Di-μ-pivalamidato-κ⁴*N:O;O:N*-bis[(2,2′-bipyridine-κ²*N,N′*)(sulfato-κ*O*)platinum(III)] tetrahydrate in a head-to-tail isomerism

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metal-organic compounds

Di-μ-pivalamidato-κ⁴N:O;O:N-bis[(2,2′-bipyridine-κ²N,N′)(sulfato-κO)platinum(III)] tetrahydrate in a head-to-tail isomerism

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The title compound, $[Pt_2^{III}(C_5H_{10}NO)_2(SO_4)_2(C_{10}H_8N_2)_2] \cdot 4H_2O$, is the first reported example of a complex in which an amidate-bridged Pt(bpy) dimer is stabilized in the oxidation level of Pt^{III} (bpy is 2,2′-bipyridine). The asymmetric unit consists of one half of the formula unit with a twofold axis passing through the center of the dimer. The intradimer Pt^{III}—Pt^{III} bond distance [2.5664 (6) Å] is comparable to those reported for α-pyridonate-bridged cis-diammineplatinum(III) dimers [2.5401 (5)–2.5468 (8) Å; Hollis & Lippard (1983). Inorg. Chem. **22**, 2605–2614], in spite of the close contact between the bpy planes within the dimeric unit. The axial Pt—$O_{sulfate}$ distance is 2.144 (7) Å.

Comment

Amidate-bridged cis-diammineplatinum dimers, $[Pt_2^{II}(NH_3)_4(\mu\text{-amidato})_2]^{2+}$ (amidate is α-pyridonate, α-pyrrolidinonate, acetamidate, etc.), have been reported to undergo one-step two-electron oxidation to give the corresponding Pt_2^{III} dimers, with a simultaneous uptake of two axial donors at both ends of the unit, as well as bond formation between the Pt^{III} centers, resulting in the formation of $[Pt_2^{III}(NH_3)_4(\mu\text{-amidato})_2X_2]^{n+}$ ions (X is an axial donor ligand and n depends on the charge of X). Reversible redox waves corresponding to the Pt_2^{II}/Pt_2^{III} couple have been observed at ~0.4–0.6 V versus SCE (Hollis & Lippard, 1983; Matsumoto & Matoba, 1986; Sakai et al., 1998). On the basis of the binding directions of the two amidate bridges, two geometric isomers, viz. head-to-head (HH) and head-to-tail (HT) isomers, are possible for this class of dimers. On the other hand, the dimers containing Pt(bpy) units instead of cis-Pt(NH₃)₂ units have been shown to exhibit irreversible redox waves corresponding to the Pt_2^{II}/Pt_2^{III} couple; irreversible oxidation–reduction waves were observed at ~1 V versus SCE for HT-$[Pt_2^{II}(bpy)_2(\mu\text{-}\alpha\text{-pyrrolidinonato})_2]$-(ClO₄)₂ (Matsumoto et al., 1992). These results suggest that

the formation of the Pt^{III}—Pt^{III} single bond in the Pt(bpy) dimers is hindered by repulsive interaction between the two bpy units. We have now found, for the first time, that an 'amidate-bridged Pt^{III}(bpy) dimer' can be isolated in a stable crystalline form, and we report here the synthesis and crystal structure of HT-$[Pt_2^{III}(bpy)_2(\mu\text{-pivalamidato})_2(SO_4)_2] \cdot 4H_2O$, (I).

(I)
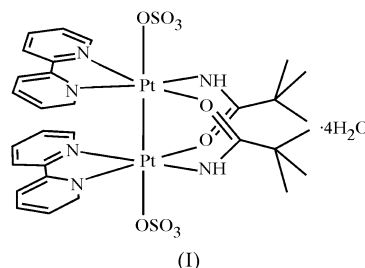
The asymmetric unit of (I) consists of one-half of the formula unit (Fig. 1). A twofold axis passes through the center of the dimeric unit. There is, therefore, a crystallographic requirement that this is a head-to-tail isomer. Analysis of the isotropic atomic displacement parameters of the O- and N-donors of pivalamidate revealed no evidence for any disorder of the O and NH moieties (see Experimental). The hydrogen-bonding geometry given in Table 3 also supports the validity of our treatment with regard to the binding direction of pivalamidate. To the best of our knowledge, this is the first structural characterization of a diplatinum(III) complex capped by two sulfate ions, even though stepwise axial sulfate-ligation equilibria were previously investigated for an α-pyr-
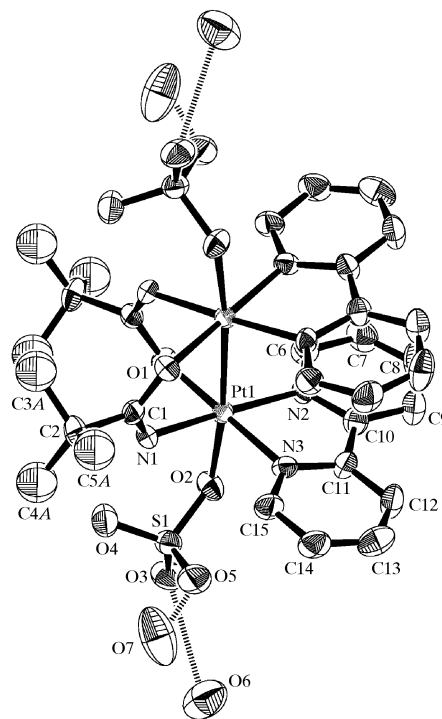

Figure 1
The structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms have been omitted for clarity and only one orientation is shown for the disordered tert-butyl groups. Dashed lines denote hydrogen bonds.

rolidinonate-bridged *cis*-diammineplatinum(III) dimer by means of spectrophotometric titration (Sakai, Tsubomura & Matsumoto, 1993).

The intradimer Pt^{III}—Pt^{III} distance in (I) [Pt1—Pt1^{i} = 2.5664 (6) Å; symmetry code: (i) $-x, y, \frac{3}{2} - z$] is unexpectedly short, in spite of the steric hindrance promoted between the bpy planes within the dimeric unit, and is comparable to those reported for α-pyridonate-bridged *cis*-diammineplatinum(III) dimers {Pt^{III}–Pt^{III} = 2.5401 (5) Å for HH-[Pt$_2^{III}$(NH$_3$)$_4$-(μ-C$_5$H$_4$NO)$_2$(H$_2$O)(NO$_3$)](NO$_3$)$_3$·2H$_2$O and Pt^{III}—Pt^{III} = 2.5468 (8) Å for HT-[Pt$_2^{III}$(NH$_3$)$_4$(μ-C$_5$H$_4$NO)$_2$(NO$_3$)$_2$]-(NO$_3$)$_2$·0.5H$_2$O (Hollis & Lippard, 1983)}. On the other hand, the Pt^{III}—Pt^{III} distance in (I) is $\sim$0.1 Å shorter than those reported for α-pyrrolidinonate-bridged *cis*-diammineplatinum(III) dimers {Pt^{III}—Pt^{III} = 2.644 (1) Å for HH-[Pt$_2^{III}$(NH$_3$)$_4$(μ-C$_4$H$_6$NO)$_2$(NO$_2$)(NO$_3$)](NO$_3$)$_2$·H$_2$O (Abe *et al.*, 1991), Pt^{III}—Pt^{III} = 2.6366 (7) Å for HH-[Pt$_2^{III}$(NH$_3$)$_4$(μ-C$_4$H$_6$NO)$_2$(Cl)$_2$](NO$_3$)$_2$ (Sakai *et al.*, 1998) and Pt^{III}—Pt^{III} = 2.6239 (9) Å for HH-[Pt$_2^{III}$(NH$_3$)$_4$(μ-C$_4$H$_6$NO)$_2$(Cl)(NO$_3$)]-(NO$_3$)$_2$·H$_2$O (Sakai *et al.*, 1998); see also Sakai, Sakamoto *et al.* (2003) and Sakai *et al.* (2004)}. Thus, a relatively short and strong Pt^{III}—Pt^{III} bond is achieved in (I). As shown in Fig. 2 and Table 2, there are some short intramolecular bpy–bpy contacts, namely N3···N2^{i}, N3···C6^{i} and C15···C6^{i}.

The mean-plane calculations performed for the four-coordinated atoms (N1, N2, N3 and O1^{i}) reveal that the Pt coordination plane is slightly deformed but is roughly planar, the four-atom r.m.s. deviation being 0.029 Å. Atom Pt1 is displaced from the mean plane defined by atoms N1, N2, N3 and O1^{i} by 0.024 (3) Å towards atom Pt1^{i} within the unit. The dihedral angle (τ) between the two Pt coordination planes within the dimeric unit and their mean torsional twist (ω) about the Pt—Pt axis are 17.1 (3) and 16.8 (4)°, respectively (see Fig. 2; see also torsion angles in Table 1). The dihedral angle between the two bpy planes within the dimeric unit is 16.3 (2)°. Thus, the bpy plane is nearly coplanar with the Pt coordination plane [they are inclined by 2.7 (3)° to one another].

The axial Pt^{III}—$O_{sulfate}$ distance [2.144 (7) Å] is comparable to those reported for α-pyridonate-bridged *cis*-diammineplatinum(III) dimers {Pt^{III}—O(axial H$_2$O) = 2.122 (6) Å and Pt^{III}—O(axial NO$_3^{-}$) = 2.193 (7) Å for HH-[Pt$_2^{III}$(NH$_3$)$_4$-(μ-C$_5$H$_4$NO)$_2$(H$_2$O)(NO$_3$)](NO$_3$)$_3$·2H$_2$O, and Pt^{III}–O(axial NO$_3^{-}$) = 2.17 (1) Å for HT-[Pt$_2^{III}$(NH$_3$)$_4$(μ-C$_5$H$_4$NO)$_2$-(NO$_3$)$_2$](NO$_3$)$_2$·0.5H$_2$O (Hollis & Lippard, 1983)}.

As shown in Fig. 3, the crystal packing is partly stabilized by relatively weak hydrophobic interactions between the tertiary butyl moieties and the bpy units, where the shortest intermolecular bpy···bpy separation is 3.69 (1) Å. The dimer–dimer interactions along the *c* axis are also stabilized by $O_{sulfate}$···O_{water}···O_{water}···$O_{sulfate}$ hydrogen bonds [*i.e.* O5···O7···O6^{ii}···O3^{ii}, where O5···O7 = 2.750 (12) Å, O7···O6^{ii} = 2.784 (14) Å and O6^{ii}···O3^{ii} = 2.864 (13) Å; symmetry code: (ii) $x, 2 - y, z - \frac{1}{2}$; see also Table 2]. The dimer is also connected to a neighboring dimer *via* an inversion center by forming $O_{sulfate}$···O_{water}···$O_{sulfate}$ hydrogen bonds [*i.e.* O5···O7···O4($\frac{1}{2} - x, \frac{5}{2} - y, 2 - z$); O7···O4($\frac{1}{2} - x, \frac{5}{2} - y, 2 - z$) = 2.828 (12) Å; see also Table 2].
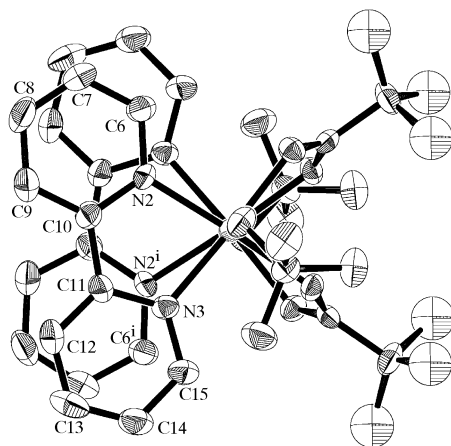

Figure 2
The structure of (I), viewed along the Pt1—Pt1^{i} vector. H atoms and water molecules have been omitted for clarity; only one orientation is shown for the disordered *tert*-butyl groups. [Symmetry code: (i) $-x, y, \frac{3}{2} - z$.]
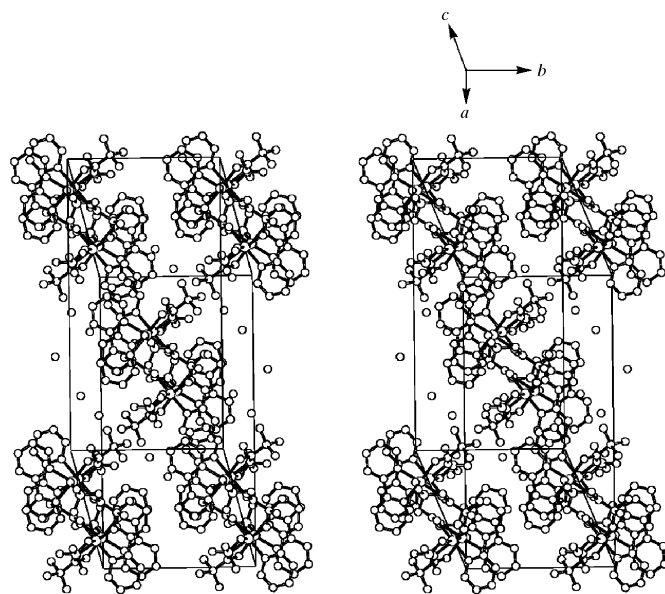

Figure 3
A stereoview of the crystal packing of (I). Non-H atoms have been drawn as ideal spheres, and H atoms and hydrogen bonds have been omitted; only one orientation is shown for the disordered *tert*-butyl groups.

Experimental

For the synthesis of (II), a suspension of PtCl$_2$(bpy) (1 mmol, 0.42 g; Morgen & Burstall, 1934), AgNO$_3$ (2 mmol, 0.34 g) and pivalamide (1.5 mmol, 0.15 g) in water (7 ml) was refluxed for 3 h in the dark, during which time the color of the solution turned deep red. The solution was then filtered while it was hot in order to remove the precipitated AgCl. Leaving the filtrate at room temperature overnight afforded (II) as deep-red block-like crystals, which were collected by filtration and air-dried (yield 65%). Complex (II) was purified by recrystallization from hot water [compound (II) (0.1 g) was dissolved in $\sim$1 ml of water; $\sim$80% of the product was recollected]. Analysis calculated for C$_{30}$H$_{46}$N$_8$O$_{13}$Pt$_2$: C 32.26, H 4.15, N 10.03%; found: C 32.30, H 3.91, N 9.99%. IR (KBr, cm^{-1}): 3421 (*w*, br), 2360 (*m*), 2341 (*w*), 1607 (*w*), 1560 (*m*), 1489 (*w*), 1454 (*w*), 1384 (*s*), 1188 (*w*), 1029 (*w*, br), 769 (*m*), 722 (*m*), 650 (*m*, br), 419 (*w*). UV–

Vis (in H_2O, 293 K): λ_{max} = 306 nm (ε = 20400 M^{-1} cm^{-1}), λ_{max} = 361 nm (ε = 2080 M^{-1} cm^{-1}), λ_{max} = 475 nm (ε = 2110 M^{-1} cm^{-1}). ^{195}Pt NMR (D_2O, 296 K, referenced to -1624 p.p.m. of K_2PtCl_4): -2064 p.p.m. (singlet characteristic of HT). Complex (II) was confirmed to be a head-to-tail isomer, part of which was reported by Sakai, Takeshita & Tsubomura (1993). For the synthesis of (I), a solution of (II) (0.25 mmol, 0.28 g) and $K_2S_2O_8$ (0.3 mmol, 0.08 g) in water (15 ml) was stirred at room temperature for 15 min. The solution was filtered to remove impurities and then evaporated to dryness. The yellow powder deposited was redissolved in a minimum amount of water ($\sim$3 ml). Leaving the solution to stand in air at room temperature for a few days afforded (I) as yellow prisms, which were collected by filtration and air-dried by suction (yield 68%). Analysis calculated for $C_{30}H_{44}N_6O_{14}Pt_2S_2$: C 30.88, H 3.80, N 7.20%; found: C 30.82, H 3.10, N 7.09%. IR (KBr, cm^{-1}): 3440 (m, br), 3077 (w, br), 2962 (w), 1606 (m), 1581 (m), 1503 (w), 1454 (m), 1426 (w), 1370 (w), 1313 (w), 1253 (w), 1182 (s), 1117 (vs), 1076 (w), 1051 (w), 1012 (vs), 917 (m), 873 (s), 777 (m), 614 (m), 587 (w). The crystals were stable in air at room temperature. A diffraction-quality single crystal was mounted on a glass fiber and used in the data collection.

Crystal data

$[Pt_2(C_5H_{10}NO)_2(SO_4)_2(C_{10}H_8N_2)_2]\cdot 4H_2O$	$D_x = 2.085$ Mg m^{-3}
$M_r = 1167.01$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 7382
$a = 22.535$ (2) Å	reflections
$b = 11.9796$ (12) Å	$\theta = 2.5$–$27.5°$
$c = 16.4774$ (17) Å	$\mu = 7.70$ mm^{-1}
$\beta = 123.285$ (2)°	$T = 296$ (2) K
$V = 3718.5$ (6) Å^3	Prism, yellow
$Z = 4$	$0.18 \times 0.11 \times 0.08$ mm

Data collection

Bruker SMART APEX CCD-detector diffractometer	4288 independent reflections
ω scans	3218 reflections with $I > 2\sigma(I)$
Absorption correction: Gaussian	$R_{int} = 0.145$
(XPREP in SAINT; Bruker, 2001)	$\theta_{max} = 27.5°$
	$h = -29 \rightarrow 29$
$T_{min} = 0.147$, $T_{max} = 0.623$	$k = -15 \rightarrow 15$
20 489 measured reflections	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.128$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.10$	$\Delta\rho_{max} = 2.78$ e Å^{-3}
4288 reflections	$\Delta\rho_{min} = -1.61$ e Å^{-3}
238 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.00183 (14)

Table 1
Selected geometric parameters (Å, °).

Pt1—O1^i	2.004 (6)	Pt1—Pt1^i	2.5664 (6)
Pt1—O2	2.144 (7)	O1—C1	1.282 (10)
Pt1—N1	1.993 (7)	N1—C1	1.302 (11)
Pt1—N2	2.027 (7)	C1—C2	1.492 (12)
Pt1—N3	2.015 (7)		
N1—Pt1—N3	96.1 (3)	O1^i—Pt1—N3	175.7 (2)
N1—Pt1—N2	176.8 (3)	O1^i—Pt1—N2	96.3 (3)
N3—Pt1—N2	80.7 (3)	O1^i—Pt1—O2	86.7 (2)
N1—Pt1—O2	94.8 (3)	O1—C1—N1	121.9 (8)
N3—Pt1—O2	90.0 (3)	O1—C1—C2	116.6 (8)
N2—Pt1—O2	85.7 (3)	N1—C1—C2	121.5 (8)
N1—Pt1—O1^i	86.9 (3)		
N1—Pt1—Pt1^i—O1	16.5 (3)	N3—Pt1—Pt1^i—N2^i	17.0 (3)

Symmetry code: (i) $-x, y, \frac{3}{2} - z$.

Table 2
Short intramolecular contacts (Å).

O3···O6	2.864 (13)	C15···C6^i	3.228 (13)
O5···O7	2.750 (12)	N2···C5B^{iv}	3.59 (3)
O7···O4^{ii}	2.828 (12)	C6···C5B^{iv}	3.60 (4)
O7···O6^{iii}	2.784 (14)	C7···C5B^{iv}	3.64 (4)
N3···N2^i	3.125 (12)	C8···C5B^{iv}	3.64 (4)
N3···C6^i	3.221 (12)	C9···C5B^{iv}	3.58 (3)
C10···C10^i	3.515 (18)	C10···C5B^{iv}	3.549 (18)
C11···N2^i	3.411 (12)	C7···C3A^{iv}	3.62 (2)
C11···C10^i	3.595 (13)	C8···C3A^{iv}	3.66 (2)
C13···C7^i	3.636 (16)	C14···C12^v	3.741 (15)
C14···C6^i	3.605 (14)		

Symmetry codes: (i) $-x, y, \frac{3}{2} - z$; (ii) $\frac{1}{2} - x, \frac{5}{2} - y, 2 - z$; (iii) $x, 2 - y, z - \frac{1}{2}$; (iv) $x, 2 - y, \frac{1}{2} + z$; (v) $\frac{1}{2} - x, \frac{3}{2} - y, 2 - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O4	0.86	2.01	2.757 (10)	144

As recently reported for several different dimers doubly bridged by chain amidate ligands (Sakai, Kurashima et al., 2003; Sakai, Ikuta et al., 2003; Sakai, Shiomi et al., 2003), it is often possible to determine the binding direction of the O- and N-donors of each amidate on the basis of the results of least-squares calculations performed for two possible directions. Moreover, when the U_{eq} values of Pt atoms are reasonably small, a disorder model based on the mixing of HH and HT isomers is not favored, since the intradimer Pt—Pt distances of the HH and HT isomers are, in general, markedly different from one another (Sakai et al., 1998). In (I), atom Pt1 has a reasonably small U_{eq} value [0.02294 (15) Å^2], indicating that the mixing of the HH and HT isomers is not likely to be promoted in this system. The locations of atoms O1 and N1 have been determined rationally from the comparison of two sets of U_{eq} values, viz. U_{eq}(O1) = 0.0277 (12) Å^2 and U_{eq}(N1) = 0.0273 (15) Å^2, and U_{eq}(N instead of O1) = 0.0152 (12) Å^2 and U_{eq}(O instead of N1) = 0.0448 (18) Å^2. The former set, corresponding to the reported combination, clearly shows a good balance and was therefore adopted as a reasonable set. As a result, the H atom on atom N1 was located at an idealized position as a riding atom, as mentioned below. The tertiary butyl group shows orientational disorder in which two sets of positions (C3A/C4A/C5A and C3B/C4B/C5B) are located around atom C2. The disordered C atoms were assumed to have the same isotropic displacement parameter. Furthermore, all six $C_{tertiary}$—C_{methyl} distances within each site were restrained to be equal, as were the three C_{methyl}—C_{methyl} distances. The occupation factors of sites A and B converged at 70.7 (15) and 29.3 (15)%, respectively. All H atoms, except for those of water molecules, were located at their idealized positions as riding atoms [C—H = 0.93 Å (for aromatic H atoms), C—H = 0.96 Å (for methyl H atoms) and N—H = 0.86 Å] and included in the refinement in the riding-motion approximation [with U_{iso}(H) = 1.2U_{eq}(carrier atom)]. Water H atoms were not located. In the final difference Fourier synthesis, 32 residual peaks in the range 1.02–2.78 e Å^{-3} were observed, not only within 1.4 Å of atom Pt1 but also near atoms O2, O3, O4, O5, O6, O7, C2, C11 and C13. The deepest hole was located 0.54 Å from atom Pt1.

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

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