Tetrabromido(di-2-pyridylamine-$\kappa^2N^2,N^{2'}$)platinum(IV)

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The Pt^{IV} ion in the title complex, [PtBr$_4$(C$_{10}$H$_9$N$_3$)], is six-coordinated in a slightly distorted octahedral environment by two pyridine N atoms from a chelating di-2-pyridylamine (dpa) ligand and four Br$^-$ anions. The complex molecule has mirror symmetry, with the Pt^{IV} atom, two Br atoms and the central N atom of the dpa ligand lying on the mirror plane. The dpa ligand is not planar, showing a dihedral angle of 34.7 (2)° between the pyridine rings. The complex molecules are connected by intermolecular N—H⋯Br hydrogen bonds, forming chains along [001]. Intermolecular C—H⋯Br hydrogen bonds and π–π interactions between the pyridine rings [centroid–centroid distance = 3.667 (4) Å] are also observed.

Related literature

For the structures of the related complexes [PtCl$_4$(dpa)] and [PtBr$_2$(dpa)], see: Ha (2011, 2012).
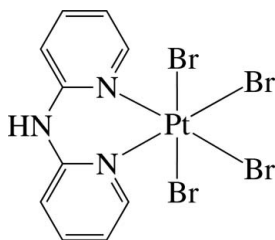
Experimental

Crystal data

[PtBr$_4$(C$_{10}$H$_9$N$_3$)]
$M_r = 685.93$

Monoclinic, $P2_1/m$
$a = 6.7876$ (7) Å
$b = 14.2860$ (14) Å
$c = 7.8893$ (8) Å
$\beta = 113.562$ (2)°
$V = 701.23$ (12) Å^3

$Z = 2$
Mo $K\alpha$ radiation
$\mu = 21.39$ mm^{-1}
$T = 200$ K
$0.28 \times 0.14 \times 0.13$ mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.459$, $T_{max} = 1.000$

4257 measured reflections
1400 independent reflections
1176 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.075$
$S = 1.04$
1400 reflections

88 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.89$ e Å^{-3}
$\Delta\rho_{min} = -1.62$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2N⋯Br2^i	0.92	2.79	3.665 (8)	161
C3—H3⋯Br1^{ii}	0.95	2.90	3.689 (7)	141

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); 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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S1. Comment

The title complex, [PtBr$_4$(dpa)] (dpa = di-2-pyridylamine, C$_{10}$H$_9$N$_3$), is a structural isomer of the previously reported chlorido Pt^{IV} complex [PtCl$_4$(dpa)] (Ha, 2011).

The Pt^{IV} ion is six-coordinated in a slightly distorted octahedral environment defined by two pyridine N atoms from a chelating dpa ligand and four Br⁻ anions (Fig. 1). The complex is disposed about a mirror plane, passing through the Pt1, Br1, Br2 and N2 atoms. The Pt—N and Pt—Br bond distances are comparable to those observed in the related Pt^{II} complex [PtBr$_2$(dpa)] (Ha, 2012). In the crystal, the dpa ligand is not planar. The dihedral angle between the least-squares planes of the pyridine rings is 34.7 (2)°. The complex molecules are stacked in columns along the *a* axis and connected by intermolecular N—H⋯Br hydrogen bonds, forming chains along the *c* axis (Fig. 2, Table 1). Intermolecular π–π interactions between the pyridine rings are present, with a centroid–centroid distance of 3.667 (4) Å. Intermolecular C—H⋯Br hydrogen bonds are also observed (Table 1).

S2. Experimental

To a solution of K$_2$PtCl$_6$ (0.240 g, 0.49 mmol) and KBr (0.745 g, 6.26 mmol) in H$_2$O (50 ml) was added di-2-pyridyl-amine (0.086 g, 0.50 mmol), and the mixture was stirred for 24 h at room temperature. The formed precipitate was separated by filtration, washed with H$_2$O and acetone, and recrystallized from a mixture of *N,N*-dimethylformamide and ether to give a red powder (0.144 g). Crystals suitable for X-ray analysis were obtained by slow evaporation from a CH$_3$CN solution at room temperature.

S3. Refinement

C-bound H atoms were positioned geometrically and allowed to ride on their respective parent atoms, with C—H = 0.95 Å and with U_{iso}(H) = 1.2U_{eq}(C). N-bound H atom was located from a difference Fourier map and then allowed to ride on its parent atom in the final cycles of refinement, with N—H = 0.92 Å and U_{iso}(H) = 1.2U_{eq}(N). The highest peak (1.89 e Å^{-3}) and the deepest hole (-1.62 e Å^{-3}) in the difference Fourier map are located 0.85 Å and 0.67 Å from atoms Pt1 and Br1, respectively.
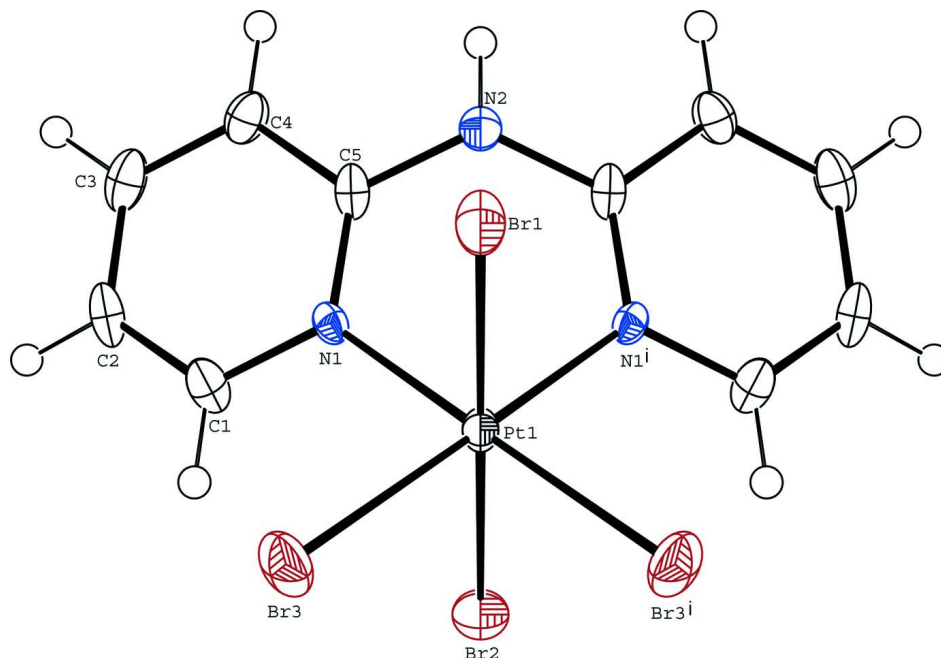
Figure 1

The molecular structure of the title complex. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) x, 1/2-y, z.]
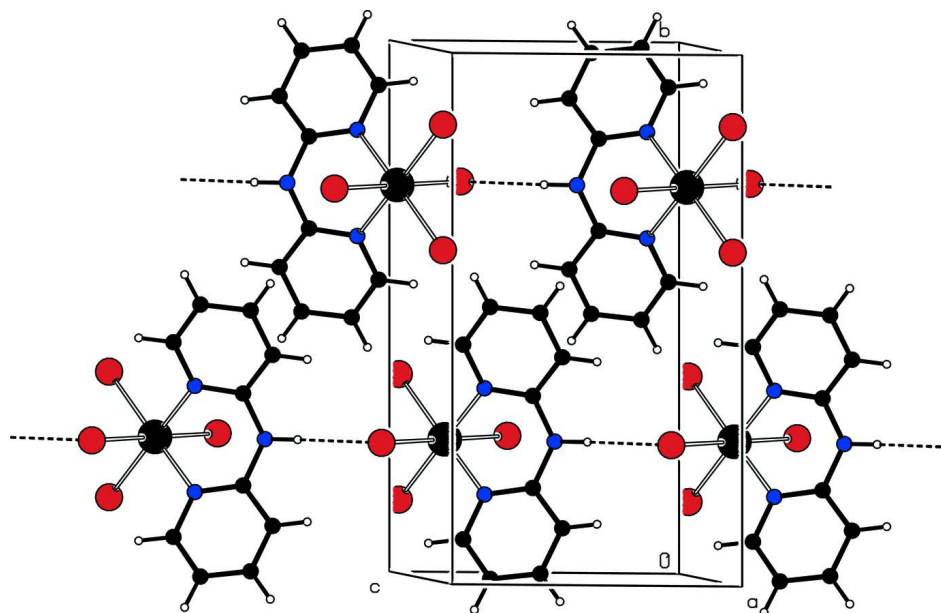
Figure 2

A view of the crystal packing of the title complex. Intermolecular N—H⋯Br hydrogen bonds are shown as dashed lines.

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Crystal data

[PtBr$_4$(C$_{10}$H$_9$N$_3$)]	$F(000) = 616$
$M_r = 685.93$	$D_x = 3.249$ Mg m^{-3}
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yb	Cell parameters from 2726 reflections
$a = 6.7876$ (7) Å	$\theta = 2.8$–26.0°
$b = 14.2860$ (14) Å	$\mu = 21.39$ mm^{-1}
$c = 7.8893$ (8) Å	$T = 200$ K
$\beta = 113.562$ (2)°	Block, red
$V = 701.23$ (12) Å^3	$0.28 \times 0.14 \times 0.13$ mm
$Z = 2$	

Data collection

Bruker SMART 1000 CCD diffractometer	4257 measured reflections
Radiation source: fine-focus sealed tube	1400 independent reflections
Graphite monochromator	1176 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.034$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$\theta_{max} = 26.0°$, $\theta_{min} = 2.8°$
$T_{min} = 0.459$, $T_{max} = 1.000$	$h = -8 \rightarrow 8$
	$k = -17 \rightarrow 15$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.028$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.075$	
$S = 1.04$	H-atom parameters constrained
1400 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 0.9524P]$ where $P = (F_o^2 + 2F_c^2)/3$
88 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 1.89$ e Å^{-3}
	$\Delta\rho_{min} = -1.61$ 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	0.02241 (6)	0.2500	0.81398 (5)	0.01565 (14)
Br1	−0.30563 (16)	0.2500	0.52614 (15)	0.0260 (3)
Br2	0.34926 (18)	0.2500	1.10292 (15)	0.0298 (3)
Br3	−0.14760 (13)	0.13183 (5)	0.93509 (11)	0.0306 (2)

N1	0.1651 (8)	0.1500 (3)	0.7074 (8)	0.0145 (11)
N2	0.1284 (13)	0.2500	0.4576 (11)	0.0193 (17)
H2N	0.1473	0.2500	0.3485	0.023*
C1	0.2280 (12)	0.0668 (5)	0.7949 (11)	0.0251 (16)
H1	0.2303	0.0591	0.9153	0.030*
C2	0.2881 (12)	−0.0059 (4)	0.7148 (11)	0.0250 (16)
H2	0.3358	−0.0632	0.7797	0.030*
C3	0.2786 (11)	0.0046 (5)	0.5396 (11)	0.0257 (17)
H3	0.3095	−0.0471	0.4784	0.031*
C4	0.2249 (11)	0.0890 (5)	0.4520 (10)	0.0224 (15)
H4	0.2227	0.0972	0.3318	0.027*
C5	0.1730 (11)	0.1634 (4)	0.5426 (10)	0.0193 (15)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.0193 (2)	0.0115 (2)	0.0184 (2)	0.000	0.00991 (17)	0.000
Br1	0.0226 (6)	0.0189 (5)	0.0313 (6)	0.000	0.0053 (5)	0.000
Br2	0.0315 (6)	0.0315 (6)	0.0222 (6)	0.000	0.0063 (5)	0.000
Br3	0.0381 (5)	0.0239 (4)	0.0393 (5)	−0.0026 (3)	0.0254 (4)	0.0072 (3)
N1	0.014 (3)	0.012 (2)	0.017 (3)	−0.002 (2)	0.005 (2)	0.003 (2)
N2	0.023 (5)	0.017 (4)	0.019 (4)	0.000	0.010 (4)	0.000
C1	0.029 (4)	0.019 (3)	0.030 (4)	0.002 (3)	0.014 (3)	0.007 (3)
C2	0.023 (4)	0.012 (3)	0.042 (5)	0.001 (3)	0.015 (4)	0.006 (3)
C3	0.022 (4)	0.018 (4)	0.041 (5)	−0.002 (3)	0.017 (4)	−0.008 (3)
C4	0.023 (4)	0.019 (3)	0.028 (4)	0.001 (3)	0.014 (3)	−0.005 (3)
C5	0.018 (4)	0.011 (3)	0.031 (4)	0.000 (3)	0.012 (3)	0.001 (3)

Geometric parameters (Å, º)

Pt1—N1	2.082 (5)	C1—C2	1.360 (10)
Pt1—Br3	2.4446 (7)	C1—H1	0.9500
Pt1—Br1	2.4642 (12)	C2—C3	1.366 (11)
Pt1—Br2	2.4647 (12)	C2—H2	0.9500
N1—C5	1.337 (9)	C3—C4	1.366 (10)
N1—C1	1.356 (8)	C3—H3	0.9500
N2—C5[i]	1.382 (7)	C4—C5	1.401 (9)
N2—C5	1.382 (7)	C4—H4	0.9500
N2—H2N	0.9200		
N1[i]—Pt1—N1	86.6 (3)	C5[i]—N2—C5	127.1 (8)
N1[i]—Pt1—Br3[i]	93.02 (13)	C5[i]—N2—H2N	111.6
N1—Pt1—Br3[i]	179.26 (15)	C5—N2—H2N	111.6
N1[i]—Pt1—Br3	179.26 (15)	N1—C1—C2	121.7 (7)
N1—Pt1—Br3	93.02 (13)	N1—C1—H1	119.1
Br3[i]—Pt1—Br3	87.35 (4)	C2—C1—H1	119.1
N1[i]—Pt1—Br1	91.29 (16)	C1—C2—C3	118.9 (7)
N1—Pt1—Br1	91.29 (16)	C1—C2—H2	120.5

Br3^i—Pt1—Br1	88.07 (3)	C3—C2—H2	120.5
Br3—Pt1—Br1	88.07 (3)	C4—C3—C2	120.3 (6)
N1^i—Pt1—Br2	88.95 (15)	C4—C3—H3	119.9
N1—Pt1—Br2	88.95 (16)	C2—C3—H3	119.9
Br3^i—Pt1—Br2	91.69 (3)	C3—C4—C5	118.8 (7)
Br3—Pt1—Br2	91.69 (3)	C3—C4—H4	120.6
Br1—Pt1—Br2	179.67 (3)	C5—C4—H4	120.6
C5—N1—C1	119.6 (6)	N1—C5—N2	120.9 (6)
C5—N1—Pt1	120.1 (4)	N1—C5—C4	120.3 (6)
C1—N1—Pt1	119.9 (4)	N2—C5—C4	118.9 (6)
N1^i—Pt1—N1—C5	−39.4 (6)	C1—C2—C3—C4	4.8 (11)
Br3—Pt1—N1—C5	139.9 (5)	C2—C3—C4—C5	−2.1 (10)
Br1—Pt1—N1—C5	51.8 (5)	C1—N1—C5—N2	−174.2 (7)
Br2—Pt1—N1—C5	−128.4 (5)	Pt1—N1—C5—N2	13.3 (9)
N1^i—Pt1—N1—C1	148.0 (4)	C1—N1—C5—C4	6.5 (10)
Br3—Pt1—N1—C1	−32.6 (5)	Pt1—N1—C5—C4	−166.1 (5)
Br1—Pt1—N1—C1	−120.7 (5)	C5^i—N2—C5—N1	34.0 (13)
Br2—Pt1—N1—C1	59.0 (5)	C5^i—N2—C5—C4	−146.7 (7)
C5—N1—C1—C2	−3.8 (10)	C3—C4—C5—N1	−3.6 (10)
Pt1—N1—C1—C2	168.8 (6)	C3—C4—C5—N2	177.0 (7)
N1—C1—C2—C3	−1.9 (11)		

Symmetry code: (i) x, −y+1/2, z.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2N⋯Br2^{ii}	0.92	2.79	3.665 (8)	161
C3—H3⋯Br1^{iii}	0.95	2.90	3.689 (7)	141

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