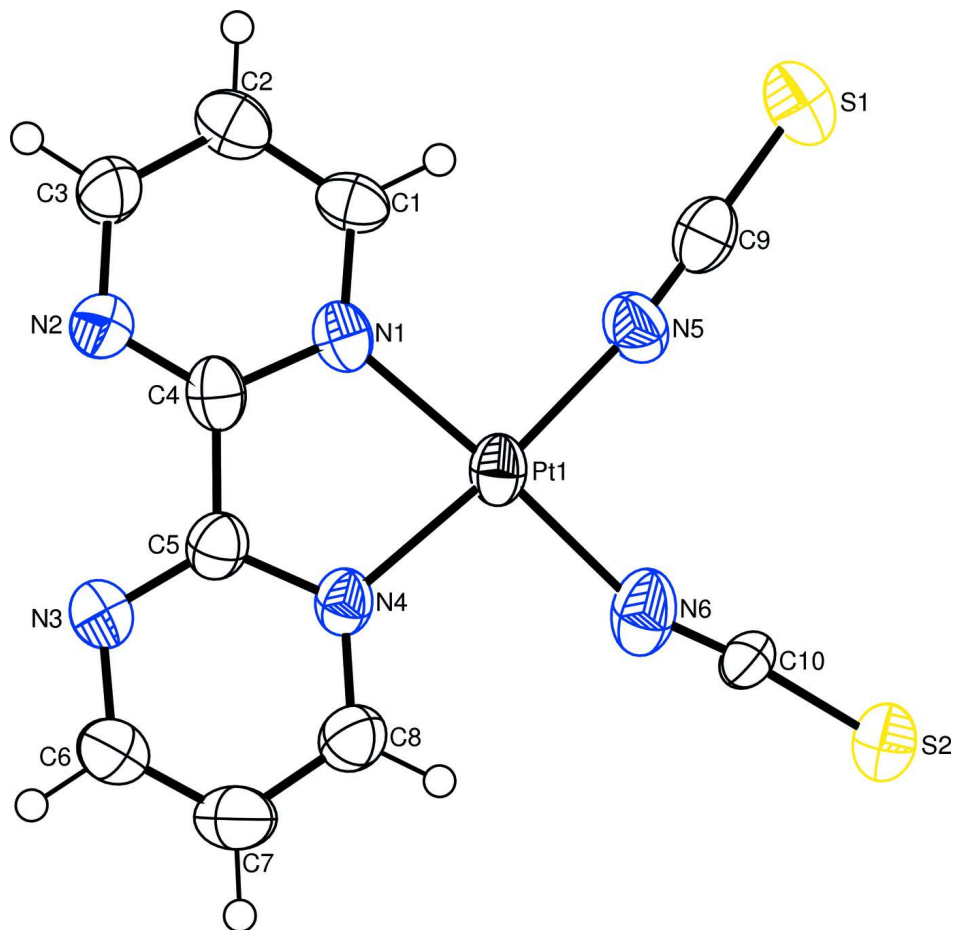
Figure 1

The molecular structure of the title complex, with atom numbering. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.
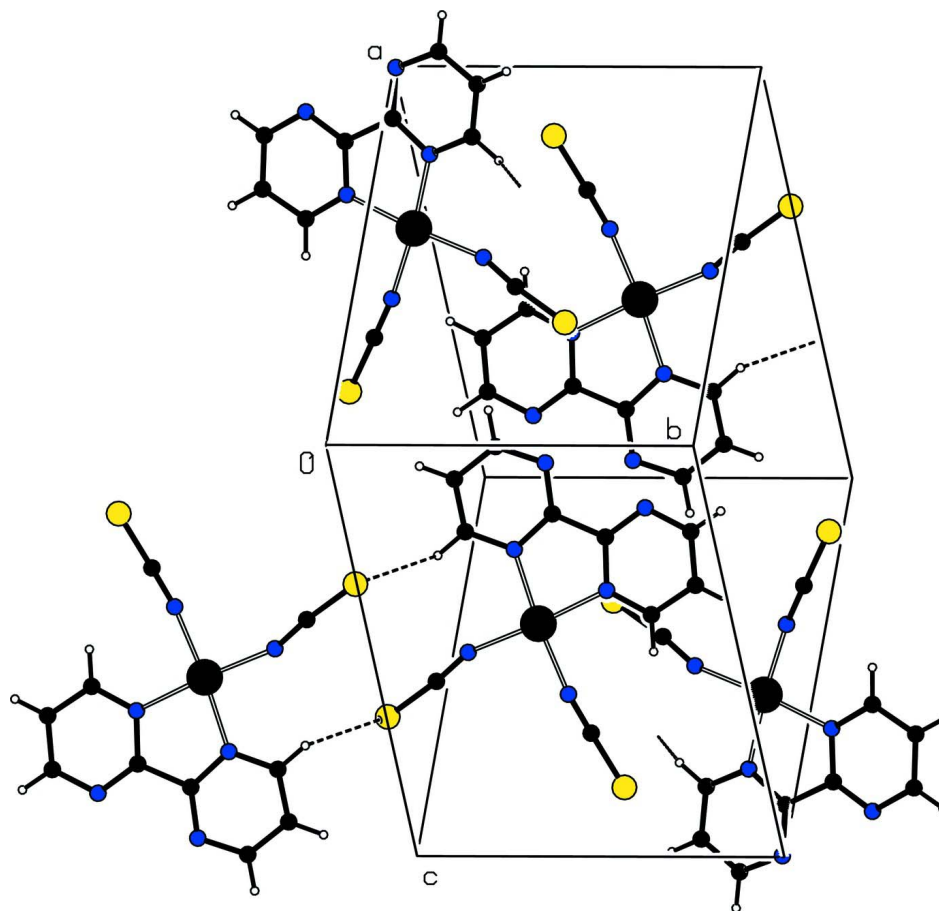
Figure 2

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-$\kappa^2 N^1,N^{1\prime}$)bis(thiocyanato- κN)platinum(II)

Crystal data

[Pt(NCS)$_2$(C$_8$H$_6$N$_4$)]	$F(000) = 872$
$M_r = 469.42$	$D_x = 2.442$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 5056 reflections
$a = 11.0871$ (8) Å	$\theta = 2.7–26.0°$
$b = 9.8779$ (7) Å	$\mu = 11.31$ mm^{-1}
$c = 12.8790$ (9) Å	$T = 200$ K
$\beta = 115.135$ (1)°	Block, orange
$V = 1276.91$ (16) Å^3	$0.34 \times 0.28 \times 0.28$ mm
$Z = 4$	

Data collection

Bruker SMART 1000 CCD diffractometer	Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
Radiation source: fine-focus sealed tube	$T_{min} = 0.680$, $T_{max} = 1.000$
Graphite monochromator	7611 measured reflections
φ and ω scans	2467 independent reflections

2179 reflections with $I > 2\sigma(I)$

$R_{int} = 0.026$

$\theta_{max} = 26.0°$, $\theta_{min} = 2.0°$

$h = -13 \rightarrow 13$

$k = -12 \rightarrow 11$

$l = -15 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.043$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.105$	
$S = 1.09$	H-atom parameters constrained
2467 reflections	$w = 1/[\sigma^2(F_o^2) + (0.030P)^2 + 21.4936P]$
172 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 4.86$ e Å^{-3}
	$\Delta\rho_{min} = -1.72$ e 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 (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
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, º)

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, º)

D—H···A	D—H	H···A	D···A	D—H···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.