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A head-to-head isomer of di- μ -pivalamidato- $\kappa^4 N, O$ -bis[(1,10-phenanthroline- $\kappa^2 N, N'$)]platinum(II) dinitrate dihydrate

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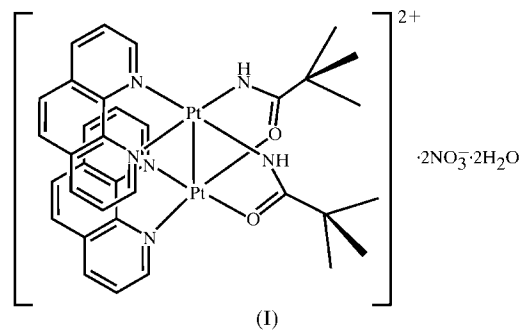
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In the title compound, $[\text{Pt}_2(\text{C}_5\text{H}_{10}\text{NO})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, the intradimer Pt–Pt distance is relatively short [2.8489 (17) Å], which must be due to the strong intramolecular π – π -stacking interactions between the phenanthroline moieties. The dimers stack along the *c* axis, forming one-dimensional columns in which very intriguing *d*–*d*, π – π and *d*– π interactions exist. Although the dimer–dimer Pt...Pt distances are very long [4.340 (2) and 4.231 (2) Å], some short interdimer Pt...C contacts leading to strong interdimer associations are found [3.325 (19) and 3.402 (19) Å].

Comment

Interest in recent years has concentrated on one-dimensional platinum chain systems consisting of dinuclear entities doubly bridged, in *cis* positions, by amidate or carboxylate ligands (Sakai, Takeshita *et al.*, 1998; Sakai, Ishigami *et al.*, 2002). One of the attractive features of such dimers lies in their structural flexibility, which allows a change in the Pt–Pt distance upon change in Pt oxidation state. Such flexibility must be considered a unique characteristic of the ‘U-shaped’ dimers mentioned above as it is not exhibited by the quadruply bridged dimers, which are known as ‘lantern dimers’. In this context, we recently succeeded in developing quite unusual Magnus-type one-dimensional double salts involving a pivalamidate-bridged Pt(bpy) dimer, namely $[\text{Pt}_2(\text{bpy})_2(\mu\text{-pivalamidato})_2]^{2+}$ (bpy = 2,2′-bipyridine; Sakai, Akiyama *et al.*, 2002). Note that two geometrical isomers, *viz.* head-to-head (HH) and head-to-tail (HT), are possible for this class of doubly bridged dimer as a result of the asymmetric feature of the amidate N–C–O units. As part of the project, we report here the crystal structure of the 1,10-phenanthroline (phen) analog in a HH arrangement, *viz.* HH- $[\text{Pt}_2(\text{phen})_2(\mu\text{-pivalamidato})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, (I). We also obtained crystals of the HT isomer, details of which will be reported elsewhere.



The asymmetric unit of (I) consists of a dimer cation, two nitrate anions, and two water molecules. The mean-plane calculations performed for the four coordinated atoms reveal that the two Pt coordination environments are planar; the four-atom r.m.s. deviation is 0.015 Å for the N1/N2/N5/N6 plane and 0.021 Å for the O1/O2/N3/N4 plane. The dihedral angle (τ) between the two Pt coordination planes within the dimer unit and their average torsional twist (ω) about the Pt–Pt axis are estimated as 21.5 (4) and 13 (3)°, respectively, where $\omega = 0^\circ$ indicates that the two Pt coordination planes stack in an eclipsed fashion. On the other hand, the two phen ligands are also found to be planar; the 14-atom r.m.s. deviation is 0.023 Å for the plane defined by atoms N1/N2/C1–C12 and 0.030 Å for the plane defined by atoms N3/N4/C13–C24. The dihedral angle between the phen planes [6.2 (3)°] is smaller by 15.3 (4)° than that between the two Pt coordination planes, indicating that a relatively strong π -stacking interaction exists in the dimer unit (Figs. 2 and 3*a*), where the interplanar spacing is 3.56 (11) Å. Atoms Pt1 and Pt2 are shifted from the individual coordination planes by 0.016 (7) and 0.028 (8) Å, respectively. They are both shifted towards the outside of the dimer unit as if they were attempting to move away to resist the attractive forces induced by the strong intradimer phen–phen stacking interaction. The intradimer Pt–Pt distance [2.8489 (17) Å] is shorter than that observed for the bpy analog [*ca* 2.87 Å for HH- $[\text{Pt}_2(\text{bpy})_2(\mu\text{-pivalami-$

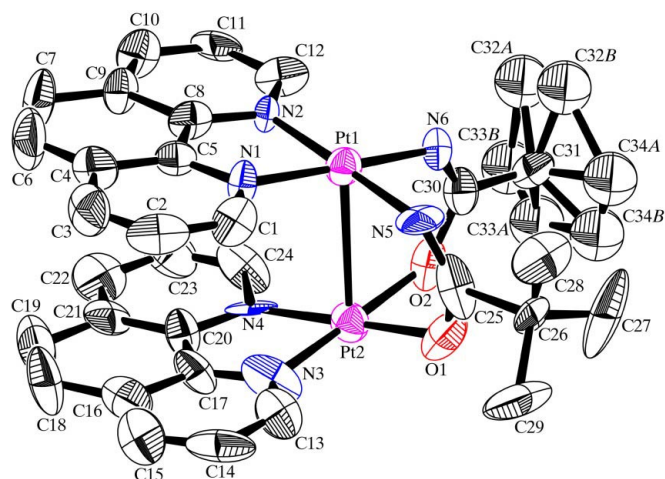


Figure 1

The structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity.

dato)₂]²⁺; unpublished results}. This is consistent with our interpretation that aromatic ligands in equatorial positions promote the attractive interaction between the two Pt coordination planes within the dimer unit.

As shown in Fig. 4, the dimer cations stack along the *c* axis, giving beautiful cationic one-dimensional columns, *viz.* [HH-Pt₂(phen)₂(μ-pivalamidato)₂]_{*n*}^{2*n+*}. The Pt1–Pt2 vector is tilted by *ca* 22° with respect to the *c* axis, resulting in relatively long interdimer Pt···Pt distances [4.340 (2) and 4.231 (2) Å; Table 1]. On the other hand, counter-ions and water molecules are inserted into the channels beside the dimer chains to give anionic one-dimensional chains [(NO₃)₂·2H₂O]_{*n*}^{2*n-*} (Fig. 4*a*), where hydrogen bonds are formed between nitrate and water atoms O9 and O10 (Table 2). This is the first example of a crystal structure in which either a Pt(bpy) or a Pt(phen) dimer doubly bridged with amidate ligands gives a ‘one-dimensional column’, in spite of the fact that several crystal structures have already been reported for dimers of this type, *viz.* HH-[Pt₂(bpy)₂(μ-3,3-dimethylglutarimidato)₂]₂(NO₃)₄ (Matsumoto & Urata, 1993) and HT-[Pt₂(bpy)₂(α-pyrrolidinonato)₂]₂(ClO₄)₂ (Matsumoto, Harashima *et al.*, 1992). All the reported compounds were prepared as Pt(bpy) dimers bridged by exocyclic amidate ligands having sterically bulky amidate rings, leading to the partial blocking of dimer–dimer associations. Importantly, the blocking effect of exocyclic amidate

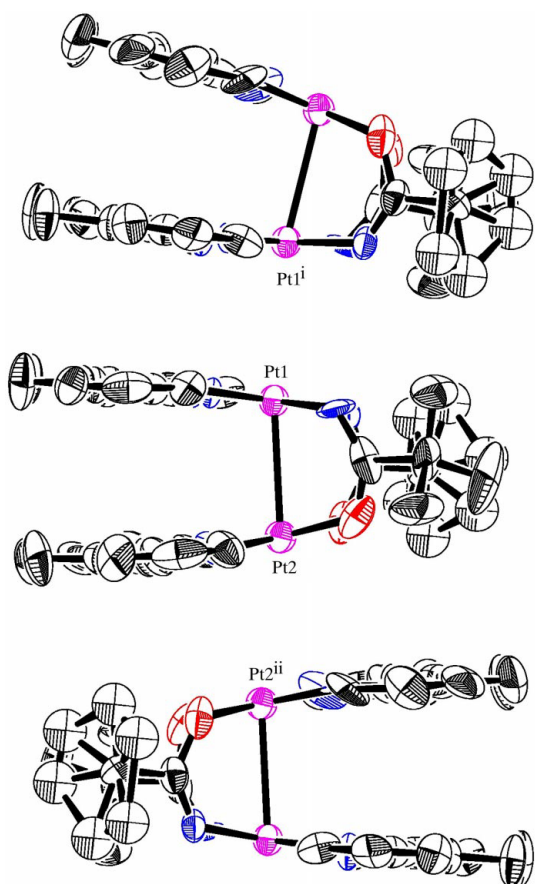


Figure 2
A view showing two crystallographically independent dimer–dimer associations. H atoms have been omitted for clarity.

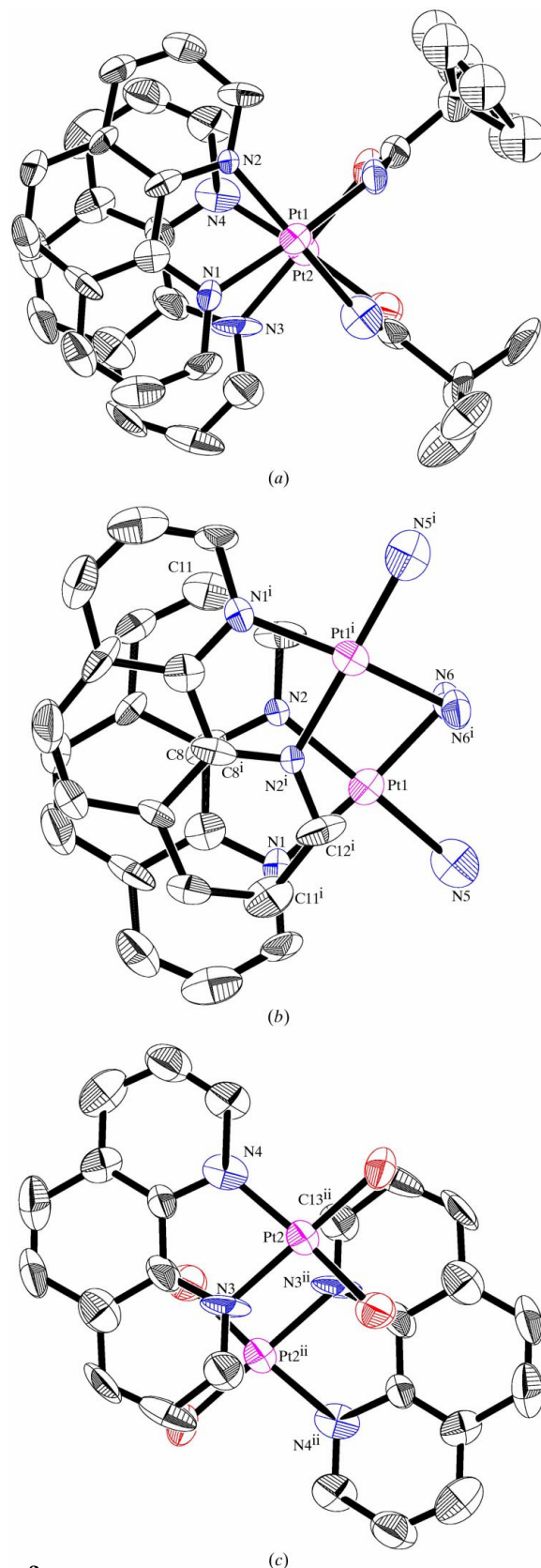


Figure 3
Views showing three different stacking interactions within the one-dimensional column: (a) an intradimer association, (b) an interdimer association through a twofold axis and (c) an interdimer association through an inversion center. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $-x, 1 - y, -z$.]

ligands can be eliminated by employing chain amidate ligands, such as acetamidate, as reported by the authors (Sakai & Matsumoto, 1989; Matsumoto, Sakai *et al.*, 1992). Thus, the one-dimensional framework observed in (I) must be promoted by the use of pivalamidate, which belongs to the chain amidate family.

Although Pt··Pt interactions are not extended in a one-dimensional manner, the dark-red (almost black) nature of (I) implies that somewhat strong intermolecular interactions are enhanced within the columnar stack of dimers. As shown in Fig. 2, two crystallographically independent dimer–dimer interactions are found. The dimer–dimer association through an inversion center [see the Pt2··Pt2ⁱⁱ geometry in Fig. 2; symmetry code: (ii) $-x, 1-y, -z$] is stabilized by several interactions discussed below. One is an edge-to-face interaction formed between the *tert*-butyl and phen moieties; the other is a dipole–dipole interaction between the *cis*-PtN₂O₂ coordination planes, as previously reported for many tetranuclear platinum complexes made up of amidate-bridged *cis*-Pt(NH₃)₂ dimers (Sakai, Tanaka *et al.*, 1998). Two reports also show that similar HH dimers stack to give a dimer of dimers based on the stack of PtO₂(bpy) units in which a crystallographic inversion center is located at the mid-point of the interaction (Trötscher *et al.*, 1990; Matsumoto & Urata,

1993). It is also quite reasonable to consider that *cis*-PtN₂O₂ units rather than PtN₄ units tend to stack through an inversion center in order to form a more stable dipole–dipole interaction, as a much larger dipole would result at the *cis*-PtN₂O₂ unit compared with the PtN₄ unit. In addition to these interactions, a relatively strong *d*– π interaction exists, Pt2··C13ⁱⁱ = 3.325 (19) Å (Fig. 3c). Other short contacts in this structure are listed in Table 2.

Two adjacent dimers are also correlated with a twofold axis [see the Pt1··Pt1ⁱ geometry in Figs. 2 and 3b; symmetry code: (i) $-x, y, \frac{1}{2} - z$]. In this case, the dimer–dimer interaction is not only stabilized by a π – π -stacking interaction between the phen moieties [the interplanar spacing is 3.36 (7) Å], but also by hydrophobic interactions between the *tert*-butyl moieties. Although two relatively weak hydrogen bonds are involved in this geometry (Table 3), they do not participate in the stabilization of the interdimer association. A considerable *d*– π interaction is also observed [Pt1··C12ⁱ = 3.402 (19) Å]. Other short contacts are summarized in Table 2.

We think that the strong *d*–*d*, π – π and *d*– π interactions observed in the present one-dimensional system may lead to unusual physical properties. Detailed studies on the luminescence and electrical-conduction properties of (I), together with those of related compounds, are still in progress in our laboratory.

Experimental

A solution of PtCl₂(phen) [0.5 mmol, 0.22 g; prepared in the same manner as reported for PtCl₂(bpy); Morgen & Burstall, 1963], AgNO₃ (1 mmol, 0.17 g) and pivalamide (1.5 mmol, 0.15 g) in water (30 ml) was refluxed in the dark for 2 d. The solution was then filtered while hot to remove precipitated AgCl. The filtrate was left to stand in air at room temperature overnight. The deposited dark-red crystals were collected by filtration (yield 50%). The compound was dissolved in water at 338 K (*ca* 0.1 g/2 ml H₂O), followed by filtration of the hot solution. Leaving the filtrate to stand in air at room temperature overnight afforded the final product, (I), as dark-red prisms (yield 30%). Analysis calculated for C₃₄H₄₀N₈O₁₀Pt₂: C 36.76, H 3.63, N 10.09%; found: C 36.58, H 3.46, N 10.02%.

Crystal data

[Pt₂(C₅H₁₀NO)₂(C₁₂H₈N₂)₂]
(NO₃)₂·2H₂O
M_r = 1110.92
Monoclinic, C2/c
a = 22.454 (10) Å
b = 13.341 (6) Å
c = 27.271 (13) Å
 β = 113.701 (14)°
V = 7480 (6) Å³
Z = 8

D_x = 1.973 Mg m⁻³
Mo K α radiation
Cell parameters from 867 reflections
 θ = 3.1–19.8°
 μ = 7.54 mm⁻¹
T = 296 (2) K
Prism, dark red
0.15 × 0.10 × 0.05 mm

Data collection

Bruker SMART APEX CCD-detector diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.509, *T_{max}* = 0.686
18 755 measured reflections
6557 independent reflections
3177 reflections with *I* > 2 σ (*I*)

R_{int} = 0.129
 θ_{\max} = 25.0°
h = –26 → 25
k = –15 → 13
l = –27 → 32
57 standard reflections
frequency: 330 min
intensity variation: 0.2%

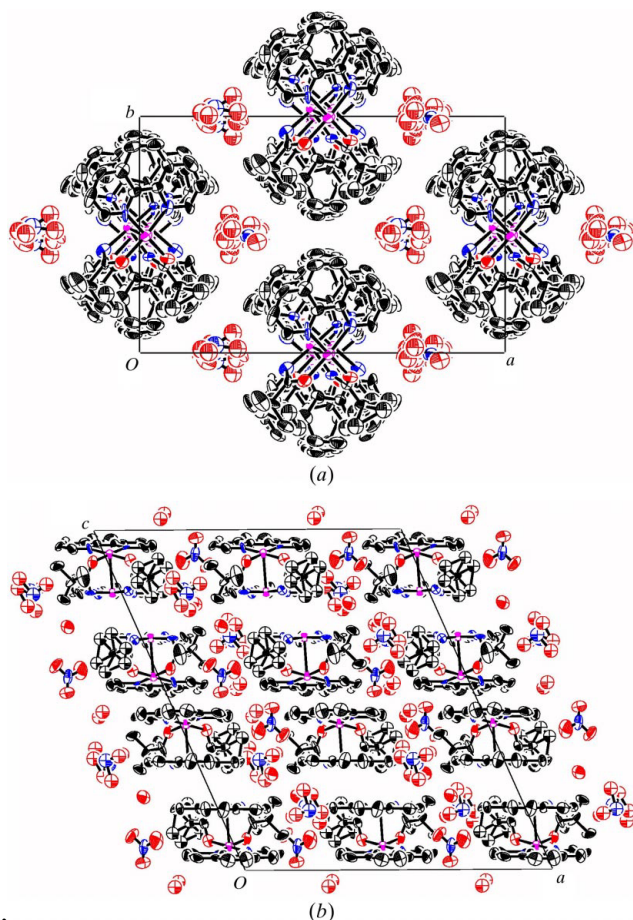


Figure 4
Crystal packing views showing one-dimensional columns consisting of dimer units (*a*) along the *c* axis and (*b*) along the *b* axis. H atoms have been omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

Pt1—Pt2	2.8489 (17)	Pt2—N4	1.980 (14)
Pt1···Pt1 ⁱ	4.340 (2)	Pt1—N5	2.009 (14)
Pt2···Pt2 ⁱⁱ	4.231 (2)	Pt1—N6	1.985 (12)
Pt1—N1	2.027 (12)	Pt2—O1	2.029 (12)
Pt1—N2	1.999 (11)	Pt2—O2	2.033 (12)
Pt2—N3	2.008 (14)		
N6—Pt1—N2	93.3 (5)	N4—Pt2—N3	81.4 (6)
N6—Pt1—N5	87.6 (5)	N4—Pt2—O1	174.9 (5)
N2—Pt1—N5	179.1 (5)	N3—Pt2—O1	94.3 (5)
N6—Pt1—N1	175.2 (5)	N4—Pt2—O2	98.5 (5)
N2—Pt1—N1	82.3 (5)	N3—Pt2—O2	179.6 (7)
N5—Pt1—N1	96.9 (5)	O1—Pt2—O2	85.8 (5)
N2—Pt1—Pt2—N4	−16.3 (5)	N5—Pt1—Pt2—O1	−12.5 (5)
N1—Pt1—Pt2—N3	−15.1 (6)	N6—Pt1—Pt2—O2	−10.6 (4)

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

Table 2
Contact distances (Å).

Pt1···C12 ⁱ	3.402 (19)	O3B···O9	2.67 (4)
Pt2···C13 ⁱⁱ	3.325 (19)	O4A···O9	3.30 (3)
Pt2···N3 ⁱⁱ	3.426 (18)	O7···O10A	2.95 (4)
N1···C11 ⁱ	3.23 (2)	O7···O10B	3.03 (4)
N2···N2 ⁱ	3.26 (3)	O9···O6 ⁱ	3.00 (2)
N6···N6 ⁱ	3.63 (3)	O10A···O5A ⁱⁱ	2.76 (5)
C8···C8 ⁱ	3.36 (4)	O10B···O4B ⁱⁱ	3.11 (5)
O1···C17 ⁱⁱ	3.53 (3)	O10B···O5B ⁱⁱ	3.27 (5)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N5—H5···O9	0.86	2.43	3.21 (2)	151

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.067$	$w = 1/[\sigma^2(F_o^2) + (0.0126P)^2]$
$wR(F^2) = 0.122$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.80$	$(\Delta/\sigma)_{\max} < 0.001$
6557 reflections	$\Delta\rho_{\max} = 2.16 \text{ e } \text{Å}^{-3}$
478 parameters	$\Delta\rho_{\min} = -1.25 \text{ e } \text{Å}^{-3}$

It is often possible to determine the binding direction of the O and NH moieties of the amidate group by comparing the results of least-squares calculations performed for two possible directions (Sakai *et al.*, 2003). On the other hand, it is not very likely that the HH and HT isomers possess the same intradimer Pt—Pt distance (Sakai, Tanaka *et al.*, 1998). We decided to abandon the possibility that the two isomers co-exist in a disorder model, since the Pt atoms possess moderately small U_{eq} values of 0.0404 (2) and 0.0450 (2) Å². Consequently, one of two possible directions of the O—C—N group was adopted for each pivalamidate ligand. The locations of atoms O1 and N5 have been rationally determined from the comparison of two sets of U_{eq} values: $U_{\text{eq}}(\text{O1}) = 0.065$ (4) Å² and $U_{\text{eq}}(\text{N5}) = 0.053$ (4) Å², and $U_{\text{eq}}(\text{N instead of O1}) = 0.040$ (4) Å² and $U_{\text{eq}}(\text{O instead of N5}) = 0.080$ (4) Å². On the other hand, it was rather difficult to evaluate the validity of our assignment of the locations of atoms O2 and N6 based on the following values: $U_{\text{eq}}(\text{O2}) = 0.063$ (4) Å² and $U_{\text{eq}}(\text{N6}) = 0.041$ (4) Å², and $U_{\text{eq}}(\text{N instead of O2}) = 0.036$ (4) Å² and $U_{\text{eq}}(\text{O$

instead of N6) = 0.067 (4) Å². Finally, we decided to select the former assignment, since it was quite reasonable to suppose this compound to be a HH isomer from many viewpoints, as discussed in the *Comment*. As a result of this selection, a relatively short contact is observed at N6—H6···H6ⁱ—N6ⁱ, where H6···H6ⁱ = 2.11 Å, N6—H6···H6ⁱ = 151°, N6···N6ⁱ = 3.63 (3) Å and N6—H6···H6ⁱ—N6ⁱ = −51° (Fig. 3*b* and Table 2). However, such an unusually short contact has been observed in many systems; for instance, H(NH₃)···H(NH₃) distances in the range 2.31 (8)–2.40 (7) Å were observed in one case (Hollis & Lippard, 1983), and H(en)···H(en) distances in the range 2.2–2.3 Å were observed in HH-[Pt^{III}(en)₂(μ-α-pyridonato)₂(NO₂)(NO₃)]²⁺ (en = ethylenediamine; O'Halloran *et al.*, 1986). These unusually short H···H contact distances are due to a strong Pt—Pt bond formed between the two *cis*-Pt(NH₃)₂ or Pt(en) moieties. Although the H6···H6ⁱ contact in (I) still seems too short, it must be taken into consideration that H6 was located geometrically. The actual H6···H6ⁱ distance could be longer than that described above to give a more reasonable/acceptable situation with only a slight modification of the H6 position.

One of the two *tert*-butyl groups shows orientational disorder in which two sets of positions (C32A/C33A/C34A and C32B/C33B/C34B) are located around atom C31. The disordered C atoms were presumed to have the same isotropic displacement parameter. Furthermore, all six C(tertiary)—C(methyl) distances and three C(methyl)—C(methyl) distances within each site were restrained to be equal. The occupation factors of sites *A* and *B* converged at 58 (2) and 42 (2)%, respectively. In the other *tert*-butyl group, the anisotropic displacement parameter (ADP) values of atom C27 are unusual. However, refinement with a reasonable disorder model was unsuccessful. One of the two nitrate ions was also regarded as being disordered over two sets of positions (N7A/O3A/O4A/O5A and N7B/O3B/O4B/O5B). All the disordered atoms within each site were assumed to have the same isotropic displacement parameter. Moreover, the N—O distances were restrained to be 1.22 (1) Å, three O···O distances within each site were restrained to be equal, and each nitrate ion was restrained to be planar. The occupation factors of sites *A* and *B* converged at 59 (2) and 41 (2)%, respectively.

All H atoms were located at idealized positions [C—H(aromatic) = 0.93 Å, C—H(methyl) = 0.96 Å and N—H = 0.86 Å] and included in the refinement in riding-motion approximation, with $U_{\text{iso}}(\text{aromatic H}) = 1.2U_{\text{eq}}(\text{C})$, $U_{\text{iso}}(\text{methyl H}) = 1.5U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. Water H atoms were not located. In the final difference Fourier synthesis, seven residual peaks in the range 1.00–2.16 e Å^{−3} were observed within 1.35 Å of the Pt atoms. The deepest hole was located 0.84 Å from Pt1. The maximum and minimum principal-axis ADP ratios of atoms N3 and N4 were 3.5 and 7.2, respectively. These abnormal ADP values might be the result of a low ratio of observed/unique reflections (48%).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; 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 *ORTEPII* (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1705). Services for accessing these data are described at the back of the journal.

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