

C(6)	0.4208 (6)	0.605 (1)	0.2264 (9)	0.075 (6)
C(7)	0.3405 (5)	0.228 (1)	0.1429 (9)	0.051 (5)
C(8)	0.2846 (6)	0.195 (2)	0.1263 (10)	0.134 (8)
C(9)	0.4200 (6)	0.095 (1)	-0.0081 (8)	0.062 (5)
C(10)	0.4122 (6)	0.013 (1)	-0.075 (1)	0.082 (6)
C(11)	0.3815 (6)	0.036 (1)	-0.165 (1)	0.085 (6)
C(12)	0.3554 (6)	0.144 (1)	-0.1921 (8)	0.068 (5)
C(13)	0.3626 (5)	0.221 (1)	-0.1240 (8)	0.046 (4)
C(14)	0.3391 (5)	0.333 (1)	-0.1449 (7)	0.043 (4)
C(15)	0.3040 (6)	0.376 (1)	-0.2297 (8)	0.066 (5)
C(16)	0.2844 (7)	0.481 (2)	-0.2411 (9)	0.081 (6)
C(17)	0.2987 (6)	0.545 (1)	-0.167 (1)	0.075 (6)
C(18)	0.3331 (6)	0.501 (1)	-0.0810 (9)	0.062 (5)

† Occupancy factor of 0.5; refined isotropically.

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mn(1)··Mn(1')	2.844 (4)	Mn(1)—O(8)	2.204 (8)
Mn(1)··Mn(2')	3.303 (3)	Mn(2)—O(1)	1.838 (6)
Mn(1)··Mn(2)	3.379 (2)	Mn(2)—O(3)	2.17 (1)
Mn(1)—O(1)	1.893 (7)	Mn(2)—O(5)	1.916 (8)
Mn(1)—O(1')	1.898 (8)	Mn(2)—O(6)	2.13 (1)
Mn(1)—O(2)	1.930 (9)	Mn(2)—N(1)	2.081 (10)
Mn(1)—O(4)	2.172 (8)	Mn(2)—N(2)	2.070 (8)
Mn(1)—O(7)	1.919 (8)		
O(1)—Mn(1)—O(1')	82.1 (2)	O(1)—Mn(2)—O(6)	93.3 (3)
O(1)—Mn(1)—O(2)	95.0 (3)	O(1)—Mn(2)—N(1)	94.8 (3)
O(1)—Mn(1)—O(4)	85.9 (3)	O(1)—Mn(2)—N(2)	172.2 (4)
O(1)—Mn(1)—O(7)	173.0 (3)	O(3)—Mn(2)—O(5)	94.7 (4)
O(1)—Mn(1)—O(8)	98.4 (3)	O(3)—Mn(2)—O(6)	170.9 (3)
O(1')—Mn(1)—O(2)	174.1 (3)	O(3)—Mn(2)—N(1)	82.5 (4)
O(1')—Mn(1)—O(4)	89.6 (4)	O(3)—Mn(2)—N(2)	85.6 (4)
O(1')—Mn(1)—O(7)	98.0 (3)	O(5)—Mn(2)—O(6)	91.8 (4)
O(1')—Mn(1)—O(8)	89.0 (3)	O(5)—Mn(2)—N(1)	167.4 (3)
O(2)—Mn(1)—O(4)	95.3 (4)	O(5)—Mn(2)—N(2)	90.1 (3)
O(2)—Mn(1)—O(7)	85.5 (4)	O(6)—Mn(2)—N(1)	89.8 (4)
O(2)—Mn(1)—O(8)	86.3 (3)	O(6)—Mn(2)—N(2)	88.0 (4)
O(4)—Mn(1)—O(7)	87.1 (3)	N(1)—Mn(2)—N(2)	77.5 (4)
O(4)—Mn(1)—O(8)	175.3 (3)	Mn(1)—O(1)—Mn(1')	97.2 (2)
O(7)—Mn(1)—O(8)	88.6 (3)	Mn(1)—O(1)—Mn(2)	129.8 (5)
O(1)—Mn(2)—O(3)	92.2 (3)	Mn(1')—O(1)—Mn(2)	124.3 (4)
O(1)—Mn(2)—O(5)	97.6 (3)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Data collection and cell refinement used *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1994a). The metal-atom positions were determined by direct methods (*SAPI90*; Fan, 1990). The remaining non-H atoms were located using the *DIRDIF* program (Parthasarathi, Beurskens & Bruins Slot, 1992) and refined anisotropically by full-matrix least squares, except for the atoms of the disordered ClO_4^- ion which were refined isotropically under a rigid-group constraint ($\text{Cl—O} = 1.44 \text{ \AA}$). The isotropic displacement parameter of each atom was independently shifted [the e.s.d.'s of these were not reported by *TEXSAN* (Molecular Structure Corporation, 1994b), so they are not presented]. In the final difference Fourier map, the largest peak (1.26 e \AA^{-3}) was located 0.53 \AA from the Cl atom, which is reflected by the relatively large reliability factors. All H atoms were located in their calculated positions ($\text{C—H} = 0.95 \text{ \AA}$) and not refined. Best-planes calculations were performed with the *BP70* program developed by Ito (1982). All other calculations were performed using *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1198). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bush, J. B. & Frinkbeiner, J. H. (1968). *J. Am. Chem. Soc.* **21**, 5903–5905.
- Fan, H.-F. (1990). *SAPI90. Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.
- Ito, T. (1982). *Acta Cryst.* **A38**, 869–870.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1994a). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1994b). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6f. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Parthasarathi, V., Beurskens, P. T. & Bruins Slot, H. J. (1983). *Acta Cryst.* **A39**, 860–864.
- Vincent, J. B., Christmas, C., Chang, H.-R., Li, Q., Boyd, P. D. W., Huffman, J. C., Hendrickson, D. N. & Christou, G. (1989). *J. Am. Chem. Soc.* **111**, 2086–2097.

Acta Cryst. (1996). **C52**, 779–783

Two Different Crystal Forms of *cis*-Diamminebis(pyrazole)platinum(II) Dinitrate

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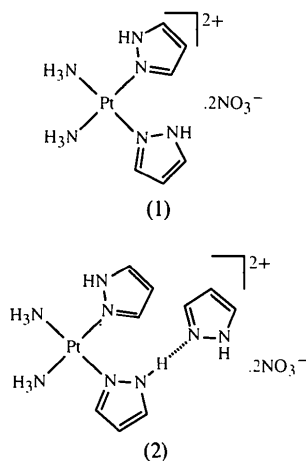
Abstract

The crystal structures of *cis*-diamminebis(pyrazole)platinum(II) dinitrate, *cis*-[Pt(NH₃)₂(C₃H₄N₂)₂](NO₃)₂, (1), and *cis*-diamminebis(pyrazole)platinum(II) dinitrate pyrazole solvate, *cis*-[Pt(NH₃)₂(C₃H₄N₂)₂](NO₃)₂·C₃H₄N₂, (2), have been determined by X-ray diffraction. Interestingly, compound (1) crystallizes in the centrosymmetric space group *P*₂/n, while compound (2) somehow crystallizes in the non-centrosymmetric space group *P*₂. In both (1) and (2), the two coordinated pyrazole planes are twisted with respect to the Pt coordination planes at angles of between 46.0 (9) and 60.5 (4)°. The free pyrazole molecule contained as a crystal solvent in compound (2) forms a strong hydrogen bond [2.82 (1) Å] with one of the two coordinated pyrazole ligands. In each crystal, the packing is electrostatically stabilized through hydrogen bonds formed

between the nitrate O atoms and the ammine and pyrazole ligands.

Comment

Minghetti and his co-workers have described convenient methods of synthesizing various pyrazolate-bridged homo- and heteronuclear Pt^{II} complexes (Minghetti, Banditelli & Bonati, 1979; Bandini, Banditelli, Minghetti & Bonati, 1979). Other pyrazolate-bridged complexes of Ru^{II} (Sullivan, Salmon, Meyer & Peedin, 1979) and Cu^{II} (ten Hoedt, Hulsbergen, Verschoor & Reedijk, 1982; Hulsbergen, ten Hoedt, Verschoor & Reedijk, 1983) have also been reported. As briefly reported previously (Sakai, 1993), we have prepared the title compound as a 'complex ligand' to be used in the preparation of new functional molecules having more than two metal centers with different reactivities. The actual use of this complex ligand will be described elsewhere. [Pt(NH₃)₂(pzH)₂](NO₃)₂, (1) (where pzH is pyrazole), was obtained almost quantitatively by the addition of 2 equivalents of pzH to an aqueous solution of *cis*-[Pt(NH₃)₂(OH₂)₂]²⁺. This compound was found to be fairly stable and the coordinated pzH does not undergo solvolysis in water, which was confirmed by ¹H NMR analysis. On the other hand, when the synthetic solution was slowly evaporated in the presence of an excess amount of pzH, *cis*-[Pt(NH₃)₂(pzH)₂](NO₃)₂·pzH, (2), was obtained instead of compound (1), indicating that crystallization of (1) from a mixed solvent consisting of pzH and water affords compound (2).



The atom-labeling scheme for compound (1) is shown in Fig. 1. Best-plane calculations have been carried out for the coordination plane defined by the four coordinated N atoms and for the two pyrazole planes, pzH(A) [N(3), N(4), C(1), C(2), C(3)] and pzH(B) [N(5), N(6), C(4), C(5), C(6)]. The results indicate that all the planes are planar; the r.m.s. deviations are 0.001, 0.012 and 0.003 Å, respectively. The Pt ion has almost ideal square-planar coordination geometry,

although it is slightly shifted out of the coordination plane by 0.015 (5) Å. The pzH(A) and pzH(B) planes are twisted with respect to the Pt coordination plane at angles of 60.5 (4) and 53.0 (4)°, respectively. The two non-coordinated N atoms of the pyrazole ligands, N(4) and N(6), are located on the same side of the Pt coordination plane. In both the pzH rings, all the C—N and C—C distances lie in a narrow range from 1.30 (1) to 1.39 (2) Å, suggesting that the *sp*²-hybridized nature is delocalized over the five atoms, as previously discussed for [Ni(pzH)₆](NO₃)₂ (Reimann, Santoro & Mighell, 1970). The nitrate O atoms form hydrogen bonds with either the ammine or the pyrazole ligands, leading to the electrostatic stabilization of the crystal packing (Table 3).

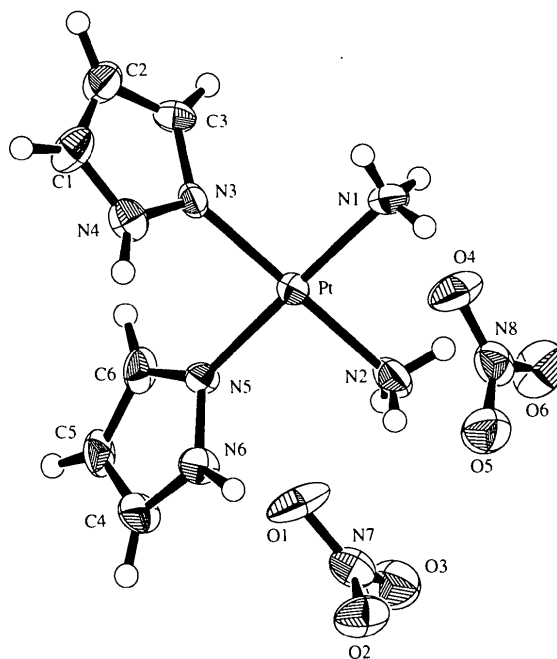


Fig. 1. The structure of *cis*-[Pt(NH₃)₂(pzH)₂](NO₃)₂ showing the atom-labeling scheme and displacement ellipsoids at the 50% probability level.

The most remarkable structural feature of compound (2) is that the non-coordinated pyrazole molecule forms a hydrogen bond with one of the coordinated pyrazoles [N(6)···N(7) 2.82 (1) Å; Fig. 2]. The structure of the *cis*-[Pt(NH₃)₂(pzH)₂]²⁺ cation involved in (2) is essentially the same as that of (1). Best-plane calculations have been performed as for compound (1). The coordination planes of the four coordinated N atoms, pzH(A) [N(3), N(4), C(1), C(2), C(3)] and pzH(C) [N(7), N(8), C(7), C(8), C(9)] are planar with r.m.s. deviations of 0.016, 0.005 and 0.018 Å, respectively. However, pzH(B) [N(5), N(6), C(4), C(5), C(6)] shows exceptional behavior, with an r.m.s. deviation of 0.051 Å. The C(5) atom is displaced out of the least-squares plane by 0.13 (4) Å, the reason for which remains unclear. The

Pt ion shows a slight distortion from ideal square-planar coordination geometry; the shift of the Pt atom from the coordination plane is 0.035 (7) Å. The twist angles of the pzH(A) and pzH(B) planes with respect to the Pt coordination plane are 46.0 (9) and 57 (1)°, respectively. The dihedral cant between the hydrogen-bonded pzH planes [pzH(B) and pzH(C)] is 24 (1)°. The crystal packing is stabilized by an extensive hydrogen-bonding network (Table 6).

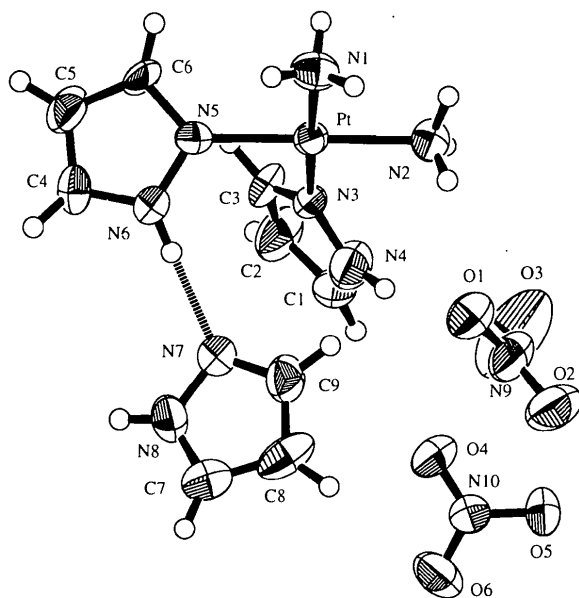


Fig. 2. The structure of *cis*-[Pt(NH₃)₂(pzH)₂](NO₃)₂.pzH showing the atom-labeling scheme and displacement ellipsoids at the 50% probability level.

As described in the experimental text, the ¹H NMR spectrum of compound (2), acquired in D₂O, displayed signals identical to those of compound (1), as well as signals of free pyrazole, revealing that the hydrogen bond between the coordinated and the uncoordinated pyrazole ligands achieved in compound (2) is completely cleaved in aqueous media.

Experimental

For the preparation of complex (1), an aqueous solution of *cis*-[Pt(NH₃)₂(OH₂)₂](NO₃)₂ (1 mmol, 7 ml) was prepared according to the method of Lim & Martin (1976). To this solution was added pyrazole (2.2 mmol) and the resulting solution was stirred at 333 K for 3 h whereupon it was evaporated to a total volume of ca 2 ml until colorless crystals appeared. Addition of a large excess of acetone (ca 50 ml) and cooling to ice temperature afforded the product as colorless prisms (yield 80–90%). Analysis: calculated for C₆H₁₄N₈O₆Pt C 14.73, H 2.88, N 22.90%; found C 15.02, H 2.85, N 22.98%. ¹H NMR (Jeol JNM-GX270; D₂O, 296 K): δ 6.52 (*pseudo-t*, 2H, *J* = 2.6 Hz), 7.77 (*d*, 2H, *J* = 2.4 Hz), 7.86 p.p.m. (*d*, 2H, *J* = 2.7 Hz). When 5 equivalents of pyrazole were employed in place of 2.2 equivalents in the above synthesis, complex (2) was deposited in the evaporation procedure. Analysis:

calculated for C₉H₁₈N₁₀O₆Pt C 19.39, H 3.26, N 25.13%; found C 19.38, H 3.17, N 25.25%. ¹H NMR (D₂O, 296 K): δ 6.43 [*t*, H (free pzH), *J* = 2.1 Hz], 6.52 (*pseudo-t*, 2H, *J* = 2.6 Hz), 7.72 [*d*, 2H (free pzH), *J* = 2.1 Hz], 7.77 (*d*, 2H, *J* = 2.4 Hz), 7.86 p.p.m. (*d*, 2H, *J* = 2.7 Hz). Crystals of (1) were recrystallized from water, while crystals of (2) were used without any treatment.

Compound (1)

Crystal data

[Pt(NH₃)₂(C₃H₄N₂)₂](NO₃)₂
M_r = 489.32
 Monoclinic
*P*2₁/*n*
a = 8.943 (1) Å
b = 9.222 (2) Å
c = 17.184 (2) Å
 β = 90.53 (1)°
V = 1417.1 (4) Å³
Z = 4
D_x = 2.2934 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 25.16–29.89°
 μ = 9.944 mm⁻¹
T = 296.0 K
 Prism
 0.30 × 0.30 × 0.10 mm
 Colorless

Data collection

Rigaku AFC-5S diffractometer
 ω/2θ scans
 Absorption correction:
 ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.702, *T_{max}* = 1.000
 3675 measured reflections
 3461 independent reflections

2458 observed reflections
 [*I* > 3σ(*I*)]
R_{int} = 0.0474
 θ_{max} = 27.5°
h = 0 → 11
k = 0 → 11
l = -22 → 22
 3 standard reflections monitored every 150 reflections
 intensity decay: 0.73%

Refinement

Refinement on *F*
R = 0.0391
wR = 0.0377
S = 3.18
 2458 reflections
 191 parameters
 H-atom parameters not refined
w = 1/σ²(*F*)
 (Δ/σ)_{max} = 0.0005

Δρ_{max} = 1.81 e Å⁻³
 Δρ_{min} = -1.61 e Å⁻³
 Extinction correction:
 Zachariasen (1967) type II, Gaussian isotropic
 Extinction coefficient:
 2.96793
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (1)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Pt	0.56356 (5)	0.39010 (5)	0.65321 (3)	0.0257 (1)
O(1)	0.9386 (10)	0.257 (1)	0.7088 (5)	0.059 (3)
O(2)	1.1457 (9)	0.259 (1)	0.7742 (5)	0.051 (3)
O(3)	1.068 (1)	0.456 (1)	0.7204 (6)	0.061 (4)
O(4)	0.6285 (10)	0.307 (1)	0.8794 (5)	0.056 (3)
O(5)	0.864 (1)	0.318 (1)	0.9009 (5)	0.059 (3)
O(6)	0.743 (1)	0.5130 (10)	0.8743 (6)	0.059 (3)
N(1)	0.437 (1)	0.430 (1)	0.7506 (6)	0.037 (3)
N(2)	0.710 (1)	0.544 (1)	0.6907 (6)	0.043 (3)
N(3)	0.417 (1)	0.2383 (10)	0.6142 (5)	0.028 (3)

N(4)	0.455 (1)	0.101 (1)	0.6032 (5)	0.036 (3)
N(5)	0.6896 (9)	0.358 (1)	0.5580 (5)	0.028 (3)
N(6)	0.837 (1)	0.334 (1)	0.5601 (5)	0.041 (3)
N(7)	1.050 (1)	0.326 (1)	0.7354 (7)	0.040 (4)
N(8)	0.745 (1)	0.382 (1)	0.8846 (5)	0.042 (3)
C(1)	0.335 (2)	0.021 (1)	0.5806 (8)	0.047 (5)
C(2)	0.216 (1)	0.111 (2)	0.5771 (7)	0.044 (4)
C(3)	0.270 (1)	0.245 (1)	0.5954 (7)	0.037 (4)
C(4)	0.898 (1)	0.327 (2)	0.4916 (7)	0.043 (4)
C(5)	0.786 (1)	0.347 (1)	0.4397 (7)	0.039 (4)
C(6)	0.658 (1)	0.365 (1)	0.4838 (6)	0.037 (4)

Table 2. Bond lengths (Å) and angles (°) for (1)

Pt—N(1)	2.061 (9)	N(5)—N(6)	1.34 (1)
Pt—N(2)	2.033 (10)	N(5)—C(6)	1.31 (1)
Pt—N(3)	2.029 (9)	N(6)—C(4)	1.30 (1)
Pt—N(5)	2.018 (9)	C(1)—C(2)	1.35 (2)
N(3)—N(4)	1.33 (1)	C(2)—C(3)	1.36 (2)
N(3)—C(3)	1.35 (1)	C(4)—C(5)	1.35 (2)
N(4)—C(1)	1.35 (1)	C(5)—C(6)	1.39 (2)
N(1)—Pt—N(2)	88.7 (4)	N(6)—N(5)—C(6)	104.0 (9)
N(1)—Pt—N(3)	91.8 (4)	N(5)—N(6)—C(4)	113.8 (9)
N(1)—Pt—N(5)	178.3 (4)	N(4)—C(1)—C(2)	107 (1)
N(2)—Pt—N(3)	179.1 (4)	C(1)—C(2)—C(3)	105 (1)
N(2)—Pt—N(5)	89.9 (4)	N(3)—C(3)—C(2)	110 (1)
N(3)—Pt—N(5)	89.7 (3)	N(6)—C(4)—C(5)	105 (1)
N(4)—N(3)—C(3)	104.9 (9)	C(4)—C(5)—C(6)	105 (1)
N(3)—N(4)—C(1)	110 (1)	N(5)—C(6)—C(5)	110 (1)

Table 3. Possible hydrogen-bond distances (Å) for (1)

O(1)···N(6)	2.79 (1)	O(4)···N(2')	3.07 (1)
O(1)···N(2')	2.94 (1)	O(5)···N(2')	3.05 (1)
O(2)···N(1 ⁱⁱ)	3.07 (1)	O(5)···N(4 ⁱⁱⁱ)	3.07 (1)
O(4)···N(1)	3.01 (1)	O(6)···N(4 ⁱⁱⁱ)	2.84 (1)

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (ii) $1+x, y, z$; (iii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.**Compound (2)***Crystal data*[Pt(NH₃)₂(C₃H₄N₂)₂]-
(NO₃)₂·C₃H₄N₂ $M_r = 557.395$

Monoclinic

 $P2_1$ $a = 10.049 (2) \text{ \AA}$ $b = 7.531 (3) \text{ \AA}$ $c = 12.298 (1) \text{ \AA}$ $\beta = 98.89 (1)^\circ$ $V = 919.5 (4) \text{ \AA}^3$ $Z = 2$ $D_x = 2.0132 \text{ Mg m}^{-3}$ D_m not measured*Data collection*

Rigaku AFC-5S diffractometer

 $\omega/2\theta$ scans

Absorption correction:

 ψ scan (North, Phillips & Mathews, 1968) $T_{\min} = 0.575, T_{\max} = 1.000$

3033 measured reflections

2886 independent reflections

Mo $K\alpha$ radiation $\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

 $\theta = 15.89\text{--}20.96^\circ$ $\mu = 7.679 \text{ mm}^{-1}$ $T = 296.0 \text{ K}$

Plate

 $0.40 \times 0.10 \times 0.10 \text{ mm}$

Colorless

2056 observed reflections
[$I > 3\sigma(I)$] $R_{\text{int}} = 0.0333$ $\theta_{\text{max}} = 30.0^\circ$ $h = 0 \rightarrow 14$ $k = 0 \rightarrow 10$ $l = -17 \rightarrow 17$

3 standard reflections

monitored every 150

reflections

intensity decay: 0.77%

*Refinement*Refinement on F $R = 0.0383$ $wR = 0.0248$ $S = 1.20$

2056 reflections

235 parameters

H-atom parameters not refined

 $w = 1/\sigma^2(F)$ $(\Delta/\sigma)_{\text{max}} = 0.019$ $\Delta\rho_{\text{max}} = 1.19 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -1.00 \text{ e \AA}^{-3}$

Extinction correction:

Zachariasen (1967) type

II, Gaussian isotropic

Extinction coefficient:

6.00601

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (2)

	x	y	z	U_{eq}
Pt	0.82899 (3)	0.2549	0.63030 (3)	0.03689 (10)
O(1)	0.4252 (9)	0.125 (2)	0.5705 (9)	0.066 (3)
O(2)	0.2121 (9)	0.161 (1)	0.5437 (8)	0.093 (4)
O(3)	0.344 (2)	0.377 (2)	0.545 (2)	0.164 (9)
O(4)	0.2708 (8)	0.677 (2)	0.7465 (7)	0.115 (5)
O(5)	0.0733 (7)	0.710 (2)	0.6619 (6)	0.072 (4)
O(6)	0.1122 (8)	0.739 (6)	0.8356 (7)	0.138 (6)
N(1)	0.9176 (9)	0.046 (1)	0.5640 (8)	0.054 (3)
N(2)	0.6885 (7)	0.272 (4)	0.4914 (6)	0.045 (3)
N(3)	0.7433 (8)	0.466 (1)	0.6894 (7)	0.040 (3)
N(4)	0.6145 (10)	0.505 (2)	0.6908 (9)	0.067 (4)
N(5)	0.9650 (7)	0.245 (5)	0.7677 (7)	0.046 (3)
N(6)	0.9290 (8)	0.237 (5)	0.8676 (7)	0.067 (5)
N(7)	0.6645 (9)	0.161 (1)	0.9022 (8)	0.056 (3)
N(8)	0.6410 (10)	0.114 (2)	1.0031 (8)	0.061 (4)
N(9)	0.323 (2)	0.237 (5)	0.559 (1)	0.090 (7)
N(10)	0.1544 (10)	0.706 (2)	0.7498 (9)	0.065 (5)
C(1)	0.598 (1)	0.670 (2)	0.736 (1)	0.063 (5)
C(2)	0.729 (1)	0.731 (5)	0.763 (1)	0.079 (7)
C(3)	0.8087 (10)	0.605 (2)	0.7351 (10)	0.043 (4)
C(4)	1.037 (1)	0.222 (2)	0.9455 (9)	0.045 (4)
C(5)	1.1459 (10)	0.254 (7)	0.8946 (10)	0.081 (5)
C(6)	1.1012 (9)	0.246 (5)	0.7822 (9)	0.060 (4)
C(7)	0.524 (2)	0.033 (4)	1.002 (3)	0.072 (7)
C(8)	0.464 (1)	0.032 (2)	0.891 (1)	0.070 (5)
C(9)	0.558 (1)	0.104 (2)	0.836 (1)	0.062 (5)

Table 5. Bond lengths (Å) and angles (°) for (2)

Pt—N(1)	2.04 (1)	N(7)—N(8)	1.34 (1)
Pt—N(2)	2.045 (7)	N(7)—C(9)	1.31 (1)
Pt—N(3)	1.997 (9)	N(8)—C(7)	1.32 (2)
Pt—N(5)	2.004 (8)	C(1)—C(2)	1.38 (2)
N(3)—N(4)	1.33 (1)	C(2)—C(3)	1.32 (3)
N(3)—C(3)	1.32 (1)	C(4)—C(5)	1.36 (2)
N(4)—C(1)	1.38 (2)	C(5)—C(6)	1.39 (1)
N(5)—N(6)	1.34 (1)	C(7)—C(8)	1.41 (4)
N(5)—C(6)	1.35 (1)	C(8)—C(9)	1.36 (2)
N(6)—C(4)	1.34 (1)		
N(1)—Pt—N(2)	90.1 (8)	N(7)—N(8)—C(7)	112 (1)
N(1)—Pt—N(3)	177.4 (4)	N(4)—C(1)—C(2)	103 (1)
N(1)—Pt—N(5)	91.4 (9)	C(1)—C(2)—C(3)	106 (2)
N(2)—Pt—N(3)	88.5 (7)	N(3)—C(3)—C(2)	113 (1)
N(2)—Pt—N(5)	178 (1)	N(6)—C(4)—C(5)	105 (1)
N(3)—Pt—N(5)	90.0 (10)	C(4)—C(5)—C(6)	106 (1)
N(4)—N(3)—C(3)	104.0 (9)	N(5)—C(6)—C(5)	107.3 (9)
N(3)—N(4)—C(1)	112 (1)	N(8)—C(7)—C(8)	105 (2)
N(6)—N(5)—C(6)	107.0 (8)	C(7)—C(8)—C(9)	104 (1)
N(5)—N(6)—C(4)	110.9 (8)	N(7)—C(9)—C(8)	113 (1)
N(8)—N(7)—C(9)	104.2 (10)		

Table 6. Possible hydrogen-bond distances (Å) for (2)

O(1)··N(2 ¹)	2.95 (3)	O(5)··N(1 ¹¹)	3.06 (1)
O(3)··N(2 ¹)	3.01 (4)	O(5)··N(1 ¹¹)	3.12 (2)
O(3)··N(1 ¹¹)	3.03 (2)	O(6)··N(8 ¹¹)	3.07 (2)
O(4)··N(2 ¹)	3.10 (1)	N(6)··N(7)	2.82 (1)

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

Data collection and cell refinement used *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994a). The metal-atom positions were determined by direct methods (*SAPI91*; Fan, 1991). The remaining non-H atoms were located using the *DIRDIF* program (Parthasarathi, Beurskens & Bruins Slot, 1983) and refined anisotropically by full-matrix least squares. The locations of the non-coordinated N atoms of the pyrazole ligands were determined by comparing the results of refinements performed for every possible location. The absolute structure of (2) was determined by comparing the final reliability factors obtained for two centrosymmetrically convertible structures. Several H atoms of the ammine ligands were visible in the difference Fourier map and were used to locate all the ammine H atoms. These H atoms were idealized (N—H 0.87 Å) and were not refined. The H atoms of the pyrazole ligands were located in their calculated positions (C—H 0.95 and N—H 0.87 Å) and were not refined. Best-planes calculations were performed with the *BP70* program developed by Ito (1982). All other calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1994b).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1060). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bandini, A. L., Banditelli, G., Minghetti, G. & Bonati, F. (1979). *Can. J. Chem.* **57**, 3237–3242.
- Fan, H.-F. (1991). *SAPI91. Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.
- Hoedt, R. W. M. ten, Hulsbergen, F. B., Verschoor, G. C. & Reedijk, J. (1982). *Inorg. Chem.* **21**, 2369–2373.
- Hulsbergen, F. B., ten Hoedt, R. W. M., Verschoor, G. C. & Reedijk, J. (1983). *J. Chem. Soc. Dalton Trans.* pp. 539–545.
- Ito, T. (1982). *Acta Cryst.* **A38**, 869–870.
- Lim, M. C. & Martin, R. B. (1976). *J. Inorg. Nucl. Chem.* **38**, 1911–1914.
- Minghetti, G., Banditelli, G. & Bonati, F. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1851–1856.
- Molecular Structure Corporation (1994a). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1994b). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6f. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Parthasarathi, V., Beurskens, P. T. & Bruins Slot, H. J. (1983). *Acta Cryst.* **A39**, 860–864.
- Reimann, C. W., Santoro, A. & Mighell, A. D. (1970). *Acta Cryst.* **B26**, 521–526.
- Sakai, K. (1993). PhD thesis, Waseda University, Japan.
- Sullivan, B. P., Salmon, D. J., Meyer, T. J. & Peedin, J. (1979). *Inorg. Chem.* **18**, 3369–3374.
- Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1996). **C52**, 783–786

Di-(μ -pyrazolato-*N:N'*)-bis[(2,2'-bipyridine-*N,N'*)platinum(II)] Bis(tetrafluoroborate) Monohydrate

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Abstract

The crystal structure of [Pt₂(C₃H₃N₂)₂(C₁₀H₈N₂)₂](BF₄)₂·H₂O, has been determined by X-ray diffraction. The six-membered ring consisting of the two Pt atoms and the four pyrazolyl N atoms has a boat-shaped conformation in which each Pt atom is located 1.14 (1) Å above the plane defined by the four pyrazolyl N atoms. The two platinum coordination planes are canted at an angle of 77.9 (3)°, which is 8.1 (6)° smaller than the dihedral angle between the two bipyridyl planes. The dihedral angle between the two pyrazolyl planes is 83.4 (6)°. These angular strains are found to be caused by the intramolecular steric repulsion between the bipyridyl H and pyrazolyl N atoms.

Comment

It was reported that Ir^I [Ir₂(μ -bridge)₂(CO)₄] dimers (bridge = pyrazolate and 3,5-dimethylpyrazolate) exhibit activity in hydrogenation catalysis and that the activity increases with shortening of the intradimer Ir···Ir distance (Nussbaum, Rettig, Storr & Trotter, 1985). This trend was later discussed in terms of the filled–filled *d*⁸–*d*⁸ interaction which promotes destabilization of the HOMO (highest occupied molecular orbital) (Lichtenberger, Copenhagen, Gray, Marshall & Hopkins, 1988). The diplatinum complex examined in this study, [Pt₂(μ -pz)₂(bpy)₂]²⁺, where pz is pyrazolate and bpy is 2,2'-bipyridine, has the same M₂(μ -pz)₂ core, with M being in the *d*⁸ configuration. This complex cation was first prepared by Minghetti, Banditelli & Bonati (1979) as the tetrachloroplatinate salt, [Pt₂(μ -pz)₂(bpy)₂][PtCl₄], which is insoluble in any solvent. With the aim of examining the structure and reactivity of this dimer complex, we have prepared both the nitrate and tetrafluoroborate salts, [Pt₂(μ -pz)₂(bpy)₂]₂X₂·nH₂O [(1) X = NO₃⁻, n = 5; (2) X = BF₄⁻, n = 1] (Sakai, 1993). Although the tetrachloroplatinate salt was prepared *via* a two-step synthesis starting with [PtCl₂(bpy)], it was found that