metal-organic compounds

A nearly planar arrangement of ions in 4,4′-bipiperidinium tetracyanido-platinate(II) monohydrate

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The title compound, $(C_{10}H_{22}N_2)[Pt(CN)_4]\cdot H_2O$, was isolated from solution as a molecular salt. The compound contains discrete 4,4′-bipiperidinium cations and tetracyano-platinate(II) anions that are involved in a hydrogen-bonding network with one water molecule of hydration. The structure differs from that of the similar acetonitrile solvate, $(C_{10}H_{22}N_2)[Pt(CN)_4]\cdot 2CH_3CN$, in the orientation of the ions relative to one another. The hydrate reported here contains layers of nearly parallel cations and anions with an angle between their mean planes of only 4.35 (11)°, while in the acetonitrile solvate the cations and anions are nearly perpendicular to one another (86.1° between mean planes). The crystal showed partial inversion twinning.

Related literature

Organic dications such as 4,4′-bipyridinium and 4,4′-bipiperidinium have been shown to be successful in crystallizing a number of square-planar metallate anions, and a large number of salts containing these two ions have been reported (Lewis & Orpen, 1998; Angeloni & Orpen, 2001; Crawford *et al.*, 2004). For the acetonitrile solvate, with a contrasting arrangement of the ions, see Crawford *et al.* (2004).
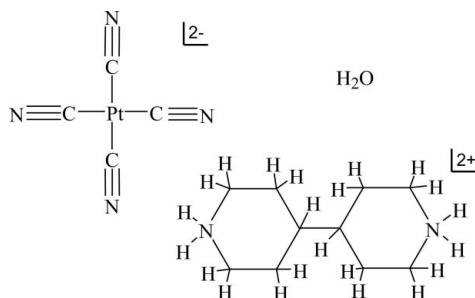
Experimental

Crystal data

$(C_{10}H_{22}N_2)[Pt(CN)_4]\cdot H_2O$	V = 1756.4 (6) Å^3
M_r = 487.48	Z = 4
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
a = 9.5246 (13) Å	μ = 8.00 mm^{-1}
b = 11.966 (3) Å	T = 290 (2) K
c = 15.411 (3) Å	$0.63 \times 0.60 \times 0.40$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	3233 independent reflections
Absorption correction: numerical (*XPREP* in *SHELXTL*; Bruker, 1998)	3030 reflections with $I > 2\sigma(I)$
	R_{int} = 0.025
	3 standard reflections
T_{min} = 0.014, T_{max} = 0.104	frequency: 120 min
3591 measured reflections	intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033	$\Delta\rho_{max}$ = 1.74 e Å^{-3}
$wR(F^2)$ = 0.088	$\Delta\rho_{min}$ = -0.69 e Å^{-3}
S = 1.10	Absolute structure: (Flack, 1983),
3233 reflections	1371 Friedel pairs
201 parameters	Flack parameter: 0.39 (10)
H-atom parameters constrained	

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N5—H5$A\cdots$O1^i	0.90	1.92	2.809 (12)	172
N5—H5$B\cdots$N2^{ii}	0.90	2.17	2.940 (12)	143
N5—H5$B\cdots$N4^{iii}	0.90	2.44	3.008 (13)	121
N6—H6$A\cdots$N4	0.90	2.25	2.976 (13)	137
N6—H6$A\cdots$N2^{iv}	0.90	2.42	3.021 (12)	125
N6—H6$B\cdots$N3^v	0.90	2.13	3.026 (12)	179
O1—H1$A\cdots$N1^{vi}	0.85	2.10	2.946 (11)	179
O1—H1$B\cdots$N3^v	0.85	2.27	3.125 (10)	180

Symmetry codes: (i) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$; (ii) $x-1, y+1, z$; (iii) $x, y+1, z$; (iv) $x-1, y, z$; (v) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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supporting information

A nearly planar arrangement of ions in 4,4′-bipiperidinium tetracyanidoplatinate(II) monohydrate

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S1. Comment

The title compound, $(C_{10}H_{22}N_2)Pt(CN)_4.H_2O$, was obtained as an unexpected product during a reaction that attempted to prepare a praseodymium tetracyanoplatinate incorporating 4,4′-bipiperidine.

The structure of (**I**) consists of separated 4,4′-bipiperidinium dications and tetracyanoplatinate anions, additionally one water molecule of crystallization is also present. Fig. 1 shows an illustration of the units of the structure along with the atomic labeling scheme. The 4,4′-bipiperidinium cations and tetracyanoplatinate anions lie in approximately the *ab* crystallographic planes and contain multiple hydrogen bonding interactions as can be seen in Fig. 2. Each of the approximately square planar anions is hydrogen bonded to four cations and each cation is also hydrogen bonded to four anions. See Table 1 for bond distances and angles of these hydrogen bonding interactions. The mean plane that passes through the 4,4′-bipiperidinium cation makes an angle of 4.35 (11)° with the mean plane of the tetracyanoplatinate anion in the structure, illustrating the nearly parallel nature of these groups relative to one another. Small cavities in these two dimensional planes are filled with water molecules that hydrogen bond within the plane to N1 and N3 atoms of the tetra-cyanoplatinate anions. Additional hydrogen bonding interactions are also present between the water molecules in one plane and H5A atoms of neighboring planes. See Table 1 for details of these H-bonding interactions.

Several major structural differences exist between **I** and the previously reported $(C_{10}H_{22}N_2)Pt(CN)_4.2CH_3CN$, **II** (Crawford *et al.*, 2004). While compound **I** contains a nearly parallel arrangement of the cations and anions, the 4,4′-bipiperidinium cations in **II** are nearly perpendicular to the tetracyanoplatinate anions. The angle between the mean planes formed by the two groups in **II** is 86.1°. This packing arrangement of the cations and anions in **II** leaves relatively large holes in the structure that accommodate acetonitrile solvate molecules. In **I**, the smallercavities contain water molecules.

S2. Experimental

$K_2Pt(CN)_4.3H_2O$ (Alfa Aesar, 99.9%), 4,4′-bipiperidine dihydrochloride (Aldrich, 97%), and $Pr(NO_3)_3.6H_2O$ (Strem Chemicals, 99.9%) were used as received without further purification. $K_2Pt(CN)_4.3H_2O$ (1 ml, 0.14 *M*) in 90%:10% $CH_3CN:H_2O$ was added to an CH_3CN solution of $Pr(NO_3)_3.6H_2O$ (1 ml, 0.10 *M*). 4,4′-bipiperidine dihydrochloride (1 ml, 0.077 *M*) in CH_3CN was then layered on this solution. Slow evaporation of the solvents over a period of several days resulted in colorless, prismatic crystals of the title compound.

S3. Refinement

H atoms of the 4,4′-bipiperidinium cation were placed in calculated positions and allowed to ride during subsequent refinement, with $U_{iso}(H) = 1.2U_{eq}(C)$ and C—H distances of 0.97 Å for H atoms bonded to the C atoms and $U_{iso}(H) = 1.2U_{eq}(N)$ and N—H distances of 0.90 Å for the H atoms bonded to the N atoms. The H atoms on the water molecule

were not located in the difference map, but were placed in calculated positions with O—H distances of 0.85 Å and $U_{iso}(H) = 1.2U_{eq}(O)$. The H atoms were not allowed to move during refinement. The crystal of **I** that was used for the diffraction study was found to be a racemic twin and therefore the refinement was carried out taking into account the inverted component.
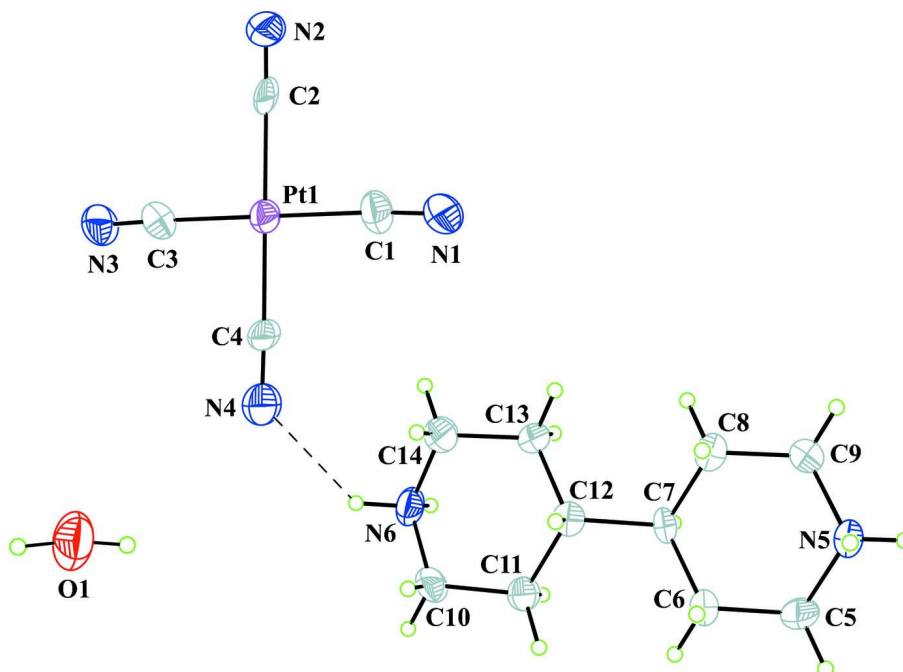

Figure 1

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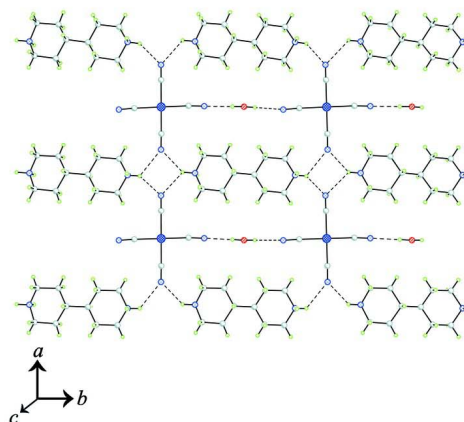

Figure 2

A representation of two-dimensional layers of 4,4′-bipiperidinium cations, tetracyanoplatinate anions and water molecules found in the *ab* plane of (I).

4,4′-bipiperidinium tetracyanidoplatinate monohydrate

Crystal data

$(C_{10}H_{22}N_2)[Pt(CN)_4]\cdot H_2O$	$F(000) = 944$
$M_r = 487.48$	$D_x = 1.843$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 25 reflections
$a = 9.5246$ (13) Å	$\theta = 8.2–11.7°$
$b = 11.966$ (3) Å	$\mu = 8.00$ mm^{-1}
$c = 15.411$ (3) Å	$T = 290$ K
$V = 1756.4$ (6) Å^3	Rectangular prism, colorless
$Z = 4$	$0.63 \times 0.60 \times 0.40$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	3233 independent reflections
Radiation source: fine-focus sealed tube	3030 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.025$
$\theta/2\theta$ scans	$\theta_{max} = 25.4°$, $\theta_{min} = 2.2°$
Absorption correction: analytical	$h = 0\rightarrow11$
(*XPREP*; Bruker, 1998)	$k = 0\rightarrow14$
$T_{min} = 0.014$, $T_{max} = 0.104$	$l = -18\rightarrow18$
3591 measured reflections	3 standard reflections every 120 min
	intensity decay: none

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 1.1497P]$
$wR(F^2) = 0.088$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
3233 reflections	$\Delta\rho_{max} = 1.74$ e Å^{-3}
201 parameters	$\Delta\rho_{min} = -0.69$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97*,
Primary atom site location: structure-invariant direct methods	Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0087 (5)
	Absolute structure: (Flack, 1983), 1371 Friedel pairs
	Absolute structure parameter: 0.39 (10)

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 $F^2 > 2\sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Pt1	0.78147 (3)	0.08308 (3)	0.143832 (18)	0.03168 (13)

C1	0.7890 (11)	0.2485 (8)	0.1344 (5)	0.0431 (18)
C2	0.9911 (9)	0.0805 (8)	0.1605 (6)	0.042 (2)
C3	0.7736 (10)	−0.0821 (7)	0.1573 (5)	0.0381 (17)
C4	0.5765 (8)	0.0854 (8)	0.1287 (6)	0.0378 (18)
C5	0.1305 (10)	0.8253 (9)	0.1135 (7)	0.044 (2)
H5C	0.0523	0.8616	0.0846	0.053*
H5D	0.1119	0.8247	0.1754	0.053*
C6	0.1454 (11)	0.7054 (7)	0.0804 (6)	0.038 (2)
H6C	0.0598	0.6646	0.0928	0.046*
H6D	0.1580	0.7066	0.0179	0.046*
C7	0.2665 (10)	0.6462 (6)	0.1210 (6)	0.0330 (18)
H7A	0.2521	0.6462	0.1840	0.040*
C8	0.3971 (12)	0.7103 (8)	0.1024 (8)	0.048 (3)
H8A	0.4145	0.7101	0.0404	0.058*
H8B	0.4760	0.6740	0.1306	0.058*
C9	0.3868 (11)	0.8308 (8)	0.1341 (9)	0.057 (3)
H9A	0.3787	0.8315	0.1969	0.068*
H9B	0.4718	0.8707	0.1185	0.068*
C10	0.1598 (12)	0.3338 (8)	0.0928 (6)	0.037 (2)
H10A	0.0749	0.2943	0.1091	0.045*
H10B	0.1741	0.3237	0.0309	0.045*
C11	0.1436 (11)	0.4557 (7)	0.1125 (6)	0.035 (2)
H11A	0.1209	0.4648	0.1735	0.042*
H11B	0.0663	0.4857	0.0789	0.042*
C12	0.2812 (11)	0.5236 (7)	0.0912 (6)	0.0336 (17)
H12A	0.2954	0.5228	0.0283	0.040*
C13	0.4053 (10)	0.4656 (8)	0.1339 (7)	0.039 (2)
H13A	0.4914	0.5003	0.1138	0.046*
H13B	0.3997	0.4765	0.1962	0.046*
C14	0.4117 (12)	0.3420 (9)	0.1151 (7)	0.045 (3)
H14A	0.4288	0.3303	0.0537	0.053*
H14B	0.4887	0.3087	0.1472	0.053*
N1	0.7856 (10)	0.3441 (7)	0.1291 (6)	0.059 (2)
N2	1.1070 (9)	0.0788 (8)	0.1678 (8)	0.070 (3)
N3	0.7651 (10)	−0.1777 (6)	0.1673 (5)	0.0474 (19)
N4	0.4565 (10)	0.0854 (9)	0.1178 (7)	0.066 (3)
N5	0.2634 (9)	0.8885 (5)	0.0956 (6)	0.0413 (18)
H5A	0.2755	0.8949	0.0379	0.050*
H5B	0.2565	0.9578	0.1179	0.050*
N6	0.2788 (8)	0.2880 (6)	0.1401 (5)	0.0383 (15)
H6A	0.2849	0.2142	0.1296	0.046*
H6B	0.2648	0.2973	0.1974	0.046*
O1	0.2238 (9)	0.0836 (6)	0.4148 (5)	0.0655 (19)
H1A	0.2210	0.0146	0.4017	0.079*
H1B	0.2269	0.1486	0.3921	0.079*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.03236 (18)	0.02454 (17)	0.03815 (18)	−0.00054 (13)	0.00362 (13)	0.00082 (13)
C1	0.051 (5)	0.028 (4)	0.050 (4)	−0.005 (4)	−0.002 (5)	−0.002 (4)
C2	0.041 (5)	0.009 (3)	0.075 (6)	0.006 (4)	0.009 (4)	0.001 (5)
C3	0.042 (4)	0.037 (5)	0.035 (3)	−0.007 (5)	−0.003 (4)	−0.002 (4)
C4	0.027 (4)	0.019 (3)	0.067 (5)	0.002 (4)	0.002 (4)	0.010 (5)
C5	0.021 (4)	0.037 (5)	0.075 (6)	0.003 (4)	0.003 (4)	0.001 (4)
C6	0.034 (5)	0.022 (4)	0.058 (5)	0.001 (4)	−0.006 (5)	−0.005 (4)
C7	0.034 (5)	0.015 (4)	0.050 (4)	−0.004 (3)	−0.002 (4)	−0.004 (3)
C8	0.036 (5)	0.027 (5)	0.082 (7)	0.003 (4)	−0.002 (5)	−0.005 (4)
C9	0.032 (5)	0.031 (5)	0.107 (9)	−0.002 (4)	−0.017 (6)	−0.007 (6)
C10	0.037 (5)	0.024 (4)	0.051 (5)	−0.007 (4)	−0.009 (4)	0.005 (4)
C11	0.032 (4)	0.024 (4)	0.050 (5)	−0.002 (4)	−0.002 (4)	0.010 (3)
C12	0.031 (4)	0.027 (4)	0.042 (4)	0.000 (4)	−0.001 (4)	−0.002 (3)
C13	0.024 (4)	0.028 (4)	0.064 (6)	0.002 (3)	−0.002 (5)	−0.001 (5)
C14	0.032 (5)	0.029 (5)	0.072 (7)	−0.004 (4)	0.006 (4)	0.000 (4)
N1	0.043 (4)	0.035 (5)	0.097 (7)	−0.008 (4)	0.005 (6)	0.004 (4)
N2	0.035 (5)	0.034 (4)	0.140 (9)	0.002 (4)	0.007 (5)	−0.003 (6)
N3	0.051 (5)	0.030 (4)	0.061 (5)	−0.006 (4)	−0.001 (4)	0.007 (3)
N4	0.049 (5)	0.030 (4)	0.118 (8)	0.000 (5)	−0.005 (5)	0.006 (6)
N5	0.036 (4)	0.021 (4)	0.067 (5)	0.002 (3)	−0.004 (4)	0.000 (3)
N6	0.040 (4)	0.021 (3)	0.054 (4)	0.003 (3)	0.005 (5)	0.000 (3)
O1	0.085 (5)	0.037 (3)	0.074 (5)	0.008 (5)	−0.007 (4)	−0.005 (4)

Geometric parameters (Å, º)

Pt1—C4	1.967 (8)	C9—H9B	0.9700
Pt1—C1	1.986 (9)	C10—N6	1.455 (12)
Pt1—C3	1.989 (8)	C10—C11	1.498 (14)
Pt1—C2	2.013 (9)	C10—H10A	0.9700
C1—N1	1.147 (12)	C10—H10B	0.9700
C2—N2	1.110 (13)	C11—C12	1.577 (14)
C3—N3	1.157 (10)	C11—H11A	0.9700
C4—N4	1.155 (12)	C11—H11B	0.9700
C5—N5	1.500 (12)	C12—C13	1.520 (14)
C5—C6	1.529 (13)	C12—H12A	0.9800
C5—H5C	0.9700	C13—C14	1.508 (13)
C5—H5D	0.9700	C13—H13A	0.9700
C6—C7	1.491 (13)	C13—H13B	0.9700
C6—H6C	0.9700	C14—N6	1.472 (13)
C6—H6D	0.9700	C14—H14A	0.9700
C7—C8	1.490 (14)	C14—H14B	0.9700
C7—C12	1.543 (10)	N5—H5A	0.9000
C7—H7A	0.9800	N5—H5B	0.9000
C8—C9	1.526 (14)	N6—H6A	0.9000
C8—H8A	0.9700	N6—H6B	0.9000

C8—H8B	0.9700	O1—H1A	0.8503
C9—N5	1.487 (13)	O1—H1B	0.8532
C9—H9A	0.9700		
C4—Pt1—C1	90.7 (4)	C11—C10—H10A	109.6
C4—Pt1—C3	89.4 (4)	N6—C10—H10B	109.6
C1—Pt1—C3	178.2 (3)	C11—C10—H10B	109.6
C4—Pt1—C2	179.5 (4)	H10A—C10—H10B	108.1
C1—Pt1—C2	89.4 (4)	C10—C11—C12	112.0 (9)
C3—Pt1—C2	90.5 (4)	C10—C11—H11A	109.2
N1—C1—Pt1	176.3 (10)	C12—C11—H11A	109.2
N2—C2—Pt1	178.5 (10)	C10—C11—H11B	109.2
N3—C3—Pt1	177.5 (9)	C12—C11—H11B	109.2
N4—C4—Pt1	178.3 (10)	H11A—C11—H11B	107.9
N5—C5—C6	109.5 (8)	C13—C12—C7	112.1 (8)
N5—C5—H5C	109.8	C13—C12—C11	108.7 (7)
C6—C5—H5C	109.8	C7—C12—C11	110.7 (8)
N5—C5—H5D	109.8	C13—C12—H12A	108.4
C6—C5—H5D	109.8	C7—C12—H12A	108.4
H5C—C5—H5D	108.2	C11—C12—H12A	108.4
C7—C6—C5	112.2 (8)	C14—C13—C12	113.4 (9)
C7—C6—H6C	109.2	C14—C13—H13A	108.9
C5—C6—H6C	109.2	C12—C13—H13A	108.9
C7—C6—H6D	109.2	C14—C13—H13B	108.9
C5—C6—H6D	109.2	C12—C13—H13B	108.9
H6C—C6—H6D	107.9	H13A—C13—H13B	107.7
C8—C7—C6	108.7 (7)	N6—C14—C13	110.2 (9)
C8—C7—C12	110.9 (8)	N6—C14—H14A	109.6
C6—C7—C12	113.4 (8)	C13—C14—H14A	109.6
C8—C7—H7A	107.9	N6—C14—H14B	109.6
C6—C7—H7A	107.9	C13—C14—H14B	109.6
C12—C7—H7A	107.9	H14A—C14—H14B	108.1
C7—C8—C9	111.8 (9)	C9—N5—C5	111.1 (7)
C7—C8—H8A	109.3	C9—N5—H5A	109.4
C9—C8—H8A	109.3	C5—N5—H5A	109.4
C7—C8—H8B	109.3	C9—N5—H5B	109.4
C9—C8—H8B	109.3	C5—N5—H5B	109.4
H8A—C8—H8B	107.9	H5A—N5—H5B	108.0
N5—C9—C8	111.2 (9)	C10—N6—C14	111.9 (7)
N5—C9—H9A	109.4	C10—N6—H6A	109.2
C8—C9—H9A	109.4	C14—N6—H6A	109.2
N5—C9—H9B	109.4	C10—N6—H6B	109.2
C8—C9—H9B	109.4	C14—N6—H6B	109.2
H9A—C9—H9B	108.0	H6A—N6—H6B	107.9
N6—C10—C11	110.2 (8)	H1A—O1—H1B	142.2
N6—C10—H10A	109.6		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5A···O1[i]	0.90	1.92	2.809 (12)	172
N5—H5B···N2[ii]	0.90	2.17	2.940 (12)	143
N5—H5B···N4[iii]	0.90	2.44	3.008 (13)	121
N6—H6A···N4	0.90	2.25	2.976 (13)	137
N6—H6A···N2[iv]	0.90	2.42	3.021 (12)	125
N6—H6B···N3[v]	0.90	2.13	3.026 (12)	179
O1—H1A···N1[vi]	0.85	2.10	2.946 (11)	179.4
O1—H1B···N3[v]	0.85	2.27	3.125 (10)	179.6

Symmetry codes: (i) −x+1/2, −y+1, z−1/2; (ii) x−1, y+1, z; (iii) x, y+1, z; (iv) x−1, y, z; (v) −x+1, y+1/2, −z+1/2; (vi) −x+1, y−1/2, −z+1/2.