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Di- μ - α -pyrrolidinonato-bis[*cis*-diammineplatinum(II)] sulfate monohydrate as a head-to-head isomer

Ken Sakai, Itsuki Sakai, Neil D. Draper and Daniel B. Leznoff

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Di- μ - α -pyrrolidinonato-bis[*cis*-diammine-platinum(II)] sulfate monohydrate as a head-to-head isomerKen Sakai,^{a*} Itsuki Sakai,^a
Neil D. Draper^b and
Daniel B. Leznoff^b^aDepartment of Applied Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan, and ^bDepartment of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC, Canada V5A 1S6Correspondence e-mail:
ksakai@rs.kagu.tus.ac.jp

Key indicators

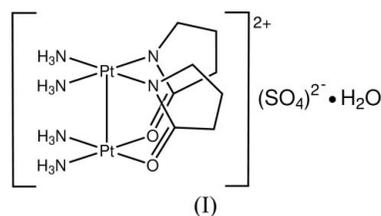
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.028\text{ \AA}$
H-atom completeness 93%
 R factor = 0.054
 wR factor = 0.126
Data-to-parameter ratio = 13.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $[\text{Pt}_2^{\text{II}}(\text{C}_4\text{H}_6\text{NO})_2(\text{NH}_3)_4](\text{SO}_4)\cdot\text{H}_2\text{O}$, the intradimer $\text{Pt}^{\text{II}}-\text{Pt}^{\text{II}}$ distance is 2.9749 (11) Å, which is clearly shorter than the value of 3.029 (2) Å reported for a different salt of the same cation, *viz.* $[\text{Pt}_2^{\text{II}}(\text{C}_4\text{H}_6\text{NO})_2(\text{NH}_3)_4]_2(\text{PF}_6)_3\cdot(\text{NO}_3)\cdot\text{H}_2\text{O}$ [Matsumoto *et al.* (1989). *Inorg. Chem.* **28**, 2959–2964]. The two Pt coordination planes are inclined to each other by 29.9 (5)°, and the average torsional twist of the ligands about the Pt–Pt axis is estimated as 4.3 (8)°.

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Comment

Dinuclear metal complexes having a d^7-d^7 configuration usually possess a single metal–metal bond within the dimeric core, and are often ligated by two extra donor ligands, one at each end of the units. We have been interested in the axial ligand substitution equilibria of some such complexes over the past decade. Up to now, a large variety of inorganic materials have been employed to test their axial ligation properties with the *cis*-diammineplatinum(III) dimers doubly bridged by amidate ligands, $[\text{Pt}_2^{\text{III}}(\text{NH}_3)_4(\mu\text{-amidato})_2L_2]^{4+}$ (L is an axial ligand, such as OH_2 , OH^- , NO_3^- , NO_2^- , SO_4^{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). It must be noted here that two geometrical isomers, head-to-head (HH) and head-to-tail (HT), are possible for this class of dimers because of the asymmetric character of amidate ligands.



The title compound, (I), exhibits HH isomerism, as a result of the same isomerism in the starting tetranuclear complex (a dimer of HH dimers) (see *Experimental*). The title compound was accidentally obtained during our recent efforts to obtain heterometallic coordination polymers involving the $[\text{Au}^{\text{I}}(\text{CN})_2]^-$ anion (Leznoff *et al.*, 2001). In the study, an acidic aqueous solution of the diaqua-coordinated HH- Pt_2^{III} dimer was titrated with a solution of $\text{K}[\text{Au}^{\text{I}}(\text{CN})_2]$. Our analysis of the spectroscopic changes induced by the titration suggested that a 2:1, a 1:1 and a 1:2 adduct of the HH- Pt_2^{III} dimer and the $[\text{Au}^{\text{I}}(\text{CN})_2]^-$ anion are formed in aqueous media. During efforts to isolate and crystallize such adducts, the title HH- Pt_2^{II} dimer was obtained as a by-product having a d^8-d^8 config-

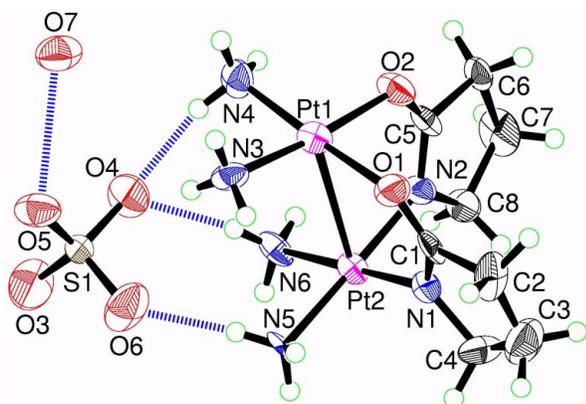


Figure 1
The structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level. Dashed lines denote hydrogen bonds.

uration, presumably due to the reduction of the $\text{HH-Pt}_2^{\text{III}}$ dimer by dimethylformamide used in the synthesis (see *Experimental*). We previously reported that the same Pt_2^{III} dimer is readily reduced to the Pt_2^{II} dimer upon addition of hydroquinone (Sakai *et al.*, 1993). We report here the crystal structure of a sulfate salt of an α -pyrrolidinonate-bridged *cis*-diammineplatinum(II) dimer, $\text{HH}[\text{Pt}_2^{\text{II}}(\text{NH}_3)_4(\mu\text{-}\alpha\text{-pyrrolidinonato})_2](\text{SO}_4)\cdot\text{H}_2\text{O}$, (I). This is the third example of a crystal structure of an α -pyrrolidinonate-bridged *cis*-diammineplatinum(II) dimer: the first was determined for a tetranuclear HH derivative, $\text{HH}[\text{Pt}_2^{\text{II}}(\text{NH}_3)_4(\mu\text{-}\alpha\text{-pyrrolidinonato})_2](\text{PF}_6)_3\cdot(\text{NO}_3)\cdot\text{H}_2\text{O}$ [(II); Matsumoto *et al.*, 1989]; the second was determined for an HT dimer, $\text{HT}[\text{Pt}_2^{\text{II}}(\text{NH}_3)_4(\mu\text{-}\alpha\text{-pyrrolidinonato})_2](\text{ClO}_4)_2$ (Sakai *et al.*, 1998).

The asymmetric unit of (I) consists of a diplatinum(II) cation, a sulfate anion, and a water molecule (Fig. 1). The intradimer $\text{Pt}^{\text{II}}\text{—Pt}^{\text{II}}$ distance [$\text{Pt1—Pt2} = 2.9749(11)\text{ \AA}$] is 0.054 \AA shorter than the value reported for (II) [$\text{Pt}^{\text{II}}\text{—Pt}^{\text{II}}$ (intradimer) = $3.029(2)\text{ \AA}$; Matsumoto *et al.*, 1989]. The considerable difference in the Pt—Pt (intradimer) distance observed between (I) and (II) clearly indicates that the dianionic sulfate has a great contribution to the fastener effect, resulting in the closer contact between the two Pt coordination planes within the dimeric unit. A similar tendency was recently observed for the pivalate-bridged *cis*-diammineplatinum(II) dimers obtained in two different salts: Pt—Pt (intradimer) = $2.9011(9)\text{ \AA}$ for $[\text{Pt}_2^{\text{II}}(\text{NH}_3)_4(\mu\text{-pivalato})_2](\text{SO}_4)\cdot\text{H}_2\text{O}$ (Sakai *et al.*, 2003a) and Pt—Pt (intradimer) = $3.0928(9)\text{ \AA}$ for $[\text{Pt}_2^{\text{II}}(\text{NH}_3)_4(\mu\text{-pivalato})_2](\text{ClO}_4)_2\cdot\text{C}_5\text{H}_{10}\text{O}_2$ (Sakai *et al.*, 2003b). The sulfate anion is hydrogen bonded to the equatorial ammine units [$\text{N4}\cdots\text{O4} = 3.00(2)\text{ \AA}$, $\text{N5}\cdots\text{O6} = 2.87(2)\text{ \AA}$ and $\text{N6}\cdots\text{O4} = 3.02(2)\text{ \AA}$; see Fig. 1 and Table 2]. The electrostatic attractive interactions achieved between the dianionic sulfate and the dicationic Pt-dimer complex are likely to promote the fastener effect discussed above. Indeed, atom Pt2 has an unusual situation in which the atom is displaced from the mean plane defined by the four coordinated N atoms by $0.022(7)\text{ \AA}$, in such a manner that it shows a shift toward the outside of the dimeric core. In other words, it

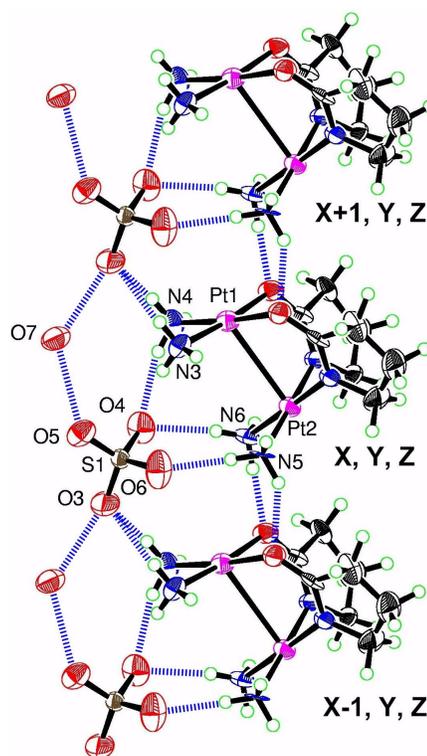


Figure 2
A view showing the manner in which the dimers stack along the *a* axis based on extensive hydrogen-bonding networks. Dashed lines denote hydrogen bonds.

can also be considered that the two ammines involving N5 and N6 are withdrawn by the sulfate anion in such a manner that they approach the ammines involving N3 and N4 (see Fig. 1). On the other hand, atom Pt1 is displaced from the mean plane defined by the four coordinated N atoms by $0.094(7)\text{ \AA}$, so that it approaches Pt2 within the dimeric unit, which is consistent with the general tendency observed thus far for many HH- and HT- Pt_2^{II} dimers of this class [see, for example, Sakai *et al.* (1998, 2003a) and Sakai & Takahashi (2003)].

In addition, the structural features of this class of dimers 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 coordinating atoms in these planes about the Pt—Pt axis (ω). The two parameters for (I) are estimated as $\tau = 29.9(5)^\circ$ and $\omega = 4.3(8)^\circ$, which compare respectively with the values of $\tau = 35.9^\circ$ and $\omega = 1.0^\circ$ reported for (II) [Matsumoto *et al.* (1989); see also Sakai *et al.* (1998), since the ω value for (II) was corrected in the latter paper]. The smaller τ value in (I) in comparison with that in (II) is directly coupled to the shorter Pt—Pt (intradimer) distance in (I) in comparison with that in (II).

As shown in Fig. 2, the dimeric cations stack along the *a* axis *via* extensive hydrogen-bonding motifs (see Table 2), giving rise to one-dimensional chains in the crystal structure. The dimer-dimer Pt—Pt distance [$\text{Pt1}\cdots\text{Pt1}(1+x, y, z) = 4.7921(16)\text{ \AA}$] is so long that no metal-metal interaction is achieved between the dimers.

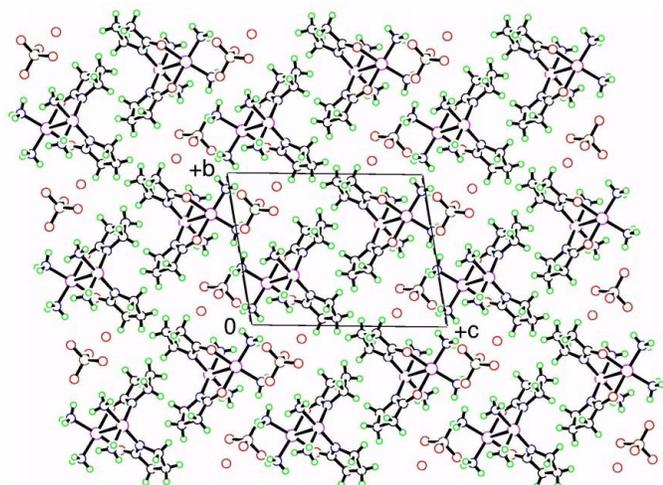


Figure 3
The crystal packing of (I), viewed along the *a* axis, with atoms drawn as spheres for clarity.

As shown in Fig. 3, the crystal packing is stabilized both by the hydrophobic interactions around the plane defined by $z = 0.5$ and by the hydrophilic interactions achieved around the plane defined by $z = 0$. Relevant hydrogen-bond distances are summarized in Table 2.

Experimental

A mixed-valence tetranuclear platinum(2.5+) complex, $[\text{HH-Pt}(2.5+)_2(\text{NH}_3)_4(\mu\text{-}\alpha\text{-pyrrolidinonato})_2]_2(\text{NO}_3)_6 \cdot 2\text{H}_2\text{O}$ (formally considered as a $\text{Pt}^{\text{II}}\text{Pt}^{\text{III}}$ complex), was prepared according to the literature method of Sakai *et al.* (1993). To a solution of $\text{K}_2\text{S}_2\text{O}_8$ (0.019 mmol, 5 mg) in water (0.5 ml) was added the tetranuclear $\text{Pt}^{\text{II}}\text{Pt}^{\text{III}}$ complex (0.012 mmol, 20 mg). The solution was then heated at 333 K for 15 min, giving a clear yellow solution, during which time all the chemical species generated after dissolution of the starting complex were converted into the dinuclear Pt_2^{III} complexes, as previously described (Sakai *et al.*, 1998). To dimethylformamide (20 ml) was added the former solution and a solution of $\text{K}[\text{Au}^{\text{I}}(\text{CN})_2]$ (0.05 mmol, 14.4 mg) in water (5 ml). The resulting yellow solution was left at room temperature for two weeks, giving a pink filtrate and (I) as colorless needles. The compound is quite stable in air at room temperature for at least a year.

Crystal data

$[\text{Pt}_2(\text{C}_4\text{H}_6\text{NO})_2(\text{NH}_3)_4](\text{SO}_4) \cdot \text{H}_2\text{O}$	$Z = 2$
$M_r = 740.59$	$D_x = 2.777 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 6.859(2) \text{ \AA}$	Cell parameters from 1567 reflections
$b = 10.229(2) \text{ \AA}$	$\theta = 5.1\text{--}68.2^\circ$
$c = 12.896(2) \text{ \AA}$	$\mu = 30.63 \text{ mm}^{-1}$
$\alpha = 99.569(10)^\circ$	$T = 293(2) \text{ K}$
$\beta = 93.538(10)^\circ$	Needle, colorless
$\gamma = 95.146(10)^\circ$	$0.13 \times 0.05 \times 0.03 \text{ mm}$
$V = 885.8(3) \text{ \AA}^3$	

Data collection

Rigaku R-Axis RAPID diffractometer	3014 independent reflections
ω scans	2176 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.072$
$T_{\text{min}} = 0.098$, $T_{\text{max}} = 0.465$	$\theta_{\text{max}} = 68.2^\circ$
10 099 measured reflections	$h = -7 \rightarrow 7$
	$k = -12 \rightarrow 12$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.054$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.127$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 2.52 \text{ e \AA}^{-3}$
3014 reflections	$\Delta\rho_{\text{min}} = -2.15 \text{ e \AA}^{-3}$
222 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.00037 (8)

Table 1
Selected geometric parameters (\AA , $^\circ$).

Pt1—N4	1.991 (14)	Pt2—N1	1.990 (14)
Pt1—O2	2.011 (11)	Pt2—N5	2.030 (11)
Pt1—N3	2.012 (12)	Pt2—N6	2.031 (14)
Pt1—O1	2.020 (12)	Pt1—Pt2	2.9749 (11)
Pt2—N2	1.978 (13)	Pt1—Pt2 ⁱ	4.7921 (16)
N4—Pt1—O2	89.7 (5)	N1—Pt2—N6	178.4 (5)
N4—Pt1—N3	87.3 (5)	N5—Pt2—N6	90.4 (5)
O2—Pt1—N3	174.4 (5)	N4—Pt1—Pt2	105.7 (4)
N4—Pt1—O1	174.0 (5)	O2—Pt1—Pt2	81.2 (3)
O2—Pt1—O1	91.5 (5)	N3—Pt1—Pt2	104.1 (4)
N3—Pt1—O1	91.0 (5)	O1—Pt1—Pt2	80.3 (4)
N2—Pt2—N1	91.0 (5)	N2—Pt2—Pt1	79.9 (4)
N2—Pt2—N5	178.8 (5)	N1—Pt2—Pt1	80.9 (4)
N1—Pt2—N5	88.7 (5)	N5—Pt2—Pt1	98.9 (4)
N2—Pt2—N6	89.8 (5)	N6—Pt2—Pt1	97.9 (4)
O2—Pt1—Pt2—N2	−3.5 (5)	N3—Pt1—Pt2—N5	−5.2 (6)
O1—Pt1—Pt2—N1	−3.9 (5)	N4—Pt1—Pt2—N6	−4.7 (5)

Symmetry code: (i) $1 + x, y, z$.

Table 2
Hydrogen-bonding and short-contact geometry (\AA , $^\circ$).

$D\text{---}H\text{---}A$	$D\text{---}H$	$H\text{---}A$	$D\text{---}A$	$D\text{---}H\text{---}A$
O5...O7			2.820 (18)	
O7...O3 ⁱ			2.888 (2)	
N4—H4B...O4	0.89	2.14	3.00 (2)	164
N5—H5C...O6	0.89	2.00	2.87 (2)	167
N6—H6A...O4	0.89	2.14	3.02 (2)	167
N3—H3B...O6 ⁱⁱ	0.89	1.97	2.798 (18)	154
N3—H3A...O3 ⁱ	0.89	2.32	3.08 (2)	143
N4—H4C...O4 ⁱⁱⁱ	0.89	2.03	2.829 (19)	149
N4—H4A...O3 ⁱ	0.89	2.44	3.18 (2)	141
N5—H5A...O5 ⁱⁱ	0.89	2.29	3.12 (2)	155
N5—H5A...O6 ⁱⁱ	0.89	2.50	3.23 (2)	140
N5—H5B...O1 ^{iv}	0.89	2.19	2.954 (17)	143
N6—H6C...O7 ⁱⁱⁱ	0.89	2.14	2.99 (2)	161
N6—H6B...O2 ^{iv}	0.89	2.05	2.862 (18)	151

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

All H atoms, except for those of the water molecules, were placed at idealized positions (methylene C—H = 0.97 \AA and ammine N—H = 0.89 \AA), and included in the refinement in a riding-model approximation, with U_{iso} (methylene H) = $1.2U_{\text{eq}}(\text{C})$ and U_{iso} (ammine H) = $1.5U_{\text{eq}}(\text{N})$. The water H atoms were not located. In the final difference Fourier synthesis, 16 residual peaks in the range 1.01–2.52 e \AA^{-3} were observed not only within 1.5 \AA of Pt atoms but also near atoms O1, N1, N3 and N6. The deepest hole was located 0.78 \AA from atom Pt1. The unusual shape of the displacement ellipsoid for atom N5 is likely due to the presence of relatively large residual electron-density peaks near atom Pt2 which is bound to N5.

Data collection: PROCESS-AUTO (Rigaku, 1998); cell refinement: PROCESS-AUTO; data reduction: PROCESS-AUTO; 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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References

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Leznoff, D. B., Xue, B.-Y., Batchelor, R. J., Einstein, F. W. B. & Patrick, B. O. (2001). *Inorg. Chem.* **40**, 6026–6034.
- Matsumoto, K., Miyamae, H. & Moriyama, H. (1989). *Inorg. Chem.* **28**, 2959–2964.
- Matsumoto, K. & Sakai, K. (1999). *Adv. Inorg. Chem.* **49**, 375–427.
- Molecular Structure Corporation (2001). *TEXSAN*, Version 1.11r1. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Sakai, K. (1993). PhD dissertation, Waseda University, Japan.
- Sakai, K. (2002). *KENX*. Graphical User Interface for *SHELXL97*. Tokyo University of Science, Japan.
- Sakai, K., Ishigami, E., Yokokawa, K., Kajiwara, T. & Ito, T. (2003a). *Acta Cryst. E59*, m443–m445.
- Sakai, K., Ishigami, E., Yokokawa, K., Kajiwara, T. & Ito, T. (2003b). *Acta Cryst. E59*, m1178–m1180.
- Sakai, K. & Takahashi, S. (2003). *Acta Cryst. E59*, m532–m535.
- Sakai, K., Tanaka, Y., Tsuchiya, Y., Hirata, K., Tsubomura, T., Iijima, S. & Bhattacharjee, A. (1998). *J. Am. Chem. Soc.* **120**, 8366–8379.
- Sakai, K., Tsubomura, T. & Matsumoto, K. (1993). *Inorg. Chim. Acta*, **213**, 11–16.
- Sakai, K., Tsubomura, T. & Matsumoto, K. (1995). *Inorg. Chim. Acta*, **234**, 157–161.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.