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Di- μ - α -pyrrolidinonato-bis[*cis*-diammine-chloroplatinum(III)] sulfate dihydrate: a head-to-head isomer

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Key indicators

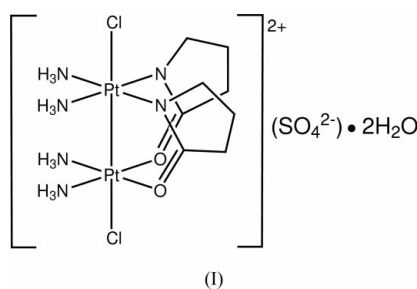
Single-crystal X-ray study
T = 296 K
Mean σ (C–C) = 0.035 Å
H-atom completeness 86%
Disorder in solvent or counterion
R factor = 0.059
wR factor = 0.153
Data-to-parameter ratio = 16.8

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

In the title compound, $[\text{Pt}^{\text{III}}_2\text{Cl}_2(\text{C}_4\text{H}_6\text{NO})_2(\text{NH}_3)_4](\text{SO}_4) \cdot 2\text{H}_2\text{O}$, the intradimer $\text{Pt}^{\text{III}}-\text{Pt}^{\text{III}}$ distance is 2.6235 (13) Å. The axial $\text{Pt}^{\text{III}}-\text{Cl}$ bond distances for the N_4 and N_2O_2 coordinated sites are 2.410 (5) and 2.446 (5) Å, respectively. The two Pt coordination planes are inclined at 16.3 (6)° and the average torsional twist of the ligands about the Pt–Pt axis is estimated as 0.4°.

Comment

We have been interested in the axial ligand substitution equilibria of *cis*-diammineplatinum(III) dimers doubly bridged by amidate ligands, having a general composition $[\text{Pt}^{\text{III}}_2(\text{NH}_3)_4(\mu\text{-amidato})_2L_2]^{4+}$ (L is an axial ligand, such as OH_2 , OH^- , NO_3^- , NO_2^- , Cl^- , Br^- etc.; amidate = α -pyrrolidinonate, acetamidate etc.; the complex charge varies as the axial ligands vary) (Sakai *et al.*, 1993, 1995, 1998; Sakai, 1993; Matsumoto & Sakai, 1999). These dimeric compounds have a d^7-d^7 configuration and therefore possess a single $\text{Pt}^{\text{III}}-\text{Pt}^{\text{III}}$ bond within the dimeric core. Another important feature is that they are usually axially ligated with two extra donor ligands at both ends of the unit, though there is an exception in which one of the two axial sites is not occupied by any extra donor, $[\text{Pt}^{\text{III}}_2(\text{NH}_3)_4(\mu\text{-1-methyluracilato})_2(\text{NO}_2)](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (Lippert *et al.*, 1986). In addition, two geometrical isomers, head-to-head (HH) and head-to-tail (HT), are possible due to the asymmetric character of amidate ligands.



The compound reported here, (I), is an HH isomer, which is obviously due to the HH isomerism established in the starting tetranuclear complex (a dimer of HH dimers; see *Experimental*). This compound was obtained accidentally as a by-product during our recent study of a reaction between the HH- Pt^{III}_2 dimer and the $[\text{PtCl}_4]^{2-}$ anion. In the study, an acidic aqueous solution of the diaqua-coordinated HH- Pt^{III}_2 dimer was titrated with a solution of K_2PtCl_4 . Our analysis of the spectroscopic changes induced by the titration suggested that a 3:1, a 2:1, and a 1:1 adduct of the HH- Pt^{III}_2 dimer and $[\text{PtCl}_4]^{2-}$ are formed in solution. Efforts to isolate such high-

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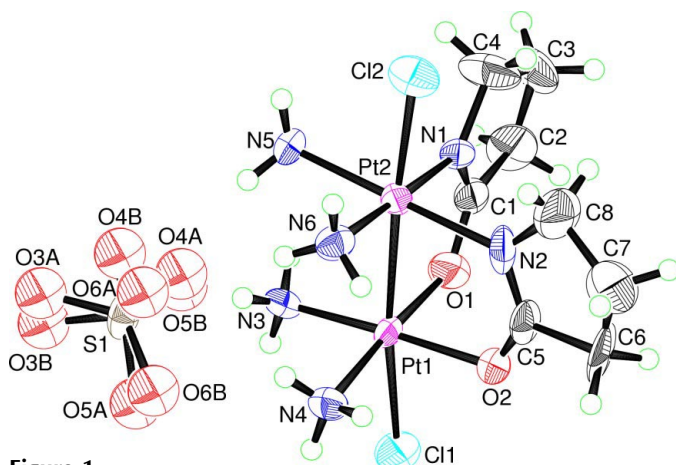


Figure 1
The structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level.

nuclearity adducts have been unsuccessful thus far. We report here the crystal structure for a sulfate salt of a dichloro-coordinated α -pyrrolidinonate-bridged *cis*-diammineplatinum(III) dimer, $\text{HH}[\text{Pt}^{\text{III}}_2(\text{NH}_3)_4(\mu\text{-}\alpha\text{-pyrrolidinonato})_2\text{Cl}_2](\text{SO}_4)\cdot 2\text{H}_2\text{O}$, (I). We previously reported the crystal structure of a nitrate salt of the same diplatinum(III) cation, *viz.* $\text{HH}[\text{Pt}^{\text{III}}_2(\text{NH}_3)_4(\mu\text{-}\alpha\text{-pyrrolidinonato})_2\text{Cl}_2](\text{NO}_3)_2$ [(II); Sakai *et al.*, 1998]. Very recently, we have also reported the crystal structure of a bromo derivative of (II), *viz.* $\text{HH}[\text{Pt}^{\text{III}}_2(\text{NH}_3)_4(\mu\text{-}\alpha\text{-pyrrolidinonato})_2\text{Br}_2](\text{NO}_3)_2$ [(III); Sakai *et al.*, 2003].

The asymmetric unit of (I) consists of a dichloro-capped diplatinum(III) cation in a head-to-head arrangement (Fig. 1), a sulfate anion (Figs. 1 and 2), and two water molecules (Fig. 2). The counter-anion and the solvent molecules suffer from disorder phenomena (see *Experimental*). The intradimer $\text{Pt}^{\text{III}}\text{—Pt}^{\text{III}}$ bond length [$\text{Pt1—Pt2} = 2.6235$ (13) Å] is almost the same as that reported for the nitrate salt of the same cation, (II) [$\text{Pt}^{\text{III}}\text{—Pt}^{\text{III}} = 2.6366$ (7) Å; Sakai *et al.*, 1998], but is significantly shorter than that recently reported for (III) [$\text{Pt}^{\text{III}}\text{—Pt}^{\text{III}} = 2.6476$ (4) Å; Sakai *et al.*, 2003]. The Pt—Cl bond length for the N_4 -coordinated Pt^{III} ion [$\text{Pt2—Cl2} = 2.410$ (5) Å] is slightly but significantly shorter than that for the N_2O_2 -coordinated Pt^{III} ion [$\text{Pt1—Cl1} = 2.446$ (5) Å]. A similar tendency was observed for (II) [$\text{Pt—Cl} = 2.395$ (3) Å at the $\text{N}_4\text{—Pt}^{\text{III}}$ ion; $\text{Pt—Cl} = 2.455$ (4) Å at the $\text{N}_2\text{O}_2\text{—Pt}^{\text{III}}$ ion; Sakai *et al.*, 1998]. On the other hand, such a tendency is rather ambiguous in the case of the bromo derivative (III), where the $\text{Pt}^{\text{III}}\text{—Br}$ distances at the $\text{N}_4\text{—Pt}^{\text{III}}$ and $\text{N}_2\text{O}_2\text{—Pt}^{\text{III}}$ ions were reported as 2.5647 (9) and 2.5889 (8) Å, respectively (Sakai *et al.*, 2003).

The structural features of this type of dimer have been evaluated by use of two structural parameters. One is the dihedral angle between the two Pt coordination planes within the dimeric unit (τ), and the other is an average torsional twist of the donor atoms in these coordination planes about the Pt—Pt axis (ω). The two parameters for (I) are estimated as $\tau = 16.3$ (6) $^\circ$ and $\omega = 0.4$ $^\circ$, which agree respectively with the values of $\tau = 18.9$ $^\circ$ and $\omega = 1.5$ $^\circ$ reported for (II) (Sakai *et al.*, 1998).

In addition, the values for (I) are also similar to the values of $\tau = 18.1$ (3) $^\circ$ and $\omega = 1.05$ $^\circ$ reported for (III) (Sakai *et al.*, 2003).

As previously reported for (II) and (III), the two Pt atoms are displaced from their individual Pt coordination planes in such a manner that they have an attractive interaction with one another. Atoms Pt1 and Pt2 are displaced from the individual mean planes defined by the coordinating atoms by 0.077 (6) and 0.018 (7) Å, where the four-atom r.m.s. deviations estimated in the mean-plane calculations are 0.008 and 0.002 Å, respectively.

The crystal packing is stabilized by an extensive three-dimensional hydrogen-bonding network (see Table 2), in which the hydrogen-bond donors are the amines and the water molecules, while the acceptors are the Cl and amidate, sulfate and water O atoms.

Experimental

Compound (I) was accidentally obtained during efforts to obtain some possible supramolecular adducts consisting of α -pyrrolidinonate-bridged $\text{HH-Pt}^{\text{III}}_2$ cations and $[\text{PtCl}_4]^{2-}$ anions as follows. The starting complex used in the synthesis was a mixed-valence tetranuclear platinum(2.5+) complex, *viz.* $[\text{HH-Pt}(2.5+)_2(\text{NH}_3)_4(\mu\text{-}\alpha\text{-pyrrolidinonato})_2]_2(\text{NO}_3)_6\cdot 2\text{H}_2\text{O}$ (formally considered as a $\text{Pt}^{\text{II}}_2\text{Pt}^{\text{III}}_2$ complex), prepared according to the literature method of Sakai *et al.* (1993). The tetranuclear $\text{Pt}^{\text{II}}_2\text{Pt}^{\text{III}}_2$ complex (20 mg) was dissolved in an aqueous 0.1 M H_2SO_4 solution (1 ml) containing $\text{K}_2\text{S}_2\text{O}_8$ (5 mg). The solution was then heated at 333 K for 15 min to give a clear yellow solution, during which time all the chemical species generated after dissolution of the starting complex were converted into the dinuclear Pt^{III}_2 complexes, as reported previously (Sakai *et al.*, 1998). After the solution had been cooled to room temperature, a solution of K_2PtCl_4 (1.25 mg) in water (0.1 ml) was added. Leaving the solution to stand at 278 K for 2 d resulted in the growth of orange plates (yield, 12.6 mg).

Crystal data

$[\text{Pt}_2\text{Cl}_2(\text{C}_4\text{H}_6\text{NO})_2(\text{NH}_3)_4](\text{SO}_4)\cdot 2\text{H}_2\text{O}$	$Z = 2$
$M_r = 829.50$	$D_x = 2.561 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$A = 8.906$ (4) Å	Cell parameters from 845 reflections
$B = 9.865$ (5) Å	$\theta = 2.3\text{--}27.2$ $^\circ$
$c = 13.619$ (7) Å	$\mu = 13.38 \text{ mm}^{-1}$
$\alpha = 88.908$ (9) $^\circ$	$T = 296$ (1) K
$\beta = 78.705$ (9) $^\circ$	Plate, orange
$\gamma = 66.753$ (9) $^\circ$	$0.21 \times 0.11 \times 0.02 \text{ mm}$
$V = 1075.7$ (9) Å 3	

Data collection

Bruker SMART APEX CCD-detector diffractometer	3904 independent reflections
ω scans	2753 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.058$
$T_{\text{min}} = 0.341$, $T_{\text{max}} = 0.818$	$\theta_{\text{max}} = 25.4$ $^\circ$
8204 measured reflections	$h = -10 \rightarrow 10$
	$k = -11 \rightarrow 11$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.059$	$w = 1/[\sigma^2(F_o^2) + (0.0927P)^2]$
$wR(F^2) = 0.153$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3904 reflections	$\Delta\rho_{\text{max}} = 5.39 \text{ e \AA}^{-3}$
233 parameters	$\Delta\rho_{\text{min}} = -1.90 \text{ e \AA}^{-3}$

Table 1
Selected geometric parameters (Å, °).

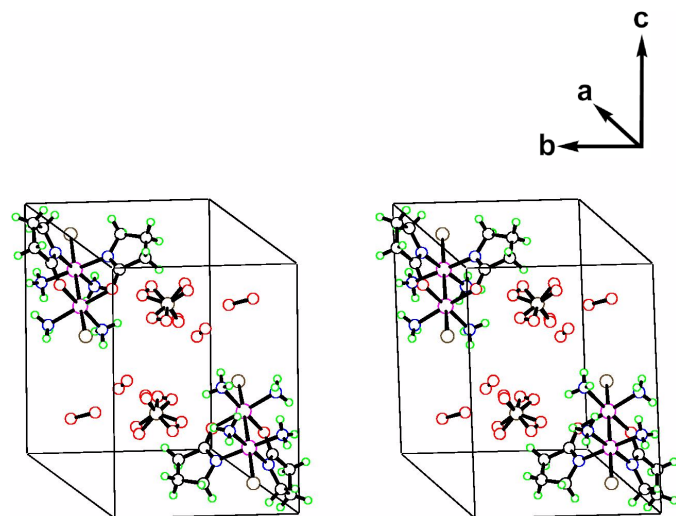
Pt1—O1	2.003 (12)	Pt2—N5	2.062 (11)
Pt1—O2	2.000 (11)	Pt2—N6	2.034 (13)
Pt2—N1	2.002 (14)	Pt1—Cl1	2.446 (5)
Pt2—N2	2.045 (12)	Pt2—Cl2	2.410 (5)
Pt1—N3	2.027 (12)	Pt1—Pt2	2.6235 (13)
Pt1—N4	2.049 (13)		
O2—Pt1—O1	90.6 (5)	N1—Pt2—N6	178.9 (5)
O2—Pt1—N3	176.0 (5)	N1—Pt2—N2	89.9 (5)
O1—Pt1—N3	88.4 (5)	N6—Pt2—N2	90.2 (5)
O2—Pt1—N4	88.3 (5)	N1—Pt2—N5	90.5 (5)
O1—Pt1—N4	175.1 (5)	N6—Pt2—N5	89.4 (5)
N3—Pt1—N4	92.3 (5)	N2—Pt2—N5	179.1 (5)
O2—Pt1—Cl1	88.5 (4)	N1—Pt2—Cl2	93.1 (4)
O1—Pt1—Cl1	87.3 (4)	N6—Pt2—Cl2	85.7 (4)
N3—Pt1—Cl1	87.6 (4)	N2—Pt2—Cl2	93.1 (4)
N4—Pt1—Cl1	87.9 (4)	N5—Pt2—Cl2	86.0 (4)
O1—Pt1—Pt2—N1	−0.6 (5)	O2—Pt1—Pt2—N2	−0.3 (5)
N4—Pt1—Pt2—N6	−1.9 (5)	N3—Pt1—Pt2—N5	1.1 (5)

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—H3A...Cl1 ⁱ	0.89	2.58	3.233 (13)	131
N3—H3C...O4A	0.89	2.08	2.93 (2)	161
N3—H3C...O5B	0.89	1.95	2.82 (2)	163
N3—H3B...O3A ⁱⁱ	0.89	1.97	2.85 (3)	171
N3—H3B...O3B ⁱⁱ	0.89	2.34	3.20 (3)	163
N4—H4B...O4A	0.89	2.41	3.21 (3)	150
N4—H4B...O5A	0.89	2.53	3.25 (3)	139
N4—H4B...O5B	0.89	2.30	3.09 (3)	148
N4—H4B...O6B	0.89	2.47	3.24 (3)	145
N4—H4C...O4B ⁱⁱⁱ	0.89	2.59	3.44 (3)	159
N4—H4C...O6A ⁱⁱⁱ	0.89	1.88	2.75 (2)	165
N4—H4C...O6B ⁱⁱⁱ	0.89	2.52	3.26 (3)	141
N5—H5B...O4A	0.89	1.94	2.81 (2)	164
N5—H5B...O5B	0.89	2.07	2.93 (2)	160.9
N5—H5C...O3A ⁱⁱ	0.89	2.20	3.07 (3)	164
N5—H5C...O3B ⁱⁱ	0.89	1.97	2.85 (3)	171
N6—H6C...O4A	0.89	2.22	3.05 (3)	156
N6—H6C...O5B	0.89	2.32	3.15 (3)	155
N6—H6C...O6A	0.89	2.54	3.30 (3)	145
N6—H6B...O5A ⁱⁱⁱ	0.89	2.21	3.02 (2)	152
N6—H6B...O6B ⁱⁱⁱ	0.89	1.76	2.637 (16)	169
N3—H3B...O3A ⁱⁱ	0.89	1.97	2.85 (3)	171
N3—H3B...O3B ⁱⁱ	0.89	2.34	3.20 (3)	163
N5—H5C...O3B ⁱⁱ	0.89	1.97	2.85 (3)	171
N5—H5C...O3B ⁱⁱ	0.89	1.97	2.85 (3)	171
N4—H4C...O6A ⁱⁱⁱ	0.89	1.88	2.75 (2)	165
N6—H6B...O5A ⁱⁱⁱ	0.89	2.21	3.02 (2)	152
N6—H6B...O6B ⁱⁱⁱ	0.89	1.76	2.637 (16)	169
N4—H4A...O7A ⁱ	0.89	2.29	3.06 (6)	145
N4—H4A...O7B ⁱ	0.89	2.48	3.25 (5)	146

Symmetry codes: (i) 1 − *x*, −*y*, 1 − *z*; (ii) −*x*, −*y*, 1 − *z*; (iii) −*x*, 1 − *y*, 1 − *z*.

The sulfate anion shows orientational disorder. Around atom S1 there are two sets of possible positions (O3A/O4A/O5A/O6A and O3B/O4B/O5B/O6B). It was assumed that the disordered O atoms have a common isotropic displacement parameter. Furthermore, S—O distances were restrained to 1.46 (1) Å and the six O...O distances were restrained to be approximately equal. The occupation factors of sites *A* and *B* were fixed at 0.5. Two water molecules were respectively assumed to be disordered over two sites (O7A/O7B and O8A/O8B). In each case, the occupation factors of sites *A* and *B* were

**Figure 2**
Stereoview of the crystal packing of (I). Atoms are drawn as spheres for clarity.

assumed to be 0.5, and the isotropic displacement parameters of sites *A* and *B* were assumed to be equal. All H atoms, except those of the water molecules, were placed at idealized positions [C—H(methylene) = 0.97 Å and N—H(ammine) = 0.89 Å], and included in the refinement as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(N)$. The water H atoms were not located. In the final difference Fourier synthesis, six residual peaks in the range 2.36–5.39 e Å^{−3} were observed within 1.08 Å of Pt atoms, and 17 other peaks in the range 1.05–1.49 e Å^{−3} were also observed around the Pt, Cl and sulfate O atoms. The deepest hole was located 0.12 Å from atom O4B.

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* and *ORTEPII* (Johnson, 1976).

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