

(*N*-Methyl-4,4'-bipyridinium)(2,2':6',2''-terpyridine)platinum(II) triperchlorate monohydrate**Ken Sakai,* Mai Kurashima, Manabu Osada and Satoru Takahashi**

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

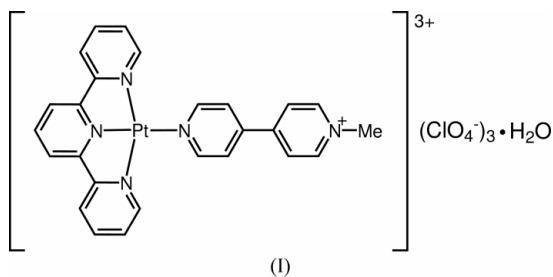
Correspondence e-mail: ksakai@rs.kagu.tus.ac.jp

Key indicatorsSingle-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
H-atom completeness 92%
Disorder in solvent or counterion
 R factor = 0.033
 wR factor = 0.089
Data-to-parameter ratio = 16.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $[\text{Pt}(\text{C}_{15}\text{H}_{11}\text{N}_3)(\text{C}_{11}\text{H}_{11}\text{N}_2)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$, the PtN_4 coordination plane is distorted from a planar geometry owing to the relatively strong intermolecular terpy-terpy interactions, giving rise to a bent structure with respect to the terpy moiety (terpy = 2,2':6',2''-terpyridine). The coordinated pyridyl plane of *N*-methyl-4,4'-bipyridinium (*MQ*) is inclined by $81.7(1)^\circ$ with respect to the Pt coordination plane. The dihedral angle between the two pyridyl planes within *MQ* is $33.5(2)^\circ$.

Comment

We previously reported that amidate-bridge Pt^{II} dimers with a general formula $[\text{Pt}_2(\text{NH}_3)_4(\mu\text{-amidato})_2]^{2+}$ (amidate = acetamidate, α -pyrrolidinonate, α -pyridonate, *etc.*) serve as effective H_2 -producing catalysts in a well known photosystem consisting of edta, $\text{Ru}(\text{bpy})_3^{2+}$ and methylviologen (Sakai *et al.*, 1993) (methylviologen = *N,N'*-dimethyl-4,4'-bipyridinium dichloride). Up to now, a large number of mono- and dinuclear Pt^{II} complexes have been prepared in our laboratory, and their catalytic activity has been evaluated by monitoring the photochemical hydrogen production from water under visible-light illumination (unpublished results). Consequently, we recently found that mononuclear Pt^{II} complexes of *N*-methyl-4,4'-bipyridinium (*MQ*), such as the title complex, (I), exhibit relatively high catalytic activity compared to the common mononuclear Pt^{II} complexes. Here we report the crystal structure of one of such complexes prepared in our laboratory.



The asymmetric unit of (I) consists of a mononuclear Pt^{II} complex cation, three perchlorate anions and a water molecule. Although various $\text{Pt}(\text{terpy})$ complexes have been reported to possess a planar geometry for the $\text{Pt}(\text{terpy})$ moiety (Cini *et al.*, 2001; Lowe *et al.*, 2001; Ross *et al.*, 2001; Yam *et al.*, 2001; Yam *et al.*, 2002), the $\text{Pt}(\text{terpy})$ moiety in (I) is found to have a bent structure. The dihedral angles between the planes $\text{N1}/\text{C1}-\text{C5}$ and $\text{N2}/\text{C6}-\text{C10}$, and between the planes $\text{N2}/\text{C6}-\text{C10}$ and $\text{N3}/\text{C11}-\text{C15}$ are $9.2(3)^\circ$ and $5.6(4)^\circ$, respectively. Moreover, the dihedral angle between the planes $\text{N1}/\text{C1}-\text{C5}$

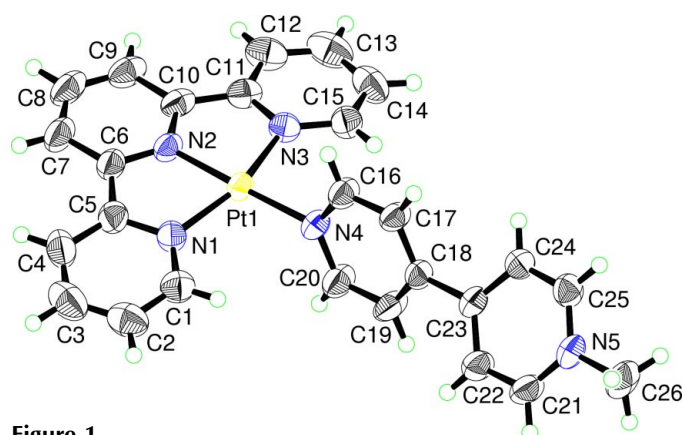


Figure 1
Structure of the cation of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

and N3/C11–C15 is $14.2(3)^\circ$. These values, together with the N–C–C–N torsion angles listed in Table 1, indicate that the two pyridyl rings at either end of terpy are twisted the same way out of the N2/C6–C10 plane. Consequently, the atom N1 shows an exceptional behavior, being displaced out of the Pt1/N2–N4 plane by $0.167(6) \text{ \AA}$, while the four-atom r.m.s. deviation from the mean plane is 0.019 \AA . The pyridyl plane of *MQ*, which is bound to the Pt^{II} atom, is inclined by $81.7(1)^\circ$ with respect to the plane Pt1/N2–N4. The pyridyl planes within *MQ* are twisted by $33.5(2)^\circ$ to each other.

The origin of the bent structure discussed above can be understood by looking at the terpy–terpy interactions in the crystal. As shown in Fig. 2*a*, there are two different types of π – π stacking interactions between the terpy moieties. It also shows that the terpy moiety has a bent structure because it is pushed down by the two adjacent cations at either end of the unit (as shown by the arrows in Fig. 2*b*). The complexes shown in Fig. 2 are related by an inversion center, where the plane-to-plane separations are $3.43(2) \text{ \AA}$ for the stacking given by the C8–C14 moiety, and $3.46(1) \text{ \AA}$ for that given by the C1–C3 unit. The Pt...Pt distances in the former and the latter stacks are $7.6411(7) \text{ \AA}$ and $8.1543(7) \text{ \AA}$, respectively, confirming the lack of any metal–metal interaction. Details of the photochemical, electrochemical and catalytic properties of (I) will be reported elsewhere.

Experimental

A solution of [PtCl(terpy)]Cl (0.1 mmol, 0.05 g; Howe-Grant & Lippard, 1980) and AgClO₄ (0.2 mmol, 0.042 g) in water (10 ml) was refluxed in the dark for 2 h. To the solution was added MQ(ClO₄) (0.1 mmol, 0.027 g; Sakai *et al.*, 2003) and the mixture was further refluxed for 4 h. After the precipitated AgCl was removed by filtration, the filtrate was evaporated to a total volume of about 5 ml until a small amount of orange precipitate started to deposit. To the solution were then added 2–3 drops of a saturated aqueous solution of sodium perchlorate. Leaving the solution to stand overnight afforded (I) as an orange precipitate. The product was recrystallized from hot water to give the final product as orange needles (yield: 51%). Analysis calculated for PtO₁₂N₅Cl₃C₂₆H₂₂ (calculated as an anhydrous form): C, 34.78; H, 2.47; N, 7.80%; found: C, 35.79; H, 2.56; N, 7.48%. ¹HNMR (D₂O, 296 K): $\delta = 4.36$ (s, 3H); 7.54–7.60 (*m*, 6H); 7.70 (*d*, 2H,

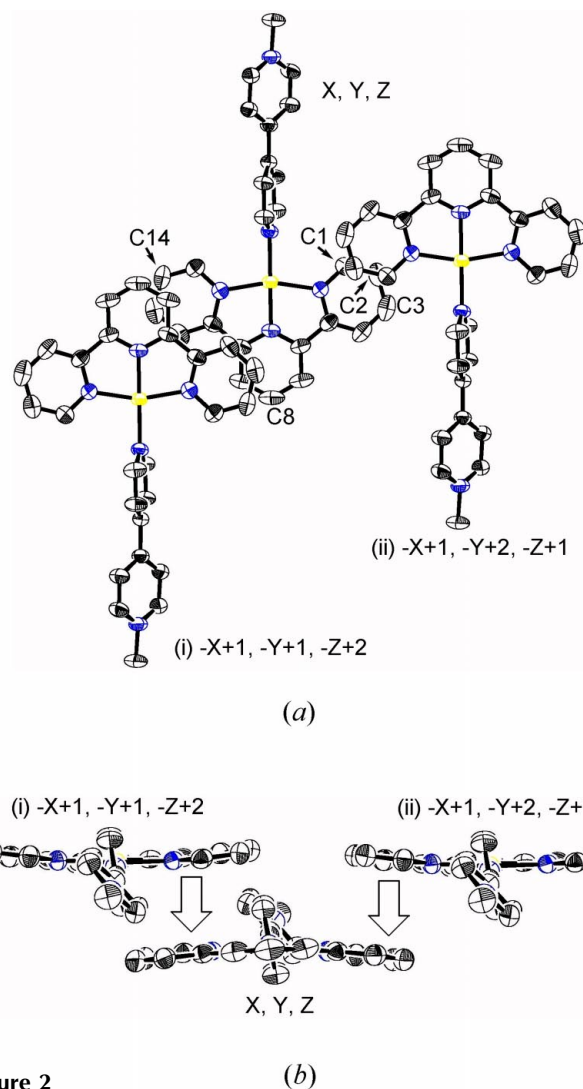


Figure 2
(*a*) Top view and (*b*) side view of the intermolecular interactions leading to a bent structure of the terpy moiety. H atoms are omitted for clarity.

$J = 5.44 \text{ Hz}$); 8.24–8.42 (*m*, 8H); 8.41 (*d*, 2H, $J = 6.93 \text{ Hz}$); 8.90 (*d*, 2H, $J = 6.93 \text{ Hz}$); 9.28 p.p.m. (*d*, 2H, $J = 6.76 \text{ Hz}$).

Crystal data

[Pt(C ₁₅ H ₁₁ N ₃)(C ₁₁ H ₁₁ N ₂)](ClO ₄) ₃ · H ₂ O	$Z = 2$
$M_r = 915.94$	$D_x = 1.974 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.2302(8) \text{ \AA}$	Cell parameters from 5125 reflections
$b = 13.4229(11) \text{ \AA}$	$\theta = 2.3\text{--}28.2^\circ$
$c = 13.6086(11) \text{ \AA}$	$\mu = 4.89 \text{ mm}^{-1}$
$\alpha = 62.287(1)^\circ$	$T = 296(2) \text{ K}$
$\beta = 83.403(1)^\circ$	Needle, orange
$\gamma = 68.990(1)^\circ$	$0.20 \times 0.09 \times 0.03 \text{ mm}$
$V = 1541.3(2) \text{ \AA}^3$	

Data collection

Bruker SMART APEX CCD- detector diffractometer	6948 independent reflections
ω scans	6193 reflections with $I > 2\sigma(I)$
Absorption correction: Gaussian (<i>XPRED</i> in <i>SAINT</i> ; Bruker, 2001)	$R_{\text{int}} = 0.067$
$T_{\text{min}} = 0.337$, $T_{\text{max}} = 0.659$	$\theta_{\text{max}} = 28.3^\circ$
13736 measured reflections	$h = -13 \rightarrow 13$
	$k = -17 \rightarrow 17$
	$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.089$
 $S = 1.01$
 6948 reflections
 423 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0448P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 1.40 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.21 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Pt1–N2	1.938 (4)	Pt1–N4	2.033 (4)
Pt1–N3	2.022 (4)	Pt1–Pt1 ⁱ	7.6411 (7)
Pt1–N1	2.024 (4)	Pt1–Pt1 ⁱⁱ	8.1543 (7)
N2–Pt1–N3	81.05 (17)	N2–Pt1–N4	177.35 (13)
N2–Pt1–N1	80.58 (17)	N3–Pt1–N4	99.26 (16)
N3–Pt1–N1	161.30 (17)	N1–Pt1–N4	99.25 (16)
N1–C5–C6–N2	4.0 (6)	N2–C10–C11–N3	–3.6 (6)

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

One of the three ClO_4^- anions shows orientational disorder. Around the atom Cl2 there are two sets of possible positions (O5A, O6A, O7A, O8A; and O5B, O6B, O7B, O8B). It was assumed that these disordered O atoms have the same isotropic displacement parameter. Furthermore, Cl–O distances were restrained to 1.43 (3) \AA and the six O–O distances within each perchlorate ion were restrained to be equal. The occupation factors for sites *A* and *B* converged at 41.9 (5) and 58.1 (5)%, respectively. A water molecule is also assumed to be disordered over two sites (O13A and O13B). These are assumed to have the same isotropic displacement parameter. The occupation factors of sites *A* and *B* converged at 33 (2) and 67 (2)%, respectively. All the H atoms except for those of the water molecule were located at idealized positions (methyl C–H = 0.96 \AA and aromatic C–H = 0.93 \AA), and included in the refinement in riding-motion approximation, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ and $1.2U_{\text{eq}}(\text{C})$ for methyl and aromatic H atoms, respectively. Water H

atoms were not located. In the final difference Fourier synthesis, eight residual peaks in the range 1.1–1.61 $\text{e } \text{\AA}^{-3}$ were observed within 0.99 \AA of the Pt atom. The deepest hole was located 1.29 \AA 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*, *TEXSAN* (Molecular Structure Corporation, 2001), *KENX* and *ORTEP* (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.
- Cini, R., Donati, A. & Giannettoni, R. (2001). *Inorg. Chim. Acta.* **315**, 73–80.
- Howe-Grant, M. & Lippard, S. J. (1980). *Inorg. Synth.* **20**, 102–103.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Lowe, G., Ross, S. A., Probert, M. & Cowley, A. (2001). *Chem. Commun.* pp. 1288–1289.
- Molecular Structure Corporation (2001). *TEXSAN*. Version 1.11r1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Ross, S. A., Lowe, G. & Watkin, D. J. (2001). *Acta Cryst.* **C57**, 275–276.
- Sakai, K., Kizaki, Y., Tsubomura, T. & Matsumoto, K. (1993). *J. Mol. Catal.* **74**, 141–152.
- Sakai, K. (2002). *KENX*. Tokyo University of Science, Japan.
- Sakai, K., Osada, M., Yokoyama, Y., Tomita, Y. & Tsubomura, T. (2003). *Acta Cryst.* **E59**, m512–m514.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Yam, V. W. W., Tang, R. P. L., Wong, K. M. C., Ko, C. C. & Cheung, K. K. (2001). *Inorg. Chem.* **40**, 571–547.
- Yam, V. W. W., Wong, K. M. C. & Zhu, N. (2002). *J. Am. Chem. Soc.* **124**, 6506–6507.