

A head-to-head isomer of bis{bis( $\mu$ -5-carboxy- $\alpha$ -pyridonato)bis[*cis*-diammineplatinum(II)]} tetranitrate tetrahydrate

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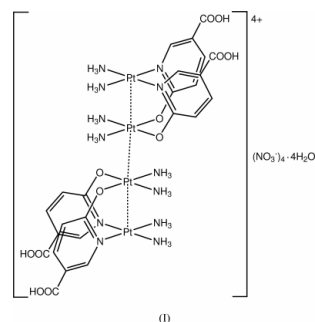
## Key indicators

Single-crystal X-ray study  
 $T = 296$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.022$  Å  
H-atom completeness 76%  
Disorder in solvent or counterion  
 $R$  factor = 0.063  
 $wR$  factor = 0.197  
Data-to-parameter ratio = 18.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound,  $[\text{Pt}_2(\text{C}_6\text{H}_4\text{NO}_3)_2(\text{NH}_3)_4]_2(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ , a head-to-head dimer has an association with another dimer unit through an inversion center to give a tetraplatinum chain structure. The interaction is stabilized not only by a metal–metal interaction but also by four hydrogen bonds formed between the amines and the O atoms of bridging amidates [ $\text{N} \cdots \text{O} = 2.988$  (17) and  $3.030$  (16) Å]. The intra- and interdimer Pt–Pt distances within the tetranuclear cation are  $2.9023$  (8) and  $3.1821$  (11) Å, respectively.

## Comment

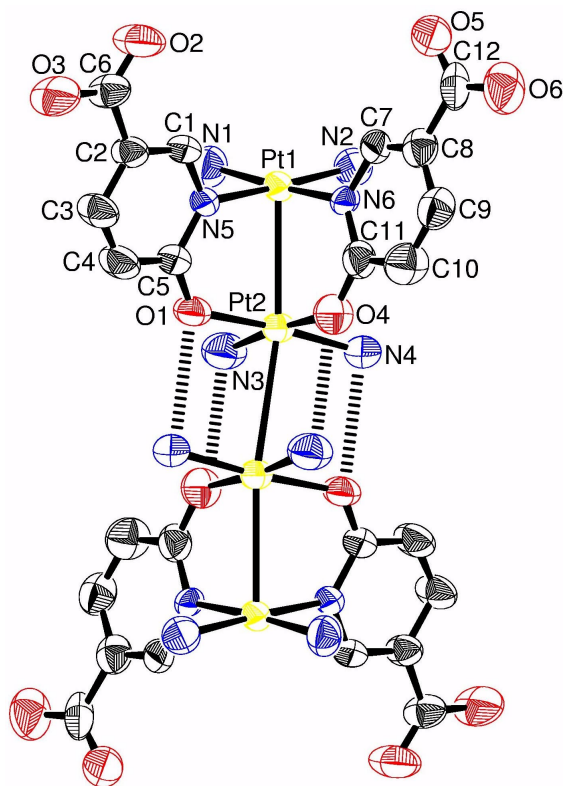
We previously reported that amidate-bridged dinuclear  $\text{Pt}^{\text{II}}$  complexes  $[\text{Pt}_2(\text{NH}_3)_4(\mu\text{-amidate})_2]^{2+}$  (amidate =  $\alpha$ -pyrrolidinonate,  $\alpha$ -pyridonate, acetamidate, *etc.*) behave as relatively efficient  $\text{H}_2$ -evolving catalysts in a well known photosystem consisting of edta,  $\text{Ru}(\text{bpy})_3^{2+}$  (bpy = 2,2'-bipyridine), and methylviologen (*N,N'*-dimethyl-4,4'-bipyridinium dichloride) (Sakai & Matsumoto, 1990; Sakai *et al.*, 1993). Since then, one of our interests has concentrated on the development of dinuclear  $\text{Pt}^{\text{II}}$  complexes tethered to tris(2,2'-bipyridine)-ruthenium(II) derivatives. Such hybrid materials may serve as efficient artificial photosynthetic devices which carry out visible-light-induced photocatalytic conversion of water into molecular hydrogen. The title compound, (I), can be regarded as an analog for the  $\alpha$ -pyridonate  $\text{Pt}_4^{\text{II}}$  complex previously reported by Hollis & Lippard (1983). (Note that it is now understood that the tetranuclear structures of this type are only stabilized in the solid state, and immediately cleave into dimers upon dissolution in aqueous media.) The carboxyl unit on the bridging ligand in (I) can be used to make a peptide bond with an amino group in an appropriate chemical component to be tethered to the diplatinum entity. We report here the crystal structure of the title compound, (I). The subsequent studies on its application will appear in future publications.



(I)

A dimer cation found in the asymmetric unit of (I) has an association to the neighboring dimer unit through an inversion

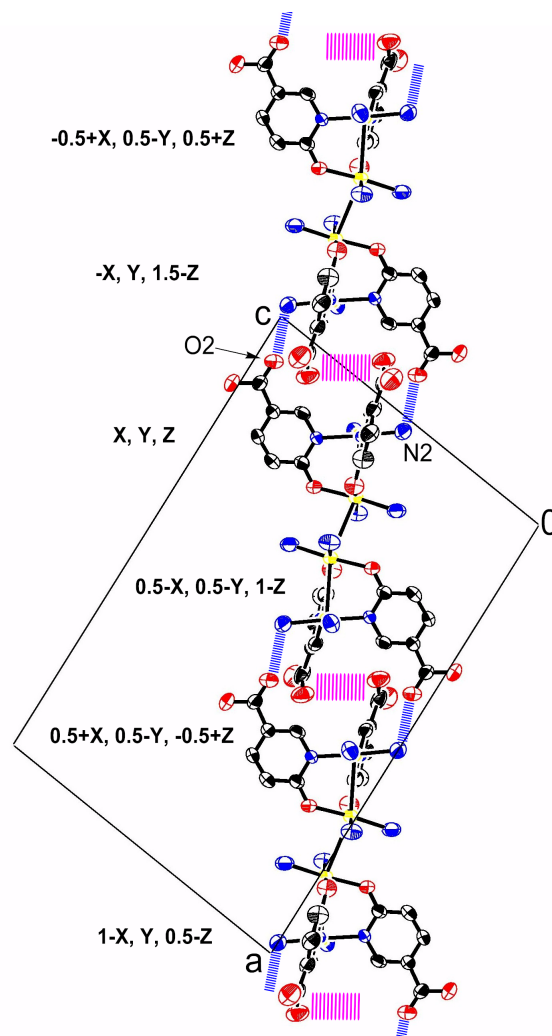
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**Figure 1**

The structure of the tetranuclear  $\text{Pt}^{\text{II}}_4$  complex cation in (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

center to give a tetranuclear structure, as observed for the  $\alpha$ -pyridonate analog  $[\text{Pt}_2(\text{NH}_3)_4(\mu\text{-}\alpha\text{-pyridonato})_2](\text{NO}_3)_4$  (Hollis & Lippard, 1983). The dimer–dimer association is stabilized by four hydrogen bonds formed between the ammine ligands and the O atoms of amidate bridges (see Fig. 1 and Table 2). Both the intra- and interdimer Pt–Pt distances within the tetranuclear cation in (I) [Pt–Pt(intradimer) = Pt1–Pt2 = 2.9023 (8) Å; Pt–Pt(interdimer) = Pt2–Pt2<sup>i</sup> = 3.1821 (11) Å; symmetry codes in Table 1] are slightly longer than those reported for the  $\alpha$ -pyridonate analog [Pt–Pt(intradimer) = 2.8767 (7) Å and Pt–Pt(interdimer) = 3.1294 (4) Å] (Hollis & Lippard, 1983). It is obvious that introduction of carboxyl unit on the  $\alpha$ -pyridonate ligand results in elongation in each Pt–Pt distance. Such a tendency has already been observed in our previous studies. For instance,  $[\text{Pt}^{\text{II}}_2(\text{NH}_3)_4(\mu\text{-glycolato})_2]^{2+}$  has a longer Pt–Pt(intradimer) distance compared to that of  $[\text{Pt}^{\text{II}}_2(\text{NH}_3)_4(\mu\text{-acetato})_2]^{2+}$  (Sakai, Takeshita *et al.*, 1998); the hydroxyl group of glycolate serves as an electron-withdrawing group. Thus, there has been a clear tendency that a decrease in electron density at the  $\text{Pt}^{\text{II}}$  centers results in elongation of Pt–Pt distances in this class of diplatinum complexes. Possibly, a dative bond formed by use of a filled Pt  $5d_{z^2}$  orbital and a vacant Pt  $6p$  orbital is weakened by the decrease in electron density at the metal centers. On the other hand, the two Pt atoms within the dimer unit are displaced out of their indi-



**Figure 2**

A view down the  $b$  axis, showing the inter-tetramer interactions leading to a one-dimensional network; hydrogen bonds formed between the tetramers are drawn by blue dotted lines and  $\pi$ – $\pi$  interactions achieved between the carboxyl units are indicated by pink lines. Hydrogen bonds formed within the basic tetrameric units have been omitted for clarity.

dual Pt coordination planes in such a manner that they have an attractive interaction with one another. Atoms Pt1 and Pt2 are respectively displaced by 0.055 (6) and 0.088 (6) Å; the four-atom r.m.s. deviations estimated in the mean-plane calculations are 0.013 and 0.012 Å, respectively. Structural features of this type of dimer have also been evaluated by use of two structural parameters. One is a dihedral angle between the two Pt coordination planes within the dimeric unit ( $\tau$ ), and the other is an average torsional twist of them about the Pt–Pt axis ( $\omega$ ). The value of  $\tau = 30.5$  (4) $^\circ$  in (I) is quite comparable to the value of  $\tau = 30.0^\circ$  reported for the  $\alpha$ -pyridonate analog (Hollis & Lippard, 1983). On the other hand, the  $\omega$  value is effectively smaller in (I) [ $\omega = 10.7^\circ$  in (I);  $\omega = 20.3^\circ$  in the  $\alpha$ -pyridonate analog], which must be due to the fact that the carboxyl units play a considerable role in the stabilization of inter-tetramer associations described below.

An intriguing feature due to the presence of carboxyl units in (I) is that the tetrameric units are strongly associated with each other to afford a one-dimensional chain (Fig. 2). A twofold axis, which is parallel to the *b* axis, is located at the mid-point between two tetramers. The interactions are not only stabilized by hydrogen bonds formed between the ammine ligands and the O atoms of carboxyl units [N2...O2(-*x*, *y*,  $\frac{3}{2} - z$ ) = 2.818 (17) Å], but also stabilized by  $\pi$ - $\pi$  stacking interactions between the carboxyl units. The plane-to-plane separation is estimated as 3.36 Å, and the shortest contact is 3.47 (2) Å for O5...C8(-*x*, *y*,  $\frac{3}{2} - z$ ). However, the inter-tetramer Pt...Pt distance [6.4394 (12) Å, see also Table 1] indicates the lack of any metal-metal interaction between the tetramers. It must also be noted that both carboxyl units have a relatively short contact with a water molecule [O3...O13 = 2.60 (2) Å and O5...O14 = 2.61 (3) Å], indicative of strong hydrogen bonds formed between these moieties.

### Experimental

To an aqueous solution of *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (0.5 mmol/3.5 ml H<sub>2</sub>O), prepared as previously described (Sakai, Takeshita *et al.*, 1998; Sakai, Tanaka *et al.*, 1998), was added 5-carboxy- $\alpha$ -pyridone (6-hydroxynicotinic acid) (0.5 mmol). The solution was heated at 353 K for 4 h followed by filtration if necessary. Leaving the resulting green solution at 278 K for a few days afforded the title compound (I) as dark green prisms, which were collected by filtration and air-dried (yield: 7%). Analysis calculated for C<sub>24</sub>H<sub>48</sub>N<sub>16</sub>O<sub>28</sub>Pt<sub>4</sub>: C 16.11, H 2.70, N 12.53%; found: C 16.34, H 2.56, N 12.28%.

#### Crystal data

[Pt <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> NO <sub>3</sub> ) <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ] <sub>2</sub> · (NO <sub>3</sub> ) <sub>4</sub> ·4H <sub>2</sub> O	<i>D<sub>x</sub></i> = 2.443 Mg m <sup>-3</sup>
<i>M<sub>r</sub></i> = 1789.14	Mo <i>K</i> $\alpha$ radiation
Monoclinic, <i>C</i> 2/ <i>c</i>	Cell parameters from 8766 reflections
<i>a</i> = 23.648 (4) Å	$\theta$ = 2.3–28.0°
<i>b</i> = 13.3574 (16) Å	$\mu$ = 11.57 mm <sup>-1</sup>
<i>c</i> = 15.5128 (19) Å	<i>T</i> = 296 (2) K
$\beta$ = 96.998 (3)°	Prism, dark green
<i>V</i> = 4863.6 (11) Å <sup>3</sup>	0.25 × 0.10 × 0.05 mm
<i>Z</i> = 4	

#### Data collection

Bruker SMART APEX CCD-detector diffractometer	5608 independent reflections
$\omega$ scans	3623 reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )
Absorption correction: Gaussian ( <i>XPREP</i> in <i>SAINT</i> ; Bruker, 2001)	<i>R</i> <sub>int</sub> = 0.101
<i>T</i> <sub>min</sub> = 0.115, <i>T</i> <sub>max</sub> = 0.325	$\theta$ <sub>max</sub> = 28.3°
20325 measured reflections	<i>h</i> = -31 → 30
	<i>k</i> = -17 → 17
	<i>l</i> = -20 → 20

#### Refinement

Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.1051P)^2 + 48.6026P]$
$R[F^2 > 2\sigma(F^2)] = 0.063$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.197$	( $\Delta/\sigma$ ) <sub>max</sub> = 0.001
<i>S</i> = 1.06	$\Delta\rho$ <sub>max</sub> = 5.48 e Å <sup>-3</sup>
5608 reflections	$\Delta\rho$ <sub>min</sub> = -1.62 e Å <sup>-3</sup>
298 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters (Å, °).

Pt1–N5	2.021 (11)	Pt2–N4	2.038 (14)
Pt1–N2	2.044 (13)	Pt2–O4	2.048 (10)
Pt1–N6	2.049 (10)	Pt1–Pt2	2.9023 (8)
Pt1–N1	2.049 (12)	Pt2–Pt2 <sup>i</sup>	3.1821 (11)
Pt2–O1	2.033 (11)	Pt1–Pt1 <sup>ii</sup>	6.4394 (12)
Pt2–N3	2.035 (13)		
N5–Pt1–N2	177.6 (5)	O1–Pt2–N4	175.7 (4)
N5–Pt1–N6	90.2 (4)	N3–Pt2–N4	91.8 (6)
N2–Pt1–N6	89.2 (5)	O1–Pt2–O4	93.5 (4)
N5–Pt1–N1	88.9 (5)	N3–Pt2–O4	174.3 (5)
N2–Pt1–N1	91.6 (5)	N4–Pt2–O4	86.8 (5)
N6–Pt1–N1	176.1 (5)	Pt1–Pt2–Pt2 <sup>i</sup>	158.74 (3)
O1–Pt2–N3	87.4 (5)		
N5–Pt1–Pt2–O1	12.8 (4)	N2–Pt1–Pt2–N4	12.4 (6)
N1–Pt1–Pt2–N3	9.3 (6)	N6–Pt1–Pt2–O4	8.1 (4)

Symmetry codes: (i)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (ii)  $-x, y, \frac{3}{2} - z$ .

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N3–H3B...O4 <sup>i</sup>	0.89	2.21	2.988 (17)	146
N4–H4A...O1 <sup>i</sup>	0.89	2.30	3.030 (16)	139
N2–H2A...O2 <sup>ii</sup>	0.89	1.97	2.818 (17)	159

Symmetry codes: (i)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (ii)  $-x, y, \frac{3}{2} - z$ .

The two nitrate ions were both treated as disordered over two sites. One of them shows orientational disorder in which two sets of positions (O7A, O8A and O9A; and O7B, O8B and O9B) are located around atom N7. For each disordered nitrate ion, the disordered O atoms were assumed to have the same isotropic displacement parameter. Furthermore, the N–O distances were restrained to 1.220 (1) Å, the three O...O distances within each nitrate ion were restrained as equal, and each nitrate ion was restrained to be planar. In each case, the two sites were assumed to be equally populated and therefore the occupation factors for all the disordered atoms were fixed at 50%. Aromatic and ammine H atoms were located at their idealized positions (C–H = 0.93 Å and N–H = 0.89 Å), and included in the refinement in riding-motion approximation, with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) and 1.5*U*<sub>eq</sub>(N) for aromatic and ammine H atoms, respectively. H atoms of the carboxyl groups and the water molecules were not located. In the final difference Fourier synthesis, four large residual peaks in the range 4.03–5.48 e Å<sup>-3</sup> were observed within 1.03 Å of Pt atoms. 12 further peaks in the range 1.00–1.84 e Å<sup>-3</sup> were located near either Pt atoms or disordered nitrate ions. The deepest hole was located 0.70 e 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* (Sheldrick, 1997), *TEXSAN* (Molecular Structure Corporation, 2001), *KENX* (Sakai, 2002) and *ORTEPII* (Johnson, 1976).

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