

Di- μ -pivalato-bis[*cis*-diammineplatinum(II)] sulfate monohydrate

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Key indicators

Single-crystal X-ray study

$T = 296$ K

Mean $\sigma(\text{C}-\text{C}) = 0.019$ Å

H-atom completeness 94%

R factor = 0.045

wR factor = 0.092

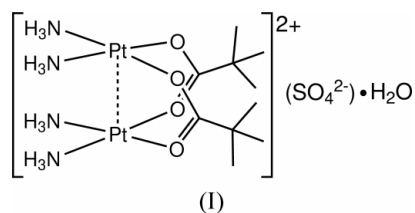
Data-to-parameter ratio = 20.3

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

The title compound, $[\text{Pt}_2(\text{NH}_3)_4(\text{C}_5\text{H}_9\text{O}_2)_2](\text{SO}_4)\cdot\text{H}_2\text{O}$, does not form an infinite chain, but has discrete dimeric cations in the crystal structure. The intradimer Pt—Pt distance in the pivalate dimer [2.9011 (9) Å] is effectively shorter than that reported for the acetate analog [2.9713 (8) Å], demonstrating the strong electron-donating property of the bridging pivalate ligand.

Comment

We previously reported that *cis*-diammineplatinum dimers doubly bridged with carboxylate ligands, $[\text{Pt}_2(\text{NH}_3)_4(\mu\text{-carboxylato})_2]^{2+}$ (carboxylate = acetate, propionate, *etc.*), tend to form quadruple hydrogen bonds with each other to give an infinite Pt chain in the crystal (Sakai *et al.*, 1998; Sakai *et al.*, 2002). However, the arrangement of dimers in the crystal is sometimes much affected by hydrophobic interactions between the ligands. Here we report the crystal structure of the title compound, (I), as an example of a structure in which the dimer cation does not stack in a one-dimensional manner, as a result of the formation of a relatively strong hydrophobic layer in the crystal.



The asymmetric unit of (I) consists of a dimer cation, a sulfate anion and a water molecule. Both the tertiary butyl moieties show relatively large atomic displacement parameters, as shown in Fig. 1. The bridged Pt—Pt distance [2.9011 (9) Å] is effectively shorter than the value of 2.9713 (8) Å reported for the acetate-bridged analog, $[\text{Pt}_2(\text{NH}_3)_4(\mu\text{-acetato})_2](\text{SiF}_6)\cdot 4\text{H}_2\text{O}$ (Sakai *et al.*, 1998). This is quite consistent with our previous observations; the introduction of an electron-withdrawing group into the carboxylate ligand leads to elongation of the bridged Pt—Pt distance (Sakai *et al.*, 1998). In (I), the tertiary butyl unit is expected to have a stronger electron-donating influence compared to the methyl unit of acetate, leading to a shorter Pt—Pt distance in (I) compared to that in the acetate analog. On the other hand, the two platinum atoms within the dimer unit are shifted out of their individual Pt coordination planes so that they have an attractive interaction with one another. The Pt1 and Pt2 atoms are shifted by 0.055 (4) and 0.018 (4) Å, respectively, where four-atom r.m.s. deviations in the mean-plane calculations are 0.034 and 0.003 Å, respectively. Structural features of this type

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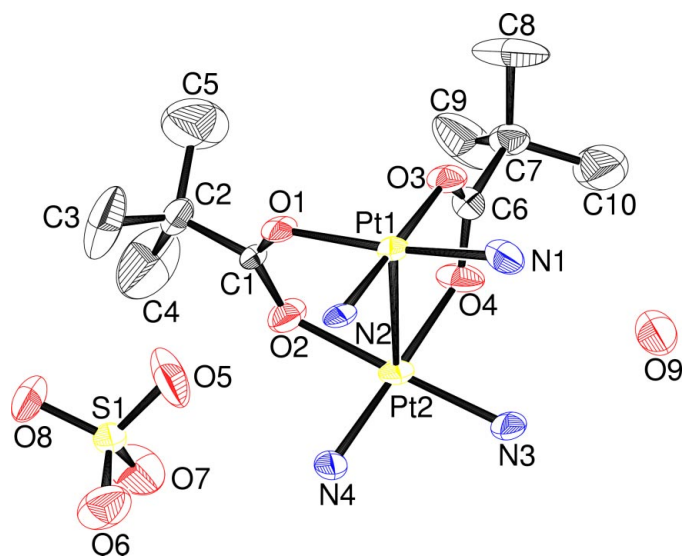


Figure 1
Structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

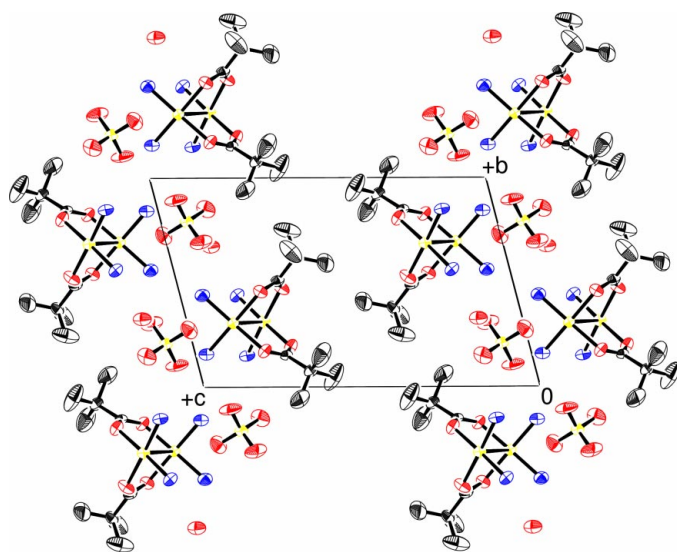


Figure 2
The packing, viewed down the *a* axis of (I).

of the dimer have been evaluated by use of the following two parameters. One is the dihedral angle between the two Pt coordination planes within a dimeric unit (τ), and the other is the average torsional twist of them about the Pt–Pt axis (ω). In this case, the values are estimated as $\tau = 28.7(3)^\circ$ and $\omega = 6.1^\circ$.

Fig. 2 shows the crystal packing diagram of (I), revealing that no interdimer metal-metal interaction is achieved in the crystal, where the shortest interdimer Pt...Pt distance is 7.8514(18) Å (see also Table 1). The figure also shows that two major factors operate in the stabilization of the crystal packing. One is a hydrophilic layer within $-0.25 < c < 0.25$, in which hydrogen bonds formed between the amines and the O atoms of sulfates or water molecule dominate the intermolecular interactions. The other is a layer within $0.25 < b <$

0.75 , in which hydrophobic interactions between the tertiary butyl units dominate the intermolecular associations. Hydrogen bonds formed by amines as hydrogen donors are summarized in Table 2. Hydrogen bonds are also formed between the water molecule and the O atoms of the sulfate: O9...O7 ($x, y - 1, z$) = 2.828(12) Å and O9...O8 ($x + 1, y - 1, z$) = 2.804(13) Å, although the H atoms were not located.

Experimental

To an aqueous solution of *cis*-[Pt(NH₃)₂(OH)₂](SO₄) (0.1 mmol/0.7 ml H₂O), prepared as previously described (Sakai *et al.*, 1998; Sakai *et al.*, 2002), was added (CH₃)₃CCO₂Na (0.1 mmol). The solution was kept at 303 K for a week to afford the title compound (I) as pale yellow needles, which were collected by filtration and air-dried (yield: 17%). Analysis calculated for Pt₂SO₉N₄C₁₀H₃₂: C, 15.51; H, 4.16; N, 7.32%; found: C, 15.39; H, 4.02; N, 7.17%.

Crystal data

[Pt₂(C₁₀H₃₀N₄O₄)]SO₄·H₂O
 $M_r = 774.64$
 Triclinic, $P\bar{1}$
 $a = 6.7043(19)$ Å
 $b = 10.672(3)$ Å
 $c = 16.100(5)$ Å
 $\alpha = 75.850(5)^\circ$
 $\beta = 88.835(6)^\circ$
 $\gamma = 75.852(5)^\circ$
 $V = 1082.1(5)$ Å³

$Z = 2$
 $D_x = 2.377$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4964 reflections
 $\theta = 20.6$ – 24.1°
 $\mu = 13.06$ mm⁻¹
 $T = 296(1)$ K
 Needle, colorless
 $0.42 \times 0.08 \times 0.07$ mm

Data collection

Bruker SMART APEX CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.317$, $T_{\max} = 0.401$
 10729 measured reflections

4964 independent reflections
 3056 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.053$
 $\theta_{\max} = 27.6^\circ$
 $h = -8 \rightarrow 8$
 $k = -13 \rightarrow 13$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.092$
 $S = 0.86$
 4964 reflections
 245 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.033P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.51$ e Å⁻³
 $\Delta\rho_{\min} = -1.90$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Pt1–N2	2.001 (9)	Pt2–N4	2.020 (8)
Pt1–N1	2.009 (9)	Pt2–O2	2.034 (7)
Pt1–O3	2.038 (8)	Pt2–N3	2.043 (8)
Pt1–O1	2.040 (7)	Pt2–O4	2.043 (7)
Pt1–Pt2	2.9011 (9)	Pt2–Pt1 ⁱⁱ	11.886 (3)
Pt1...Pt1 ⁱ	7.8514 (18)		
N2–Pt1–N1	90.3 (4)	N4–Pt2–O2	89.8 (3)
N2–Pt1–O3	178.8 (3)	N4–Pt2–N3	92.5 (4)
N1–Pt1–O3	89.3 (4)	O2–Pt2–N3	177.6 (3)
N2–Pt1–O1	91.4 (3)	N4–Pt2–O4	178.3 (4)
N1–Pt1–O1	174.6 (3)	O2–Pt2–O4	89.0 (3)
O3–Pt1–O1	88.8 (3)	N3–Pt2–O4	88.8 (4)
N2–Pt1–Pt2–N4	6.7 (4)	N1–Pt1–Pt2–N3	6.4 (4)
O1–Pt1–Pt2–O2	6.0 (3)	O3–Pt1–Pt2–O4	5.3 (3)

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

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>
N2—H6···O5	0.89	2.04	2.923 (12)	170
N4—H12···O7	0.89	2.35	3.133 (13)	148
N3—H7···O9	0.89	2.11	2.920 (12)	150
N1—H3···O9 ⁱ	0.89	2.38	3.086 (13)	137
N1—H1···O8 ⁱⁱ	0.89	2.29	3.128 (13)	156
N3—H8···O3 ⁱⁱⁱ	0.89	2.15	3.027 (11)	169
N4—H11···O1 ⁱⁱⁱ	0.89	2.24	3.071 (11)	156

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

Some of the methyl C atoms of tertiary butyl units seemed to possess unusually large displacement parameters. However, refinement of them using a disordered model has been unsuccessful. Therefore, these C atoms were treated normally in anisotropic mode. All H atoms except for those of a water molecule were placed at their idealized positions as riding atoms (C—H = 0.96 Å for methyl group, N—H = 0.89 Å for ammine group). H atoms of the water molecule were not located. In the final difference Fourier synthesis, 10 residual peaks in the range 1.06–2.51 e Å⁻³ were observed within 1.05 Å of the Pt atoms.

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* (Sakai, 2002), and *ORTEP* (Johnson, 1976).

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