

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.

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

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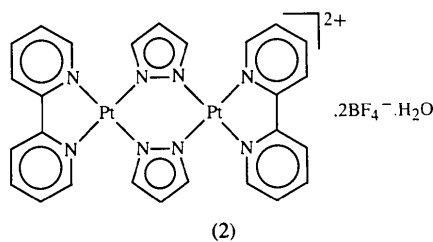
Abstract

The crystal structure of $[\text{Pt}_2(\text{C}_3\text{H}_3\text{N}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$, 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 $\text{Ir}^{\text{I}} [\text{Ir}_2(\mu\text{-bridge})_2(\text{CO})_4]$ 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, $[\text{Pt}_2(\mu\text{-pz})_2(\text{bpy})_2]^{2+}$, where pz is pyrazolate and bpy is 2,2'-bipyridine, has the same $M_2(\mu\text{-pz})_2$ core, with *M* being in the d^8 configuration. This complex cation was first prepared by Minghetti, Banditelli & Bonati (1979) as the tetrachloroplatinate salt, $[\text{Pt}_2(\mu\text{-pz})_2(\text{bpy})_2][\text{PtCl}_4]$, 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, $[\text{Pt}_2(\mu\text{-pz})_2(\text{bpy})_2]X_2 \cdot n\text{H}_2\text{O}$ [(1) $X = \text{NO}_3^-$, $n = 5$; (2) $X = \text{BF}_4^-$, $n = 1$] (Sakai, 1993). Although the tetrachloroplatinate salt was prepared *via* a two-step synthesis starting with $[\text{PtCl}_2(\text{bpy})]$, it was found that

a one-step reaction of [PtCl₂(bpy)] with a slight excess of pyrazole in the presence of two equivalents of AgNO₃ affords compound (1) in high yield. This compound shows good solubility in various solvents and the ¹H NMR spectrum (CD₃OD, 296 K; Jeol-JNM-GX270) displayed well resolved signals [δ 6.66 (*t*, 2H2, *J* = 2.4 Hz), 7.78 (*ddd*, 4H5, *J*₄₅ = 7.6, *J*₆₅ = 5.9, *J*₃₅ = 1.5 Hz), 7.96 (*d*, 4H1, *J* = 2.4 Hz), 8.43 (*pseudo-td*, 4H4, *J*₁ = 7.9, *J*₆₄ = 1.5 Hz), 8.54 (*broad d*, 4H6, *J*₅₆ = 5.9 Hz) and 8.58 p.p.m. (*broad d*, 4H3, *J*₄₃ = 8.2 Hz), where the proton-numbering scheme is the same as that shown in Fig. 1 and the assignments are based on the ¹H-¹H COSY spectrum obtained on the same solution]. The temperature dependence of ¹H NMR spectra acquired at 200–333 K exhibited neither signal broadening nor sharpening in the pyrazolyl domain, suggesting that the possible ‘butterfly-like’ flipping of the Pt₂(μ -pz)₂ core is not favored in this system. In order to better understand the structure of this dimer, the crystal structure of (2) has been determined.



A fourth of a dimer cation is found in the asymmetric unit and is reflected through two crystallographic mirrors to generate the rest of the molecule (Fig. 1). The six-membered ring consisting of the two Pt atoms and the four pyrazolyl N atoms has a boat-shaped conformation, with each Pt atom occupying a position 1.14 (1) Å above the plane defined by the four pyrazolyl N atoms. The Pt coordination plane defined by the four coordinated N atoms is crystallographically planar and the shift of the Pt atom from the coordination plane [0.007 (5) Å] is negligibly small. The remarkable structural feature is that the two platinum coordination planes within the dimer unit are canted at an angle of 77.9 (3)°. Moreover, this angle is smaller than the dihedral angle between the two bpy planes [86.0 (4)°]; the bpy plane is canted at an angle of 4.1 (3)° with respect to the Pt coordination plane, which must be relevant to the steric contact of the H(6) atom with the pz plane. The shortest contact is N(1)···H(6) of 2.691 Å and the distance of the H(6) atom from the pz plane is 2.44 (1) Å. Due to this repulsive interaction, the dihedral cant between the two pz planes is 83.4 (6)°, which is smaller than the dihedral angle [98.3 (3)°] between the trapezoid Pt—N_{pz}—N_{pz}—Pt planes. There are no intermolecular interactions in the crystal, except for the hydrogen bonds formed between the F atoms of the BF₄⁻ anions and the water molecules, with F···O distances of 2.81 (2) Å (Fig. 2).

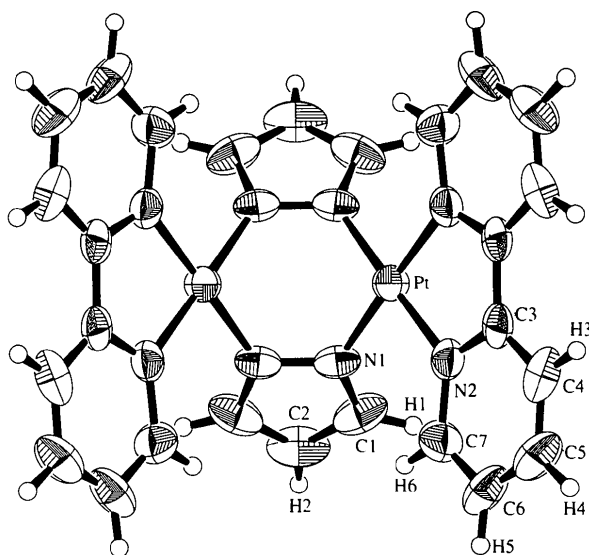


Fig. 1. The structure of the [Pt₂(μ -pz)₂(bpy)₂]²⁺ cation, viewed along the *c* axis, showing the atom-labeling scheme. Displacement ellipsoids are shown at the 40% probability level.

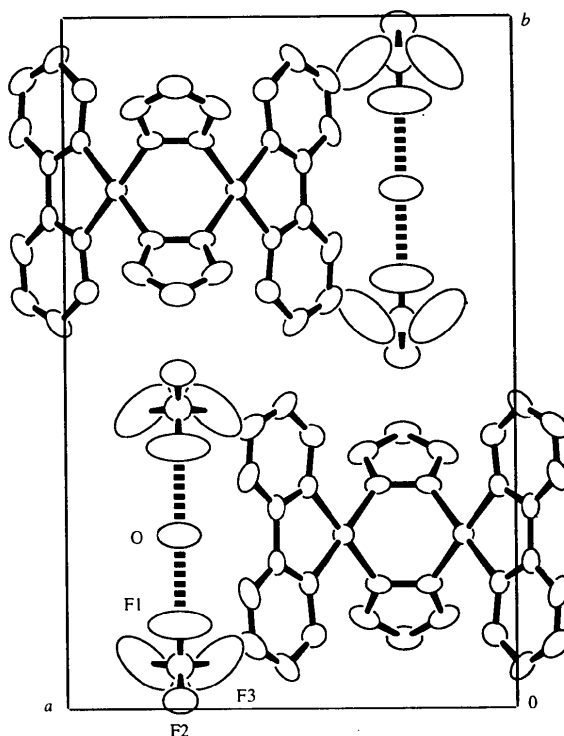


Fig. 2. The crystal packing of the title molecules (30% displacement ellipsoids) showing the hydrogen bonds.

An EHMO (extended Hückel molecular orbital) calculation was also performed using the geometric parameters obtained above, in which the energy splitting between the antibonding σ^* and bonding σ combinations for the d_{z^2} - d_{z^2} interaction was estimated to be 0.41 eV. This value is indicative of the presence of a metal-

metal interaction, but is not so large compared to the value of 1.1 eV reported for the Ir^I dimer having an Ir...Ir distance of 3.245 Å (Lichtenberger, Copenhagen, Gray, Marshall & Hopkins, 1988). The reactivity of this platinum complex is now under investigation.

Experimental

A solution made up of [PtCl₂(bpy)] (1 mmol), pyrazole (1.1 mmol), AgNO₃ (2 mmol) and H₂O (5 ml) was refluxed for 3 h in the dark followed by filtration while hot to remove the precipitated AgCl. The filtrate was allowed to stand at 278 K overnight, whereupon [Pt₂(μ-pz)₂(bpy)₂](NO₃)₂·5H₂O, (1), was obtained as bright yellow fine needles, which were collected by filtration and air dried (yield 75%). Analysis: calculated for C₂₆H₃₂N₁₀O₁₁Pt₂ C 29.72, H 3.07, N 13.33%; found C 29.40, H 3.08, N 13.32%. To an aqueous solution of (1) (0.10 g in 3 ml) was added an aqueous solution of NaBF₄ (0.11 g in 1 ml) at 303 K, which resulted in the immediate deposition of (2) as pale yellow microcrystals in quantitative yield. The crystals were filtered, washed with a minimum amount of cold water and air dried. Analysis: calculated for C₂₆H₂₄B₂F₈N₈OPt₂ C 30.37, H 2.35, N 10.90%; found C 30.52, H 2.14, N 11.14%. Recrystallization of (2) from hot water (*ca* 0.005 g in 0.7 ml of H₂O) gave single crystals of suitable quality for X-ray diffraction analysis. The density *D_m* was measured by flotation in chloroform/bromoform solution.

Crystal data

[Pt₂(C₃H₃N₂)₂(C₁₀H₈N₂)₂-(BF₄)₂·H₂O]
M_r = 1028.32
 Orthorhombic
Pmmn
a = 12.120 (3) Å
b = 18.425 (3) Å
c = 7.110 (6) Å
V = 1587.7 (14) Å³
Z = 2
D_x = 2.151 Mg m⁻³
D_m = 2.27 Mg m⁻³

Data collection

Rigaku AFC-5S diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.818, *T_{max}* = 1.000
 2702 measured reflections
 2639 independent reflections

Refinement

Refinement on *F*
R = 0.0577
wR = 0.0334
S = 1.840
 1073 reflections

Mo K α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 28.3–31.9°
 μ = 8.884 mm⁻¹
T = 296.0 K
 Needle
 0.30 × 0.20 × 0.10 mm
 Pale yellow
 1073 observed reflections
 $[I > 3\sigma(I)]$
R_{int} = 0.0108
 θ_{max} = 30.0°
h = 0 → 16
k = 0 → 24
l = 0 → 9
 3 standard reflections monitored every 150 reflections
 intensity decay: 0.32%

$\Delta\rho_{\text{max}}$ = 2.27 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -1.48 e Å⁻³
 Extinction correction:
 Zachariasen (1967) type II, Gaussian isotropic

114 parameters
 H-atom parameters not refined
 $w = 1/\sigma^2(F)$
 $(\Delta/\sigma)_{\text{max}} = 0.006$

Extinction coefficient:
 2.32743
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{\text{iso}} \text{ for B; } U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j \text{ for all other atoms.}$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}/U_{iso}</i>
Pt	0.11669 (7)	1/4	0.0377 (1)	0.0556 (2)
F(1)	-1/4	0.1216 (9)	0.057 (3)	0.27 (1)
F(2)	-1/4	0.0124 (6)	-0.009 (2)	0.124 (5)
F(3)	-0.329 (1)	0.0675 (9)	0.227 (2)	0.34 (1)
O	-1/4	1/4	0.271 (3)	0.128 (10)
N(1)	0.1937 (7)	0.1783 (5)	0.199 (1)	0.061 (4)
N(2)	0.0379 (9)	0.1800 (6)	-0.130 (2)	0.061 (4)
C(1)	0.162 (1)	0.1309 (7)	0.336 (2)	0.081 (6)
C(2)	1/4	0.101 (1)	0.423 (3)	0.086 (10)
C(3)	-0.033 (1)	0.2104 (7)	-0.258 (2)	0.059 (5)
C(4)	-0.094 (1)	0.1657 (10)	-0.375 (2)	0.082 (6)
C(5)	-0.087 (1)	0.0918 (10)	-0.370 (2)	0.094 (7)
C(6)	-0.013 (1)	0.0607 (9)	-0.245 (2)	0.085 (7)
C(7)	0.049 (1)	0.1057 (9)	-0.127 (2)	0.075 (6)
B	-1/4	0.063 (2)	0.122 (6)	0.09 (1)

Table 2. Selected geometric parameters (Å, °)

Pt—Pt ⁱ	3.231 (1)	N(1)—N(1 ⁱ)	1.37 (2)
Pt—N(1)	1.981 (9)	N(1)—C(1)	1.37 (1)
Pt—N(2)	2.00 (1)	C(1)—C(2)	1.35 (2)
N(1)—Pt—N(1 ⁱ)	83.7 (5)	Pt—N(1)—N(1 ⁱ)	118.1 (3)
N(1)—Pt—N(2)	98.0 (4)	N(1 ⁱ)—N(1)—C(1)	106.4 (8)
N(1)—Pt—N(2 ⁱ)	178.2 (4)	N(1)—C(1)—C(2)	111 (1)
N(2)—Pt—N(2 ⁱ)	80.3 (7)	C(1)—C(2)—C(1 ⁱ)	104 (1)

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

Data collection and cell refinement used *MSCI/AF C Diffractometer Control Software* (Molecular Structure Corporation, 1988). The Pt-atom position was determined by direct methods (*SAPI91*; Fan, 1991). The remaining non-H atoms were located using *DIRDIF* (Parthasarathi, Beurskens & Bruins Slot, 1983) and refined by full-matrix least squares. All non-H atoms were treated anisotropically, except for the B atom which was treated isotropically. The H atoms of the pz and bpy ligands were located in calculated positions (C—H 0.95 Å) and not refined. Water H atoms were not located. The relatively large positive and negative peaks in the final difference Fourier maps were located near the Pt atom and BF₄⁻ ions. Best-planes calculations were performed with the *BP70* program developed by Ito (1982). All other calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1994).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1064). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dimeric Aqua(3,5-dinitrobenzoato)(triethylene glycol)calcium(II) 3,5-Dinitrobenzoate Hydrate

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Abstract

The title dimeric compound, bis(μ -3,5-dinitrobenzoato-*O*:*O'*)bis[(triethylene glycol-*O*:*O'*,*O''*,*O'''*)-calcium(II)] bis(3,5-dinitrobenzoate) dihydrate, {[Ca(C₇H₃N₂O₆)(C₆H₁₄O₄)(H₂O)](C₇H₃N₂O₆)·H₂O}₂, has seven-coordinate Ca centres with distorted pentagonal bipyramidal geometry. Four O atoms in the coordination sphere belong to the triethylene glycol ligand, one belongs to the water molecule and the two remaining O atoms are from two different symmetry-related carboxylate groups belonging to two symmetry-related 3,5-dinitrobenzoate anions. The second dinitrobenzoate anion in the asymmetric unit does not participate in coordination, but is involved in hydrogen bonding to the hydroxy groups of the triethylene glycol ligand.

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Comment

In complexes of 3,5-dinitrobenzoate (DNB) with alkali and alkaline earth metal cations, the carboxylate group of DNB exhibits a variety of coordination modes. It can act as a monodentate (Hundal, Hundal, Kapoor & Poonia, 1991), an unsymmetrical bridging bidentate (Ward, Popov & Poonia, 1984) and a chelating bidentate ligand (Cradwick & Poonia, 1977). The DNB ligand is also capable of forming a homoconjugate of the type [DNB·H-DNB]⁻, which can act as a bidentate ligand to form complexes called acid salts (Tiekink, Hundal, Hundal, Kapoor & Poonia, 1990). The behaviour of DNB⁻ as a counteranion is the result of a balance of various factors such as the charge on the cation and the steric crowding around it, operative solvent–cation interactions, flexibility of the neutral ligand and its role as a double-action species. As a net result, DNB⁻ complexes can be either ion paired or charge separated. Our ongoing studies of [M(anion)(ligand)(solvent)] systems (where *M* is an alkaline earth cation) aim at distinguishing between the chemistry of Ca, Sr and Ba through crystallographic examination of the related complexes. The title compound, (I), is the first compound to be investigated in a series of complexes having triethylene glycol (TRIEG) as a neutral ligand and DNB as counteranion.

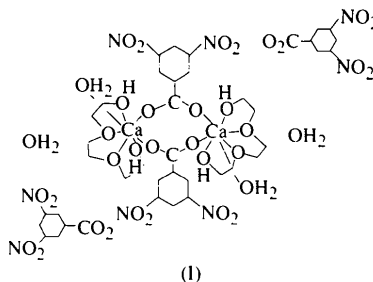


Fig. 1 is an ORTEP drawing (Johnson, 1965) of the title complex. Of the two DNB residues in the asymmetric unit, only one, *i.e.* DNBA, is coordinated to Ca²⁺, while DNBB is involved only in hydrogen bonding. Ca²⁺ is in a distorted pentagonal bipyramidal environment where all the four O atoms of TRIEG (O7, O8, O9 and O10) and atom O1A of DNBA form a pentagon and the water O11 atom and the carboxy O2A atom of the symmetry-related DNBA molecule occupy the apical positions. The carboxylate group of DNBA thus acts as a symmetrical bridge between two centrosymmetric Ca²⁺ ions. The Ca···Ca distance of 5.663(2) Å in the dimer is very long in comparison to that of 4.401(1) Å in the structure of [Sr(DNB)₂(tetraethylene glycol)]·H₂O (Kanters, Harder & Poonia, 1987). In the latter complex, the cluster is much more tightly packed because the bridging groups of DNB are triply coordinated to the Sr ion, whereas in the former the carboxylate groups are bidentate only. The two DNB anions of the title complex differ from