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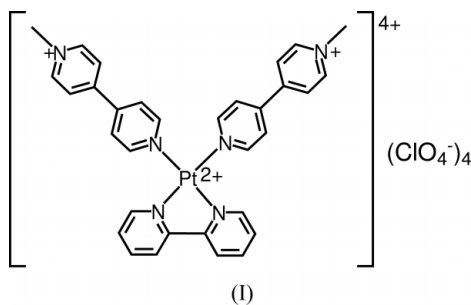
## Key indicators

Single-crystal X-ray study  
*T* = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$   
Disorder in solvent or counterion  
*R* factor = 0.047  
*wR* factor = 0.126  
Data-to-parameter ratio = 18.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.(2,2'-Bipyridine)bis(*N*-methyl-4,4'-bi-  
pyridinium)platinum(II) tetraperchlorate

In the title compound,  $[\text{Pt}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{C}_{11}\text{H}_{11}\text{N}_2)_2](\text{ClO}_4)_4$ , the square-planar  $\text{PtN}_4$  coordination geometry is slightly deformed, with the coordinated N atom of one of the *N*-methyl-4,4'-bipyridinium (*MQ*) ligands 0.262 (8) Å out of the plane defined by the rest of the coordinated N atoms and the Pt atom. The exceptional behavior of this *MQ* ligand is interpreted in terms of the electrostatic interactions between the positively charged *MQ* ligands and the perchlorate anions, where the  $\text{N}(\text{MQ}) \cdots \text{O}(\text{perchlorate})$  distances are in the range 2.932 (12)–3.259 (13) Å.

## Comment

We previously reported that amidate-bridge  $\text{Pt}^{\text{II}}$  dimers with a general formula of  $[\text{Pt}_2(\text{NH}_3)_4(\mu\text{-amidate})_2]^{2+}$  (amidate = acetamidate,  $\alpha$ -pyrrolidinonate,  $\alpha$ -pyridonate, *etc.*) serve as effective  $\text{H}_2$ -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  $\text{Pt}^{\text{II}}$  complexes have been prepared by us, and their catalytic activity has been evaluated, based on the amount of  $\text{H}_2$  evolved under visible-light illumination (unpublished results). Consequently, we recently found that mononuclear  $\text{Pt}^{\text{II}}$  complexes of *N*-methyl-4,4'-bipyridinium (*MQ*), such as the title compound, (I), exhibit relatively high catalytic activity compared to the common mononuclear platinum(II) complexes. We report here the crystal structure of one of such complexes prepared in our laboratory.

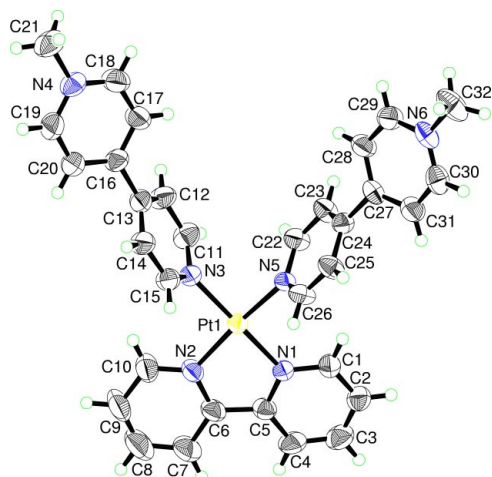


The asymmetric unit of (I) consists of a mononuclear  $\text{Pt}^{\text{II}}$  complex cation and four perchlorate anions. The stereochemistry of the Pt ion can be described as a distorted square-planar geometry, in which atom N5 is displaced by 0.262 (8) Å from the Pt coordination plane defined by the remainder of the coordinated N atoms and the Pt atom (the r.m.s. deviation of these four atoms is 0.0181 Å). This distortion is not only due to the relatively strong intermolecular  $\pi$ - $\pi$ -stacking interactions achieved between the bpy ligands (see Fig. 2), but also

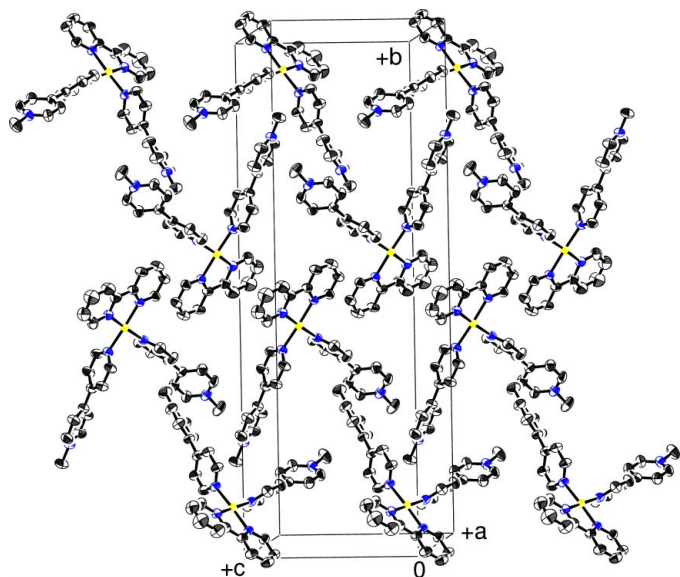
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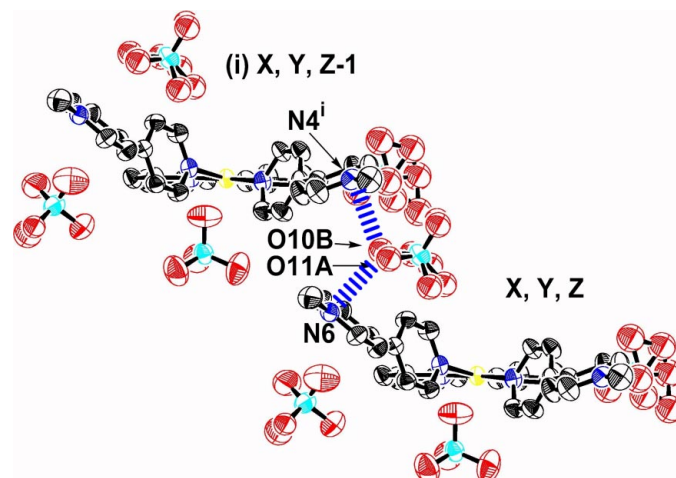


**Figure 1**  
The structure of the cation in (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**  
Crystal packing view of (I), showing the  $\pi$ - $\pi$  stacking interactions in the crystal structure. Perchlorate anions and H atoms have been omitted for clarity.

due to the fact that the positively charged *MQ* ligands have strong electrostatic interactions with one of  $\text{ClO}_4^-$  ions (Fig. 3). The strong interactions between *MQ* and the  $\text{ClO}_4^-$  ion can be recognised from the following contacts:  $\text{O10B}-\text{N6} = 2.932$  (12) Å,  $\text{O11A}-\text{N6} = 2.996$  (12) Å,  $\text{O10B}-\text{N4}^i = 2.998$  (12) Å and  $\text{O11A}-\text{N4}^i = 3.259$  (13) Å [symmetry code: (i)  $x, y, z - 1$ ]. The two pyridyl units within bpy are twisted by  $7.7$  ( $5$ )° relative to each other. The bpy plane is tilted with respect to the  $\text{N1}-\text{N3}/\text{Pt1}$  plane by an angle of  $3.8$  ( $3$ )°, which is also relevant to the intermolecular associations achieved in the crystal. On the other hand, the coordinated pyridyl ligands within the *MQ* ligands are steeply inclined with respect to the  $\text{N1}-\text{N3}/\text{Pt1}$  plane [ $75.8$  ( $2$ )° for the ring involving N3 and  $75.6$  ( $2$ )° for that involving N5]. The dihedral angle between



**Figure 3**  
A view nearly parallel to the  $\text{N1}-\text{N3}/\text{Pt1}$  plane, showing the electrostatic interactions between the *MQ* ligands and the perchlorate ions. H atoms have been omitted for clarity.

the two aromatic rings within each *MQ* is  $47.5$  ( $2$ )° for the *MQ* involving N3 and N4, and is  $42.9$  ( $2$ )° for that involving N5 and N6.

The shortest  $\text{Pt}\cdots\text{Pt}$  distance is  $7.9822$  (6) Å, confirming the lack of any  $\text{Pt}\cdots\text{Pt}$  interaction in (I) (see also Table 1). As shown in Fig. 2, the cations are arranged in a stair-like fashion to give a sort of one-dimensional  $\pi$ -stacked array. An inversion center is located midway between pairs of stacked rings. The  $\text{N1}/\text{C1}-\text{C5}$  ring is  $\pi$ -stacked with a neighbouring ring through an inversion center, and the average plane-to-plane separation is estimated as  $3.469$  (6) Å. The  $\text{N2}/\text{C6}-\text{C10}$  ring is similarly stacked with a neighbouring ring through an inversion center, with an average plane-to-plane separation of  $3.574$  (17) Å.

## Experimental

*N*-Methyl-4,4'-bipyridinium perchlorate, used in the following synthesis, was prepared as follows: a solution of *N*-methyl-4,4'-bipyridinium iodide (3.4 mmol; Van Emon *et al.*, 1986) and  $\text{AgClO}_4$  (3.5 mmol) in water (10 ml) was heated in the dark at 333 K for 2 h, followed by hot filtration in order to remove the precipitated  $\text{AgCl}$ . Leaving the filtrate at 278 K overnight afforded the perchlorate salt of *MQ* as colorless needles, which were collected by filtration and air-dried (yield: 78%). The purity was satisfactorily confirmed by  $^1\text{H}$  NMR.

Compound (I) was prepared as follows: a solution of  $\text{PtCl}_2(\text{bpy})$  (0.10 mmol, 0.042 g; Morgan & Burstall, 1963) and  $\text{AgClO}_4$  (0.20 mmol, 0.042 g) in water (20 ml) was refluxed in the dark for 2 h. To the solution was added *N*-methyl-4,4'-bipyridinium perchlorate (0.20 mmol, 0.054 g) and the mixture was further refluxed for 4 h. After the precipitated  $\text{AgCl}$  was removed by filtration, the filtrate was evaporated to a total volume of about 5 ml until a small amount of yellow precipitate started to deposit. To the solution were then added 2–3 drops of a saturated aqueous sodium perchlorate solution. Leaving the solution overnight afforded (I) as a yellow precipitate. The product was recrystallized from hot water to give the final product as yellow plates (yield: 67%).  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 296 K):  $\delta$  4.30 (s, 6H), 7.47 (m, 2H), 7.60 (m, 2H), 8.07 (d, 4H,  $J = 6.80$  Hz), 8.26 (d,

4H,  $J = 6.80$  Hz), 8.81 ( $d$ , 4H,  $J = 6.80$  Hz), 9.22 p.p.m. ( $d$ , 4H,  $J = 6.98$  Hz).

Crystal data

[Pt(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)(C<sub>11</sub>H<sub>11</sub>N<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>  
 $M_r = 1091.51$   
 Monoclinic,  $P2_1/n$   
 $a = 10.0690$  (9) Å  
 $b = 35.111$  (3) Å  
 $c = 11.7298$  (10) Å  
 $\beta = 101.835$  (2)°  
 $V = 4058.8$  (6) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.786$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 6625 reflections  
 $\theta = 2.4$ – $28.2$ °  
 $\mu = 3.80$  mm<sup>-1</sup>  
 $T = 296$  (2) K  
 Plate, pale yellow  
 0.18 × 0.05 × 0.03 mm

Data collection

Bruker SMART APEX CCD-detector diffractometer  
 $\omega$  scans  
 Absorption correction: Gaussian (XPREP in SAINT; Bruker, 2001)  
 $T_{\min} = 0.251$ ,  $T_{\max} = 0.531$   
 25 018 measured reflections  
 9347 independent reflections  
 7198 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.080$   
 $\theta_{\text{max}} = 28.3$ °  
 $h = -10 \rightarrow 13$   
 $k = -45 \rightarrow 41$   
 $l = -15 \rightarrow 14$

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.126$   
 $S = 1.01$   
 9347 reflections  
 511 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0668P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 2.53$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.09$  e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

Pt1–N1	1.997 (4)	Pt1–Pt1 <sup>i</sup>	7.9822 (6)
Pt1–N2	2.009 (4)	Pt1–Pt1 <sup>ii</sup>	8.3972 (6)
Pt1–N3	2.015 (4)	Pt1–Pt1 <sup>iii</sup>	8.5707 (6)
Pt1–N5	2.028 (4)		
N1–Pt1–N2	80.93 (18)	N1–Pt1–N5	96.22 (17)
N1–Pt1–N3	177.29 (19)	N2–Pt1–N5	173.5 (2)
N2–Pt1–N3	98.04 (19)	N3–Pt1–N5	85.05 (17)

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

For two of the four ClO<sub>4</sub><sup>-</sup> ions, O atoms (O9–O16) were treated as disordered over two sites. For each disordered anion, isotropic displacement parameters of O atoms were defined with a common value. In each case, the occupation factors of the two sites were refined, showing that they were equal. As a result, their occupation factors were all fixed at 50%. In the refinement of these disordered groups, the Cl–O distances were restrained to 1.43 (3) Å and the six

O···O distances within each perchlorate ion were restrained as equal. One of the remaining ClO<sub>4</sub><sup>-</sup> ions was also judged to be partially disordered, in which only one of the four O atoms was assumed to be disordered over two sites (O8A and O8B) with 50% population each. Since a void problem was suggested by PLATON (Spek, 2003), an O atom was located and refined isotropically, assuming the presence of a water molecule. However, the occupation factor of the atom converged at 18 (1)%. Moreover, the difference Fourier map, without inclusion of this atom in the model, did not show sufficient electron density in the void so we decided not to locate any atom within the void, which has an estimated volume of 41 Å<sup>3</sup>. All H atoms were located at their idealized positions (methyl C–H = 0.96 Å and aromatic C–H = 0.93 Å), 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. In the final difference Fourier synthesis, six residual peaks in the range 1.17–2.53 e Å<sup>-3</sup> were observed within 1.08 Å from Pt1. The deepest hole was located 0.18 Å from atom O16B.

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 ORTEPII (Johnson, 1976).

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