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Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(\text{C}-\text{C}) = 0.012 \text{ \AA}$
 Disorder in solvent or counterion
 R factor = 0.036
 wR factor = 0.092
 Data-to-parameter ratio = 24.9

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

A head-to-head isomer of di- μ - α -pyrrolidinonato-bis[*cis*-diammine-bromoplatinum(III)] dinitrate

In the title compound, $[\text{Pt}_2\text{Br}_2(\text{C}_4\text{H}_6\text{NO})_2(\text{NH}_3)_4](\text{NO}_3)_2$, the intradimer Pt—Pt distance is 2.6476 (4) Å. The axial Pt^{III}—Br bond distances at the N₄⁻ and N₂O₂-coordinated sites are 2.5647 (9) and 2.5889 (8) Å, respectively. The two Pt coordination planes are tilted by 18.1 (3)°, and the average torsional twist of the ligands about the Pt—Pt axis is estimated as 1.0°.

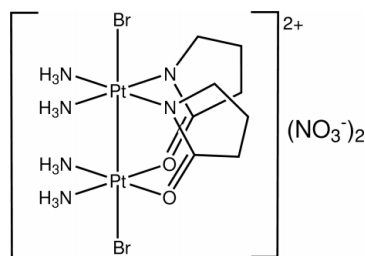
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Comment

Pt^{III} ions are generally obtained as a result of two-electron one-step oxidation of dinuclear Pt^{II} complexes. The electrochemistry of such Pt^{III} dimers was first investigated on the α -pyridonate-bridged *cis*-diammineplatinum(III) dimers, $[\text{Pt}^{\text{III}}_2(\text{NH}_3)_4(\mu\text{-}\alpha\text{-pyridonato})_2L_2]^{4+}$ (*L* is an axial ligand, such as OH₂, NO₃⁻, NO₂⁻, Cl⁻, Br⁻, etc.; Hollis & Lippard, 1983). It should be noted here that two geometrical isomers, head-to-head (HH) and head-to-tail (HT), are possible due to the asymmetric feature of the bridging amidate ligands (hereafter, HH and HT will be used as prefixes to distinguish these two isomers). Upon oxidation of Pt₂^{II} to Pt₂^{III}, a Pt—Pt single bond is formed between the two 5*d*⁷ centers and 0.3–0.4 Å of shortening in the Pt—Pt distance is induced. Moreover, the Pt₂^{III} cores generally accept two additional ligands at the axial sites. As far as the doubly bridged dimers mentioned above are concerned, around 21 crystal structures have been determined by X-ray diffraction (see, for example, Matsumoto & Sakai, 1999). Six of these compounds possess one or two halide ions at the axial sites, and α -pyridonate, α -pyrrolidinonate, and 1-methyluracilate are used as the bridging ligands. As for the α -pyrrolidinonate family investigated in this report, mono- and dichloro-coordinated HH dimers were previously reported by the authors (Sakai *et al.*, 1998). On the other hand, only one bromo compound, HT-[Pt^{III}₂(NH₃)₄(μ - α -pyridonato)₂Br₂]²⁺, has been reported up to now (Hollis *et al.*, 1983). Here we report the crystal structure of HH-[Pt^{III}₂(NH₃)₄(μ - α -pyrrolidinonato)₂Br₂](NO₃)₂, (I).



(I)

The crystal of (I) is isomorphous with the dichloro analog, HH-[Pt^{III}₂(NH₃)₄(μ - α -pyrrolidinonato)₂Cl₂](NO₃)₂ [(II);

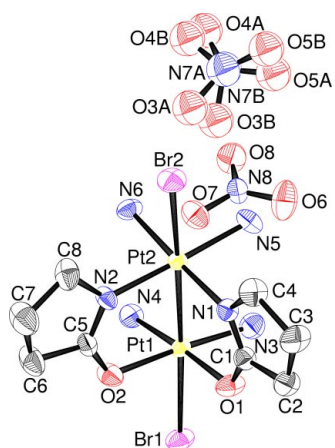


Figure 1
The structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Both components of the disordered nitrate anion are shown.

Sakai *et al.*, 1998]. The cell volume of (I) [$V = 1052.94(11) \text{ \AA}^3$] is larger than that reported for (II) [$V = 1026.8(4) \text{ \AA}^3$], reflecting a larger covalent radius of Br compared to that of Cl. The intradimer Pt—Pt distance [$2.6476(4) \text{ \AA}$] is *ca* 0.1 \AA longer than that reported for (II) [$2.6366(7) \text{ \AA}$]; this must be interpreted in terms of the difference between Cl and Br either in the *trans* influence or in the electronegativity. If the former is a predominant factor, the Pt—Pt bond distance is expected to be longer in the Cl system, for Cl has a stronger *trans* influence compared to Br; however, this is not the case. If the latter effect applies, the net charge (corresponding to the ‘net oxidation state’) in the Cl system is expected to be higher than that in the Br system. Since the Pt—Pt distance is shortened upon oxidation of Pt_2^{II} to Pt_2^{III} , the higher net oxidation state would cause shortening in the Pt—Pt distance. Thus the explanation seems to be valid. The Pt^{III}—Br distances in (I) (see Table 1) are quite comparable to those reported for $\text{HT}[\text{Pt}_2^{\text{III}}(\text{NH}_3)_4(\mu\text{-}\alpha\text{-pyridonato})_2\text{Br}_2]^{2+} [\text{Pt}^{\text{III}}\text{—Br} = 2.573(1)$ and $2.562(1) \text{ \AA}$; Hollis *et al.*, 1983].

On the other hand, structural features of this class of dimers have often been evaluated by use of the following two structural parameters. One is the dihedral angle between the two Pt coordination planes within a dimeric unit (τ), and the other is an average torsional twist of the ideally eclipsed ligands about the Pt—Pt axis (ω). The values for (I) are estimated as $\tau = 18.1(3)^\circ$ and $\omega = 1.0^\circ$, which are quite comparable to the values of $\tau = 18.9^\circ$ and $\omega = 1.5^\circ$ in (II). As reported thus far for related compounds, the two Pt atoms are shifted out of 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 coordinated atoms by $0.079(3)$ and $0.017(3) \text{ \AA}$, respectively. The crystal packing is stabilized with extensive hydrogen bonds formed between the amines and the oxygen atoms of nitrates/amidates and also between the amines and the Br atoms (see Table 2).

Experimental

The title compound was prepared in the same manner as reported for the dichloro-coordinated analog (II), $\text{HH}[\text{Pt}^{\text{III}}_2(\text{NH}_3)_4(\mu\text{-}\alpha\text{-pyrrolidinonato})_2\text{Cl}_2](\text{NO}_3)_2$ (Sakai *et al.*, 1998), except that HBr was used instead of HCl. The dimeric compound (0.024 mmol) was dissolved in an aqueous solution prepared by mixing 0.1 M HBr (0.5 ml) and concentrated HNO_3 (0.2 ml). The solution was left at 278 K for a few days to afford (I) as orange needles.

Crystal data

$[\text{Pt}_2\text{Br}_2(\text{C}_4\text{H}_6\text{NO})_2(\text{NH}_3)_4](\text{NO}_3)_2$	$Z = 2$
$M_r = 910.35$	$D_x = 2.871 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.0092(5) \text{ \AA}$	Cell parameters from 2413 reflections
$b = 10.1125(6) \text{ \AA}$	$\theta = 2.6\text{--}23.3^\circ$
$c = 12.0131(7) \text{ \AA}$	$\mu = 17.12 \text{ mm}^{-1}$
$\alpha = 80.164(1)^\circ$	$T = 293(2) \text{ K}$
$\beta = 78.041(1)^\circ$	Needle, orange
$\gamma = 84.540(1)^\circ$	$0.15 \times 0.07 \times 0.07 \text{ mm}$
$V = 1052.94(11) \text{ \AA}^3$	

Data collection

Bruker SMART APEX CCD-detector diffractometer	6122 independent reflections
ω scans	4127 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.036$
$T_{\text{min}} = 0.140$, $T_{\text{max}} = 0.302$	$\theta_{\text{max}} = 30.0^\circ$
13222 measured reflections	$h = -12 \rightarrow 12$
	$k = -14 \rightarrow 14$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2]$
$wR(F^2) = 0.092$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.95$	$(\Delta/\sigma)_{\text{max}} < 0.001$
6122 reflections	$\Delta\rho_{\text{max}} = 2.90 \text{ e \AA}^{-3}$
246 parameters	$\Delta\rho_{\text{min}} = -2.21 \text{ e \AA}^{-3}$

Table 1

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

Pt1—Pt2	2.6476 (4)	Pt1—N4	2.036 (5)
Pt1—Br1	2.5889 (8)	Pt2—N2	2.025 (6)
Pt2—Br2	2.5647 (9)	Pt2—N1	2.028 (5)
Pt1—O1	2.009 (5)	Pt2—N6	2.065 (5)
Pt1—O2	2.023 (5)	Pt2—N5	2.067 (6)
Pt1—N3	2.034 (6)		
O1—Pt1—O2	92.4 (2)	N2—Pt2—N6	88.9 (2)
O1—Pt1—N3	87.3 (2)	N1—Pt2—N6	177.7 (2)
O2—Pt1—N3	176.0 (2)	N2—Pt2—N5	178.3 (2)
O1—Pt1—N4	175.0 (2)	N1—Pt2—N5	87.6 (2)
O2—Pt1—N4	87.7 (2)	N6—Pt2—N5	90.2 (3)
N3—Pt1—N4	92.3 (3)	N2—Pt2—Br2	94.04 (17)
O1—Pt1—Br1	89.17 (15)	N1—Pt2—Br2	95.66 (17)
O2—Pt1—Br1	87.82 (14)	N6—Pt2—Br2	83.70 (17)
N3—Pt1—Br1	88.21 (19)	N5—Pt2—Br2	84.39 (18)
N4—Pt1—Br1	85.84 (17)	N2—Pt2—Pt1	83.33 (17)
N3—Pt1—Pt2	96.96 (18)	N1—Pt2—Pt1	83.15 (17)
N4—Pt1—Pt2	97.82 (17)	N6—Pt2—Pt1	97.60 (17)
Br1—Pt1—Pt2	173.52 (2)	N5—Pt2—Pt1	98.26 (18)
N2—Pt2—N1	93.3 (2)	Br2—Pt2—Pt1	177.03 (2)
O1—Pt1—Pt2—N1	0.1 (2)	N4—Pt1—Pt2—N6	−2.3 (2)
O2—Pt1—Pt2—N2	−1.5 (2)	N3—Pt1—Pt2—N5	−0.3 (2)

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—H3C...Br1	0.89	2.86	3.242 (6)	107
N3—H3A...O1	0.89	2.56	2.790 (8)	96
N3—H3B...O7	0.89	2.37	3.183 (9)	152
N4—H4C...Br1	0.89	2.81	3.176 (6)	107
N4—H4A...O7	0.89	2.18	2.927 (8)	141
N5—H5C...Br2	0.89	2.72	3.132 (7)	110
N5—H5A...O3A	0.89	2.81	3.226 (14)	110
N5—H5A...O3B	0.89	2.33	2.866 (14)	119
N5—H5A...O6	0.89	2.43	3.225 (9)	150
N6—H6C...Br2	0.89	2.70	3.111 (6)	110
N6—H6C...O3A	0.89	2.40	2.868 (13)	113
N6—H6B...O3B	0.89	2.63	3.063 (14)	111
N6—H6B...O7	0.89	2.11	2.982 (9)	165
N3—H3A...O5A ⁱ	0.89	2.24	3.051 (14)	151
N3—H3A...O5B ⁱ	0.89	2.03	2.910 (13)	168
N3—H3C...O4A ⁱⁱ	0.89	2.50	3.120 (17)	127
N3—H3C...O4B ⁱⁱ	0.89	2.11	2.786 (18)	132
N4—H4C...O3A ⁱⁱⁱ	0.89	2.64	3.130 (15)	115
N4—H4C...O4A ⁱⁱⁱ	0.89	2.33	3.170 (17)	158
N4—H4C...O4B ⁱⁱⁱ	0.89	2.09	2.934 (16)	158
N4—H4B...O7 ⁱⁱⁱ	0.89	2.58	3.217 (8)	129
N4—H4B...O8 ⁱⁱⁱ	0.89	2.19	3.038 (9)	160
N5—H5B...O5A ⁱ	0.89	1.81	2.700 (14)	177
N5—H5C...O6 ⁱ	0.89	2.46	3.153 (9)	135
N6—H6A...O7 ⁱⁱⁱ	0.89	2.61	3.053 (8)	112
N6—H6A...O8 ⁱⁱⁱ	0.89	2.24	3.093 (8)	161

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

One of the two nitrate anions was regarded as being disordered over two sites. All the disordered atoms were assumed to have the same isotropic displacement parameter, and the occupation factors were fixed at 50%. The N—O distances were restrained at 1.22 (1) Å, the three O...O distances in each disordered nitrate unit were restrained to be equal, and each nitrate unit was restrained to be

planar. All H atoms were located at their idealized positions (C—H = 0.97 Å and N—H = 0.89 Å) and included in the refinement in riding-motion approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{N})$. In the final difference Fourier synthesis, most of the 20 residual peaks in the range 1.01–2.42 e Å⁻³ were observed within 1.59 Å of the Pt atoms. The deepest hole was located 0.84 Å from Pt2.

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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