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Di-μ-pivalato-bis[*cis*-diammineplatinum(II)] bis(perchlorate) pivalic acid solvate

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.019 Å
H-atom completeness 98%
Disorder in solvent or counterion
R factor = 0.041
wR factor = 0.079
Data-to-parameter ratio = 20.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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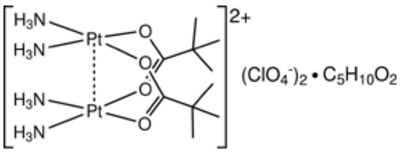
The intradimer Pt—Pt distance [3.0928 (9) Å] in the title compound, $[Pt_2(\mu\text{-}C_5H_9O_2)_2(NH_3)_4](ClO_4)_2\cdot C_5H_{10}O_2$, is much longer than that reported for $[Pt_2(\mu\text{-}C_5H_9O_2)_2(NH_3)_4](SO_4)\cdot H_2O$ [2.9011 (9) Å; Sakai, Ishigami, Yokokawa, Kajiwara & Ito (2003). *Acta Cryst.* E**59**, m443–m445]. The complex cation has a crystallographic mirror plane perpendicular to the Pt—Pt bond. The crystal packing is stabilized by both the hydrophilic and hydrophobic layers, which stack alternately along the c axis.

Comment

We have previously reported that *cis*-diammineplatinum dimers doubly bridged by carboxylate ligands, $[Pt_2(NH_3)_4(\mu\text{-carboxylato})_2]^{2+}$ (carboxylate is acetate, propionate *etc.*), tend to form quadruple hydrogen bonds with one another, giving an infinite Pt chain in the crystal structure (Sakai *et al.*, 1998, 2002). However, the arrangement of dimers is also affected by the hydrophobic interactions between the ligands. We recently reported the crystal structure of a sulfate salt of the same pivalate-bridged *cis*-diammineplatinum(II) dimer $[Pt_2(NH_3)_4(\mu\text{-pivalato})_2](SO_4)\cdot H_2O$, (II); Sakai *et al.*, 2003]. We report here the crystal structure of the title compound, (I), as another example of a structure in which the hydrophobic interactions rather than the hydrogen-bonding interactions between the dimers govern the arrangement of the dimers.



(I)

As shown in Fig. 1 and Table 1, a crystallographic mirror plane passes through the center of the diplatinum cation in (I); the asymmetric unit consists of one-half of the formula unit. As a result, the two platinum coordination planes within a dimeric unit are positioned in a perfectly eclipsed fashion, leading to $\omega = 0°$, where ω is the average torsional twist of these coordination planes about the Pt—Pt axis. On the other hand, the dihedral angle between the two Pt coordination planes within a dimeric unit [τ = 43.8 (1)°] is much larger than the value observed for (II) (τ = 28.7°; Sakai *et al.*, 2003). This discrepancy is strongly correlated with the intradimer Pt—Pt distance, which is longer in (I) [3.0928 (9) Å] than in (II) [2.9011 (9) Å]. These prominent structural differences can be interpreted in terms of the difference in the location of the counter-anions with respect to the dimer cations, as follows. In (II), four ammines within a dimer unit grab a sulfate anion by forming several hydrogen bonds between the ammines and the

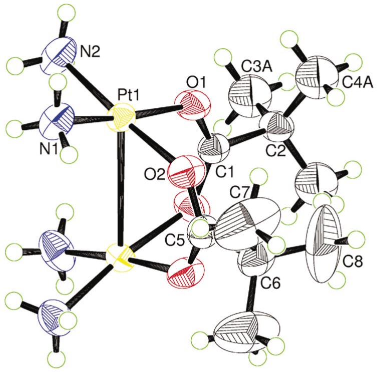


Figure 1
Structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level. One of the two disordered components of the tertiary butyl moiety involving atoms C2–C4 has been omitted for clarity.

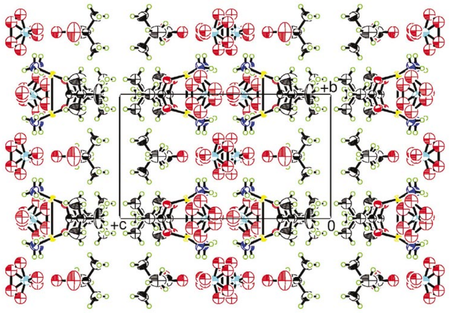


Figure 2
Crystal packing of (I), viewed along the *a* axis. One of the disordered components of the tertiary butyl moiety involving atoms C2–C4 has been omitted for clarity.

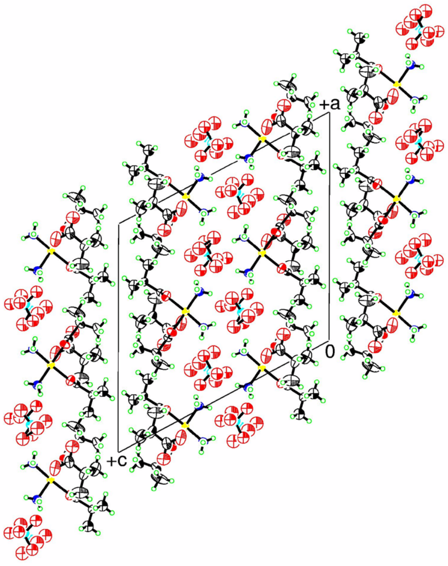


Figure 3
Crystal packing of (I), viewed along the *b* axis. One of the disordered components of the tertiary butyl moiety involving atoms C2–C4 has been omitted for clarity.

sulfate O atoms, leading to a shorter intradimer Pt—Pt distance. In (I), the perchlorate ions are not only located between the ammines within a dimeric unit but also between two neighboring dimer cations (Figs. 2 and 3, and Table 2), giving rise to the observed increase in the intradimer Pt—Pt distance in (I). It should also be noted that one pivalic acid molecule in its protonated form is involved in the crystal structure and is located on a mirror plane, as are the cations and anions.

Experimental

To an aqueous solution of *cis*-$[Pt(NH_3)_2(OH_2)_2](ClO_4)_2$ (0.1 mmol, 0.7 ml H_2O), prepared as described previously (Sakai *et al.*, 1998, 2002), was added $(CH_3)_3CCO_2Na$ (0.1 mmol). The solution was held at 303 K for a week to give the product as pale yellow needles, which were collected by filtration and air dried (yield 8%). Analysis calculated for $Pt_2Cl_2O_{14}N_4C_{15}H_{40}$: C 18.74, H 4.19, N 5.83%; found: C 18.34, H 4.00, N 5.76%.

Crystal data

$[Pt_2(C_5H_9O_2)_2(NH_3)_4](ClO_4)_2\cdot C_5H_{10}O_2$
$M_r = 961.59$
Monoclinic, $C2/m$
$a = 18.194$ (4) Å
$b = 9.874$ (2) Å
$c = 18.987$ (4) Å
$\beta = 118.155$ (5)°
$V = 3007.4$ (10) Å^3
$Z = 4$
$D_x = 2.124$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3676 reflections
$\theta = 7.0$–19.9°
$\mu = 9.54$ mm^{-1}
$T = 296$ (1) K
Prism, colorless
0.20 × 0.10 × 0.05 mm

Data collection

Bruker SMART APEX CCD detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.391$, $T_{max} = 0.563$
11 137 measured reflections
3676 independent reflections
2271 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 27.6°$
$h = -23 \rightarrow 23$
$k = -11 \rightarrow 12$
$l = -16 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.079$
$S = 0.86$
3676 reflections
183 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.43$ e Å^{-3}
$\Delta\rho_{min} = -0.88$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—N1	1.997 (6)	C2—C3*B*	1.407 (10)
Pt1—O2	2.018 (5)	C2—C4*B*	1.421 (9)
Pt1—N2	2.025 (6)	C2—C3*A*	1.422 (10)
Pt1—O1	2.025 (6)	C2—C4*A*	1.429 (9)
Pt1—Pt1^{i}	3.0928 (9)	C5—C6	1.531 (16)
Pt1—Pt1^{ii}	6.7816 (16)	C6—C8	1.457 (19)
O1—C1	1.246 (7)	C6—C7	1.501 (12)
O2—C5	1.237 (7)	C9—C10	1.52 (2)
O3—C9	1.248 (18)	C10—C12	1.538 (12)
O4—C9	1.227 (16)	C10—C11	1.56 (2)
C1—C2	1.568 (15)		
N1—Pt1—O2	86.8 (3)	N1—Pt1—O1	173.1 (3)
N1—Pt1—N2	92.0 (3)	O2—Pt1—O1	91.7 (2)
O2—Pt1—N2	174.7 (3)	N2—Pt1—O1	88.9 (3)

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

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Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1C···O4	0.89	2.60	3.304 (10)	136
N2—H2B···O9	0.89	2.54	3.15 (2)	126
N2—H2C···O5^{ii}	0.89	2.27	3.030 (15)	145
N2—H2B···O11^{i}	0.89	2.38	3.255 (16)	168
N1—H1C···O10^{iii}	0.89	2.55	3.172 (14)	128
N1—H1A···O6^{iv}	0.89	2.43	3.204 (19)	146
N1—H1A···O6^{v}	0.89	2.24	3.043 (17)	149

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

Perchlorate ions are located at two sites, each being disordered across a mirror plane. It was assumed that the disordered O atoms of each perchlorate ion have an occupation factor of 0.5 and the same isotropic displacement parameter. Furthermore, the Cl—O distances were restrained to 1.43 (1) Å, and the six O···O distances within each perchlorate ion were restrained to be equal. One of the three independent tertiary butyl groups shows orientational disorder, in which two sets of positions (C3A/C4A and C3B/C4B) are located around atom C2. The disordered C atoms were assigned the same isotropic displacement parameter. Furthermore, all six C(tertiary)—C(methyl) distances within each site were restrained to be equal, as were all three C(methyl)···C(methyl) distances within each site. All H atoms, except for those of an uncoordinated carboxyl group and a disordered tertiary butyl group, were placed at their idealized positions [C—H(methyl) = 0.96 Å and N—H(ammine) = 0.89 Å] and included in the refinement in the riding model approximation, with $U_{\rm iso}$(disordered tertiary butyl H) = 1.2$U_{\rm eq}$(C), $U_{\rm iso}$(tertiary butyl H without disorder phenomena) = 1.5$U_{\rm eq}$(C) and $U_{\rm iso}$(ammine H) = 1.5$U_{\rm eq}$(N). An H atom on the uncoordinated carboxyl group was not located. In the final difference Fourier synthesis, three residual peaks in the range 1.09–1.43 e Å^{-3} were observed within 1.05 Å of atom Pt1. The deepest hole was 0.99 Å from atom O7.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *KENX* (Sakai, 2002); software used to prepare material for publication: *SHELXL*97 and *TEXSAN* (Molecular Structure Corporation, 2001), *KENX* and *ORTEP* (Johnson, 1976).

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