A head-to-head isomer of bis(μ-N-methyl-isonicotinamidato)bis[cis-diammineplatinum(II)] tetraperchlorate

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In the title compound, $[Pt_2(C_7H_8N_2O)_2(NH_3)_4](ClO_4)_4$, the head-to-head isomer of the Pt^{II} dimer has a mirror plane through the Pt—Pt bond axis. The intradimer Pt—Pt distance is 3.0569 (8) Å, while the shortest interdimer Pt···Pt distance is 7.2325 (9) Å. Two adjacent dimers are associated with one another, with a π-stacking interaction between the N-methyl-pyridinium moieties, where the plane-to-plane separation is 3.27 (1) Å.

Comment

A photochemical system made up of $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) and methylviologen (usually, N,N'-dimethyl-4,4'-bipyridinium dichloride) has been thought of as one of the promising candidates to achieve artificial photosynthetic devices (Borgarello *et al.*, 1981). In this context, we previously reported that some amidate-bridged platinum dimers, $[Pt_2(NH_3)_4(\mu\text{-amidato})_2]^{2+}$ (amidate = acetamidate, α-pyrrolidinonate, α-pyridonate, *etc.*), serve as effective H_2-producing catalysts in the photosystem mentioned above (Sakai & Matsumoto, 1990; Sakai *et al.*, 1993). Since then, various efforts have been made to develop a single molecular device in which visible-light-induced reduction of water to molecular hydrogen is carried out in a sophisticated manner. In order to confirm the validity of our approach, various amidate-bridged platinum dimers tethered to methylviologen and derivatives have also been prepared. Here we report the crystal structure of the title compound, (I), which is one of such platinum dimers prepared in our laboratory. The H_2-producing activity of (I) has been confirmed to be comparable to those examined in our original report in 1990.


(I)
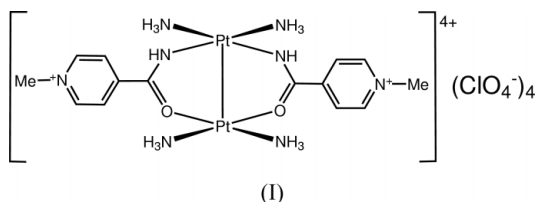
The asymmetric unit of (I) consists of one half of a dinuclear Pt^{II} cation and two perchlorate anions. Since two Pt atoms are both located on a mirror plane, there is a crystallographic requirement that this is a head-to-head dimer in which two amidate N—C—O units are arranged in the same direction within the dimeric unit (Fig. 1 and Table 1). However, one might contend that this could be a mixture of both the head-to-head and the head-to-tail isomers. Nevertheless, it is often possible to determine the correct direction of N—C—O in least-sqares refinement, as carried out in the present study
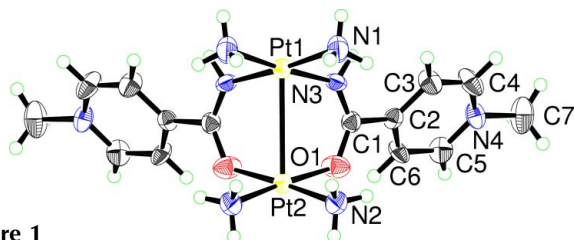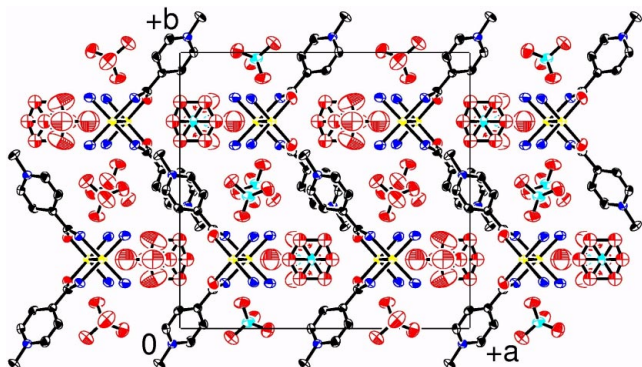
Figure 1
The structure of the dinuclear Pt_2^{II} cation in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Figure 2
Crystal packing view along the *c* axis of (I). H atoms have been omitted for clarity.

(see Experimental). Moreover, we also have a good argument against such a contention, as discussed below. As previously described (Sakai, Tanaka *et al.*, 1998; Matsumoto & Sakai, 1999), the intradimer $Pt^{II}-Pt^{II}$ distance in this class of head-to-head dimers is generally 0.02–0.05 Å shorter than that for the head-to-tail dimer having the same bridging amidate ligands. Importantly, the donor–acceptor properties of Pt^{II} centres are greatly affected by the electronegativities of coordinated atoms. In other words, the Pt atoms possess different donor–acceptor properties owing to the effective difference between the electronegativities of O and N. The head-to-head isomer has a shorter intradimer $Pt^{II}-Pt^{II}$ distance because it is an interaction between a good donor (N_4-coordinated Pt) and a good acceptor (N_2O_2-coordinated Pt). On the other hand, the head-to-tail isomer has a longer Pt—Pt distance because it is an interaction between the two N_3O-coordinated Pt atoms having an intermediate donor–acceptor property. Such Pt···Pt interactions are considered to be reinforced by a sort of dative bond formed between a filled Pt 5 d_{z^2} orbital and a vacant $6p_z$ orbital (Nova *et al.*, 1995; Connick *et al.*, 1997) (we call such bonds 'mutual dative bonds'). These indicate that, if the two isomers coexist, the displacement ellipsoid of each Pt atom must show considerable distortion or elongation along the intradimer Pt—Pt axis. However, the displacement ellipsoids of the Pt centres are observed to be quite normal [U_{eq}(Pt1) = 0.0316 (2) Å^2 and U_{eq}(Pt2) = 0.0313 (2) Å^2], supporting the conclusion that (I) is a pure form of a head-to-head isomer.

The observed intradimer Pt—Pt distance [3.0569 (8) Å] shows that it is longer than those reported for the analogous Pt^{II} dimers bridged by other amidate ligands [2.8767 (7) Å for

the α-pyridonate analogue (Hollis & Lippard, 1983); 2.9023 (8) Å for the 5-carboxy-α-pyridonate analogue (Sakai & Takahashi, 2003); 3.029 (2) Å for the α-pyrrolidinonate analogue (Matsumoto *et al.*, 1989); 2.89–2.93 Å for the acetamidate analogue (unpublished results)]. These suggest that the $Pt^{II}-Pt^{II}$ bond in the title compound is weaker than those in the reported compounds. Our tentative interpretation is that the positively charged *N*-methylpyridinium moiety in (I) plays a role as an electron-withdrawing group to diminish the electron density at the Pt^{II} centres, leading to the weakening of 'mutual dative bonds' within the diplatinum cation.

The dihedral angle between the two Pt coordination planes within the dimeric unit (τ) and the average torsional twist of them about the Pt—Pt axis (ω) are estimated as τ = 37.7 (2)° and ω = 0°. As observed thus far for related compounds, the two Pt atoms, Pt1 and Pt2, are displaced from their coordination planes by 0.067 (5) and 0.049 (5) Å in such a manner that they have an attractive interaction with one another. The pyridinium plane (N4/C2–C6) is inclined by 33.3 (9)° with respect to the carbamoyl unit (O1/C1/N3).

Fig. 2 shows a crystal packing view of (I). The shortest interdimer Pt···Pt distance is 7.2325 (9) Å (see Table 1), confirming the lack of any intermolecular Pt—Pt interaction in the crystal. As shown in Fig. 2, the dimers form a zigzag chain along the *b* axis, with π-stacking interactions achieved between the pyridinium units. Each stack is formed through an inversion centre, and the plane-to-plane separation is 3.27 (1) Å. The crystal packing is also stabilized by hydrogen bonds formed between the ammines and the O atoms of perchlorate ions (see Table 2).

Experimental

N-Methyl-4-carbamoylpyridinium perchlorate was prepared as follows [this is quite similar to the synthesis of *N*-(carbamoyl-methyl)pyridinium perchlorate (Sakai *et al.*, 1997)]: a solution of isonicotinamide (10 mmol) and methyl bromide (10.7 mmol) in CH_3CN (20 ml) was stirred at room temperature for 48 h. The deposited colourless precipitate was collected by filtration and air-dried. A solution of the bromide salt of *N*-methyl-4-carbamoyl-pyridinium (10 mmol) and an equivalent of $AgClO_4$ (10 mmol) in water (30 ml) was heated in the dark at 333 K for 1 h. After the AgBr precipitate was removed by filtration, the filtrate was evaporated to a total volume of *ca* 1 ml (Caution: Perchlorate salts are potentially explosive and must be handled with care. Be careful not to evaporate to dryness). A large excess of ethanol was added to the filtrate to reprecipitate the product. The product was recrystallized from methanol to give the final product as colourless needles (yield: 91%). Analysis calculated for $C_7H_9ClN_2O_5$: C 35.53, H 3.83, N 11.84%; found: C 35.47, H 3.68, N 11.52%. ^{1}H NMR (D_2O, 296 K): δ 4.47 (*s*, 3H); 8.36 (*d*, 2H, *J* = 6.1 Hz); 8.98 p.p.m. (*d*, 2H, *J* = 6.6 Hz).

Compound (I) was prepared as follows: to an aqueous solution of *cis*-[Pt(NH$_3$)$_2$(OH$_2$)$_2$](ClO$_4$)$_2$ (0.2 mmol Pt/2 ml H$_2$O), prepared as previously described (Sakai, Takeshita *et al.*, 1998), was added *N*-methyl-4-carbamoylpyridinium perchlorate (0.32 mmol). The solution was heated at 333 K for 5 h. To the solution was added a solution of NaClO$_4$ (6 mmol) in water (*ca*. 0.30 ml) while it was hot, followed by filtration if necessary. Allowing the filtrate to stand at room temperature for a few days afforded (I) as pale yellow–green

plates (yield 8%). Analysis calculated for $C_{14}H_{28}Cl_4N_8O_{18}Pt_2$: C 14.90, H 2.50, N 9.93%; found: C 14.75, H 2.63, N 9.68%. ^{1}H NMR (D_2O, 296 K): δ 4.33–4.41 (m, 3H); 8.18–8.41 (m, 2H); 8.72–8.88 p.p.m. (m, 2H).

Crystal data

$[Pt_2(C_7H_8N_2O)_2(NH_3)_4](ClO_4)_4$	Mo $K\alpha$ radiation
$M_r = 1128.42$	Cell parameters from 2336
Orthorhombic, $Pnma$	reflections
$a = 17.9590\,(7)$ Å	$\theta = 2.3$–$22.0°$
$b = 17.0728\,(7)$ Å	$\mu = 9.44$ mm^{-1}
$c = 10.1189\,(4)$ Å	$T = 296\,(2)$ K
$V = 3102.6\,(2)$ Å^3	Plate, pale yellow–green
$Z = 4$	$0.06 \times 0.05 \times 0.03$ mm
$D_x = 2.416$ Mg m^{-3}	

Data collection

Bruker SMART APEX CCD-detector diffractometer	2317 independent reflections
ω scans	1576 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.117$
(*SADABS*; Sheldrick, 1996)	$\theta_{max} = 23.3°$
$T_{min} = 0.540$, $T_{max} = 0.753$	$h = -19 \rightarrow 19$
16797 measured reflections	$k = -18 \rightarrow 18$
	$l = -11 \rightarrow 8$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.035$	$w = 1/[\sigma^2(F_o^2) + (0.0194P)^2]$
$wR(F^2) = 0.062$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.88$	$(\Delta/\sigma)_{max} = 0.001$
2317 reflections	$\Delta\rho_{max} = 1.43$ e Å^{-3}
221 parameters	$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—N3	2.007 (7)	Pt2—N2	2.025 (6)
Pt1—N1	2.049 (7)	Pt2—O1	2.038 (6)
Pt1—Pt2	3.0569 (8)	Pt1$\cdots$Pt2^i	7.2325 (9)
N3—Pt1—N3^{ii}	93.0 (4)	N2^{ii}—Pt2—N2	87.6 (4)
N3—Pt1—N1^{ii}	176.2 (3)	N2^{ii}—Pt2—O1	177.0 (3)
N3—Pt1—N1	87.4 (3)	N2—Pt2—O1	91.1 (3)
N1^{ii}—Pt1—N1	91.9 (4)	O1—Pt2—O1^{ii}	90.1 (4)
N3—Pt1—Pt2	76.1 (2)	N2—Pt2—Pt1	101.8 (2)
N1—Pt1—Pt2	107.7 (2)	O1—Pt2—Pt1	81.15 (18)
N1—Pt1—Pt2—N2	4.0 (3)	N3—Pt1—Pt2—O1	−2.6 (3)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H4$\cdots$O4	0.89	2.65	3.136 (11)	116
N1—H4$\cdots$O8	0.89	2.43	3.213 (13)	146
N1—H3$\cdots$O10A	0.89	2.41	3.180 (12)	146
N3—H1$\cdots$O4	0.86	2.38	3.118 (11)	143
N2—H5$\cdots$O3^{iii}	0.89	2.52	3.058 (11)	119
N2—H6$\cdots$O2^{iv}	0.89	2.58	2.988 (10)	109
N2—H5$\cdots$O5^{iii}	0.89	2.29	3.174 (10)	171
N2—H7$\cdots$O11B^{ii}	0.89	2.17	2.96 (4)	148

Symmetry codes: (ii) $x, \frac{1}{2} - y, z$; (iii) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (iv) $x, y, 1 + z$.

The binding direction of O and NH for the bridging amidate could be easily determined by comparing the results of least-squares calculations performed for two possible arrangements as follows. A wrong combination gave an asymmetric feature with regard to the equivalent displacement parameters of the supposed O and N atoms;

$U_{eq}(O) = 0.060\,(2)$ Å^2 and $U_{eq}(N) = 0.022\,(2)$ Å^2 {the reliability factors were also high: $R[F^2 > 2\sigma(F^2)] = 0.036$ and $wR(F^2) = 0.065$}. On the other hand, the reported combination, judged to be correct, gave a moderate balance in these values: $U_{eq}(O) = 0.047\,(2)$ Å^2 and $U_{eq}(N) = 0.032\,(2)$ Å^2. There are three independent ClO_4^- ions in the asymmetric unit; two are located on a mirror plane and one is located at a general position. One of the ClO_4^- ions located on a mirror shows an orientational disorder around the Cl3 atom. In this disorder model, it was assumed that the Cl3 and O9 atoms on the mirror plane are not disordered. The remaining three O atoms were considered to be disordered over two sites (O10A and O11A) and (O10B and O11B), where both O11A and O11B are also located on the same mirror plane. These four disordered O atoms were supposed to have the same isotropic displacement parameter. No other restraint was applied to this model. The occupation factors of site A and B converged at 0.740 (9) and 0.260 (9), respectively. All H atoms were placed at their idealized positions (methyl C—H = 0.96 Å, aromatic C—H = 0.93 Å and ammine N—H = 0.89 Å) and included in the refinement in the riding-motion approximation, with U_{iso} values equal to 1.2–1.5 times the U_{eq} of the carrier atom. The highest peak was located 2.21 Å from O7, while the deepest hole was located 0.56 Å from O7.

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, *TEXSAN* (Molecular Structure Corporation, 2001), *KENX* and *ORTEP*II (Johnson, 1976).

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