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

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In the title compound, [Pt₂(C₇H₈N₂O)₂(NH₃)₄](ClO₄)₄, the head-to-head isomer of the Pt⁴⁺ 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-methylpyridinium moieties, where the plane-to-plane separation is 3.27 (1) Å.

Comment

A photochemical system made up of Ru(bpy)₃²⁺ (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, [Pt₂(NH₃)₄(μ-amidato)₂]²⁺ (amidate = acetamidate, α-pyrrolidonate, α-pyridonate, etc.), serve as effective H₂-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 H₂-producing activity of (I) has been confirmed to be comparable to those examined in our original report in 1990.

The asymmetric unit of (I) consists of one half of a dinuclear Pt⁴⁺ 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-squares refinement, as carried out in the present study.
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Figure 1
The structure of the dinuclear PtII cation in (I), showing the atomlabelling 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 et al., 1998; Matsumoto & Sakai, 1999), the intradimer PtII–PtII 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. Such Pt–Pt interactions are considered to be reinforced by a sort of dative bond formed between a filled Pt 5dz² orbital and a vacant 6pz 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 [Ueq(Pt1) = 0.0316 (2) Å² and Ueq(Pt2) = 0.0313 (2) Å²], 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 PtII 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-pyrrrolidinonate analogue (Matsumoto et al., 1989); 2.89–2.93 Å for the acetamide analogue (unpublished results)]. These suggest that the PtII–PtII bond in the title compound is weaker than those in the reported compounds. Our tentative interpretation is that the positively charged N-methylpyrrolidinium moiety in (I) plays a role as an electron-attracting group to diminish the electron density at the PtII 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-carbamoylpyrrolidinium perchlorate was prepared as follows [this is quite similar to the synthesis of N-(carbamoylmethyl)pyrrolidinium perchlorate (Sakai et al., 1997)]: a solution of isonicotinamide (10 mmol) and methyl bromide (10.7 mmol) in CH3CN (20 ml) was stirred at room temperature for 48 h. The deposited colourless precipitate was collected by filtration and dried. A solution of the bromide salt of N-methyl-4-carbamoylpyrroldinium (10 mmol) and an equivalent of AgClO4 (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 C7H9ClN2O5: C 35.53, H 3.83, N 11.84%; found: C 35.53, H 3.83, N 11.84%; 1H NMR (D2O, 296 K): δ 3.54 (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(NH3)2(OH)2][ClO4]2 (0.2 mmol Pt/2 ml H2O), prepared as previously described (Sakai, Takeshita et al., 1998), was added N-methyl-4-carbamoylpyrrolidinium perchlorate (0.32 mmol). The solution was heated at 333 K for 5 h. To the solution was added a solution of NaClO4 (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_{4}N_{8}O_{18}Pt_{2}: C 14.90, H 2.50, N 9.93%; found: C 14.75, H 2.63, N 9.68%. H NMR (D_{2}O, 296 K): 8.43–4.41 (m, 4H); 8.18–8.41 (m, 2H); 8.72–8.88 p.p.m. (m, 2H).

**Crystal data**

\[ \text{[Pt}_{2}(C_{7}H_{8}N_{2}O)_{2}](\text{NH}_{3})_{4}][\text{ClO}_{4}]_{4} \]

*M* = 1128.42

Orthorhombic, *Pmnna*

\( a = 17.9590 \) (7) \( \AA \)

\( b = 17.0728 \) (7) \( \AA \)

\( c = 10.1189 \) (4) \( \AA \)

\( V = 3102.6 \) (2) \( \AA^{3} \)

\( Z = 4 \)

\( D_{x} = 2.416 \text{ Mg m}^{-3} \)

**Data collection**

Bruker SMART APEX CCD-detector diffractometer

\( \omega \) scan

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

\( T_{\text{min}} = 0.540, T_{\text{max}} = 0.753 \)

16797 measured reflections

221 parameters

**Refinement**

Refinement on \( F^{2} \)

\( R(F^{2}) = 0.062 \)

\( wR(F^{2}) = 0.035 \)

\( S = 0.88 \)

2317 reflections

221 parameters

**Table 1**

Selected geometric parameters (\( \AA, ^{\circ} \)).

| Pt1...N3 | 2.007 (7) | 2.025 (6) |
| Pt1...N1 | 2.049 (7) | 2.038 (6) |
| Pt1...P1 | 3.0569 (8) | 7.2325 (9) |
| N3...Pt1...N1 | 93.0 (4) | 87.6 (4) |
| N3...Pt1...N1 | 176.2 (3) | 177.0 (3) |
| N3...Pt1...N1 | 87.4 (3) | 91.3 (3) |
| N3...Pt1...N1 | 91.9 (4) | 90.1 (4) |
| N3...Pt1...P1 | 76.1 (2) | 101.8 (2) |
| N1...Pt1...P1 | 107.7 (2) | 81.15 (18) |

**Table 2**

Hydrogen-bonding geometry (\( \AA, ^{\circ} \)).

\begin{align*}
N1 - H4 & - O4 & 0.89 & 2.65 & 3.136 (11) & 116 \\
N1 - H4 & - O6 & 0.89 & 2.43 & 3.213 (13) & 146 \\
N1 - H3 & - O10A & 0.89 & 2.41 & 3.108 (12) & 146 \\
N3 - H1 & - O4 & 0.86 & 2.38 & 3.118 (11) & 143 \\
N2 - H5 & - O3III & 0.89 & 2.52 & 3.058 (11) & 119 \\
N2 - H6 & - O2III & 0.89 & 2.58 & 2.988 (10) & 109 \\
N2 - H5 & - O5III & 0.89 & 2.29 & 3.174 (10) & 171 \\
N2 - H7 & - O11B & 0.89 & 2.17 & 2.96 (4) & 148 \\
\end{align*}

**References**


Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*, University of Göttingen, Germany.

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