Bis(2-aminopyridine)(2,2'-bipyridine)platinum(II) bis(oxalato)platinate(II) dihydrate

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Bis(2-aminopyridine)(2,2′-bipyridine)-platinum(II) bis(oxalato)platinate(II) dihydrate

Cations and anions in \([\text{Pt(C}_{10}\text{H}_{8}\text{N}_{2})(\text{C}_{5}\text{H}_{6}\text{N}_{2})_{2}]\text{[Pt(C}_{2}\text{O}_{4})_{2}] \cdot \text{2H}_{2}\text{O}\) stack alternately along the \(a\) axis, giving a one-dimensional chain of the Magnus’s green salt type. Intrachain \(\pi-\pi\)-stacking interactions are achieved between the oxalate and the 2,2′-bipyridine moieties, where the plane-to-plane separations are 3.41 (7) and 3.46 (1) \(\text{Å}\). Two different Pt···Pt distances [3.9294 (6) and 5.0302 (7) \(\text{Å}\)] alternate along the chain.

Comment

Three or four decades ago, Magnus’s green salt (MGS), \([\text{Pt(NH}_{3})_{4}]\text{[PtCl}_{4}]\), was studied extensively owing to its unusual color and the attractive one-dimensional framework in the crystal structure (Atoji \textit{et al.}, 1957). However, it was suggested that further experiments were still required to understand the system fully (Miller, 1982). In this context, we recently started exploring new types of MGS-like systems (see, for example, Sakai \textit{et al.}, 2000). Unique MGS-type one-dimensional double salts involving dinuclear platinum compounds have also been prepared by the authors (Sakai \textit{et al.}, 2002). As part of this project, we report here the crystal structure of the title compound, together with a description of the unique diffusion method used to grow good-quality single crystals of the title double salt, \([\text{Pt(bpy)(ampy)}_{2}\text{[P-t(ox)}_{2}]\cdot \text{2H}_{2}\text{O}]\) (I) (bpy = 2,2′-bipyridine, ampy = 2-aminopyridine and ox = oxalate).

A cation, an anion, and two water molecules are found in the asymmetric unit of (I) (Fig. 1). Relatively strong interactions are found within this ion pair (hereafter, interactions within this pair will be regarded as intrapair interactions, while those of this pair with an adjacent pair will be called interpair interactions). As shown in Fig. 2, the pairs further stack along the \(a\) axis, giving a one-dimensional network. The intrapair Pt···Pt distance \([\text{Pt1} \cdot \cdot \cdot \text{Pt2} = 3.9294 (6) \text{Å}]\) is far shorter than the interpair one \([\text{Pt2} \cdot \cdot \cdot \text{Pt1}(x-1, y, z) = 5.0302 (7) \text{Å}]\). However, the plane-to-plane separation estimated for the intrapair interaction [3.46 (1) \(\text{Å}\)] is only slightly longer than that for the interpair interaction [3.41 (7) \(\text{Å}\)].
The Pt2 ion in [Pt(ox)₂]²⁻ adopts a nearly planar stereochemistry, with an r.m.s. deviation of the four coordinated O atoms of 0.002 Å. On the other hand, the mean-plane calculation performed for the four coordinated N atoms in [Pt(bpy)(ampy)₂]²⁺ reveals that the Pt1 coordination plane has relatively large distortion toward a tetrahedral geometry, the four-atom r.m.s. deviation being 0.060 Å. As shown above in Fig. 2, the normals to these planes are tilted relative to the a axis by ca 22° for the O1/O2/O5/O6 plane and ca 27° for the N1/N2/N3/N5 plane. The Pt1 and Pt2 atoms are displaced out of their individual coordination planes by 0.031 (4) and 0.012 (3) Å, respectively, in which they are shifted such that they have an attractive interaction with one another.

As shown in Fig. 3, the interchain interactions are stabilized by hydrogen bonds formed between the water molecules and the amino groups of ampy ligands (see Tables 1 and 2). In addition to these hydrophilic interactions, interchain interactions are also stabilized by the π–π-stacking associations formed between the ampy ligands. The plane-to-plane separation for the stacking through an inversion center at (1/2, 1/2, 1/2) is estimated as 3.57 (2) Å. On the other hand, the plane-to-plane separation of the ampy ligands through an inversion center at (1/2, 0, 1/2) is estimated as 4.04 (2) Å, indicating that no π–π-stacking association is achieved in this case.

Experimental

Single crystals of (I) were prepared using our unique diffusion method as follows: a solution of [Pt(bpy)(ampy)₂][NO₃]₂·2H₂O (0.01 mmol, 0.0068 g; Sakai et al., 2003) in water (4 ml) and a solution of K₂[Pt(ox)₂]·2H₂O (0.01 mmol, 0.0049 g; Werner & Grebe, 1899) in water (4 ml) were prepared separately. A petri dish having a diameter of ca 60 mm and a depth of ca 15 mm was separated into three zones using filter papers; the central zone (zone 2) must be sandwiched by the other two zones (zones 1 and 3). In other words, zone 1 and 2 (or zones 2 and 3) should be separated by 2–3 pieces of filter paper, while contact between zones 1 and 3 should be avoided. 5 ml of water was
then added to the petri dish to fill up all three zones. Finally, the two solutions mentioned above were added dropwise, at the same time, to zones 1 and 3. The solution was left to stand overnight, affording (I) as pale-yellow prisms (yield: 30%). Analysis calculated for C₃₂H₂₆N₈O₁₀Pt₂: C 30.45, H 2.56, N 8.88%; found: C 30.45, H 2.23, N 8.86%.

Crystal data

\[
\text{[Pt(C₃H₈N₄)]·[Pt(C₃H₈N₄)]·2H₂O} \quad Z = 2
\]

\[
D_r = 2.272 \text{Mg m}^{-3}
\]

Mo Kα radiation

Cell parameters from 3079 reflections

\[
a = 7.4507 (8) \text{ Å} \\
b = 12.3998 (13) \text{ Å} \\
c = 15.5348 (17) \text{ Å} \\
\alpha = 93.21 \text{°} \\
\beta = 98.602 (2) \text{°} \\
\gamma = 101.703 (2) \text{°} \\
V = 1384.0 (3) \text{ Å}^3
\]

Data collection

Brucker SMART APEX CCD-detector diffractometer

Absorption correction: Gaussian scans

\[
\theta_{	ext{max}} = 26.4^\circ \\
th = -9 \rightarrow 9 \\
k = -10 \rightarrow 15 \\
l = -19 \rightarrow 17
\]

5485 independent reflections

3605 reflections with |F| > 2σ(F)

wR = 0.039

\[
S = 0.85
\]

5485 reflections

379 parameters

Refinement

H-atom parameters constrained

w = 1/[σ²(F²) + (0.0191P)²]

where P = (F² + 2F')/3

\[
\Deltaρ_{	ext{max}} = 1.61 \text{ e Å}^{-3} \\
\Deltaρ_{	ext{min}} = -0.74 \text{ e Å}^{-3}
\]

Table 1

Selected geometric parameters (Å, °).

\[
\begin{array}{lll}
\text{Pt}1-\text{N}2 & 1.997 (9) & \text{Pt}2-\text{O}1 & 2.011 (6) \\
\text{Pt}1-\text{N}1 & 2.008 (7) & \text{Pt}1-\text{Pt}2 & 3.9294 (6) \\
\text{Pt}1-\text{N}3 & 2.041 (8) & \text{Pt}2-\text{Pt}1' & 5.0302 (7) \\
\text{Pt}1-\text{N}5 & 2.043 (7) & \text{O}4-\text{O}9 & 2.852 (11) \\
\text{Pt}2-\text{O}2 & 1.974 (6) & \text{O}4-\text{O}10'^{\text{ii}} & 3.151 (12) \\
\text{Pt}2-\text{O}6 & 1.977 (6) & \text{O}8-\text{O}10 & 2.738 (11) \\
\text{Pt}2-\text{O}5 & 1.992 (6) & \text{O}9-\text{O}10'^{\text{ii}} & 2.878 (12) \\
\text{N}2-\text{Pt}1-\text{N}1 & 80.4 (3) & \text{O}2-\text{Pt}2-\text{O}6 & 97.2 (3) \\
\text{N}2-\text{Pt}1-\text{N}3 & 173.7 (3) & \text{O}2-\text{Pt}2-\text{O}5 & 178.6 (3) \\
\text{N}1-\text{Pt}1-\text{N}3 & 96.1 (3) & \text{O}6-\text{Pt}2-\text{Pt}5 & 81.7 (3) \\
\text{N}2-\text{Pt}1-\text{N}5 & 96.7 (3) & \text{O}2-\text{Pt}2-\text{O}1 & 81.9 (3) \\
\text{N}1-\text{Pt}1-\text{N}5 & 176.6 (3) & \text{O}6-\text{Pt}2-\text{O}1 & 178.9 (3) \\
\text{N}3-\text{Pt}1-\text{N}5 & 86.9 (3) & \text{O}5-\text{Pt}2-\text{O}1 & 99.2 (3)
\end{array}
\]

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

Table 2

Hydrogen-bonding geometry (Å, °).

\[
\begin{array}{cccccc}
D-\text{H} & \cdots & A & D-\text{H} & \cdots & A & D-\text{H} & \cdots & A & D-\text{H} & \cdots & A \\
N6-\text{H}6b-\cdots & O9'^{\text{ii}} & 0.86 & 2.07 & 2.919 (10) & 168 \\
N6-\text{H}6a-\cdots & O7'^{\text{ii}} & 0.86 & 2.22 & 2.937 (11) & 140 \\
N4-\text{H}4b-\cdots & O3'^{\text{ii}} & 0.86 & 2.31 & 3.091 (11) & 151 \\
N4-\text{H}4a-\cdots & O1 & 0.86 & 2.36 & 2.993 (10) & 130
\end{array}
\]

Symmetry codes: (iv) x, y, -z; (v) 1+x, y, z; (vi) 1-x, 2-y, 1-z.

All H atoms except for those of water molecules were placed at their idealized positions (C-\text{H} = 0.93 Å and N-\text{H} = 0.86 Å), and included in the refinement in the riding-motion approximation, with U_{iso} = 1.2U_{eq} of the carrier atom. Water H atoms were not located. In the final difference Fourier synthesis, 11 residual peaks in the range 1.13-1.60 e Å⁻³ were observed within 1.1 Å of the Pt atoms. The deepest hole was located 0.56 Å from Pt2.

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).

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References


