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trans-Bis(2-aminopyridine)dichloropalladium(II), $[PdCl_2(C_5H_6N_2)_2]$

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Abstract. $M_r = 365.54$, monoclinic, $P2_1/n$, $a = 5.922$ (2), $b = 16.589$ (12), $c = 6.722$ (3) Å, $\beta = 104.52$ (3)°, $V = 639.3$ (6) Å^3, $D_x = 1.899$ Mg m^{-3}, $F(000) = 360$, $Z = 2$, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.5934$ mm^{-1}, room temperature, final $R = 0.045$, $R_w = 0.054$ ($w = 1.0$) for 1737 observed reflections. The Pd atom is four-coordinate in a square-planar environment with Pd—Cl = 2·310 (2), Pd—N = 2·024 (4) Å. There is a bifurcated intra- and intermolecular N—H···Cl hydrogen bond which, together with one more intermolecular hydrogen bond of the same kind, is responsible for the packing of the molecules.

Introduction. Since the discovery of the antitumor activity of some Pd and Pt compounds, the importance of these metals has markedly increased in bio-inorganic chemistry. We are involved in a program of synthesizing new Pd complexes and studying their reactions and structures in solution and in the solid state, in particular considering complexes with N bases.

The structure of the title compound was solved as part of this program considering substituted amines as ligands, with the aim of providing information on the structural features of this complex and confirming the structure established by chemical and spectral data (Gómez Vaamonde, Alvarez-Valdés, Navarro-Ranninger & Masaguer, 1984).

Experimental. Crystals grown by slow crystallization from dimethylformamide. Needle-shaped orange-yellow prism approximately 0·15 × 0·30 × 0·20 mm. Enraf–Nonius CAD-4 computer-controlled four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters determined by least-squares refinement of values for 25 reflections. ω–2θ scan technique. h 0 to 9, k 0 to 26, l 10 to −10. Two standard reflections ($\bar{3}21$, $32\bar{1}$) measured after every 90 reflections, no significant change in intensities. Total of 2807 independent reflections collected in the range $0 < 2\theta < 30°$; 1737 for which $I \geq 2\sigma(I)$ used in further calculations; $R_{\rm int} = 1.2\%$. Lorentz–polarization factors applied, but no absorption correction. Structure solved by the heavy-atom technique. Pd and Cl positions were derived from a three-dimensional Patterson function; a subsequent Fourier map yielded the complete non-H skeleton. The structure was refined (on F) by full-matrix least-squares calculations using unit weights. Five cycles of isotropic refinement for all non-hydrogen atoms followed by four cycles of anisotropic refinement gave $R = 0.050$. H atoms were located in a difference Fourier map and included in the calculations with a fixed isotropic temperature factor. A further refinement cycle gave a final $R = 0.045$, $R_w = 0.054$, $(\Delta/\sigma)_{\max} = 0.18$, $S = 1.4$. The final difference Fourier map showed a peak of 1·4 e Å^{-3} close to the Pd atom; the largest hole was −0·5 e Å^{-3}. Anomalous-dispersion corrections for Pd and Cl and atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations performed with *XRAY76* (Stewart, 1976) and *PARST* (Nardelli, 1983) on a VAX-11750 computer.

Discussion. Final positional parameters and geometrical characteristics of the complex are given in Tables 1 and 2,* and the atomic numbering is presented in Fig. 1.

The environment of the Pd atom is perfectly planar – an approximately regular square. The Pd which is at the symmetry center has bond lengths Pd—Cl 2·310 (2) and Pd—N 2·024 (4) Å which are within the ranges previously found in Pd$^{\rm II}$ complexes: Pd—Cl 2·307 (1), Pd—N 2·005 (3)–2·011 (4) Å (Navarro-Ranninger, Martínez-Carrera & García-Blanco, 1983).

Bond lengths and angles within the 2-aminopyridine molecules of the title compound are normal. The differences between those in the aminopyridine ligand

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* Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms and hydrogen parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39726 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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and those in the crystal of the uncomplexed ligand are not statistically significant, except for the angle N(1)–C(2)–N(2) which is significantly larger in the complex, probably as a consequence of steric interaction between the amino group and the $\mathrm{Cl^-}$ ion.

The maximum atomic displacement from the best-fit plane through the pyridine ring is 0·005 (6) Å. It seems worth noting that the displacement of N(2) from this plane [0·016 (6) Å] is the same as that found in the uncomplexed ligand (Chao, Schempp & Rosenstein, 1975).

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å² × 10⁴)

$$U_{\mathrm{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j \cos(a_i,a_j).$$

	x	y	z	U_{eq}
Pd	0	0	0	252 (1)
Cl(1)	−0·3288 (2)	0·0714 (1)	−0·1643 (2)	347 (4)
N(1)	0·0826 (8)	0·0887 (3)	0·2125 (6)	275 (12)
N(2)	−0·2160 (9)	0·0517 (4)	0·3621 (8)	375 (16)
C(2)	−0·0305 (10)	0·0989 (3)	0·3612 (8)	288 (14)
C(3)	0·0451 (11)	0·1583 (4)	0·5157 (10)	394 (21)
C(4)	0·2307 (13)	0·2055 (4)	0·5102 (11)	466 (23)
C(5)	0·3459 (12)	0·1952 (4)	0·3551 (11)	416 (21)
C(6)	0·2667 (10)	0·1373 (4)	0·2108 (9)	331 (16)

Table 2. *Geometrical characteristics* [*distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*]

A prime indicates the atom at $\bar{x}, \bar{y}, \bar{z}$.

Pd–Cl	2·310 (2)	Cl–Pd–N(1)	89·4 (1)
Pd–N(1)	2·024 (4)	Cl′–Pd–N(1)	90·6 (1)
N(1)–C(2)	1·346 (8)	Pd–N(1)–C(6)	118·6 (4)
N(1)–C(6)	1·358 (8)	Pd–N(1)–C(2)	122·5 (4)
C(2)–C(3)	1·419 (8)	C(2)–N(1)–C(6)	118·8 (5)
C(3)–C(4)	1·357 (10)	N(1)–C(2)–N(2)	119·2 (5)
C(4)–C(5)	1·392 (12)	N(2)–C(2)–C(3)	120·5 (5)
C(5)–C(6)	1·362 (9)	N(1)–C(2)–C(3)	120·4 (5)
C(2)–N(2)	1·350 (8)	C(2)–C(3)–C(4)	119·3 (6)
		C(3)–C(4)–C(5)	120·1 (7)
		C(4)–C(5)–C(6)	118·3 (7)
		N(1)–C(6)–C(5)	123·1 (6)

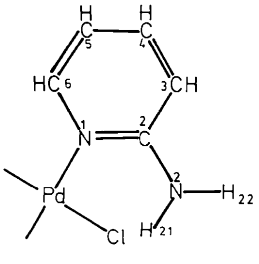

Fig. 1. View of the coordination around Pd.

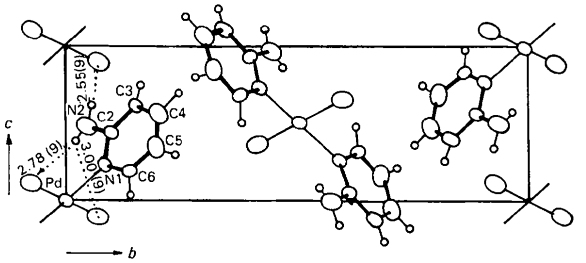

Fig. 2. The contents of the unit cell. (Distances in Å.)

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

D–H···A	D–H	D···A	H···A	∠D–H···A
N(2)–H(21)···Cl	0·76 (9)	3·448 (6)	3·00 (9)	121 (8)
N(2)–H(21)···$\mathrm{Cl^{i}}$	0·76 (9)	3·378 (6)	2·78 (9)	138 (8)
N(2)–H(22)···$\mathrm{Cl^{ii}}$	0·91 (10)	3·429 (6)	2·55 (9)	162 (8)

Symmetry code: (i) $\bar{x}-1, \bar{y}, \bar{z}$; (ii) $x, y, z+1$.

The dihedral angle between the plane of the pyridine ring and the square plane around Pd is 73·0 (2)°.

Crystal packing and hydrogen bonding. The packing of the molecules, shown in Fig. 2, is completely determined by the N–H···Cl hydrogen bonding. There is one bifurcated hydrogen bond involving H(21) which is shared by N(2) and Cl(x,y,z) (intramolecular), and by Cl($\bar{x}-1$, $\bar{y}$, $\bar{z}$) (intermolecular). Another intermolecular hydrogen bond involves H(22) (see Table 3). The distances of this hydrogen bond agree well with the values published for other palladium chloride/2-aminopyridine complexes (Reck, Heyn & Schröer, 1982).

References

CHAO, M., SCHEMPP, E. & ROSENSTEIN, R. D. (1975). *Acta Cryst.* B**31**, 2922–2924.

GÓMEZ VAAMONDE, C., ALVAREZ-VALDÉS, A., NAVARRO-RANNINGER, M. C. & MASAGUER, J. R. (1984). *Transition Met. Chem.* **9**, 52–54.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.

NAVARRO-RANNINGER, M. C., MARTÍNEZ-CARRERA, S. & GARCÍA-BLANCO, S. (1983). *Acta Cryst.* C**39**, 186–188, 188–190.

RECK, G., HEYN, B. & SCHRÖER, H. P. (1982). *Cryst. Struct. Commun.* **11**, 179–184.

STEWART, J. M. (1976). Editor. The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.