

Crystal Structure of Nitrato(2,2',2''-terpyridyl)platinum(II) Hydrogen Dinitrate, [Pt(terpy)ONO₂][H(ONO₂)₂]

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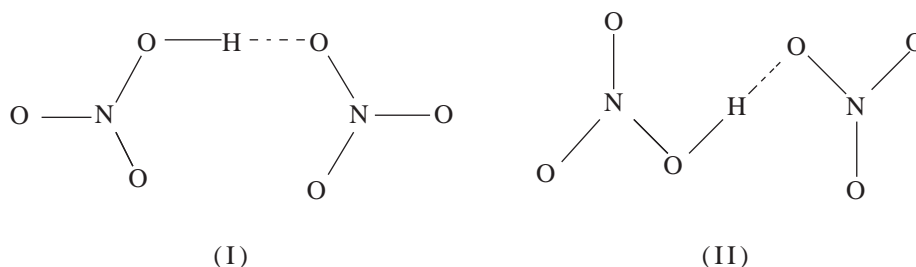
The title compound, C₁₅H₁₂N₆O₉Pt, consists of [Pt(terpy)ONO₂]⁺ cation and [H(ONO₂)₂]⁻ anion, in which 2 nitrate groups are linked by a strong hydrogen bond [O···O 2449(1) Å]. In the cation, the terpyridine is coordinated to Pt as a tridentate ligand and the fourth position is occupied by the nitrate ion's oxygen. The coordination around Pt is square-planar. The coordinated nitrate moiety adopts a distorted trigonal-planar configuration. It belongs to the space group P $\bar{1}$ with $a = 8.605(2)$, $b = 10.220(3)$ Å, $c = 10.517(2)$ Å and $\alpha = 89.51(1)$, $\beta = 82.78(2)$, $\gamma = 76.90(2)^\circ$.

Key Words: X-ray structure, terpyridine, hydrogen, nitrate, platinum, complex.

Introduction

Hydrogen-bonded species of the type (XHX)⁻ are fairly common and new examples occur frequently¹. Although there have been several studies on the salts that contain hydrogen dinitrate (HDN), the number of compounds studied using X-ray and neutron data is rather limited, and those known from diffraction works containing HDN anions are listed in Table 1.

Two distinct conformations are known for the anions (**I** and **II**) as follows:



A preliminary infrared and Raman investigation of CsHDN has been published together with the X-ray structure determination². A quasi-tetrahedral coordination of the proton was postulated in this

work, similar to the one proposed previously for the HDN ion in the $[\text{Rhpy}_4\text{Br}_2]^+$ complex⁴. The subsequent neutron diffraction investigation of CsHDN has shown that the tetrahedral coordination was foreshadowed by orientational disorder and the HDN ion has in fact structure **I** containing a short linear hydrogen bond with an $\text{O} \cdots \text{O}$ contact of about 2.5 \AA^3 . Structure **II** was derived from the X-ray diffraction of tetraphenylarsonium hydrogen dinitrate crystals⁶. The 2 nitrate groups are coplanar and the $\text{O} \cdots \text{O}$ contact is also short. Recently, the single crystal X-ray structure of 9-cyano-10-methylacridinium hydrogen dinitrate has shown that the HDN ion contains a short linear hydrogen bond with $\text{O} \cdots \text{O}$ contact of $2.440(4) \text{ \AA}$, as in other inorganic and organic compounds containing this anion⁷. Thus the existence of 2 types of HDN ions has been demonstrated.

Table 1. Structures of hydrogen dinitrate salts.

	Conformation	X-ray/neutron	Reference
$\text{CsH}(\text{NO}_3)_2$	I	X and n	2, 3
<i>trans</i> - $[\text{Rhpy}_4\text{Cl}_2]\text{H}(\text{NO}_3)_2$	I	n	4
<i>trans</i> - $[\text{Rupy}_4\text{Cl}_2]\text{H}(\text{NO}_3)_2$	I	X	5
$\text{Ph}_4\text{AsH}(\text{NO}_3)_2$	II	X	6
$\text{C}_{15}\text{H}_{11}\text{N}_2^+ \cdot \text{H}(\text{NO}_3)_2^-$	II	X	7

The infrared and Raman spectra of oligonitric acid adducts have also been investigated, and only one crystal structure has been determined, that of $\text{NH}_4\text{NO}_3 \cdot 2\text{HNO}_3^8$.

A large number of HDN anions and oligonitric acid adducts have been proposed as components of the troposphere and stratosphere¹.

Due to the stereochemical duality of the HDN ion and the controversy about hydrogen bonding, collecting further examples of the existence of the ion will surely prove to be beneficial.

Instrumentation

The unit cell parameters and intensity data were recorded at 150 K on a Delft Instruments FAST TV area detector diffractometer using the routines ENDEX, REFINE and MADONL in the MADNES software⁹; details of the procedures are described elsewhere¹⁰. Data reduction: ABSMAD¹¹, program to solve structures: SHELXS86¹², and program to refine structures: SHELXL93¹³. H atoms were placed geometrically and refined with a 'riding model' with $\text{C-H} = 0.93 \text{ \AA}$, $\text{O-H} = 0.82 \text{ \AA}$ and $U_{iso}(\text{H}) = 1.2U_{eq}$. WinGX¹⁴ version 1.64.05 and SHELXL93 were used to prepare the material for publication. Further details concerning data collection and refinement are given in Table 2.

Synthesis

To a solution of $[\text{Pt}(\text{terpy})\text{Cl}]\text{Cl} \cdot 2\text{H}_2\text{O}^{15}$ (2.4 g, 4.5 mmol) in water (100 cm^3) was added silver nitrate (1.52 g, 9 mmol) in water (ca. 5 cm^3) and the mixture heated at reflux for 2 h. The white precipitate of silver chloride was filtered through Celite and the filtrate cooled to room temperature. The trace amount of silver chloride was removed by centrifuge 3 times. The pH of the resulting clear yellow solution was adjusted to 5-6 with nitric acid and the excess of sodium nitrate in water (10 cm^3) was added with vigorous stirring. The yellow-orange precipitate was collected by filtration, washed with ether, and air-dried. Crystallization from a 1:1 mixture of conc. nitric acid and water yielded orange-red crystals.

Table 2. Crystallographic data and details of the structure refinement.

Empirical formula	C ₁₅ H ₁₂ N ₆ O ₉ Pt
Formula weight	615.40
Temperature	150(2) K
Wavelength	0.71069 Å
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	$a = 8.605(2)$ Å, $b = 10.220(3)$ Å, $c = 10.517(2)$ Å $\alpha = 89.51(1)^\circ$, $\beta = 82.78(2)^\circ$, $\gamma = 76.90(2)^\circ$
V	893.5(4) Å ³
Z	2
Density (calculated)	2.287 Mg/m ³
Absorption coefficient	7.922 mm ⁻¹
$F(000)$	588
Crystal	Orange; needle
Crystal size (mm)	0.24 x 0.18 x 0.10
θ range for data collection	2.05 – 25.01°
Index ranges	$-9 \leq h \leq 6$, $-11 \leq k \leq 11$, $-11 \leq l \leq 10$
Reflections collected	4027
Independent reflections	2568 [$R_{int} = 0.0398$]
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2568 / 0 / 281
Goodness-of-fit on F^2	1.094
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0263$, $wR2 = 0.0640$
R indices (all data)	$R1 = 0.0277$, $wR2 = 0.0643$
Largest diff. peak and hole	1.491 and -1.483 e Å ⁻³

UV/Vis in water ($C = 4.06 \times 10^{-5}$ M) λ_{max} (nm), ϵ (dm³mol⁻¹): 342 (13.4 x 10³), 327 (15.3 x 10³), 278 (29.9 x 10³), 249 (35.9 x 10³).

Results and Discussion

The molecular structure and packing diagram of the [Pt(terpy)ONO₂][H(ONO₂)₂] are depicted in Figures 1 and 2, respectively. Selected bond lengths and angles of the compound are presented in Table 3. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 4.

The title compound was prepared from the chloro complex by halide abstraction with silver nitrate in aqueous solution and subsequent recrystallization from concentrated nitric acid to yield orange crystals

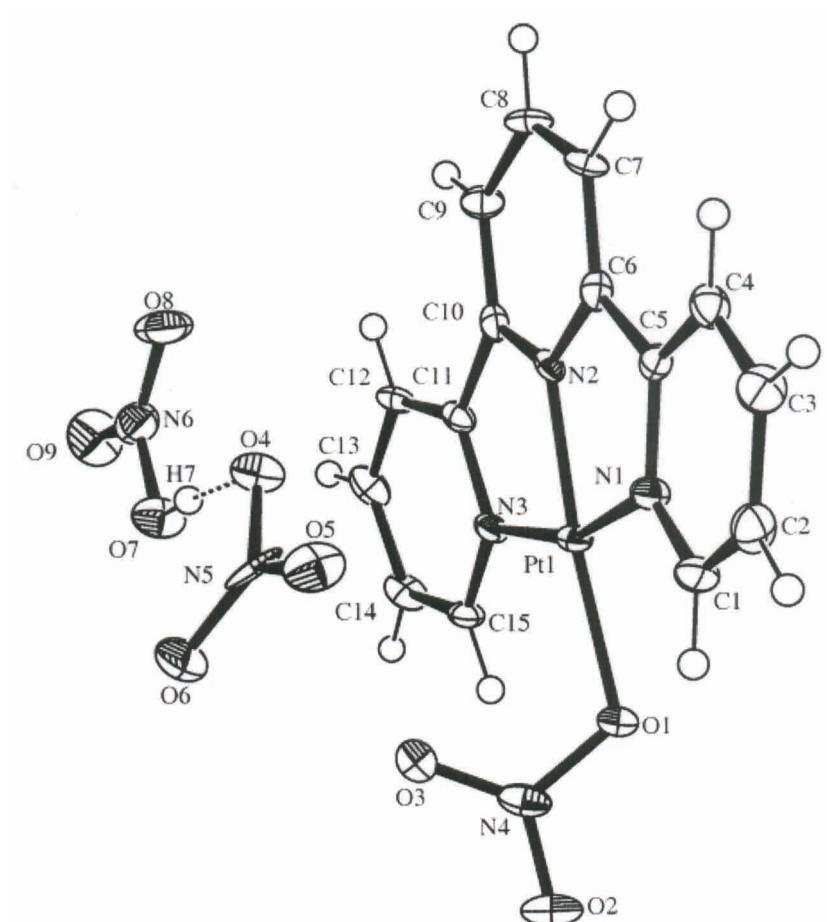


Figure 1. A drawing of the title compound with atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. Hydrogen bond is shown by the dashed line.

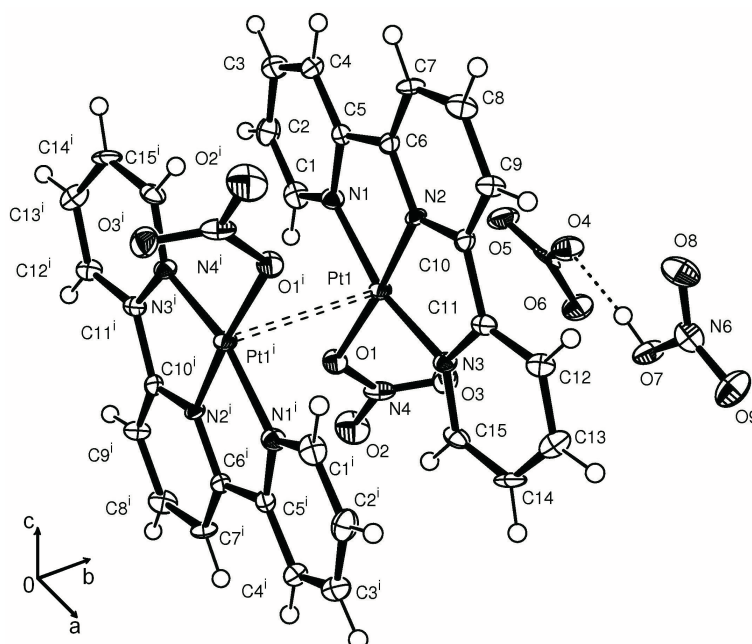


Figure 2. A packing diagram. Hydrogen bonds and Pt...Pt contacts are shown by the dashed lines. Symmetry code: (i) $-x, -y, -z$.

Table 3. Selected bond lengths [Å] and angles [°].

Pt1-N2	1.916(5)
Pt1-N1	2.014(5)
Pt1-N3	2.031(5)
Pt1-O1	2.043(4)
N4-O1	1.318(7)
N4-O2	1.224(6)
N4-O3	1.238(6)
N5-O4	1.302(6)
N5-O5	1.193(6)
N5-O6	1.277(6)
N6-O7	1.311(7)
N6-O8	1.233(7)
N6-O9	1.223(7)
N1-Pt1-N2	81.6(2)
N1-Pt1-N3	162.6(2)
N2-Pt1-N3	81.1(2)
N1-Pt1-O1	95.9(2)
N2-Pt1-O1	175.0(2)
N3-Pt1-O1	101.5(2)
N4-O1-Pt1	117.2(3)
O1-N4-O2	116.6(5)
O2-N4-O3	124.0(5)
O1-N4-O3	119.4(5)
O4-N5-O5	119.7(5)
O4-N5-O6	116.8(5)
O7-N6-O8	117.9(5)
O8-N6-O9	125.6(5)
O7-N6-O9	116.5(5)

Table 4. Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] and site occupancy factors. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
Pt1	-801(1)	1260(1)	-785(1)	14(1)
O1	-2403(5)	63(4)	-813(4)	21(1)
O2	-4340(6)	-422(5)	-1706(5)	38(1)
O3	-3125(5)	1070(4)	-2582(4)	25(1)
O4	-1255(5)	3858(4)	-3001(4)	25(1)
O5	-3525(5)	4163(4)	-1781(4)	30(1)
O6	-3420(5)	3608(4)	-3787(4)	29(1)
O7	-18(5)	2923(4)	-5122(4)	26(1)
O8	1865(6)	3897(5)	-4691(5)	35(1)
O9	2116(6)	2757(5)	-6481(5)	38(1)
N1	-1904(6)	2305(5)	820(5)	16(1)
N2	740(6)	2319(5)	-614(4)	12(1)
N3	755(6)	600(5)	-2386(5)	15(1)
N4	-3328(6)	252(5)	-1738(5)	20(1)
N5	-2782(6)	3868(5)	-2814(5)	23(1)
N6	1384(7)	3213(5)	-5448(5)	26(1)
C1	-3344(7)	2279(6)	1452(6)	21(1)
C2	-3956(8)	3056(6)	2546(6)	23(1)
C3	-3059(7)	3867(6)	3018(6)	23(1)
C4	-1569(7)	3898(6)	2367(6)	19(1)
C5	-997(7)	3110(6)	1268(5)	16(1)
C6	516(7)	3118(6)	450(5)	15(1)
C7	1664(7)	3822(6)	637(6)	17(1)
C8	3016(7)	3694(6)	-275(6)	20(1)
C9	3201(7)	2884(6)	-1370(6)	18(1)
C10	2028(7)	2190(6)	-1512(5)	15(1)
C11	2000(7)	1247(5)	-2553(6)	15(1)
C12	3070(7)	1023(6)	-3653(6)	16(1)
C13	2949(7)	130(6)	-4569(6)	21(1)
C14	1756(7)	-566(6)	-4362(6)	20(1)
C15	652(7)	-313(6)	-3264(6)	18(1)

suitable for X-ray analysis. The cation consists of tridentate terpy coordinated to the platinum with an oxygen atom of the nitrate ion completing the coordination as shown in Figure 1. The coordination geometry around the platinum center is distorted square-planar as a result of the constraints of the terpy ligand. The average deviation of the platinum, oxygen and 3 nitrogen atoms from the best plane through all 5 atoms is 0.04(3) Å, with a maximum of 0.06(1) Å for N2. The Pt-N2 distance, 1.916(5) Å, is slightly shorter than the distances of platinum to the other 2 nitrogen atoms, N1 with 2.014(5) Å, and N3 with 2.031(5) Å. This pattern commonly occurs in the structure of analogous terpyridyl platinum complexes¹⁵. The N-Pt-N angles of 81.6(2)° and 81.1(2)° in [Pt(terpy)ONO₂][H(ONO₂)₂] are significantly smaller than the theoretical 90° values expected for a square-planar complex. This effect is also seen in [Pt(terpy)Cl]Cl·2H₂O¹⁵, where these angles are 79.9(2)° and 81.0(2)°.

The nitrate is coordinated to platinum through 1 oxygen atom. The Pt-O bond length of 2.043(4) Å is comparable to those found in *cis*-bis(DMSO)dinitratoplatinum(II)¹⁶, 2.040(9) and 2.059(9) Å, and in bis(bipyridyl)dinitratoplatinum(II)¹⁷, 2.036(6) and 2.031(5) Å. The N-Pt-O angles in the [Pt(terpy)ONO₂][H(ONO₂)₂] are 101.5(2) and 95.9(2)°, again reflecting the strain caused by the terpy chelation, and are comparable to the N-Pt-S angles in the [Pt(terpy)(HET)]NO₃¹⁸ (HET = 2-hydroxyethanethiolate or mercaptoethanol) of 100.4(1)° and 98.1(2)°. The best mean plane calculated through the platinum atom, oxygen atom and terpy ligand shows some puckering of the py rings. The dihedral angles between the metal square plane and the py rings of N1, N2 and N3 are 7.6(3)°, 6.7(3)° and 5.6(3)°, respectively. The bond lengths and angles for the coordinated nitrate in the present compound are comparable to those found in [Pt(bpy)(NO₃)₂].0.5(CH₃)₂CO¹⁷. In both structures, the bond distance of the coordinated O atom to the N atom O1-N4 is greater than the other O-N bond distances O3-N4 and O2-N4. The O3 atom has a longer O-N bond, which may be due to intermolecular interactions. The nitrate adopts a distorted trigonal-planar conformation, deviating from the theoretical 120° for the ideal trigonal-planar conformation. The free nitrate ion in the [Pt(terpy)(HET)]NO₃¹⁸ adopts a trigonal-planar configuration with a small deviation of less than 0.025(6) Å.

The analogous compound [Pt(terpy)(HET)]⁺ is known to bind to DNA by intercalation. In this compound, the hydrogen bonding ability is facilitated by the mercaptoethanol ligand. The head-to-tail stacking of the 2 cations related by a center of inversion is common to the structures of [Pt(terpy)Cl]Cl·2H₂O¹⁵ and [Pt(terpy)(HET)]NO₃¹⁸, and the red form of [Pt(bpy)Cl₂]¹⁹. Hydrogen bonding to the phosphates and bases is possible¹⁸. The tendency to self-stack is an indication of ability to intercalate¹⁸. The Pt-Pt separation found here, 3.185(2) Å, is significantly shorter than the values of 3.57(1), 3.39(4) and 3.45(5) Å for the other head-to-tail stacked complexes, namely [Pt(terpy)(HET)]NO₃¹⁸ and [Pt(terpy)Cl]Cl·2H₂O¹⁵, and the red form of [Pt(bpy)Cl₂]¹⁹, respectively.

The crystal structure consists of [Pt(terpy)NO₃]⁺ and H(NO₃)₂⁻ anions that sit between the layers (Figure 2). In the crystalline phase, there is an ordered arrangement of the HDN. The dihedral angle between the planes of the 2 nitrate groups is 22.5(4)°, smaller than those of 96(3) and 91(4)° found in *trans*-[Rhpy₄Cl₂]H(NO₃)₂. The O7-H7-O6 bond between the nitrate groups constitutes a significantly smaller bending with a value of 175.7(6)°, which is comparable to those found in the other inorganic compounds containing HDN ion. The O4···O7 distance for the hydrogen bond is 2.449(1) Å [symmetry code: -x, 1-y, 1-z], similar to those found in *trans*-[Rhpy₄Cl₂]H(NO₃)₂, 2.461(18) and 2.480(18) Å, and in the 9-cyano-

10-methylacridinium hydrogen dinitrate, 2.440(4) Å. It is possible that in all cases the hydrogen dinitrate ion can be described as 2 nitrate groups linked by a very short and possibly symmetric hydrogen bond.

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