

## $\pi$ - $\pi$ Dimerization of a mono(pyridyl-imine) platinum(II) chelate

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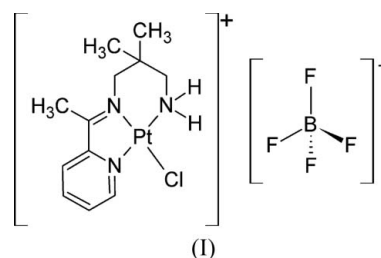
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The cation of the title complex salt, chlorido{2,2-dimethyl-*N*-[(*E*)-1-(pyridin-2-yl)ethylidene]propane-1,3-diamine}platinum(II) tetrafluoroborate, [PtCl(C<sub>12</sub>H<sub>19</sub>N<sub>3</sub>)]BF<sub>4</sub>, exhibits a nominally square-planar Pt<sup>II</sup> ion coordinated to a chloride ion [Pt—Cl = 2.3046 (9) Å] and three unique N-atom types, *viz.* pyridine, imine and amine, of the tridentate Schiff base ligand formed by the 1:1 condensation of 1-(pyridin-2-yl)ethanone and 2,2-dimethylpropane-1,3-diamine. The cations are  $\pi$ -stacked in inversion-related pairs (dimers), with a mean plane separation of 3.426 Å, an intradimer Pt···Pt separation of 5.0785 (6) Å and a lateral shift of 3.676 Å. The centroid (*C*<sub>g</sub>) of the pyridine ring is positioned approximately over the Pt<sup>II</sup> ion of the neighbouring cation (Pt···*C*<sub>g</sub> = 3.503 Å).

### Comment

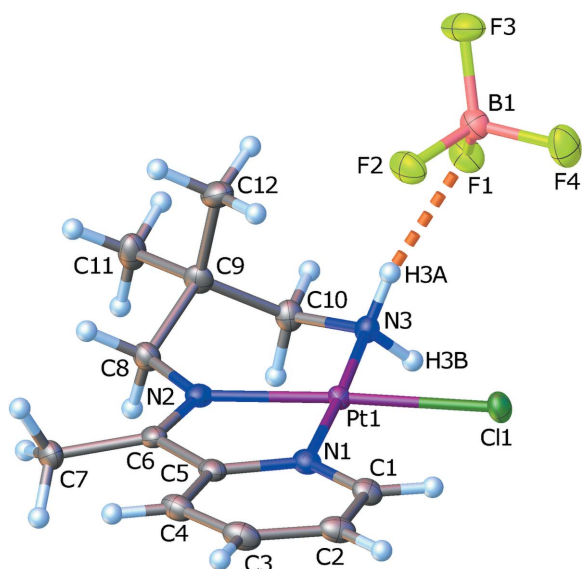
Mono(cationic) polypyridine complexes of Pt<sup>II</sup> are well known for their ability to form  $\pi$ -stacks in the crystalline solid state (Abel *et al.*, 1994; Bardwell *et al.*, 1994; Consorti *et al.*, 2004). In the simplest type of stacking, discrete dimers are formed and the cations typically stack in a head-to-head fashion (Rotondo *et al.*, 2003; Shafaatian *et al.*, 2007; Kui *et al.*, 2006). The Pt<sup>II</sup> ions within these stacks span a range of Pt···Pt separations from *ca* 3.32 Å to beyond 7 Å, giving rise to several classes of stacked species based upon the lateral shift (LS) of one cation relative to the other (as derived by consideration of the metal ion coordinates). A recent systematic geometric and trigonometric analysis of  $\pi$ -stacked centrosymmetric dimers in terpyridine complexes of Pt<sup>II</sup> (Field *et al.*, 2011) showed that there are three categories of dimer based on the metrics of their interactions. Type-I dimers have short lateral shifts, typically ranging from 0 to 1.6 Å, exhibit head-to-head overlap, and are governed by stabilizing Pt···Pt  $5dz^2$ ··· $5dz^2$  orbital interactions as well as  $\pi$ - $\pi$  interactions between stacked pyridine rings. The Pt···Pt orbital overlaps in type-I dimers lead to characteristic and potentially exploitable long-lived <sup>3</sup>MMLCT emissive states (MMLCT is metal-to-metal-ligand charge transfer) in the crystalline solids (Field *et al.*, 2008; Field & Grimmer *et al.*, 2010; Mathew &

Sun, 2010). Type-II dimers exhibit head-to-head overlap and have longer lateral shifts (1.8–3.5 Å), consequently lacking Pt···Pt orbital overlaps, and are stabilized by  $\pi$ - $\pi$  interactions and cation··· $\pi$  interactions. These dimers have normal <sup>3</sup>MLCT emission in the solid state (Wen *et al.*, 2011; Field & Gertenbach *et al.*, 2010). The third category of dimers (type III) have long-range head-to-tail overlap, LS values in the range 5.5–7.5 Å and are stabilized mainly by  $\pi$ - $\pi$  interactions. In each class of dimeric species,  $\pi$ - $\pi$  interactions are prevalent between the pyridine rings of the stacked cations. Furthermore, the interplanar spacings, or mean plane separation (MPS) values, span the range 3.2–3.5 Å (Field *et al.*, 2011) and are similar in magnitude to that of graphite (3.35 Å; Bacon, 1951), the archetypal  $\pi$ -stacked aromatic system.



Our initial objective in this study was to synthesize and structurally characterize dicationic tetradentate bis(pyridyl-imine) chelates of Pt<sup>II</sup> in an effort to determine whether or not the charge on the cation impacts on the  $\pi$ -stacking, the photophysics of this class of compounds, and the ability of such species to bind to DNA, particularly in view of a significant body of recent literature highlighting the DNA-targeting behaviour of cytotoxic Pt<sup>II</sup> complexes bearing pyridine-based ligands (Rubino *et al.*, 2011; Shi *et al.*, 2010; Ruiz *et al.*, 2010). The tetradentate ligand chosen for our study, 2,2-dimethyl-*N,N'*-bis[(pyridin-2-yl)ethylene]propane-1,3-diamine, was synthesized by the condensation of two molar equivalents of 1-(pyridin-2-yl)ethanone with one molar equivalent of 2,2-dimethylpropane-1,3-diamine and was fully characterized prior to use in reaction with K<sub>2</sub>[PtCl<sub>4</sub>]. However, hydrolysis of one of the Schiff base imine units occurred during metallation and resulted in the isolation of a novel tridentate bis(chelate) of Pt<sup>II</sup>, namely chlorido{2,2-dimethyl-*N*-[(*E*)-1-(pyridin-2-yl)ethylidene]propane-1,3-diamine}platinum(II) tetrafluoroborate, hereafter (I). This mono(pyridyl-imine) complex of Pt<sup>II</sup> has a net positive charge and is still sufficiently planar and aromatic to assemble into  $\pi$ -stacked dimers in the crystalline solid state. Interestingly, two other mono(pyridyl-imine) complexes of Pt<sup>II</sup> have been analysed by single-crystal X-ray diffraction (Mandal *et al.*, 2010; Hinman *et al.*, 2000) and show similar  $\pi$ -stacking behaviour to (I), suggesting that the presence of a single pyridine moiety as part of a chelating ligand for Pt<sup>II</sup> might be a sufficient structural motif for  $\pi$ -stacking.

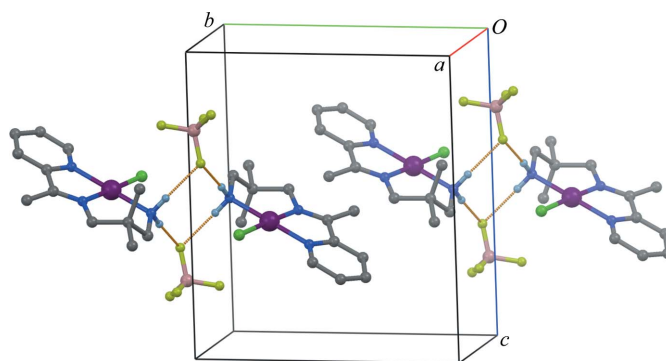
The cation of (I) is predominantly planar with the exception of the central C atom (C9) of the substituted propyl bridge linking the imine (N2) and amine (N3) N atoms, which is canted above the plane of the metal ion and four coordinated ligand atoms. The six-membered chelate ring based on these


**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of an arbitrary radius. The hydrogen bond between amine atom H3A and atom F1 of the anion is shown as a broken cylinder.

two N-atom donors adopts a typical half-chair conformation. The nominally square-planar Pt<sup>II</sup> ion is coordinated to three chemically distinct N-atom types: pyridine (N1), imine (N2) and amine (N3), as shown in Fig. 1. The Pt–N<sub>pyridine</sub> and Pt–N<sub>imine</sub> distances are equivalent at 2.007 (3) and 2.003 (3) Å, respectively, consistent with the fact that both of these N-atom types exhibit *sp*<sup>2</sup>-hybridization and are donors within a five-membered chelate ring (Table 1). The Pt–N<sub>pyridine</sub> bond distance is consistent with those observed between pyridine and Pt<sup>II</sup> in a variety of polypyridine complexes of the metal, including terpyridine derivatives (Field *et al.*, 2011). This suggests that the five-membered chelate ring incorporating the pyridine and imine groups in (I) is not substantially different from the five-membered chelate rings in polypyridine chelates of the metal. The Pt–N<sub>amine</sub> distance, being part of a six-membered chelate ring and *sp*<sup>3</sup>-hybridized, is commensurately longer at 2.038 (3) Å. The fourth coordination site of the metal ion is occupied by a chloride ligand, consistent with similar coordination interactions for Pt<sup>II</sup> derivatives in the literature (Che *et al.*, 2011; Panda *et al.*, 2005). The Pt1–Cl1 bond length is 2.3046 (9) Å.

Because the pyridyl-imine ligand of (I) comprises adjacent five- and six-membered chelate rings, the bond angles subtended at the Pt<sup>II</sup> ion deviate significantly from the ideal 90° angles expected for a truly square-planar geometry. From Table 1 it is evident that the N1–Pt1–N2 angle within the five-membered chelate ring is particularly acute at 80.25 (12)°, while the N2–Pt1–N3 angle of the six-membered chelate ring is correspondingly quite obtuse, measuring 97.62 (12)°. This significant difference in the *cis*-N–Pt–N angles is in fact large enough to be clearly evident upon visual inspection of Fig. 1. The distortion of the coordination sphere of the metal

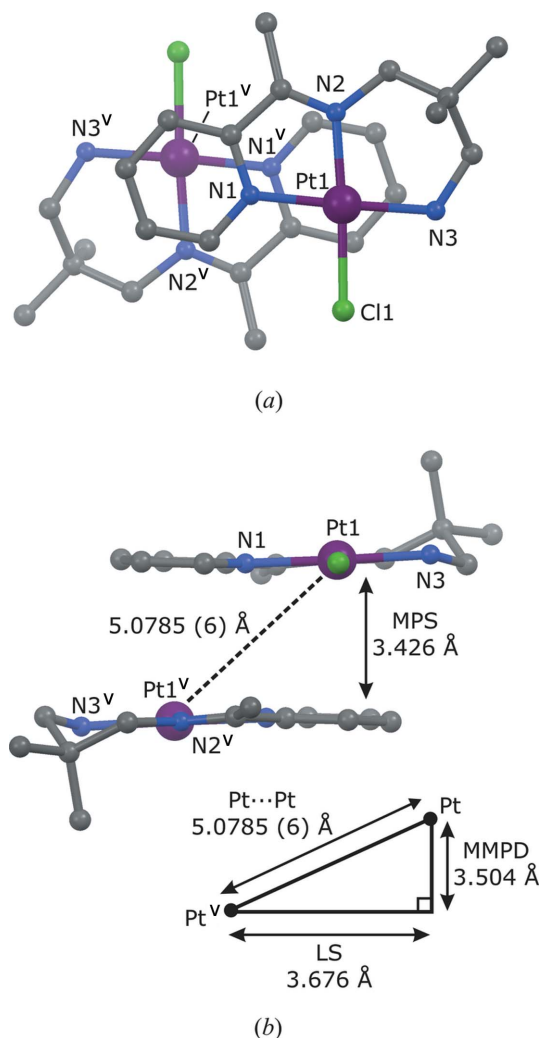

**Figure 2**

A view of the unit-cell packing of (I). Pairs of cations and hydrogen-bonded anions are related by centres of inversion at  $[0, 0, \frac{1}{2}]$  and  $[1, 1, \frac{1}{2}]$ . Atoms are rendered as spheres of arbitrary radii and bonds as cylinders. Only H atoms involved in hydrogen bonding are shown for clarity.

ion away from an idealized square-planar geometry is further reflected by the *cis*-N–Pt–Cl angles, which are 96.48 (9) and 85.68 (8)° for N1–Pt1–Cl1 and N3–Pt1–Cl1, respectively. The perpendicular displacements of the four ligand donor atoms from their mean plane are –0.022 (2), 0.023 (1), –0.021 (1) and 0.019 (1) Å for N1, N2, N3 and Cl1, respectively. These out-of-plane displacements of the ligand donor atoms from the plane containing the metal ion are small and confirm the fundamentally square-planar *5d*<sup>8</sup> geometry and electron configuration for the Pt<sup>II</sup> ion. Moreover, if we define the nine-atom mean plane of the cation by all *sp*<sup>2</sup>-hybridized C and N atoms plus the metal ion, the perpendicular displacements of the individual atoms from this mean plane are not inconsistent with a generally planar chelate system: N1 0.034 (3) Å; C1 0.039 (3) Å; C2 –0.002 (3) Å; C3 –0.053 (3) Å; C4 –0.014 (3) Å; C5 0.024 (3) Å; C6 0.061 (3) Å; N2 –0.050 (2) Å; Pt1 –0.039 (2) Å. (For this set of atomic displacements, negative values indicate a displacement perpendicular to the nine-atom mean plane in the same direction as the out-of-plane C atom of the six-membered chelate ring, C9, in Fig. 1.)

Inspection of the extended structure of (I) in Figs. 1 and 2 reveals that the tetrafluoroborate anion is hydrogen bonded to the coordinated amino group H atoms (H3A and H3B) of two adjacent non-interacting cations (related by an inversion centre). From Table 2, the N···F distances are inequivalent. The two inversion-related ion pairs therefore make up an asymmetric tetrad comprising two cations and their charge-balancing anions. Several other less conventional hydrogen bonds with longer donor–acceptor distances are also present (Table 2) and primarily involve C–H donors and acceptors such as the F atoms from nearby BF<sub>4</sub><sup>–</sup> ions, as well as the coordinated chloride ligand of a nearby cation. Collectively, the data suggest that ion pairing in (I) mediated mainly by the shorter conventional N–H···F interactions is probably one of the more significant contributors to the stability of the salt in the solid state.

As noted earlier, pyridine complexes of Pt<sup>II</sup> are well known for their ability to  $\pi$ -stack principally in the solid state, but also



**Figure 3**

(a) Selectively labelled view of an inversion-related cation pair (*i.e.* dimer) perpendicular to the nine-atom mean plane of the upper cation defined by the pyridine ring, the imine N and C atoms, and the Pt<sup>II</sup> ion. Using the Pt–Cl bond vectors to define the relative orientations of the cations, the geometry of the dimer is best described as an offset head-to-head  $\pi$ -stacked pair. (b) An edge-on view of the dimer down the Cl–Pt bond vector of the upper cation. The Pt $\cdots$ Pt distance and MPS are indicated. The trigonometric relationships involving the Pt<sup>II</sup> ions are shown on the triangle below the dimer. MMPD is the metal-to-metal perpendicular distance. Because the Pt<sup>II</sup> ions are displaced above and below the nine-atom mean plane of the top and bottom cations by 0.039 Å, respectively, the MMPD is not equivalent to the MPS. The LS is calculated using Pythagoras' theorem from the MMPD and Pt $\cdots$ Pt ion separation. [Symmetry code: (v)  $-x + 1, -y, -z + 2$ .]

in solution depending on the solvent used (Tam *et al.*, 2008). In the crystal structure of (I), pairs of cations are  $\pi$ -stacked in a head-to-head orientation (Figs. 3a and 3b) to form inversion pairs or dimers (we use the Pt–Cl bond vectors of the interacting cations to define the relative orientations of the stacked cations). The MPS between the nine-atom mean planes of the interacting cations is 3.426 Å. This is slightly larger than the graphite interlayer spacing of 3.35 Å (Bacon, 1951), but consistent with the normal range (3.33–3.48 Å) observed for terpyridine complexes of Pt<sup>II</sup> (Field *et al.*, 2011) and that for

$\pi$ -stacked ring systems in general (Hunter & Sanders, 1990; Janiak, 2000). Since the Pt<sup>II</sup> cation has a perpendicular displacement of 0.039 (2) Å above the nine-atom mean plane in a direction away from the intradimer space, the metal-to-metal perpendicular displacement (MMPD) for the cations within the dimer is 3.504 Å. Together with the Pt $\cdots$ Pt separation of 5.0785 (6) Å, these values can be used to calculate the LS for the stacked cations (3.676 Å) based on the metal ion coordinates (Fig. 3b). The LS value for (I) is larger than that for many considerably more aromatic terpyridine complexes of Pt<sup>II</sup>, for which LS values are typically < 3 Å (Field *et al.*, 2011; Buchner *et al.*, 1999). This presumably reflects two factors unique to (I): (a) the geometry of the ligand, which obviously lacks the central pyridine ring of terpyridine-based dimers (stacking of the central pyridine rings of two interacting terpyridine ligands favours modestly offset cation $\cdots$ cation interactions), and (b) the likely existence of a significantly stabilizing metal $\cdots$  $\pi$  interaction (Mecozzi *et al.*, 1996) involving the Pt<sup>II</sup> ion of one cation and the pyridine ring of the second chelate of the dimer. The distance for this interaction is Pt1 $\cdots$ Cg1<sup>v</sup> = 3.503 Å, where Cg1 is the centre of gravity of the pyridine ring of the second ligand in the dimer [symmetry code: (v)  $-x + 1, -y, -z + 2$ ] and may be thought of as being predominantly electrostatic in origin (an electron-rich  $\pi$ -system donating electron density to an electron-deficient metal cation). (The MMPD is within 0.001 Å of the Pt1 $\cdots$ Cg1<sup>v</sup> distance, but is only coincidentally similar as the two vectors are physically distinct.) Fig. 3(a) illustrates the slightly offset Pt $\cdots$  $\pi$  interaction more clearly when the dimer is viewed perpendicular to the nine-atom mean plane of the upper cation. The  $\pi$ -stacking in (I) is similar, as far as the overall arrangement of the cations is concerned, to that observed for centrosymmetric dimers of *mer*-methyl(2-[[2-(di3*N,N',N''*)platinum(II) trifluoromethanesulfonate (Hinman *et al.*, 2000) [Cambridge Structural Database (Allen, 2002) refcode KERQAZ]. Interestingly, the latter complex has larger MPS, LS and Pt $\cdots$ Pt distances [3.60, 4.99 and 6.1501 (3) Å, respectively] than those observed for dimers of (I). These structural differences can be traced principally to the steric repulsion between one of the two N–CH<sub>3</sub> groups of one ligand pointing into the space between the stacked cations and hence directly at the pyridine ring of the second ligand within the dimer. This effect is clearly absent in (I) because the bulky methyl groups appended to the six-membered chelate ring are positioned above the nine-atom mean plane of the chelate and away from the intradimer space, enabling a tighter interaction for the stacked cation pairs.

## Experimental

All reagents were purchased from Aldrich and were used as received. Standard solvent purification and instrumental analysis methods for compound characterization were used.

For the synthesis of 2,2-dimethyl-*N,N'*-bis[(pyridin-2-yl)ethylene]propane-1,3-diamine, 2,2-dimethylpropane-1,3-diamine (10 mmol) was stirred in methanol (20 ml). 2-Acetylpyridine (20 mmol) was added and the temperature increased; the reaction mixture was refluxed for

8 h. The solvent was reduced in volume. MgSO<sub>4</sub> was added and then filtered off, washing with dichloromethane (10 ml). An orange oil was obtained (yield: 2.723 g, 89%). UV-vis (CH<sub>3</sub>OH; λ<sub>max</sub>, nm): 259.0 (sh), 266.0, 280.0 (sh), 299.0. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.56 (d, J = 4.5 Hz, 2H, N<sub>py</sub>CHCH), 7.73 (d, J = 7.90 Hz, 2H, N<sub>py</sub>CHCHCHCHC), 7.65 (t of d, J = 7.5, 1.8 Hz, 2H, N<sub>py</sub>CHCHCHCHC), 7.14 (t of d, J = 6.1, 1.3 Hz, 2H, N<sub>py</sub>CHCHCHCHC), 2.52 (d, J = 13.1 Hz, 2H, N—CHHC—), 2.38 (d, J = 13.0 Hz, 2H, N—CHHC—), 1.38 [s, 6H, —C(CH<sub>3</sub>)=N—], 1.11 [s, 6H, C(CH<sub>3</sub>)<sub>2</sub>]. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 163.6 (N=C), 155.7 [N<sub>py</sub>=C—C(CH<sub>3</sub>)=N], 148.9 (N<sub>py</sub>CHCH), 136.6 (N<sub>py</sub>CHCHCHCHC), 127.0 (N<sub>py</sub>CHCHCHCHC), 121.6 (N<sub>py</sub>CHCHCHCHC), 71.0 [C(CH<sub>3</sub>)<sub>2</sub>], 53.2 (—CH<sub>2</sub>—), 31.6 [C(CH<sub>3</sub>)=N], 23.5 [C(CH<sub>3</sub>)<sub>2</sub>]. IR ν(cm<sup>-1</sup>): 3323, 3315, 3052, 3004, 2950, 2924, 2902, 2864, 1699, 1641, 1587, 1567, 1465, 1429, 1384, 1365, 1297, 1283, 1239, 1201, 1150, 1097, 1045, 993, 953, 909, 865, 834, 781, 743, 719, 645, 621, 574, 509, 491, 420, 404. HR-ESI-MS: m/z 309.2076 [M]<sup>+</sup>; calculated for C<sub>19</sub>H<sub>25</sub>N<sub>4</sub>: 309.2079.

For the synthesis of (I), 2,2-dimethyl-*N,N'*-bis[(pyridin-2-yl)ethyl-ene]propane-1,3-diamine (0.3 mmol) was dissolved in acetonitrile (1 ml). The metal salt potassium tetrachloroplatinate (0.3 mmol) dissolved in distilled water (1.5 ml) was added dropwise. Silver hexafluorophosphate(V) (1.2 mmol) as a suspension in acetonitrile (5 ml) was added to the solution dropwise. The mixture was refluxed for more than 30 h. After cooling to room temperature overnight, the solution was filtered. Aliquots of the filtrate were placed in test tubes and layered with ethanol; the remainder of the solution was left to evaporate slowly. An amorphous solid formed after slow evaporation of the solvent and was dissolved in 2-methoxyethanol (or distilled H<sub>2</sub>O) and layered in test tubes with diethyl ether (or ethanol). Spectroscopic analysis (<sup>1</sup>H NMR) of the bulk powder precipitates from these tubes unfortunately revealed a mixture of products. However, an X-ray-quality crystal was isolated from a generally amorphous precipitate in one of these crystallization attempts. The X-ray structure revealed the presence of the tetrafluoridoborate salt of an unintended reaction product, specifically salt (I). Analysis of the commercial source of AgPF<sub>6</sub> used in our laboratory by LC-MS and <sup>11</sup>B NMR identified the presence of the BF<sub>4</sub><sup>-</sup> ion as a minor impurity (< 1.5%).

Salt (I) is evidently an unintended reaction product from the above method and reflects partial hydrolysis of the bis(pyridyl-imine) ligand as well as crystallization of the cation with a minor impurity anion. Clearly the synthetic method described here is not optimal for a general synthesis of (I). Given the paucity of structures such as (I) in the literature and studies on this class of compounds in general, a higher yielding and more direct method for preparing (I) as well as a range of derivatives with different diamine precursors is currently being developed in our laboratory and will be reported on elsewhere.

Crystal data

[PtCl(C <sub>12</sub> H <sub>19</sub> N <sub>3</sub> )]BF <sub>4</sub>	V = 1634.6 (4) Å <sup>3</sup>
M <sub>r</sub> = 522.65	Z = 4
Monoclinic, P <sub>2</sub> <sub>1</sub> /n	Mo Kα radiation
a = 11.0907 (16) Å	μ = 8.79 mm <sup>-1</sup>
b = 11.1644 (16) Å	T = 100 K
c = 13.480 (2) Å	0.25 × 0.25 × 0.20 mm
β = 101.664 (2)°	

Data collection

Bruker APEXII CCD diffractometer	some modification]
Absorption correction: for a cylinder mounted on the φ axis [the interpolation procedure of Dwiggin (1975) was used with	T <sub>min</sub> = 0.062, T <sub>max</sub> = 0.088
	9381 measured reflections
	3829 independent reflections
	3594 reflections with I > 2σ(I)
	R <sub>int</sub> = 0.029

Table 1

Selected geometric parameters (Å, °).

C1—N1	1.338 (4)	C10—N3	1.478 (4)
C1—N1—Pt1	126.2 (2)	C10—N3—Pt1	118.1 (2)
C5—N1—Pt1	113.9 (2)	N1—Pt1—N3	177.51 (11)
C6—N2—Pt1	116.6 (2)	N2—Pt1—Cl1	176.53 (9)
C8—N2—Pt1	123.9 (2)		

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N3—H3A...F1	0.90 (2)	2.08 (2)	2.963 (4)	169 (1)
N3—H3B...F1 <sup>i</sup>	0.90 (2)	2.11 (2)	3.005 (4)	177 (2)
C1—H1...F4 <sup>ii</sup>	0.95	2.40	3.055 (4)	126
C2—H2...Cl1 <sup>ii</sup>	0.95	2.69	3.496 (4)	144
C3—H3...F4 <sup>iii</sup>	0.95	2.47	3.353 (4)	154
C7—H7B...F2 <sup>iv</sup>	0.98	2.32	3.301 (5)	178

Symmetry codes: (i) -x + 1, -y + 1, -z + 2; (ii) -x + ½, y - ½, -z + ¾; (iii) x, y - 1, z; (iv) -x + ¾, y - ½, -z + ¾.

Refinement

R[F <sup>2</sup> > 2σ(F <sup>2</sup> )] = 0.029	H atoms treated by a mixture of constrained and independent refinement
wR(F <sup>2</sup> ) = 0.075	
S = 1.08	Δρ <sub>max</sub> = 2.72 e Å <sup>-3</sup>
3829 reflections	Δρ <sub>min</sub> = -2.98 e Å <sup>-3</sup>
203 parameters	

All H atoms were positioned geometrically. For amino atom N3, the N—H distances were allowed to refine while being constrained to be equal with ideal orientations of the N—H vectors. The remaining H atoms were refined using a riding model, with C—H = 0.93 (aromatic), 0.98 (methyl) or 0.99 Å (methylene) and with U<sub>iso</sub>(H) = 1.5U<sub>eq</sub>(C) for methyl H atoms and 1.2U<sub>eq</sub>(C,N) otherwise. For methyl H atoms, the torsion angle about the parent C—C bond was optimized to fit the electron density.

Data collection: APEX2 (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: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 and Mercury (Macrae *et al.*, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3105). Services for accessing these data are described at the back of the journal.

References

Abel, E. W., Orrell, K. G., Osborne, A. G., Pain, H. M., Sik, V., Hursthouse, M. B. & Malik, K. M. A. (1994). *J. Chem. Soc. Dalton Trans.* pp. 3441–3449.  
 Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.  
 Bacon, G. E. (1951). *Acta Cryst.* **4**, 558–561.

- Bardwell, D. A., Crossley, J. G., Jeffery, J. C., Orpen, A. G., Psillakis, E., Tilley, E. E. M. & Ward, M. D. (1994). *Polyhedron*, **13**, 2291–2300.
- Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Buchner, R., Cunningham, C. T., Field, J. S., Haines, R. J., McMillin, D. R. & Summerton, G. C. (1999). *J. Chem. Soc. Dalton Trans.* pp. 711–717.
- Che, C. M., Chow, C. F., Yuen, M. Y., Roy, V. A. L., Lu, W., Chen, Y., Chui, S. S. Y. & Zhu, N. Y. (2011). *Chem. Sci.* **2**, 216–220.
- Consorti, C. S., Ebeling, G., Rodembusch, F., Stefani, V., Livotto, P. R., Rominger, F., Quina, F. H., Yihwa, C. & Dupont, J. (2004). *Inorg. Chem.* **43**, 530–536.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Dwiggins, C. W. (1975). *Acta Cryst.* **A31**, 395–396.
- Field, J. S., Gertenbach, J. A., Jaganyi, D., McMillin, D. R., Shaira, A. & Stewart, D. J. (2010). *Z. Naturforsch. Teil B*, **65**, 1318–1326.
- Field, J. S., Grimmer, C. D., Munro, O. Q. & Waldron, B. P. (2010). *Dalton Trans.* **39**, 1558–1567.
- Field, J. S., Ledwaba, L. P., Munro, O. Q. & McMillin, D. R. (2008). *CrystEngComm*, **10**, 740–747.
- Field, J. S., Wilson, C. R. & Munro, O. Q. (2011). *Inorg. Chim. Acta*, **374**, 197–204.
- Hinman, J. G., Baar, C. R., Jennings, M. C. & Puddephatt, R. J. (2000). *Organometallics*, **19**, 563–570.
- Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.
- Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
- Kui, S. C., Chui, S. S., Che, C. M. & Zhu, N. (2006). *J. Am. Chem. Soc.* **128**, 8297–8309.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Mandal, S., Castineiras, A., Mondal, T. K., Mondal, A., Chattopadhyay, D. & Goswami, S. (2010). *Dalton Trans.* **39**, 9514–9522.
- Mathew, I. & Sun, W. F. (2010). *Dalton Trans.* **39**, 5885–5898.
- Mecozzi, S., West, A. P. & Dougherty, D. A. (1996). *J. Am. Chem. Soc.* **118**, 2307–2308.
- Panda, M., Das, S., Mostafa, G., Castineiras, A. & Goswami, S. (2005). *Dalton Trans.* pp. 1249–1255.
- Rotondo, E., Bruschetta, G., Bruno, G., Rotondo, A., Di Pietro, M. L. & Cusumano, M. (2003). *Eur. J. Inorg. Chem.* pp. 2612–2618.
- Rubino, S., Portanova, P., Giammalva, F., Girasolo, M. A., Orecchio, S., Calvaruso, G. & Stocco, G. C. (2011). *Inorg. Chim. Acta*, **370**, 207–214.
- Ruiz, J., Rodriguez, V., de Haro, C., Espinosa, A., Perez, J. & Janiak, C. (2010). *Dalton Trans.* **39**, 3290–3301.
- Shafaatian, B., Akbari, A., Nabavizadeh, S. M., Heinemann, F. W. & Rashidi, M. (2007). *Dalton Trans.* pp. 4715–4725.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Shi, C. Y., Gao, E. J., Ma, S. A., Wang, M. L. & Liu, Q. T. (2010). *Bioorg. Med. Chem. Lett.* **20**, 7250–7254.
- Tam, A. Y. Y., Lam, W. H., Wong, K. M. C., Zhu, N. Y. & Yam, V. W. W. (2008). *Chem. Eur. J.* **14**, 4562–4576.
- Wen, H. M., Wu, Y. H., Xu, L. J., Zhang, L. Y., Chen, C. N. & Chen, Z. N. (2011). *Dalton Trans.* **40**, 6929–6938.