metal-organic papers

(4-Amino-2,2′-bipyridine)dichloroplatinum(II) dihydrate

Ken Sakai,* Yoshimi Yokoyama, Ken Okamoto and Satoru Takahashi

Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan

Correspondence e-mail: ksakai@rs.kagu.tus.ac.jp

In the crystal structure of the title compound, $[PtCl_2(C_{10}H_9N_3)]\cdot 2H_2O$, the square-planar platinum complexes form one-dimensional columns based on the π–π-stacking interactions between the 4-amino-2,2′-bipyridine ligands, where the plane-to-plane separations are 3.45 (1) and 3.47 (1) Å. The Pt···Pt distances in the column are 5.1214 (7) and 6.1648 (7) Å, suggesting no metal–metal interaction. Intermolecular hydrogen bonds are formed among the water molecules, the amino groups, and the coordinated Cl atoms.

Comment

Since we discovered that some dinuclear platinum complexes are active as catalysts in the reduction of water to molecular hydrogen (Sakai *et al.*, 1993), continuous efforts have been made to develop bifunctional metal complexes consisting of light-harvesting centres and catalytically active centres. The title platinum compound, $[PtCl_2(4\text{-amino-2,2′-bipyridine})]\cdot 2H_2O$, (I), has been prepared and characterized as one of the precursors for our ideal systems. The amino group on the compound can be used to accommodate a photosensitizer, such as a tris(2,2′-bipyridine)ruthenium(II) derivative. In addition, this compound must be viewed as related to the yellow and red forms of $[PtCl_2(2,2′\text{-bipyridine})]$ (Herber *et al.*, 1994). Their difference in colour was rationally interpreted in terms of the difference in the Pt—Pt distance observed by X-ray diffraction (3.45 Å for the red form and 4.44 Å for the yellow form). The lowest energy transition was assigned as a metal-to-ligand charge transfer transition (Herber *et al.*, 1994).

(I)
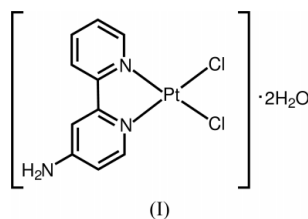
Atom Pt1 shows slight distortion toward a tetrahedral geometry (Fig. 1 and Table 1). The structure can be described in terms of a distortion from ideal square-planar coordination, whereby one of the four coordinated atoms (Cl2) is displaced by 0.13 (1) Å from the plane defined by the rest of the coordinated atoms (N1, N2 and Cl1), and the displacement of Pt1 from this plane is neglibly small. The 4-amino-2,2′-bipyridine ligand has a planar geometry, with the 13-atom r.m.s. deviation of 0.011 Å. This plane is tilted by 2.6 (2)° with respect to the N1/N2/Cl1 plane.

As shown in Fig. 2, the mononuclear units stack along the *a* axis, such that two types of π–π stacks are generated, with the
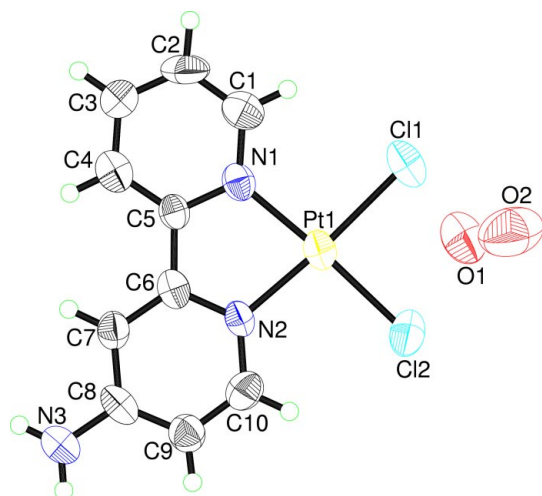
Figure 1
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level. Water H atoms were not located.

plane-to-plane separations of 3.45 (1) and 3.47 (1) Å. The Pt···Pt distances along the stack [5.1214 (7) and 6.1648 (7) Å, see Table 1] indicate that there is no metal–metal interaction in (I). There are hydrogen bonds between the Cl atoms and the water molecules (Table 1), between the water molecules, and between the amino groups and the water molecules (Table 2).

Experimental

4-Amino-2,2′-bipyridine was prepared according to the literature method (Jones *et al.*, 1967). The title Pt^{II} complex was prepared in the same manner as reported for [PtCl₂(2,2′-bipyridine)] (Morgan & Burstall, 1963) (yield: 96%). The crystals of (I) were obtained by slow cooling of a hot aqueous solution of the complex.

Crystal data

|	
[PtCl₂(C₁₀H₉N₃)]·2H₂O	$D_x = 2.276$ Mg m⁻³
$M_r = 473.22$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2848
$a = 7.3136$ (6) Å	reflections
$b = 10.1125$ (9) Å	$\theta = 2.3–23.9°$
$c = 18.7166$ (16) Å	$\mu = 10.54$ mm⁻¹
$\beta = 93.784$ (1)°	$T = 293$ (2) K
$V = 1381.2$ (2) Å³	Needle, yellow
$Z = 4$	$0.36 \times 0.05 \times 0.02$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	3188 independent reflections
	2165 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.061$
Absorption correction: Gaussian (*XPREP* in *SAINT*; Bruker, 2001)	$\theta_{max} = 28.3°$
	$h = -9 \rightarrow 9$
	$k = -13 \rightarrow 10$
$T_{min} = 0.323, T_{max} = 0.785$	$l = -23 \rightarrow 24$
8387 measured reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0267P)^2]$
$wR(F^2) = 0.085$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.89$	$(\Delta/\sigma)_{max} = 0.001$
3188 reflections	$\Delta\rho_{max} = 1.81$ e Å⁻³
163 parameters	$\Delta\rho_{min} = -0.93$ e Å⁻³
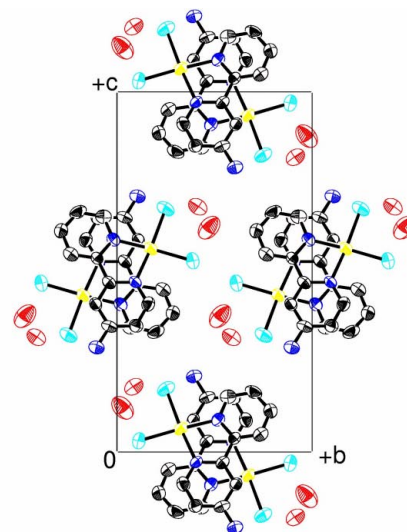
(a)
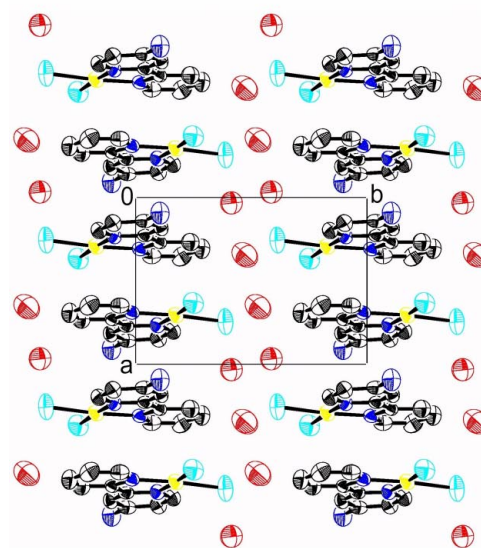
(b)

Figure 2
The crystal packing in (I), showing the one-dimensional π–π-stacking interactions (*a*) along the *a* axis and (*b*) along the *c* axis ($\frac{1}{4} < z < \frac{3}{4}$). Hydrogen bonds are not shown.

Table 1
Selected geometric parameters (Å, °).

Pt1—N2	1.995 (6)	Pt1···Pt1^{ii}	6.1648 (7)
Pt1—N1	1.997 (6)	Cl1···O2	3.197 (8)
Pt1—Cl2	2.284 (3)	Cl1···O1	3.362 (7)
Pt1—Cl1	2.303 (2)	Cl2···O2^{iii}	3.240 (8)
Pt1···Pt1^{i}	5.1214 (7)	O2···O1^{iv}	2.657 (11)
N2—Pt1—N1	80.6 (3)	N2—Pt1—Cl1	175.71 (19)
N2—Pt1—Cl2	95.8 (2)	N1—Pt1—Cl1	95.1 (2)
N1—Pt1—Cl2	175.25 (19)	Cl2—Pt1—Cl1	88.45 (9)
Cl1—Pt1—N1—C1	−0.3 (6)	N2—C6—C5—N1	−2.0 (9)
Cl2—Pt1—N2—C10	4.9 (6)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N3—H3B⋯O1^{ii}	0.86	2.35	3.194 (10)	167

Symmetry code: (ii) $-x, 2-y, 1-z$.

All H atoms except for those of water molecules were located at their idealized position (C—H = 0.93 Å and N—H = 0.86 Å), and included in the refinement in riding-motion approximation, with $U_{iso} = 1.2U_{eq}$ of the carrier atom. Water H atoms were not located. In the final difference Fourier synthesis, seven residual peaks in the range 1.01–1.56 e Å^{-3} were observed within 1.00 Å of the Pt atom. The deepest hole was located 1.44 Å from Pt1.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *KENX* (Sakai, 2002); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997), *TEXSAN* (Molecular Structure Corporation, 2001), *KENX* (Sakai, 2002) and *ORTEP*II (Johnson, 1976).

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