

Crystal and Molecular Structure of the Yellow Form of Chloro(2,2':6',2''-terpyridine)platinum (II)chloride dihydrate, [Pt(terpy)Cl]Cl·2H₂O

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The synthesis, characterization, and X-ray crystal structure of the yellow dimorph, [Pt(terpy)Cl]Cl·2H₂O, are reported. The yellow acicular crystals are monoclinic: space group $P2_1/n$, $a = 6.908(3)$ Å, $b = 17.06700(11)$ Å, $c = 13.8390(10)$ Å, $\beta = 98.607(4)^\circ$, and $D_{calc} = 2.204$ Mg m⁻³ for $Z = 4$. The cation consists of platinum coordinated to tridentate terpyridine ligand and to chloride ion. The coordination geometry is essentially square-planar with distortions arising from the constraints of the terpyridine ligand. Bond distances are within the acceptable limits of predicted values. The cations stack in a head-to-tail orientation with an intermolecular Pt–Pt distance of 3.39 Å

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

Introduction

Cationic, planar complexes of platinum(II) having 2,2'-bipyridine (bpy), 2,2':6',2''-terpyridine (terpy), or related ligands can bind to nucleic acids by intercalation¹ and one of these platinum metallo-intercalators has been shown to inhibit genetic recombination in *pneumococci*². The recently ongoing interest in these square-planar d^8 complexes arises from the fact that they display intriguing spectroscopic and photophysical properties³. In addition, several mononuclear complexes have been shown to form linear-chain materials with striking spectroscopic properties. One such complex,⁴ [Pt(terpy)Cl]⁺, precipitates from different solvents (or with different counterions) to give salts of various colors. In our work on the preparation of dimorphic (red and yellow) [Pt(terpy)Cl]Cl·2H₂O (hereafter **I**·2H₂O) and the novel conversion in the solid state of red to yellow, we found that the different solid state colors are due to variations in the stacking arrangements of the planar cations.

In this communication, we report the single crystal X-ray structure of the yellow form to establish firmly the geometry of the complex and to ascertain whether the observed spectral properties are indicative of either an unusual structure or one in which unusual molecular interactions are present.

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Experimental

Apparatus

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 software⁵; detailed procedures are described elsewhere⁶. Data reduction: ABSMAD⁷, program to solve structures: SHELXS86⁸, and program to refine structures: SHELXL93⁹. WinGX¹⁰ version 1.64.05 and SHELXL93 were used to prepare the material for publication. Details concerning data collection and refinement are given in Table 1.

Table 1. Crystallographic data and details of the structure refinement of [Pt(terpy)Cl]Cl·2H₂O.

Empirical formula	C ₁₅ H ₁₅ Cl ₂ N ₃ O ₂ Pt
Formula weight	535.29
Temperature	150(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ /n
Unit cell dimensions	<i>a</i> = 6.908(3) Å, <i>b</i> = 17.06700(11) Å, <i>c</i> = 13.8390(10) Å <i>β</i> = 98.607(4)°
<i>V</i>	1613.0(6) Å ³
<i>Z</i>	4
Density (calculated)	2.204 Mg/m ³
Absorption coefficient	9.042 mm ⁻¹
<i>F</i> (000)	1016
Crystal	Yellow, needles
Crystal size (mm)	0.18 x 0.16 x 0.10
<i>θ</i> range for data collection	1.91 – 24.96°
Index ranges	-8 ≤ <i>h</i> ≤ 7, -20 ≤ <i>k</i> ≤ 14, -13 ≤ <i>l</i> ≤ 16
Reflections collected	4748
Independent reflections	2272 [<i>R</i> _{int} = 0.0384]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.952 and 0.742
Refinement method	Full-matrix least-squares on <i>F</i> ₂
Data/restraints/parameters	2272 / 6 / 208
Goodness-of-fit on <i>F</i> ²	0.873
Final <i>R</i> indices [<i>F</i> ² > 2σ(<i>F</i> ²)]	<i>R</i> 1 = 0.0230, <i>wR</i> 2 = 0.0443
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0334, <i>wR</i> 2 = 0.0455
Largest diff. peak and hole	0.704 and -0.788 e Å ⁻³

Synthesis

The synthesis and spectroscopic characterization of the compound were reported before¹¹. Single crystals were grown by dissolving the pure compound in a 1:1 water-ethanol solution and then allowing the solvent to evaporate slowly at room temperature over 2 weeks. Stable yellow crystals were formed as long needles belonging to the monoclinic crystal system.

Results and Discussion

The cation consists of a tridentate terpyridine ligand coordinated to platinum with a chloride atom completing the square-planar shown in Figure. 1. The cations stack in a head-to-tail fashion forming a dimer in the solid state (Figure 2). The selected bond lengths and angles are listed in Table 2. Atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are given in Table 3. The Pt–N distance to the middle nitrogen atom (N2) of the terpyridine ligand, 1.940 (5) Å, is slightly shorter than the distances of platinum to the other 2 nitrogen atoms, N1, 2.002 (5) Å, and N3, 2.004 (5) Å. This pattern also occurs in the structure of [Pd(terpy)Cl]Cl·2H₂O¹². The N–Pt–N angles of 79.9 (2) and 81.0 (2)° in [Pt(terpy)Cl]Cl·2H₂O are significantly smaller than the theoretical 90° values expected for a square-planar complex. This result is also seen in [Pd(terpy)Cl]Cl·2H₂O, where these angles are 82 (2) and 79 (2)°.

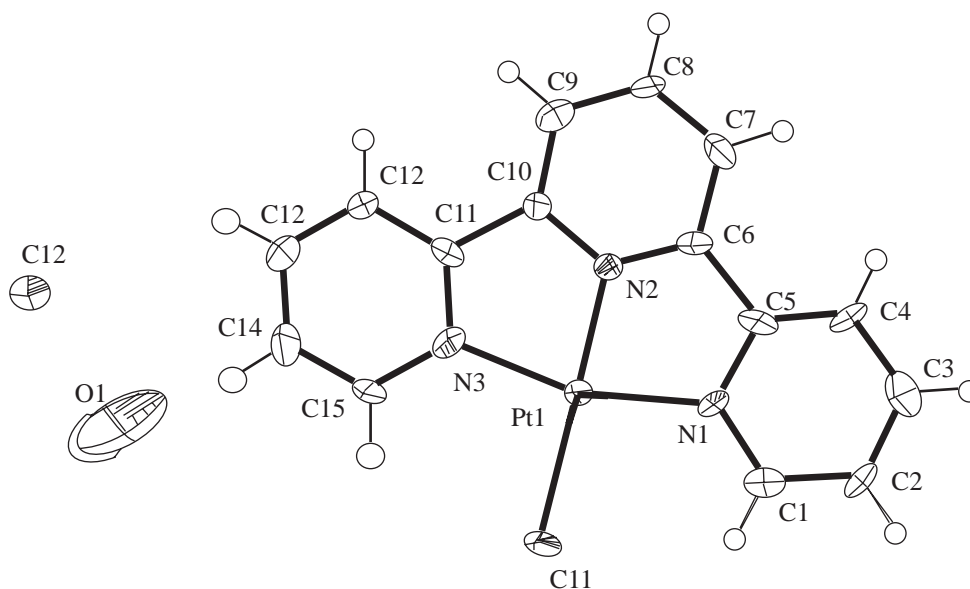


Figure 1. ORTEP drawing of Chloro(2,2':6',2''-terpyridine)platinum(II)chloride dihydrate. Displacement ellipsoids are shown at the 50% probability level.

The Pt–Cl bond length of 2.296 (2) Å is comparable to the Pt–Cl distance of 2.307 (1) Å in **I**·CF₃SO₃³, and to the Pd–Cl distance of 2.313 (7) Å. The N–Pt–N angles in **I**·2H₂O can also be compared to those found in **I**·CF₃SO₃ of 80.8 (2) and 81.1 (2)°, and to the N–Pd–N angles in [Pd(terpy)Cl]Cl·2H₂O of 96 (2) and 101 (2)°. The internal bond distances and angles for the terpyridine ligand given in Table 2 are unexceptional.

A weak interaction between 2 [Pt(terpy)Cl]⁺ cations is anticipated in the solid state. According to previous studies, such an interaction would lead to a red shift in the absorption spectrum from monomer to dimer as found for the orange-red color of solid [Pt(terpy)Cl]Cl·CF₃SO₃³, where the Pt–Pt distance is 3.329 (1) Å, smaller than the distance of 3.39 (5) Å in yellow solid [Pt(terpy)Cl]Cl·2H₂O.

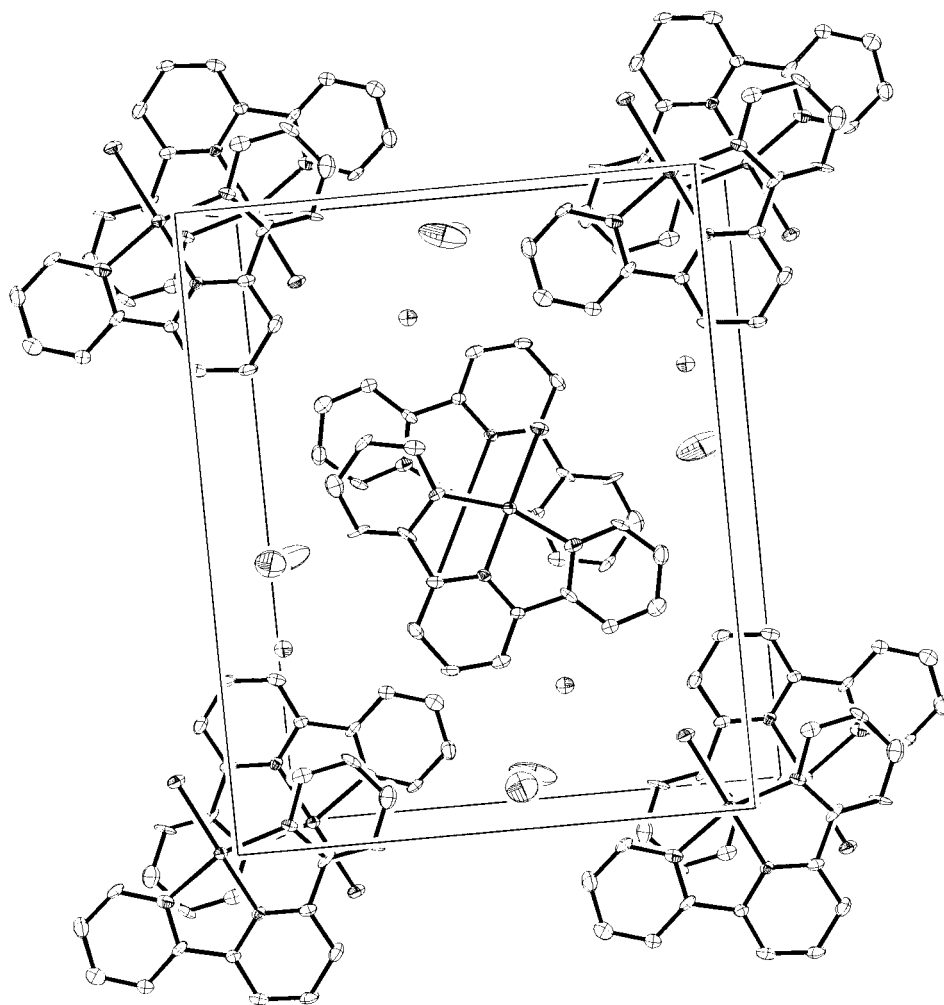


Figure 2. ORTEP packing diagram of $[\text{Pt}(\text{terpy})\text{Cl}]\text{Cl}\cdot 2\text{H}_2\text{O}$ (**I** $\cdot 2\text{H}_2\text{O}$). Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths [\AA] and angles [$^\circ$] of $[\text{Pt}(\text{terpy})\text{Cl}]\text{Cl}\cdot 2\text{H}_2\text{O}$.

Pt(1)-N(2)	1.940 (5)
Pt(1)-N(3)	2.004 (5)
Pt(1)-N(1)	2.002 (5)
Pt(1)-Cl(1)	2.296 (2)
N(1)-C(1)	1.386 (8)
N(2)-C(10)	1.352 (8)
N(3)-C(15)	1.376 (8)
N(2)-Pt(1)-N(1)	79.9 (2)
N(1)-Pt(1)-N(3)	160.8 (2)
N(1)-Pt(1)-Cl(1)	100.12 (9)
N(2)-Pt(1)-N(3)	81.0 (2)
N(2)-Pt(1)-Cl(1)	178.67 (9)
N(3)-Pt(1)-Cl(1)	99.0 (2)
N(2)-C(6)-C(5)	113.3 (6)
N(2)-C(10)-C(11)	112.8 (6)

Table 3. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for $[\text{Pt}(\text{terpy})\text{Cl}]\text{Cl}\cdot 2\text{H}_2\text{O}$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
Pt (1)	2311(1)	58(1)	620(1)	15(1)
Cl (1)	2111(2)	-1147(1)	13335(1)	23(1)
Cl (2)	2814(2)	1927(1)	6011(1)	30(1)
O (1)	5730(8)	661(3)	5445(6)	91(3)
O (2)	-415(8)	639(3)	5539(5)	68(2)
N (1)	2625(6)	-270(3)	-737(4)	15(1)
N (2)	2545(6)	1076(3)	24(4)	14(1)
N (3)	2153(7)	736(3)	1787(4)	21(1)
C (1)	2663(8)	-1032(4)	-1079(5)	22(2)
C (2)	2866(8)	-1189(4)	-2038(5)	23(2)
C (3)	3057(9)	-555(4)	-2664(6)	30(2)
C (4)	2992(7)	191(3)	-2290(5)	18(2)
C (5)	2805(8)	319(4)	-1376(5)	17(2)
C (6)	2778(8)	1105(4)	-915(5)	19(2)
C (7)	2959(9)	1830(4)	-1372(5)	24(2)
C (8)	2896(9)	2503(4)	-763(5)	24(2)
C (9)	2635(9)	2441(4)	199(6)	26(2)
C (10)	2459(8)	1714(3)	596(5)	14(1)
C (11)	2290(8)	1511(4)	1614(5)	17(2)
C (12)	2329(8)	2062(4)	2364(5)	22(2)
C (13)	2227(8)	1823(4)	3298(5)	26(2)
C (14)	2071(9)	1021(4)	3469(5)	27(2)
C (15)	2043(9)	490(4)	2724(5)	23(2)

These results indicate that the coordination geometry is essentially square-planar with distortions arising from constraints of the terpyridine ligand, as found in several related structures^{13,14}.

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References

1. M. Howe-Grant, K.C. Wu, W.R. Bauer, and S.J. Lippard, **Biochemistry**, **15**, 4339 (1976).
2. Y.S. Wong and S.J. Lippard, **J. Chem. Soc. Chem. Comm.**, 825 (1977).
3. H.K. Yip, L.K. Cheng, K.K. Cheung and C.M. Che, **J. Chem. Soc. Dalton Trans.** 2933 (1993).
4. G. Annibale, M. Brandolisio and B. Pitteri, **Polyhedron**, **14**, 451 (1995).
5. J.W. Pflugrath and A. Messerschmidt, MADNES. Distributed by Delft Instruments, Delft, The Netherlands, 1989
6. J.A. Darr, S.R. Drake, M.B. Hursthouse and K. M.A. Malik, **Inorg. Chem.**, **32**, 5704 (1993).
7. A.I. Karaulov, ABSMAD. Program for FAST Data Processing. University of Wales, Cardiff, Wales, 1991.

8. G.M. Sheldrick, **Acta Cryst**, **A46**, 467 (1990).
9. G.M. Sheldrick, SHELXL93. Program for the Refinement of Crystal Structures. University of Gottingen, Germany, 1993.
10. L.J. Farrugia, **J. Appl. Cryst.**, **32**, 837 (1999).
11. R.D. Gillard, A. Sengul and A. Oldroyd, **Transition Met. Chem.**, **26**, 339 (2001).
12. G.M. Intille, C.E. Pfluger and W.A. Baker, JR, **J. Cryst. Mol. Struct.**, **3**, 47 (1973).
13. K.W. Jennette, T.J. Gill, J.A. Sadownik and S.J. Lippard, **J. Am. Chem. Soc.**, **98**, 6159 (1976).
14. R.S. Osborn and D. Rogers, **J. Chem. Soc. Dalton Trans**, 1002 (1974).