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[2,6-Bis(5-methyl-2-pyridyl)phenyl-κ^3N,C^1,N']chloridoplatinum(II)

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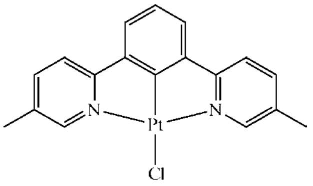
In the title compound, [Pt($C_{18}H_{15}N_2$)Cl], the Pt^{II} centre adopts a distorted square-planar coordination geometry due to the pincer-type monoanionic N–C–N tridentate ligand. The planar complexes stack *via* π–π interactions to form two-dimensional accumulated sheets. This packing pattern is in contrast to that in related pincer-type N–C–N complexes, which exhibit a one-dimensional columnar stacking.

Comment

We have been investigating the luminescence color tuning of transition-metal complex crystals due to vapochromism. For example, [Ru(dbb)$_2$(CN)$_2$] (dbb is di-*tert*-butyl-2,2′-bipyridine) shows a reversible color change from dark red to bright orange in the presence of moisture (Abe & Shinozaki, 2005). We have demonstrated luminescence vapochromism to organic solvent vapors using a Pt compound with a pincer-type tridentate monoanionic N–C–N ligand, *viz*. 2,6-di-2-pyridylphenyl. Moreover, luminescence mechanochromism, which is the luminescence color change observed upon grinding crystals of the complex, was found for the title compound, (I) (Abe, 2007). However, mechanochromism has not been reported for chlorido(2,6-di-2-pyridylphenyl-κ^3N,C^1,N')platinum(II), which has no methyl groups in the N–C–N ligand (Cárdenas & Echavarren, 1999). We report here a single-crystal X-ray structure analysis of (I).



(I)

The molecular structure of the title Pt^{II} complex is illustrated in Fig. 1 and selected geometric parameters are given in Table 1. The coordination bond lengths and the bite angles of the N–C–N ligand are typical, compared with those of the analogous platinum(II) N—C—N tridentate complexes [PtCl{1-*R*-3,5-(2-py)$_2$C$_6$H$_2$}] (py is pyridyl) [*R* = H, (II) (Cárdenas & Echavarren, 1999), *R* = COOMe, (III) (Williams *et al.*, 2003), *R* = Me, (IV), and *R* = 4-PhC$_6$H$_4$, (V) (Farley *et al.*, 2005)] [Pt—C = 1.903 (4)–1.912 (3) Å, Pt—N = 2.033 (6)–2.045 (2) Å, Pt—Cl = 2.405 (1)–2.4221 (8) Å, C—Pt—N = 80.1 (3)–80.9 (2)° and N—Pt—N 161.1 (2)–161.4 (2)°]. Unlike in complexes (II)–(V), the two N—Pt—Cl angles in (I) differ slightly from one another, which is indicative of the distortion of the Cl$^-$ coordination from the ideal molecular C_{2v} symmetry. The Pt^{II} coordination plane is almost coplanar with that of the benzene ring and with the plane of the N2/C12–C16 pyridyl ring, the dihedral angles being 1.54 (8) and 3.02 (8)°, respectively. The other pyridyl ring (N1/C7–C11) is, however, slightly twisted from the Pt^{II} coordination plane; the dihedral angle is 6.57 (8)°. This twisting is also related to the packing structure of (I) (see below).

The crystal packing of (I) (Figs. 2 and 3) contrasts with the packing in related 1-*R*-3,5-(2-py)$_2$C$_6$H$_2$ complexes (II)–(V), where one-dimensional stacking columns are constructed *via* intermolecular π–π interactions (Fig. 4). In the crystal structure of (I), all the molecules are aligned with their coordination planes parallel to the crystallographic (101) plane (Fig. 2), and the aligned molecules compose a two-dimensional sheet

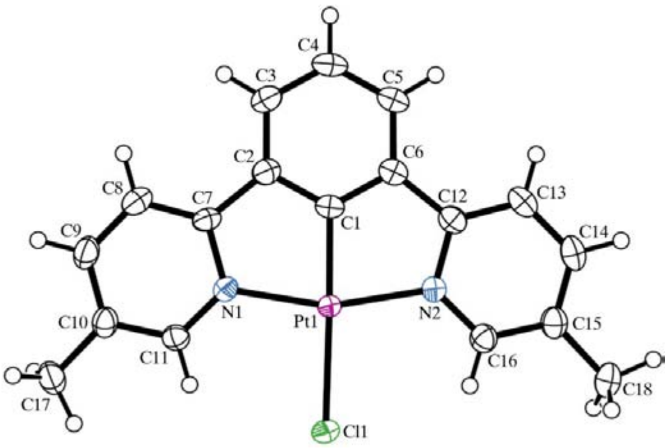


Figure 1
An *ORTEP-3* (Farrugia, 1997) view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

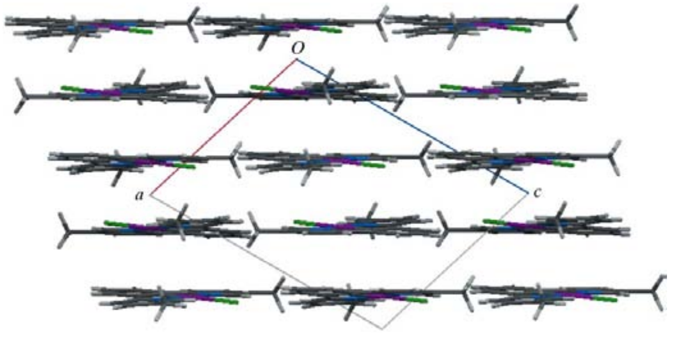


Figure 2
The structure of (I), viewed along the *b* axis.

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parallel to the ($\bar{1}01$) plane. In the sheet (Fig. 3, middle), two molecules are paired by a π–π interaction in an antiparallel fashion (stack *A* at the bottom of Fig. 3); the distances of the closest contacts between the Pt^{II} complex molecules are 3.477 (2) Å for Pt1$\cdots$C12^{i} and 3.412 (3) Å for N1$\cdots$C14^{i} [symmetry code: (i) $-x + 2$, $-y$, $-z + 2$]. The antiparallel arrangement of molecules results primarily from the electrostatic interaction due to the large dipole moment of the Pt^{II} complex, which we have estimated as 4.5 D by a density functional theory calculation using the Amsterdam Density Functional package (*ADF 2004.01*; Te Velde *et al.*, 2001; Ziegler, 1991). On the other side of the molecular plane, however, two neighboring molecules participate in π–π stacking interactions (stack *B* at the top of Fig. 3) [C8$\cdots$C14^{ii} = 3.376 (3) Å and C7$\cdots$C13^{ii} = 3.364 (3) Å; symmetry code: (ii) $-x + \frac{3}{2}$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$]. Thus, a molecule in the crystal structure of (I) interacts in total with three neighbors. This unit expands over the crystallographic ($\bar{1}01$) plane, forming a two-dimensional sheet (Fig. 3, middle). The difference between the packing in (I) and that in (II)–(V) can be traced to the introduction of methyl substituents at the 5-positions of both pyridyl rings of the N–C–N ligand. The Me groups seem to impede sterically the formation of one-dimensional stacking columns, affording a different packing structure for (I) from those of (II)–(V) and thereby providing a structural rationalization for the novel luminescence properties of (I).

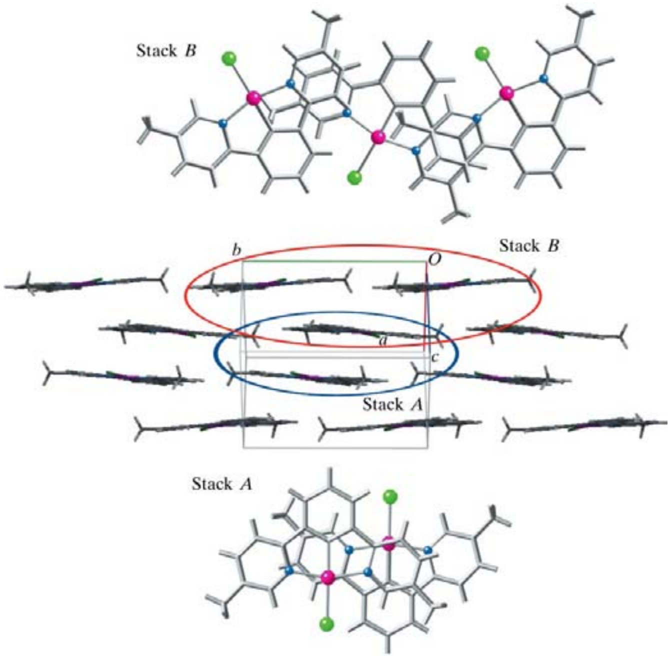

Figure 3
A complementary view of the crystal structure of (I), showing an accumulated sheet in the ($\bar{1}01$) plane (middle), and the two stacking patterns (*A* at the bottom and *B* at the top) present in the sheet.

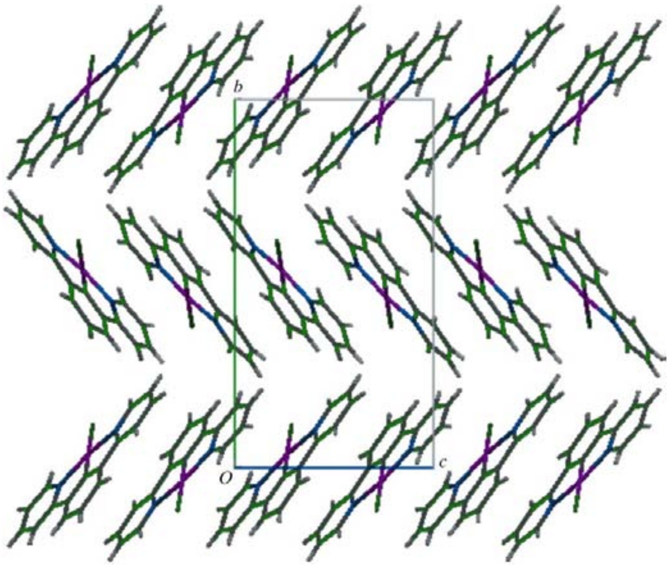

Figure 4
The packing of (II) (Cárdenas & Echavarren, 1999), viewed along the *a* axis.

Experimental

1,3-Bis(5-methyl-2-pyridyl)benzene (5Hdpb) was synthesized from 1,3-diacetylbenzene, methacrolein and ammonium acetate according to the procedure described by Krönke (1963). [Pt(5dpb)Cl] was prepared from K_2PtCl_4 (200 mg) and 5Hdpb (140 mg) by refluxing in acetic acid (100 ml) for 24 h. Partial removal of solvent by evaporation gave yellow crystals. These were collected by filtration, redissolved in $CHCl_3$ and purified by passage through a silica-gel column (1.5 cm in diameter and 30 cm in length), eluting with $CHCl_3$ (200 ml) three times. Addition of hexane to the solution gave bright-yellow crystals (yield 50%). ^{1}H NMR (270 MHz, $CDCl_3$, 298 K, TMS): δ 9.06 (2H, *s*, CH), 7.68 (2H, *d*, CH), 7.51 (2H, *d*, CH), 7.32 (2H, *d*, CH), 7.13 (1H, *t*, CH), 2.37 (6H, *s*, CH_3); ESI–MS *m*/*z*: 454 $[M - Cl]^+$, 491 $[M + H]^+$. A single crystal suitable for X-ray analysis was obtained by the slow evaporation of solvent from an ethanol–toluene (1:1) solution.

Crystal data

$[PtCl(C_{18}H_{15}N_2)]$
M_r = 489.86
Monoclinic, $P2_1/n$
a = 9.657 (4) Å
b = 12.969 (5) Å
c = 12.962 (6) Å
β = 107.092 (17)°
V = 1551.7 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 9.21 mm^{-1}
T = 200 (2) K
0.20 × 0.15 × 0.12 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: numerical (*SHAPE*; Higashi, 1999) T_{min} = 0.260, T_{max} = 0.459
14606 measured reflections
3524 independent reflections
3301 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.039
S = 1.07
3524 reflections
203 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.92 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 e Å^{-3}

Methyl H atoms were located from ΔF syntheses and refined as rigid groups which were allowed to rotate but not tip or distort [C—H = 0.98 Å and U_{iso}(H) = $1.2U_{eq}$(C)]. Aromatic H atoms were placed geometrically and constrained to ride on their parent atoms [C—H = 0.95 Å and U_{iso}(H) = $1.2U_{eq}$(C)].

Table 1
Selected geometric parameters (Å, °).

Pt1—C1	1.915 (3)	Pt1—N2	2.041 (2)
Pt1—N1	2.027 (2)	Pt1—Cl1	2.4091 (10)
C1—Pt1—N1	80.87 (11)	C11—N1—Pt1	126.45 (19)
C1—Pt1—N2	80.61 (11)	C7—N1—Pt1	114.43 (18)
N1—Pt1—N2	161.47 (9)	C16—N2—Pt1	126.13 (19)
C1—Pt1—Cl1	177.56 (9)	C12—N2—Pt1	114.19 (18)
N1—Pt1—Cl1	97.56 (7)	C6—C1—Pt1	118.8 (2)
N2—Pt1—Cl1	100.94 (7)	C2—C1—Pt1	118.5 (2)

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2005); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3040). Services for accessing these data are described at the back of the journal.

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