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Key indicators

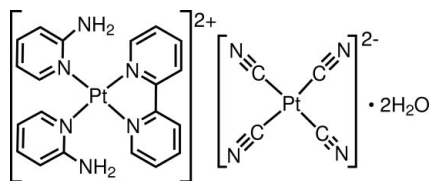
Single-crystal X-ray study
 $T = 296\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.018\text{ \AA}$
H-atom completeness 84%
 R factor = 0.047
 wR factor = 0.131
Data-to-parameter ratio = 14.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(2-aminopyridine)(2,2'-bipyridine)-
platinum(II) tetracyanoplatinate(II)
dihydrate

In the title compound, $[\text{Pt}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{C}_5\text{H}_6\text{N}_2)_2][\text{Pt}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$, cations and anions alternate along the a axis, giving a one-dimensional chain of the Magnus green salt type. The electrostatic interactions between the divalent cations and anions, together with the π - π stacking associations between the 2,2'-bipyridine moieties, contribute to the stabilization of the crystal packing. Two different Pt...Pt distances [5.2034 (6) and 4.5599 (6) Å] alternate along the one-dimensional stack.

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Comment

Considerable attention has been paid in our laboratory to the studies of one-dimensional substances (Sakai, Ishigami *et al.*, 2002; Sakai, Takeshita *et al.*, 1998; Sakai, Tanaka *et al.*, 1998). In the hope of obtaining robust materials, we recently started to explore the one-dimensional double salts related to the Magnus green salt (MGS), $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ (Atoji *et al.*, 1957). Such complexes have attracted considerable attention due to their electrical conduction properties (Miller, 1982), photoluminescence properties (Houling & Frank, 1985) and vapochromic behaviours (Buss *et al.*, 1998). Here we report the crystal structure of the title compound, $[\text{Pt}(\text{bpy})(\text{ampy})_2][\text{Pt}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ (I), which has a relevance to our recent reports on $[\text{Pt}(\text{bpy})(\text{ampy})_2][\text{Pt}(\text{ox})_2] \cdot 2\text{H}_2\text{O}$ [(II); bpy = 2,2'-bipyridine, ampy = 2-aminopyridine; Sakai *et al.*, 2003*b*] and $[\text{Pt}(\text{bpy})(\text{ampy})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ [(III); Sakai *et al.*, 2003*a*].



(I)

A cation, an anion and two water molecules are found in the asymmetric unit of (I) (Fig. 1). Selected bond distances and angles are listed in Table 1. Possible hydrogen-bonding geometries are also summarized in Tables 2 and 3. As shown in Fig. 2, cations and anions alternate along the a axis. Importantly, the one-dimensional stacking associations are not only stabilized with electrostatic interactions but also with π - π stacking interactions between the part of bpy units. As shown in Fig. 2*b*, one pyridyl ring (N1/C1-C5) forms a stack with the $[\text{Pt}(\text{CN})_4]^{2-}$ anion, while the other ring (N2/C6-C10) gives a one-dimensional π -stacking array along the $(x, \frac{1}{2}, \frac{1}{2})$ axis. Two independent interplanar separations between the $[\text{Pt}(\text{CN})_4]^{2-}$ anion and the N1/C1-C5 plane alternate along the a axis; these are 3.59 (2) and 3.54 (2) Å, which are respectively estimated as

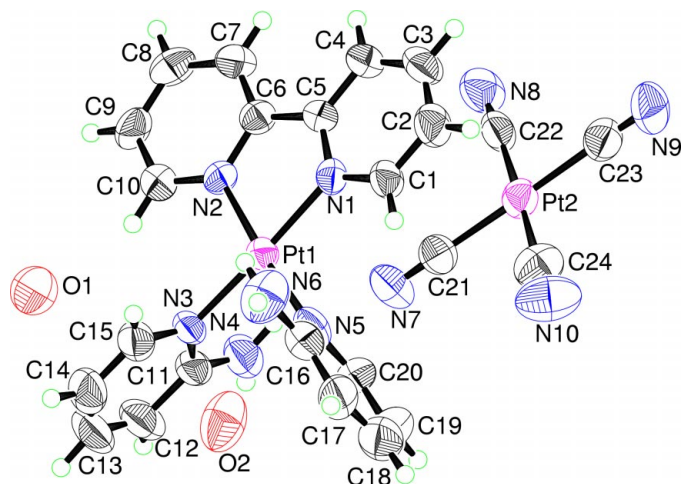
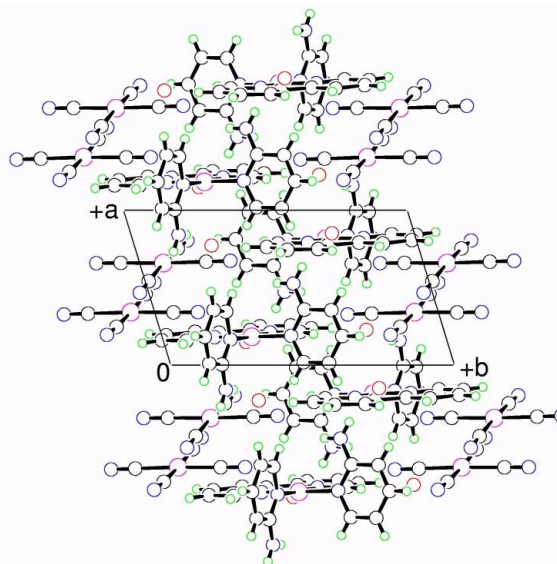


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

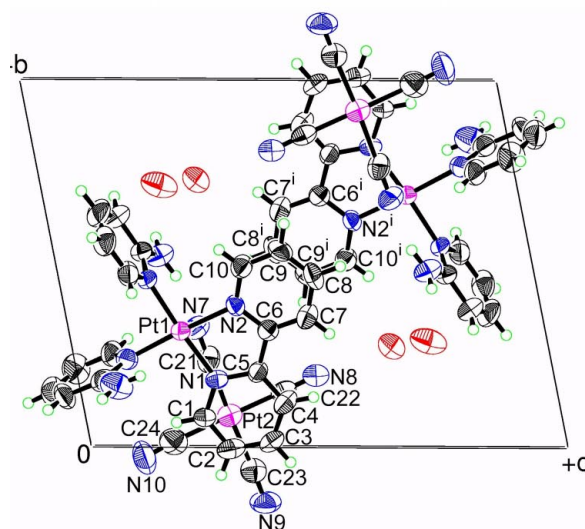
a separation between Pt2/C21/N7/C22/N8 and N1/C1–C5 and that between Pt2/C21/N7/C22/N8 and N1ⁱ/C1ⁱ–C5ⁱ [symmetry code: (i) $x + 1, y, z$]. On the other hand, two independent π – π separations between the pyridyl rings also alternate along the a axis; these are 3.567 (1) Å for the separation between C7–C10 and C7ⁱ–C10ⁱ, and 3.425 (1) Å for that between C7–C10 and C7ⁱⁱ–C10ⁱⁱ [symmetry codes: (i) $1 - x, 1 - y, 1 - z$ (ii) $-x, 1 - y, 1 - z$]. As previously reported, the one-dimensional stack in (II) is primarily stabilized with alternating stacks of cations and anions, in which the bpy unit shows a good fit to the molecular shape of the [Pt(ox)₂]²⁻ anion and no bpy–bpy stacking interaction is achieved in (II).

The Pt...Pt distances in (II) are reported as 3.9294 (6) and 5.0302 (7) Å (Sakai *et al.*, 2003*b*), while those in (I) are Pt1...Pt2 = 5.2034 (6) Å and Pt1...Pt2($x - 1, y, z$) = 4.5599 (6) Å. The short Pt...Pt distance [3.9294 (6) Å] observed in (II) reflects a good fit between the bpy and the [Pt(ox)₂]²⁻ units, as discussed above. This is also relevant to the fact that the ampy ligands sterically block the approach of either [Pt(ox)₂]²⁻ or [Pt(CN)₄]²⁻. The steric factor arising from the ampy ligand well explains the relatively long Pt...Pt distances observed in (I) and (II). A similarly long Pt...Pt distance was previously observed for a unique double salt [Pt(pzH)₄][PtCl₄][*cis*-PtCl₂(pzH)₂]₂ (pzH = pyrazole; Pt...Pt = 3.9388 (1) Å; Sakai *et al.*, 2000), in which the pyrazole rings block the approach of the neighbouring [PtCl₄]²⁻ ions.

The mean-plane calculation performed for the four coordinated N atoms in [Pt(bpy)(ampy)₂]²⁺ reveals that the coordination of Pt1 is nearly planar (the four-atom r.m.s deviation is 0.017 Å). The coordination of [Pt(CN)₄]²⁻ involving Pt2 is slightly distorted toward a tetrahedral geometry, where the four-atom r.m.s deviation is 0.040 Å. The dihedral angle between the two Pt coordination planes is 17.4 (2)°. The atoms Pt1 and Pt2 are displaced from their individual coordination planes by 0.026 (4) and 0.022 (6) Å, respectively. On the other hand, the two pyridyl planes within bpy are twisted by 4.35 (3)° with respect to one another. The Pt coordination



(a)



(b)

Figure 2
Projections of the crystal structure of (I) (a) along the c axis, and (b) along the a axis. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

plane involving Pt1 and the bpy plane are inclined at an angle of 4.35 (2)°. The pyridyl planes of the 2-aminopyridines are inclined with respect to the Pt1 coordination plane by 82.86 (3)° for the plane defined by N3/N4/C11–C15 and by 83.94 (3)° for that defined by N5/N6/C16–C20.

Experimental

Single crystals of (I) were prepared by our unique diffusion method as follows: a solution of [Pt(bpy)(2-aminopyridine)₂](NO₃)₂·2H₂O (0.01 mmol, 0.0068 g; Sakai *et al.*, 2003*a*) in water (4 ml) and a solution of K₂[Pt(CN)₄]·3H₂O (0.01 mmol, 0.0043 g) in water (4 ml) were prepared separately. A Petri dish having a diameter of *ca* 60 mm and a depth of *ca* 15 mm was separated into three zones using filter

papers; the central zone (zone 2) must be sandwiched by the other two zones (zones 1 and 3), while zones 1 and 3 have no direct contact. Water (5 ml) was then added to the Petri dish to fill all three zones. Finally, the two solutions mentioned above were added dropwise, at the same time, to zones 1 and 3. The solution was left to stand at room temperature overnight, affording (I) as colourless needles (yield 77%). Analysis calculated for $C_{24}H_{24}N_{10}O_2Pt_2$: C 32.96, H 2.77, N 16.01%; found: C 33.32, H 2.48, N 15.85%.

Crystal data

$[Pt(C_{10}H_8N_2)(C_5H_6N_2)_2][Pt(CN)_4] \cdot 2H_2O$
 $M_r = 874.71$
 Triclinic, $P\bar{1}$
 $a = 7.2972$ (5) Å
 $b = 12.7313$ (8) Å
 $c = 15.7612$ (10) Å
 $\alpha = 98.266$ (1)°
 $\beta = 98.963$ (1)°
 $\gamma = 105.187$ (1)°
 $V = 1369.45$ (15) Å³
 $Z = 2$
 $D_x = 2.121$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4752 reflections
 $\theta = 2.4$ – 25.4 °
 $\mu = 10.25$ mm⁻¹
 $T = 296$ (2) K
 Needle, colourless
 $0.32 \times 0.07 \times 0.07$ mm

Data collection

Bruker SMART APEX CCD-detector diffractometer
 ω scans
 Absorption correction: Gaussian (XPREP in SAINT; Bruker, 2001)
 $T_{min} = 0.215$, $T_{max} = 0.604$
 7239 measured reflections
 4918 independent reflections
 4030 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.082$
 $\theta_{max} = 25.4$ °
 $h = -8 \rightarrow 8$
 $k = -15 \rightarrow 15$
 $l = -17 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.131$
 $S = 1.10$
 4918 reflections
 343 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.5602P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 4.09$ e Å⁻³
 $\Delta\rho_{min} = -3.13$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------|------------|----------------------|------------|
| Pt1–N1 | 2.002 (7) | Pt2–C21 | 2.003 (12) |
| Pt1–N2 | 2.003 (8) | Pt2–C23 | 2.016 (13) |
| Pt1–N3 | 2.030 (7) | Pt2–C24 | 2.048 (16) |
| Pt1–N5 | 2.032 (9) | Pt1–Pt2 | 5.2034 (6) |
| Pt2–C22 | 1.940 (13) | Pt1–Pt2 ⁱ | 4.5599 (6) |
| N1–Pt1–N2 | 80.0 (3) | C22–Pt2–C21 | 87.1 (4) |
| N1–Pt1–N3 | 176.1 (3) | C22–Pt2–C23 | 90.1 (5) |
| N2–Pt1–N3 | 96.2 (3) | C21–Pt2–C23 | 177.0 (5) |
| N1–Pt1–N5 | 96.6 (3) | C22–Pt2–C24 | 176.4 (5) |
| N2–Pt1–N5 | 175.9 (3) | C21–Pt2–C24 | 92.7 (5) |
| N3–Pt1–N5 | 87.2 (3) | C23–Pt2–C24 | 90.2 (5) |

Symmetry code: (i) $x - 1, y, z$.

Table 2

Contact distances (Å).

| | | | |
|-----------------------|------------|------------------------|------------|
| O1...O2 ⁱ | 2.774 (14) | O1...N9 ⁱⁱⁱ | 3.071 (16) |
| O1...N8 ⁱⁱ | 2.807 (15) | O2...N9 ⁱⁱⁱ | 2.899 (14) |

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $x, 1 + y, z$.

Table 3

Hydrogen-bonding geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|----------------------------|-------|--------------|--------------|----------------|
| N6–H6B...N10 ^{iv} | 0.86 | 2.53 | 3.316 (17) | 153 |
| N4–H4A...N7 | 0.86 | 2.36 | 3.121 (13) | 147 |
| N4–H4B...O2 | 0.86 | 2.01 | 2.835 (13) | 161 |

Symmetry code: (iv) $-x, -y, -z$.

All H atoms, except for those of the water molecules, were located at idealized positions [$C-H$ (aromatic) = 0.93 Å and $N-H$ (amino) = 0.86 Å], and included in the refinement in a riding-model approximation, with $U_{iso} = 1.2U_{eq}$ of the carrier atom. Water H atoms were not located. In the final difference Fourier synthesis, a relatively large residual electron density with a height of 4.09 e Å⁻³ was observed 0.86 Å from Pt2. In addition, 7 more peaks in the range 1.00–1.44 e Å⁻³ were observed within 0.96 Å of Pt atoms. The deepest hole (–3.13 e Å⁻³) was located 0.77 Å from Pt2.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: KENX (Sakai, 2002) and ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97, TEXSAN (Molecular Structure Corporation, 2001) and KENX.

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