Bis[μ-3-(N-methyl-4,4'-bipyridinium-1-yl)propionamidato]bis[cis-diammineplatinum(II)] hexaperchlorate dihydrate: a head-to-tail isomer

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Bis[µ-3-(N'-methyl-4,4'-bipyridinium-1-yl)propionamidato]bis[cis-diammineplatinum(II)] hexaperchlorate dihydrate: a head-to-tail isomer

In the title compound, [Pt₂(µ-μ-C₄H₆N₃O)₂(NH₃)₄][ClO₄]₂·2H₂O, the diplatinum(II) cation is found to be a head-to-tail isomer. The intradimer Pt–Pt distance [3.0304 (7) Å] is much shorter than the value of 3.0852 (13) Å reported for the analogous cis-diammineplatinum(II) dimer bridged by 2-(N'-methyl-4,4'-bipyridinium-1-yl)acetamidates [Sakai, Ikuta, Tsubomura, Kato, Yokoyama, Kajiwara & Ito (2003). Acta Cryst. E59, m780–m783], showing that the electron density at the metal centers is higher in the title system than in the previously reported system. The shortest interdimer Pt···Pt distance is 8.4585 (8) Å.

Comment

We previously reported that amide-bridged cis-diammineplatinum(II) dimers, viz. [Pt₂(NH₃)₄(µ-amidato)₂]²⁺ (amide is acetamidate, α-pyrolidininolate, α-pyridonate etc.), are generally active as H₂-evolving catalysts in a well known photosystem consisting of edta (usually, ethylenediaminetetraacetic acid disodium salt), Ru(bpy)₃²⁺ (bpy is 2,2'-bipyridine), and methylviologen (usually, N,N'-dimethyl-4,4'-bipyridinium dichloride) (Sakai & Matsumoto, 1990; Sakai et al., 1993). It should be noted here that two geometrical isomers, head-to-head (HH) and head-to-tail (HT), are possible for this class of doubly-bridged dimers, because of the asymmetric feature of amide N—C—O units. In addition, edta, Ru(bpy)₃²⁺ and methylviologen, respectively, serve as a sacrificial electron donor, a photosensitizer and an electron relay. One of our interests over many years has concentrated on the development of molecular devices which replace three major components, that is, Ru(bpy)₃²⁺, methylviologen and the PtII dimer. Such devices are considered as one-component systems. Considerable attention has also been paid to the studies on two-component systems in which the photo-chemical reduction of water into H₂ by edta is driven by Ru(bpy)₃²⁺ and a hybrid compound made up of both the methylviologen and the H₂-evolving PtII units. In this context, the title compound, HT-[Pt₂(NH₃)₄(µ-L₁)₂][ClO₄]₂·2H₂O [[I]: L₁ is 3-(N'-methyl-4,4'-bipyridinium-1-yl)propionamidate], together with an analogus dimer, HT-[Pt₂(NH₃)₄(µ-L₂)₂][ClO₄]₂·2H₂O [[II]: Sakai, Ikuta et al., 2003; L₂ is 2-(N'-methyl-4,4'-bipyridinium-1-yl)acetamidate], were first prepared in 1994 (Ikuta et al., 1994), and were found to be somewhat effective. It has been confirmed that the H₂-evolving activity of (I), evaluated under the three-component system, is slightly higher than that of the acetamidate-bridged analog (Sakai et al., 1993), and is ca 1.5 times higher than that of (II) (Sakai et al., 1995). Importantly, preliminary experiments have shown that the photolysis of a solution containing edta, Ru(bpy)₃²⁺, and either (I) or (II), in the absence of...
methylviologen, also results in evolution of H₂ in a relatively high quantum efficiency (Sakai et al., 1995). Nevertheless, it took a long time to refine the reliable synthetic methods yielding (I), (II) and the related complexes (Sakai, Shiomi et al., 2003; Sakai, Ikuta et al., 2003). We now report the synthesis and crystal structure of (I).

A dinuclear Pt²⁺ cation, six perchlorate anions and apparently 1.5 molecules of water are found in the asymmetric unit of (I). As previously reported for several analogous dimers doubly bridged by chain amidates, the binding directions of two bridging amidates could be rationally determined (see Experimental). As a result, the complex has been shown to be a head-to-tail isomer in the crystal structure, even though the complex is likely to give a mixture of both the HH and the HT isomer in solution, as previously observed for the related amidate-bridged Pt²⁺ dimers (see, for example, Sakai, Tanaka et al., 1998).

The intradimer Pt—Pt distance in (I) [3.0304 (7) Å] is much shorter than that reported for (II) [3.0852 (13) Å] (Sakai, Ikuta et al., 2003). The considerably long Pt²⁺—Pt²⁺ distance in (II) was previously interpreted in terms of the fact that the positively charged bipyridinium moieties in (II) serve as electron-withdrawing groups to diminish the electron density at the Pt²⁺ centers, leading to the weakening of the ‘mutual dative bonds’ within the diplatinum cation [two Pt²⁺ centers in close proximity are considered to form a dative Pt(5dz²) → Pt(6p or 6s) bond with one another; Connick et al., 1997]. The shorter Pt—Pt distance in (I) is consistent with the fact that the bipyridinium moieties in (I) serve as poorer electron-withdrawing groups, because the distance between the bipyridinium unit and the Pt²⁺ core in (I) is longer than that in (II). The N(bipyridinium)—C(briding amidate) distances in (I) [N2—C1 = 3.831 (18) Å and N5—C15 = 3.781 (17) Å] are ca 1.4 Å longer than those reported for (II) [2.41 (3) and 2.46 (3) Å; Sakai, Ikuta et al. 2003], where the N(bipyridinium) atom denotes the N atom of a viologen unit which is closer to the diplatinum entity.

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 = 37.8 (3)° and ω = 3.8 (9)° (see also Table 1), where ω = 0° denotes that the two Pt coordination planes stack in an eclipsed fashion. The corresponding values were reported as τ = 40.8 (5)° and ω = 5 (1)° for (II) (Sakai, Ikuta et al., 2003). Atoms Pt1 and Pt2
are shifted out of their coordination planes by 0.073 (5) and 0.065 (5) Å, respectively, in such a manner that they have an attractive interaction with one another.

The pyridinium plane directly attached to the propionamidine unit is inclined with respect to the bridging O—C—N unit by 89.8 (7°) for N2/C4—C8 and 6.8 (24°) for N5/C18—C22. The twist angles of the two pyridinium planes within the individual bipyridinium moieties are 32.0 (7°) for the bipyridinium involving N2 and N3, and 16.2 (6°) for that involving N5 and N6. As previously discussed for (II) (Sakai, Ikuta et al., 2003), these values are both effectively larger than that observed for the uncoordinated ligand N6. As previously discussed for (II) (Sakai, Ikuta et al., 2003), these values are both effectively larger than that observed for the uncoordinated ligand N6.

Crystal data

\[ \text{[Pt} (\text{C}_6 \text{H}_8 \text{N}_3 \text{O}_2)\{\text{NH}_3\}_2\text{]}\cdot \\text{(ClO}_4\text{)}_2 \cdot 2\text{H}_2\text{O} \]

\[ M_r = 1575.64 \]

Triclinic, Pt

\[ a = 10.0927 (5) \text{ Å} \]

\[ b = 11.0827 (5) \text{ Å} \]

\[ c = 24.4798 (10) \text{ Å} \]

\[ \alpha = 78.116 (2)^\circ \]

\[ \beta = 79.305 (2)^\circ \]

\[ \gamma = 74.210 (2)^\circ \]

\[ V = 2553.9 (2) \text{ Å}^3 \]

Data collection

Bruker SMART APEX CCD-detector diffractometer

\[ \omega \text{ scans} \]

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

\[ T_{	ext{min}} = 0.666, T_{	ext{max}} = 0.831 \]

24 579 measured reflections

Refinement

Refinement on \( F^2 \)

\[ R(F^2) = 0.121 \]

\[ S = 0.79 \]

11 715 independent reflections

633 parameters

Selected geometric parameters (Å, °).

Table 1

\begin{align*}
\text{Pt} &- \text{O} & 2.041 (11) & \text{Pt} &- \text{N} & 1.985 (9) \\
\text{Pt} &- \text{N} & 2.007 (11) & \text{Pt} &- \text{N} & 2.009 (10) \\
\text{Pt} &- \text{N} & 2.038 (10) & \text{Pt} &- \text{N} & 2.057 (8) \\
\text{Pt} &- \text{N} & 2.021 (9) & \text{Pt} &- \text{N} & 3.034 (7) \\
\text{Pt} &- \text{O} & 1.997 (9) & \text{Pt} &- \text{N} & 8.458 (8) \\
\text{N} &- \text{Pt} &- \text{N} & 88.3 (4) & \text{N} &- \text{Pt} &- \text{O} & 92.1 (4) \\
\text{N} &- \text{Pt} &- \text{N} & 90.2 (4) & \text{N} &- \text{Pt} &- \text{N} & 87.4 (7) \\
\text{N} &- \text{Pt} &- \text{O} & 92.5 (4) & \text{O} &- \text{Pt} &- \text{N} & 87.5 (4) \\
\text{N} &- \text{Pt} &- \text{O} & 88.8 (4) & \text{N} &- \text{Pt} &- \text{N} & 92.6 (4) \\
\text{N} &- \text{Pt} &- \text{N} & 177.4 (4) & \text{O} &- \text{Pt} &- \text{N} & 175.9 (4) \\
\text{N} &- \text{Pt} &- \text{O} & 173.9 (3) & \text{N} &- \text{Pt} &- \text{N} & 176.7 (4) \\
\text{O} &- \text{Pt} &- \text{N} &- \text{O} & 3.8 (4) & \text{N} &- \text{Pt} &- \text{N} & 5.0 (4) \\
\text{N} &- \text{Pt} &- \text{N} &- \text{O} & 3.0 (4) & \text{Pt} &- \text{N} &- \text{N} & 3.3 (4) \\
\end{align*}

Symmetry code: (i) \( x, y-1, z \).
Table 2
Contact distances (Å).

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<tr>
<td>O8â–O28</td>
<td>3.17 (3)</td>
<td>O27â–O5a</td>
<td>3.10 (6)</td>
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<tr>
<td>O22A–O27</td>
<td>2.74 (4)</td>
<td>O28â–O7Bc</td>
<td>3.07 (3)</td>
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<td>O22B–O27</td>
<td>3.17 (5)</td>
<td>O28â–O7Aa</td>
<td>3.19 (5)</td>
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</table>

Symmetry codes: (i) 1 – x, – y, 1 – z; (ii) 1 – x, 1 – y, – z.

Table 3
Hydrogen-bonding geometry (Å, °).

<table>
<thead>
<tr>
<th>D–H–A</th>
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<th>H–A</th>
<th>D–A</th>
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<tr>
<td>N7–H7C â– O13Bw</td>
<td>0.89</td>
<td>2.64</td>
<td>2.94 (3)</td>
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<tr>
<td>N8–H8C â– O26b</td>
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<td>2.28</td>
<td>3.159 (15)</td>
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<td>N8–H8A â– O21Aa</td>
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<td>2.06</td>
<td>2.92 (2)</td>
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<tr>
<td>N8–H8B â– O13Aa</td>
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<td>2.48</td>
<td>3.003 (18)</td>
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<tr>
<td>N8–H8B â– O16Bc</td>
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<td>2.20</td>
<td>3.01 (2)</td>
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<td>2.34</td>
<td>3.155 (15)</td>
<td>152</td>
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<tr>
<td>N9–H9A â– O22Aa</td>
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<td>2.29</td>
<td>3.155 (18)</td>
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<tr>
<td>N9–H9C â– O13Bf</td>
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<td>2.42</td>
<td>3.22 (3)</td>
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<td>N9–H9C â– O14Aa</td>
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<td>3.148 (18)</td>
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<tr>
<td>N10–H10A â– O18Bf</td>
<td>0.89</td>
<td>2.49</td>
<td>3.00 (3)</td>
<td>117</td>
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<td>N10–H10A â– O20Aa</td>
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<td>2.31</td>
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<td>N4–H4A â– O9A</td>
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<td>3.09 (2)</td>
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<tr>
<td>N7–H7C â– O25b</td>
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<td>2.59</td>
<td>3.151 (14)</td>
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<tr>
<td>N7–H7C â– O26b</td>
<td>0.89</td>
<td>2.15</td>
<td>3.042 (14)</td>
<td>177</td>
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</table>

Symmetry codes: (ii) 1 – x, – y, 1 – z; (iv) x – 1, y, 1 – z; (v) 1 – x, 1 – y, 1 – z.

As recently reported for several different dimers doubly bridged by chain amidate ligands (Sakai, Kurashima et al., 2003; Sakai, Ikuta et al., 2003; Sakai, Shiomori et al., 2003), the binding directions of O and N for the amidate ligands were rationally determined by the results of least-squares calculations performed for two possible arrangements for each ligand as follows. A wrong combination gave an asymmetric feature with regard to the equivalent displacement parameters of the assumed O and N atoms, while an appropriate combination gave an idealized feature with regard to the equivalent displacement parameters of the assumed O and N atoms, while an appropriate combination gave an idealized feature with regard to the equivalent displacement parameters of the assumed O and N atoms, while an appropriate

### References


Molecular Structure Corporation (2001). TExSAN. Version 1.1r1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.


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