

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

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

Ken Sakai, Yoshimi Yokoyama, Ken Okamoto and Satoru Takahashi

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site provided that this cover page is retained. Republication of this article or its storage in electronic databases or the like is not permitted without prior permission in writing from the IUCr.

(4-Amino-2,2'-bipyridine)dichloroplatinum(II)
dihydrateKen Sakai,* Yoshimi Yokoyama,
Ken Okamoto and Satoru
TakahashiDepartment of Applied Chemistry, Faculty of
Science, Tokyo University of Science,
Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601,
JapanCorrespondence e-mail:
ksakai@rs.kagu.tus.ac.jp

In the crystal structure of the title compound, $[\text{PtCl}_2(\text{C}_{10}\text{H}_9\text{N}_3)] \cdot 2\text{H}_2\text{O}$, 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.

Received 13 June 2003

Accepted 17 June 2003

Online 30 June 2003

Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.012$ Å

H-atom completeness 70%

R factor = 0.046

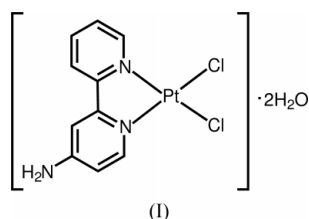
wR factor = 0.085

Data-to-parameter ratio = 19.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

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, $[\text{PtCl}_2(4\text{-amino-2,2'-bipyridine})] \cdot 2\text{H}_2\text{O}$, (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 $[\text{PtCl}_2(2,2'\text{-bipyridine})]$ (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).



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 negligibly 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

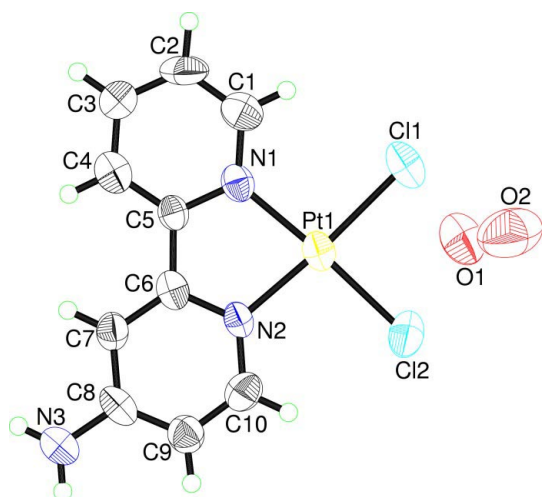


Figure 1
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level. Water H atoms were not located.

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

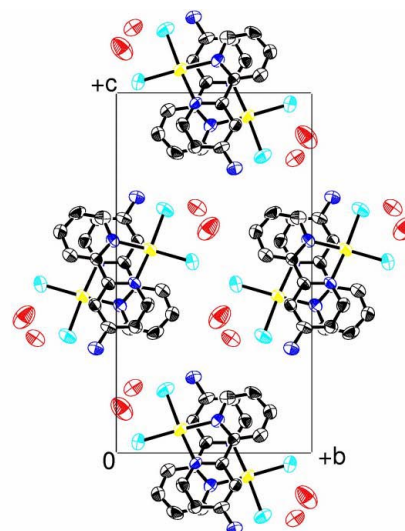
[PtCl ₂ (C ₁₀ H ₉ N ₃)]·2H ₂ O	$D_x = 2.276 \text{ Mg m}^{-3}$
$M_r = 473.22$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2848 reflections
$a = 7.3136 (6) \text{ \AA}$	$\theta = 2.3\text{--}23.9^\circ$
$b = 10.1125 (9) \text{ \AA}$	$\mu = 10.54 \text{ mm}^{-1}$
$c = 18.7166 (16) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 93.784 (1)^\circ$	Needle, yellow
$V = 1381.2 (2) \text{ \AA}^3$	$0.36 \times 0.05 \times 0.02 \text{ mm}$
$Z = 4$	

Data collection

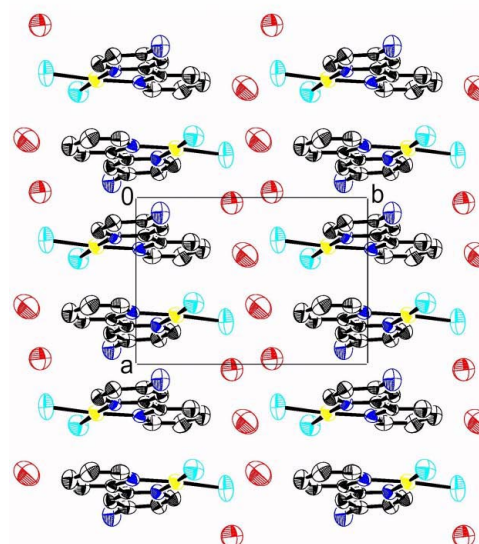
Bruker SMART APEX CCD area-detector diffractometer	3188 independent reflections
ω scans	2165 reflections with $I > 2\sigma(I)$
Absorption correction: Gaussian (XPRED in SAINT; Bruker, 2001)	$R_{\text{int}} = 0.061$
$T_{\text{min}} = 0.323$, $T_{\text{max}} = 0.785$	$\theta_{\text{max}} = 28.3^\circ$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

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 $P = (F_o^2 + 2F_c^2)/3$
$S = 0.89$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3188 reflections	$\Delta\rho_{\text{max}} = 1.81 \text{ e \AA}^{-3}$
163 parameters	$\Delta\rho_{\text{min}} = -0.93 \text{ e \AA}^{-3}$



(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, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N3-H3B\cdots O1^{ii}$	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: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *KENX* (Sakai, 2002); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997), *TEXSAN* (Molecular Structure Corporation, 2001), *KENX* (Sakai, 2002) and *ORTEPII* (Johnson, 1976).

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 14340223) from the Ministry of Education, Science, Sports, and Culture of Japan.

References

- Bruker (2001). *SAINT* (Version 6.22) and *SMART* (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
- Herber, R. H., Croft, M., Coyer, M. J., Bilash, B. & Sahiner, A. (1994). *Inorg. Chem.* **33**, 2422–2426.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Jones, R. A., Roney, B. D., Sasse, W. H. F. & Wade, K. O. (1967). *J. Chem. Soc. B*, pp. 106–111.
- Molecular Structure Corporation (2001). *TEXSAN*. Version 1.11r1. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
- Morgan, G. T. & Burstall, F. H. (1963). *J. Chem. Soc.* pp. 965–971.
- Sakai, K. (2002). *KENX*. Tokyo University of Science, Japan.
- Sakai, K., Kizaki, Y., Tsubomura, T. & Matsumoto, K. (1993). *J. Mol. Catal.* **74**, 141–152.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.