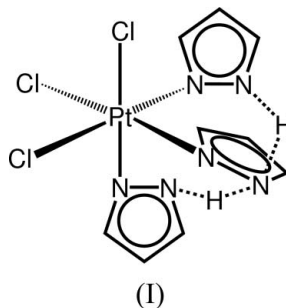


fac-Trichloro(pyrazolato)bis(pyrazole)platinum(IV)Anatoly V. Khripun,^a Matti Haukka,^{b*} Dina N. Nikolaeva^a and Vadim Yu. Kukushkin^a^aDepartment of Chemistry, St Petersburg State University, 198504 Stary Petergof, Russian Federation, and ^bDepartment of Chemistry, University of Joensuu, PO Box 111, FIN-80101 Joensuu, FinlandCorrespondence e-mail:
matti.haukka@joensuu.fi**Key indicators**Single-crystal X-ray study
T = 120 K
Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$
R factor = 0.031
wR factor = 0.081
Data-to-parameter ratio = 16.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Pt}(\text{C}_3\text{H}_3\text{N}_2)\text{Cl}_3(\text{C}_3\text{H}_4\text{N}_2)_2]$, has mirror symmetry. The Pt^{IV} atom has a slightly distorted octahedral geometry, with three facial Cl atoms and three N atoms, the latter from one pyrazolate (pz) and two pyrazole (pzH) ligands. There is an intramolecular N—H···N···H—N hydrogen-bonding system, with N···N distances of 2.747 (7) Å.

Comment

Complexes containing various pyrazole ligands currently attract significant attention, due to their intrinsic biological, synthetic, catalytic and magnetic properties (Ardizzoia *et al.*, 1991, 1994; Trofimenko, 1993; Sakai *et al.*, 2000; Bigmore *et al.*, 2005). During our ongoing studies of platinum complexes with N-donor ligands (Kukushkin & Pombeiro, 1999, 2002, 2005; Bokach & Kukushkin, 2005), the title complex, (I), was obtained as a by-product in the synthesis of *cis*-[PtCl₄(pzH)₂] by the known method of Minacheva *et al.* (2001) or as the target compound in the reaction described in the *Experimental* section. In this work, complex (I) has been characterized by X-ray crystallography, elemental analyses and ¹H NMR spectroscopy.



Complex (I) belongs to a class of octahedral platinum(IV) species bearing three Cl[−] ligands in the *fac* arrangement (Fig. 1). The remaining coordination sites are occupied by one negatively charged pyrazolate (pz; N3/N4/C4–C6) and two neutral pyrazole ligands (pzH; N1/N2/C1–C3 and its symmetry-equivalent). There is a crystallographic mirror plane containing Pt1, Cl1 and the negatively charged pz ligand. The bond distances and angles in the heterocyclic rings are comparable with those previously reported for free pyrazole molecules (Berthou *et al.*, 1970; Larsen *et al.*, 1970; la Cour *et al.*, 1973) and coordinated pyrazoles in *cis*-[PtCl₄(pzH)₂] (Minacheva *et al.*, 2001; Khripun *et al.*, 2005) and *trans*-[PtCl₄(pzH)₂] (Khripun *et al.*, 2005).

An intramolecular N2—H2N···N4···H2Nⁱ—N2ⁱ hydrogen-bonding system is formed (Table 2 gives geometric details and

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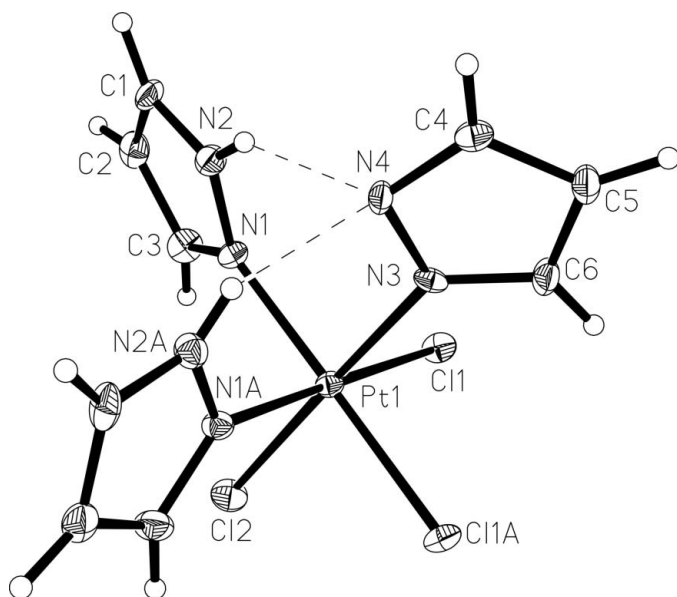


Figure 1
A view of (I), with displacement ellipsoids drawn at the 50% probability level. Atoms N1A/N2A/Cl1A and unlabelled atoms are related to atoms N1/N2/Cl1 and other labelled atoms by the symmetry operation $(x, \frac{1}{2} - y, z)$. Dashed lines indicate hydrogen bonds.

the symmetry code). The $N \cdots N$ distances [2.747 (7) Å] are similar to those observed in *fac*-[Re(pz)(pzH)₂(CO)₃] [2.749 (7)–2.883 (6) Å; Ardizzoia *et al.*, 1998]. Structurally characterized complexes with *fac*-*M*(pyrazole/ate)₃ moieties (Trofimenko, 1993), are known and include compounds with a *fac*-*M*(pz)₂(pzH) or *fac*-*M*(pz)(pzH)₂ structural unit, namely [Ir(η^5 -C₅Me₅)(pz)₂(pzH)] (Carmona *et al.*, 1986), [Ru(η^6 -*p*-cymene)(pz)₂(pzH)] (*p*-cymene is 1-isopropyl-4-methylbenzene; Carmona *et al.*, 1990), [Ru(η^6 -mesitylene)(pz)₂(pzH)] (Carmona *et al.*, 1996), [Ru(η^6 -*p*-cymene)(pz)(pzH)₂][BF₄] (Carmona *et al.*, 1990) and [Re(pz)(pzH)₂(CO)₃] (Ardizzoia *et al.*, 1998). Thus, complex (I) represents the first example of a platinum complex of the *fac*-*M*(pyrazole/ate)₃ type and the second example of a structurally characterized complex with a *fac*-*M*(pz)(pzH)₂ hydrogen-bonding system. In [Ru(η^6 -*p*-cymene)(pz)(pzH)₂][BF₄] (Carmona *et al.*, 1990), there is an intramolecular hydrogen bond between one of the pzH ligands and a pz anion, while the NH group of the second pzH ligand is involved in an intermolecular hydrogen bond with the counter-ion.

Experimental

Compound (I) was obtained as a by-product in the synthesis of *cis*-[PtCl₄(pzH)₂] (Minacheva *et al.*, 2001). A mixture of K₂[PtCl₆] (0.131 g, 0.27 mmol) and pzH (0.046 g, 0.68 mmol) was heated in water (10 ml) at 343 K for 30 min. The yellow solid which formed was collected by filtration, washed with one 5 ml portion of water and air-dried at room temperature. Under these conditions, a mixture of the target complex *cis*-[PtCl₄(pzH)₂] and complex (I) was formed (0.017 g; molar ratio of the products 2:1 by ¹H NMR integration). We also found that, when one more equivalent of pzH (0.018 g,

0.27 mmol) was added to the filtrate and the solution was further heated at 343 K for 10 h, a yellow precipitate of the title compound was formed. The solid was collected by filtration, washed with one 5 ml portion of water and air-dried at room temperature (yield 0.082 g, 60%, based on the starting K₂[PtCl₆]). Suitable crystals of (I) for X-ray study were obtained by slow evaporation of an acetone solution at room temperature. Analysis calculated for C₉H₁₁N₆Cl₃Pt: C 16.65, H 2.20, N 21.42%; found: C 16.55, H 2.22, N 21.50%; ¹H NMR (acetone-*d*₆, δ , p.p.m.): 6.56 (pseudo-*t*, $J = 2.4$ Hz, 1H, ⁴CH), 7.92 (*d*, $J = 2.4$ Hz, 1H, ⁵CH), 7.94 (*d*, $J = 2.4$ Hz, 1H, ³CH). It should be noted that, in the ¹H NMR spectrum, the equivalence of both pyrazole and pyrazolate ligands, on the one hand, and the absence of signals from the NH protons, on the other, was observed, indicating exchange processes in the solution.

Crystal data

[Pt(C₃H₃N₂)Cl₃(C₃H₄N₂)₂]
 $M_r = 504.68$
 Monoclinic, $P2_1/m$
 $a = 6.8307$ (6) Å
 $b = 13.5005$ (7) Å
 $c = 7.6421$ (7) Å
 $\beta = 94.888$ (3)°
 $V = 702.18$ (10) Å³
 $Z = 2$

$D_x = 2.387$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4975 reflections
 $\theta = 3.0$ – 27.4 °
 $\mu = 10.56$ mm⁻¹
 $T = 120$ (2) K
 Plate, yellow
 0.24 × 0.16 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans, and ω scans with κ offset
 Absorption correction: analytical (de Meulenaer & Tompa, 1965)
 $T_{\min} = 0.189$, $T_{\max} = 0.631$
 4975 measured reflections

1645 independent reflections
 1522 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\max} = 27.4$ °
 $h = -8 \rightarrow 7$
 $k = -17 \rightarrow 14$
 $l = -8 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.081$
 $S = 1.03$
 1645 reflections
 101 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 1.4982P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 1.82$ e Å⁻³
 $\Delta\rho_{\min} = -2.94$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|------------------------|------------|--------------------------|-------------|
| Pt1–N3 | 2.041 (6) | Pt1–Cl1 | 2.3026 (12) |
| Pt1–N1 | 2.060 (4) | Pt1–Cl2 | 2.3274 (19) |
| N3–Pt1–N1 | 92.07 (18) | Cl1–Pt1–Cl1 ⁱ | 90.59 (6) |
| N1–Pt1–N1 ⁱ | 91.8 (2) | N3–Pt1–Cl2 | 178.21 (17) |
| N3–Pt1–Cl1 | 89.14 (13) | N1–Pt1–Cl2 | 89.18 (13) |
| N1–Pt1–Cl1 | 88.78 (13) | Cl1–Pt1–Cl2 | 89.60 (5) |

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

Table 2

Hydrogen-bond geometry (Å, °).

| | | | | |
|---------------------------|----------|--------------|--------------|----------------|
| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
| N2–H2N ⁱ ···N4 | 0.81 (7) | 2.06 (7) | 2.747 (7) | 142 (6) |

The NH H atom (H2N) was located in a difference Fourier map and refined isotropically. Other H atoms were placed in idealized

positions and constrained to ride on their parent atoms, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The highest peak is located 1.38 Å from atom N4 and the deepest hole 0.94 Å from atom Pt1.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2005); software used to prepare material for publication: *SHELXL97*.

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