

Crystal and Molecular Structures of *cis*- and *trans*-Dichlorobispyridine-platinum(II)

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The crystal structures of *cis*- and *trans*-dichlorobispyridineplatinum(II) [(I) and (II)] have been determined. Crystals of (I) are monoclinic, space group $C2/c$, with $a = 9.408(5)$, $b = 17.110(14)$, $c = 15.270(7)$ Å, $\beta = 98.53(4)^\circ$, $Z = 8$; crystals of (II) are triclinic, space group $P\bar{1}$, with $a = 7.695(6)$, $b = 7.091(5)$, $c = 5.542(5)$ Å, $\alpha = 87.6(1)^\circ$, $\beta = 83.7(1)^\circ$, $\gamma = 79.3(1)^\circ$, $Z = 1$. The structures were solved by heavy-atom techniques from 1 000 (I) and 1 032 (II) observed intensities, measured by diffractometer, and refined by least-squares methods to R 0.041 (I) and 0.068 (II).

Both complexes consist of discrete molecules with platinum showing the usual square-planar co-ordination. Shortest mean Pt...Pt distances are 4.967 (I) and 5.542 Å (II). Molecules of (I) pack in a manner similar to that of *cis*-[Pt(NH₃)₂Cl₂], but the large Pt...Pt distances preclude any metal-metal interaction.

DURING an investigation of the relationships between crystal structure and antitumour activity of certain platinum(II) complexes,¹ the structures of *cis*-, (I), and *trans*-dichlorobispyridineplatinum(II), (II), have been determined by X-ray diffraction. A discussion of the relation of the biological activity of (I) to its solid-state structure has been published.² We report here details of the crystal and molecular structures of the two complexes.

EXPERIMENTAL

Crystal Data.—(a) *cis*-[Pt(py)₂Cl₂], (I). C₁₀H₁₀Cl₂N₂Pt, $M = 424.20$, Monoclinic, $a = 9.408(5)$, $b = 17.110(14)$, $c = 15.270(7)$ Å, $\beta = 98.53(4)^\circ$, $U = 2\,430.8$ Å³, $Z = 8$, $D_c = 2.32$ g cm⁻³. Mo- K_α radiation, $\lambda = 0.7107$ Å; $\mu(\text{Mo-}K_\alpha) = 125.5$ cm⁻¹. Space group $C2/c$ or Cc from systematic absences, the former confirmed by the successful refinement of the structure.

(b) *trans*-[Pt(py)₂Cl₂], (II). C₁₀H₁₀Cl₂N₂Pt, $M = 424.20$, Triclinic, $a = 7.695(6)$, $b = 7.091(5)$, $c = 5.542(5)$ Å, $\alpha = 87.6(1)^\circ$, $\beta = 83.7(1)^\circ$, $\gamma = 79.3(1)^\circ$, $U = 295.3$ Å³, $Z = 1$, $D_c = 2.39$ g cm⁻³. $\mu(\text{Mo-}K_\alpha) = 129.1$ cm⁻¹. Space group $P\bar{1}$.

Data Collection.—(a) *cis*-[Pt(py)₂Cl₂], (I). Crystals were prepared by the method of ref. 3. The crystal used for data collection was a plate with edges $0.13 \times 0.48 \times 0.42$ mm, which were later found to be parallel to [001], [010], and [110], respectively.

Without any prior knowledge of cell constants and orientation, the crystal was mounted on a Philips automatic diffractometer. The 'peak-hunting' routine⁴ readily gave a triclinic cell, which, after Dirichlet reduction, was shown unambiguously to be monoclinic C -centred with the above cell constants. 25 Reflections were used for the least-squares refinement of cell constants and orientation matrix. Intensity data were collected with a ω - 2θ scan technique at a scan rate of 0.1° s⁻¹ and a constant scan range of 1.6° in ω . Stationary-counter background counts of 8 s (half the total scan time) were taken at each end of the scan range. The take-off angle was 4.5° and graphite-monochromatized Mo radiation was used. Of 1 124 reflections measured in the range $0 < 2\theta < 40^\circ$, 1 000 having $I > 2\sigma(I)$ were considered observed. After correction for the background, the standard deviation $\sigma(I)$ of the corrected

intensity was estimated according to the expression: $\sigma(I) = [P + B_1 + B_2 + (kI)^2]^{1/2}$, where P is the total peak count, and B_1 and B_2 the background counts. The value of k , determined by a least-squares analysis of the intensities of three reflections monitored periodically, was 0.008. No systematic drift in these standards was observed. Intensities were corrected for Lorentz, polarization, and absorption effects. Transmission factors were calculated by numerical methods, using the program ABSOR, a local modification of the original GONO9 by W. C. Hamilton. Input for the program are the dimensions of the crystal and the indices of the faces delimiting it.

(b) *trans*-[Pt(py)₂Cl₂], (II). This was also prepared as described in ref. 3. The crystal used for cell-constant determination and intensity collection was a fragment without definite crystal faces, with dimensions *ca.* $0.06 \times 0.14 \times 0.46$ mm. Least-squares refinement of cell constants and collection of the intensity data were performed as for (I). In this way 1 034 reflections were measured in the range $0 < 2\theta < 50^\circ$, and only two, with $I < 2\sigma(I)$, were considered unobserved. Correction of the intensities and evaluation of the standard deviations was as already described, the intensity-correction factor k being 0.007. The evaluation of the absorption correction caused some problems, owing to the irregular crystal shape. Because of the approximation made in describing the crystal habit, absorption effects were only partially corrected, and this was probably the cause of some difficulties encountered in the least-squares refinement (see later).

Structure Determination.—(a) (I). A three-dimensional Patterson synthesis readily gave the positions of the platinum and chlorine atoms. An electron-density synthesis phased by these atoms clearly showed all non-hydrogen atom positions. Two cycles of isotropic refinement for all atoms and two cycles with anisotropic temperature factors for platinum, chlorine, and nitrogen, followed by inclusion of the hydrogen atoms in calculated positions, gave a final conventional R of 0.041. Hydrogen atoms were assigned temperature factors equal to those of the atoms to which they are attached. The weighted factor, R' , $\{R' = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}\}$ was 0.038. The mean shift-to-error ratio in the last cycle was 0.54. The function minimized in the refinement was $\Sigma w(|F_o| - |F_c|)^2$ with weights from counting statistics taken as $4F_o^3/\sigma^2(F_o^2)$. Atomic scattering factors for (I) and (II) were taken from ref. 5, those for platinum and chlorine being corrected for both the real and

¹ B. Rosenberg and L. Van Camp, *Cancer Res.*, 1970, **30**, 1799.

² P. L. Orioli, P. Colamarino, P. Nannelli, B. P. Block, *Atti VII Convegno Nazionale di Chimica Inorganica*, Sept. 1974, Pesaro, Italy.

³ G. B. Kauffman, *Inorg. Synth.*, 1951, **7**, 249.

⁴ Philips, *Serving Science and Industry*, 1972, **18**, 22.

⁵ D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

TABLE 1

Positional parameters ($\times 10^4$) and thermal parameters * ($\text{\AA}^2 \times 10^3$), with estimated standard deviations in parentheses

(a) (I)									
Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt \dagger	15 569(7)	38 182(4)	52 521(6)	297(4)	338(5)	342(5)	-31(4)	-73(3)	31(6)
Cl(1)	1 039(5)	4 258(3)	3 817(3)	52(3)	58(4)	37(4)	-6(3)	-10(3)	12(3)
Cl(2)	35(5)	2 775(3)	4 960(4)	52(3)	50(4)	73(4)	-23(3)	-14(3)	0(3)
N(1)	2 911(13)	4 716(8)	5 564(10)	30(9)	35(10)	55(12)	-1(7)	-1(8)	10(9)
N(2)	1 987(13)	3 447(8)	6 532(10)	33(8)	37(10)	37(11)	-6(7)	0(7)	11(9)
Atom	x/a	y/b	z/c	U	Atom	x/a	y/b	z/c	U
C(1)	4 291(18)	4 569(11)	5 951(13)	45(5)	C(6)	1 683(18)	3 926(11)	7 177(14)	47(5)
C(2)	5 215(20)	5 175(12)	6 227(14)	55(6)	C(7)	1 978(19)	3 698(12)	8 045(14)	60(6)
C(3)	4 770(22)	5 910(13)	6 129(16)	68(7)	C(8)	2 560(21)	2 989(13)	8 241(16)	65(6)
C(4)	3 400(19)	6 084(12)	5 715(14)	59(6)	C(9)	2 936(20)	2 527(12)	7 610(16)	62(6)
C(5)	2 498(18)	5 465(11)	5 458(13)	42(5)	C(10)	2 636(18)	2 751(11)	6 717(14)	48(5)
H(1)	4 636	3 960	6 039	45	H(6)	1 255	4 499	7 011	47
H(2)	6 333	5 056	6 522	55	H(7)	1 734	4 091	8 566	60
H(3)	5 475	6 397	6 367	68	H(8)	2 687	2 780	8 930	65
H(4)	3 019	6 665	5 598	59	H(9)	3 490	1 981	7 782	62
H(5)	1 421	5 586	5 158	42	H(10)	2 929	2 378	6 188	48
(b) (II)									
Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt \dagger	0	0	0	284(6)	386(6)	287(6)	-18(4)	33(4)	22(4)
Cl	-2 122(7)	2 758(7)	490(10)	40(3)	48(3)	57(3)	7(2)	12(2)	7(2)
N	-1 509(17)	-1 283(20)	2 409(24)	21(6)	39(7)	34(7)	10(5)	-26(6)	-9(6)
C(1)	-3 221(27)	-1 453(30)	2 135(39)	40(11)	50(11)	51(12)	-8(9)	-5(9)	-4(9)
C(2)	-4 244(30)	-2 363(32)	3 763(46)	46(12)	48(12)	72(15)	-17(10)	11(11)	-5(11)
C(3)	-3 568(30)	-3 215(31)	5 795(41)	53(13)	49(12)	53(12)	-14(10)	21(10)	-2(10)
C(4)	-1 780(31)	-3 174(27)	6 157(36)	71(14)	32(10)	37(10)	-5(9)	10(9)	-2(8)
C(5)	-797(25)	-2 247(27)	4 452(33)	38(10)	41(10)	35(9)	-7(8)	0(8)	2(7)
Atom	x/a	y/b	z/c	U	Atom	x/a	y/b	z/c	U
H(1)	-3 748	-861	612	57	H(4)	-1 233	-3 822	7 645	57
H(2)	-5 522	-2 408	3 466	57	H(5)	499	-2 247	4 669	57
H(3)	-4 345	-3 872	7 039	57					

* Anisotropic thermal factors are of the form: $\exp(-2\pi^2 \sum_{i,j=1}^3 h_i h_j a_i^* a_j^* U_{ij})$. \dagger Positional parameters $\times 10^5$, thermal parameters $\text{\AA}^2 \times 10^4$. \ddagger Thermal parameters $\text{\AA}^2 \times 10^4$.

imaginary parts of the anomalous dispersion terms.⁶ The 'X-Ray '72' system of programs, adapted for the CII 10070 computer of the University of Florence by Dr. C. Mealli, was used for all calculations.

(b) (II). With the platinum atom at 0,0,0 an electron-density synthesis readily showed all the non-hydrogen atom positions. Two cycles of isotropic and two of anisotropic least-squares, with inclusion of hydrogen atoms in calculated positions, reduced R to 0.068 and R' to 0.085. The mean shift-to-error ratio in the last cycle was 0.13. Hydrogen atoms were assigned a fixed temperature factor, U 0.057 \AA^2 . Weights were initially assumed from counting statistics as $4F_o^2/\sigma^2(F_o^2)$. However, during anisotropic refinement the temperature factor of the nitrogen atom went non-positive definite, probably due to the presence of some systematic errors, such as the partially uncorrected absorption effects. It was then decided to assume a Hughes-type weighting scheme, with $\sqrt{w} = 1$ for reflections with $F_o \leq 40$ and $\sqrt{w} = 40/F_o$ for $F_o > 40$. With these weights the anisotropic refinement was successful. Atomic parameters and their standard deviations are reported in Table 1 for (I) and (II). Structure factors are listed in Supplementary Publication No. SUP 21337 (3 pp., 1 microfiche).^{*}

^{*} See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

⁶ 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

⁷ 'X-Ray '72,' Technical Report TR 192, 1972, University of Maryland, U.S.A., eds. J. M. Stewart, F. A. Kendell, and J. C. Baldwin.

⁸ F. R. Hartley, *Quart. Rev.*, 1973, **2**, 163.

DISCUSSION AND DESCRIPTION OF THE STRUCTURES

Structure of (I).—The structure (Figure 1) consists of discrete molecules in which the platinum atoms show the

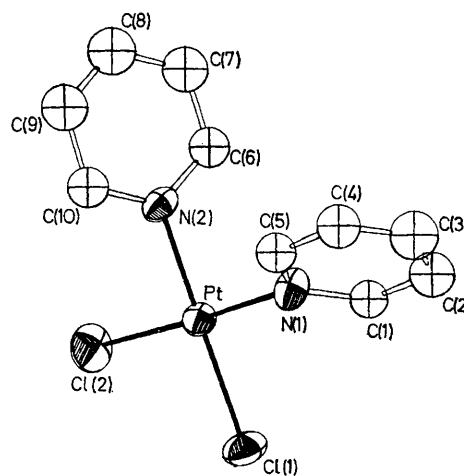


FIGURE 1 ORTEP diagram of *cis*-[Pt(py)₂Cl₂] (I), showing the atom labelling

usual square-planar co-ordination, with mean Pt-Cl 2.296(5) and Pt-N 2.02(1) \AA , in agreement with analogous distances reported previously.⁸ Table 2 shows

bond lengths and angles, and Table 3 equations of least-square planes through the co-ordination plane and the pyridine rings. The pyridine rings [planes (2) and

TABLE 2

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(a) (I)			
Pt-N(2)	2.04(1)	N(2)-Pt-N(1)	89.0(6)
Pt-N(1)	2.01(1)	N(1)-Pt-Cl(1)	90.7(4)
Pt-Cl(1)	2.300(5)	Cl(1)-Pt-Cl(2)	91.8(2)
Pt-Cl(2)	2.291(5)	Cl(2)-Pt-N(2)	88.5(4)
N(1)-C(1)	1.37(2)	Pt-N(1)-C(1)	119(1)
C(1)-C(2)	1.38(3)	C(1)-N(1)-C(5)	118(1)
C(2)-C(3)	1.33(3)	C(5)-N(1)-Pt	123(1)
C(3)-C(4)	1.38(3)	N(1)-C(1)-C(2)	121(2)
C(4)-C(5)	1.38(3)	C(1)-C(2)-C(3)	120(2)
C(5)-N(1)	1.34(2)	C(2)-C(3)-C(4)	121(2)
		C(3)-C(4)-C(5)	117(2)
		C(4)-C(5)-N(1)	123(2)
N(2)-C(6)	1.34(3)	Pt-N(2)-C(6)	118(1)
C(6)-C(7)	1.37(3)	C(6)-N(2)-C(10)	122(2)
C(7)-C(8)	1.35(3)	C(10)-N(2)-Pt	120(1)
C(8)-C(9)	1.33(3)	N(2)-C(6)-C(7)	120(2)
C(9)-C(10)	1.40(3)	C(6)-C(7)-C(8)	119(2)
C(10)-N(2)	1.35(2)	C(7)-C(8)-C(9)	121(2)
		C(8)-C(9)-C(10)	120(2)
		C(9)-C(10)-N(2)	118(2)
(b) (II)			
Pt-Cl	2.308(5)	N-Pt-Cl	88.0(4)
Pt-N	1.98(1)		
N-C(1)	1.37(3)	Pt-N-C(1)	124(1)
C(1)-C(2)	1.35(3)	C(1)-N-C(5)	116(2)
C(2)-C(3)	1.36(3)	C(5)-N-Pt	120(1)
C(3)-C(4)	1.42(3)	N-C(1)-C(2)	124(2)
C(4)-C(5)	1.37(3)	C(1)-C(2)-C(3)	120(2)
C(5)-N	1.41(2)	C(2)-C(3)-C(4)	119(2)
		C(3)-C(4)-C(5)	118(2)
		C(4)-C(5)-N	123(2)

TABLE 3

Least-squares plane equations, in the form $Ax + By + Cz = D$, referred to the crystallographic axes, with deviations (Å) of the atoms from the plane in square brackets

	A	B	C	D
(a) (I)				
Plane (1): Pt, Cl(1), Cl(2), N(1), N(2)	-7.515	9.431	5.449	5.302
[Pt -0.009, Cl(1) 0.013, Cl(2) -0.009, N(1) -0.010, N(2) 0.015]				
Plane (2): N(1), C(1)-(5)	-4.186	-0.275	14.529	6.729
[N(1) 0.006, C(1) -0.005, C(2) -0.007, C(3) 0.017, C(4) -0.016, C(5) 0.005]				
Plane (3): N(2), C(6)-(10)	8.489	7.270	-0.936	3.601
[N(2) -0.020, C(6) 0.010, C(7) 0.013, C(8) -0.026, C(9) 0.016, C(10) 0.007]				
(b) (II)				
Plane (1): Pt, Cl, N	4.709	2.832	4.458	0
Plane (2): N, C(1)-(5)	-0.795	5.841	2.815	0.023
[N 0.026, C(1) -0.015, C(2) -0.006, C(3) 0.014, C(4) -0.002, C(5) -0.018]				

(3)] form angles of 55.8 and 62.0° with the co-ordination plane [plane (1), Table 3(a)]. The molecules

⁹ G. H. W. Milburn and M. R. Truter, *J. Chem. Soc. (A)*, 1966, 1609.

pack in the crystal in columns, [110] being approximately the stacking direction (Figure 2). Pairs of molecules in the column are centrosymmetrically related. This packing, similar to that found in *cis*-[Pt(NH₃)₂Cl₂] (ref. 9) and *cis*-[Pt(en)₂Cl₂] (ref. 10), probably minimizes the potential energy between the permanent dipoles of the molecules. However, in (I) the Pt...Pt distances in the column are 4.986(1) and 4.949(1) Å, whereas in *cis*-[Pt(NH₃)₂Cl₂] and [Pt(en)₂Cl₂] they are *ca.*

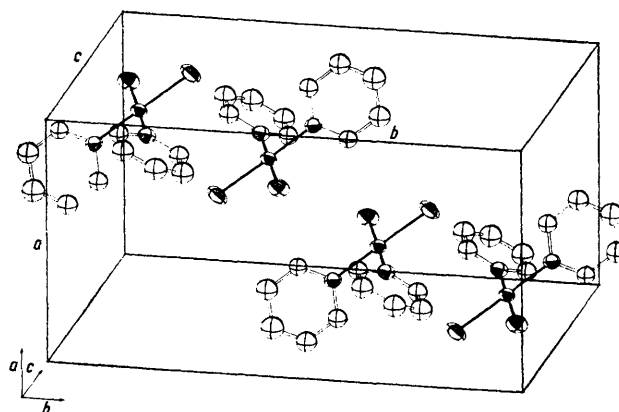


FIGURE 2 ORTEP diagram of (I) showing the packing of the molecules along [110]

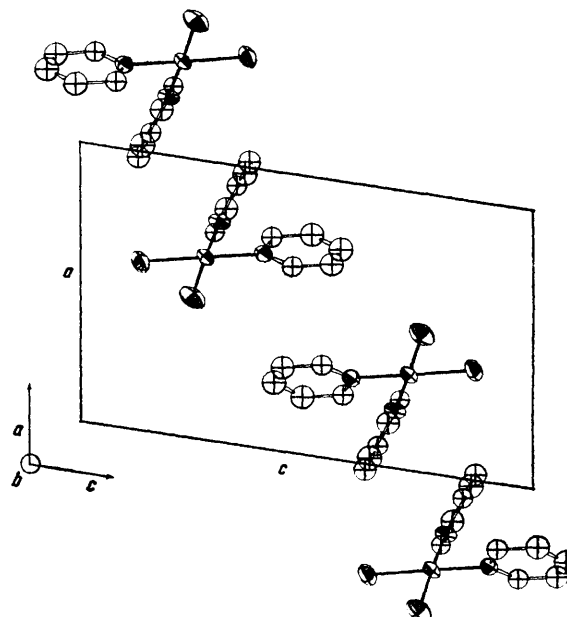


FIGURE 3 ORTEP packing diagram of (I), showing the orientation of the pyridine rings

3.40 Å, which was assumed to be an indication of metal-metal interaction. Further, in (I) the platinum atoms are not colinear, the angle with the two nearest neighbours in the column being 158.63(4)°. All this evidence clearly rules out the presence of any Pt...Pt interaction. It is reasonable to assume that a closer approach of the molecules is precluded by the pyridine rings, which

¹⁰ D. S. Martin, L. D. Hunter, R. Kroening, and P. F. Coley, *J. Amer. Chem. Soc.*, 1971, **93**, 5433.

are rotated with respect to the co-ordination plane in order to minimize intramolecular repulsions.

A further contribution to the stability of the crystal is given by the interaction of pyridine rings from adjacent molecules. Figure 3 shows that pairs of pyridine rings of different molecules lie in approximately parallel planes, *ca.* 3.40 Å apart, almost the same as for the carbon atom planes in graphite. Some significant contact distances between the atoms of these rings are in Table 4.

TABLE 4

Some significant intermolecular distances (Å) in (I)

Cl(1) ... C(2 ^I)	3.67	Cl(1) ... H(6 ^{II})	3.15 *
N(1) ... C(2 ^I)	3.47	C(6) ... C(6 ^{III})	3.45
C(1) ... C(3 ^I)	3.52	C(6) ... C(7 ^{III})	3.43
C(2) ... C(1 ^I)	3.45	H(1) ... Cl(2 ^{IV})	3.37 *
H(5) ... Pt ^{II}	2.96 *	H(10) ... Pt ^{IV}	3.09 *
H(5) ... Cl(1 ^{II})	2.99 *	H(9) ... Cl(1 ^{IV})	3.31 *
H(4) ... Cl(2 ^{II})	3.03 *		

* These molecules are above and below the reference molecule in the direction approximately parallel to [110] (see text).

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

I 1 - <i>x</i> , 1 - <i>y</i> , 1 - <i>z</i>	III - <i>x</i> , <i>y</i> , $\frac{3}{2}$ - <i>z</i>
II - <i>x</i> , 1 - <i>y</i> , 1 - <i>z</i>	IV $\frac{1}{2}$ - <i>x</i> , $\frac{1}{2}$ - <i>y</i> , 1 - <i>z</i>

Bond lengths and angles in the pyridine rings are as expected.

Structure of (II).—The structure of this complex is also composed of discrete molecules (Figure 4). The platinum atom is on a crystallographic centre of symmetry and shows square-planar co-ordination with Pt-N 1.98(1) and Pt-Cl 2.308(5) Å. The slight shortening of the former and lengthening of the latter bonds, compared

to values for (I), is in accord with the higher *trans*-effect of chlorine compared to nitrogen.⁸

Least-squares planes through the co-ordination plane [plane (1), Table 3(b)] and the pyridine ring [plane (2)]

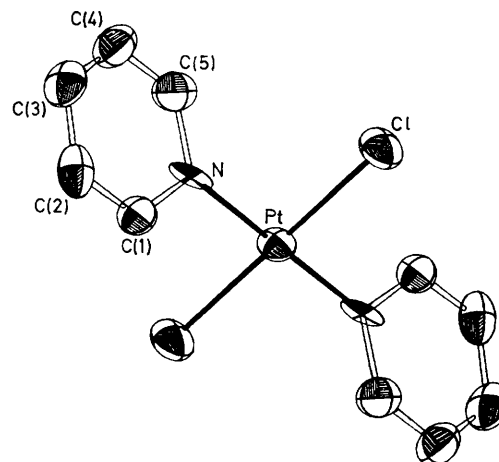


FIGURE 4 ORTEP diagram of *trans*-[Pt(py)₂Cl₂], (II), showing the atom labelling

with deviations of the atoms from the plane are reported in Table 3. The pyridine rings make angles of 56.2° with the co-ordination plane. The shortest Pt ... Pt distance is 5.542 Å. Bond lengths and angles in the pyridine ring (Table 2) are as expected.

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