Di-μ-2-aminopyridinato-bis[(2,2′-bipyridine)platinum(II)] dinitrate tetrahydrate as a head-to-tail isomer

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Di-μ-2-aminopyridinato-bis[(2,2′-bipyridine)-platinum(II)] dinitrate tetrahydrate as a head-to-tail isomer

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In the title compound, $[Pt_2(C_{10}H_8N_2)_2(C_5H_5N_2)_2](NO_3)_2\cdot4H_2O$, two 2-aminopyridinate ligands bridge two Pt atoms in a head-to-tail fashion, the Pt—Pt distance being 2.8724 (6) Å. The dimers form a one-dimensional stack based on π–π stacking interactions between the bpy (2,2′-bipyridine) units, where the interplanar separations are estimated as 3.44 (2) and 3.45 (1) Å. No metal–metal interaction exists between the dimers.

Comment

We recently reported the syntheses and crystal structures of several platinum(II) complexes of 2-aminopyridine (ampyH): $[Pt(bpy)(ampyH)_2](NO_3)_2\cdot2H_2O$ [(II); bpy is 2,2′-bipyridine and ampyH is 2-aminopyridine; Sakai *et al.*, 2003a], $[Pt(bpy)(ampyH)_2][Pt(ox)_2]\cdot2H_2O$ (ox is oxalate; Sakai *et al.*, 2003b) and $[Pt(bpy)(ampyH)_2][Pt(CN)_4]\cdot2H_2O$ (Sakai *et al.*, 2004). Our initial interest in the use of ampyH lay in the exploration of multinuclear platinum(II) complexes having 2-aminopyridinate (ampy) as a bridging ligand. Nevertheless, only the mononuclear complex (II), except for such multinuclear complexes, was obtained in our previous studies. In our hope to obtain a trinuclear platinum(II) chain complex, $[(bpy)Pt(\mu\text{-ampy})_2Pt(\mu\text{-ampy})_2Pt(bpy)]^{2+}$, complex (II) was reacted with a variety of platinum(II) complexes, such as $[Pt(NH_3)_4]^{2+}$, *cis*-$[Pt(NH_3)_2(OH_2)_2]^{2+}$, *cis*-$PtCl_2(dimethyl\text{-}sulfoxide)_2$, *etc*. However, it was found that the title dinuclear complex, HT-$[Pt_2(bpy)_2(\mu\text{-ampy})_2](NO_3)_2\cdot4H_2O$ [abbreviated as (I), HT = head-to-tail], was always obtained as the main product. As a result, we found that a simple decomposition reaction of (II) in aqueous media results in the formation of (I) (see *Experimental*).
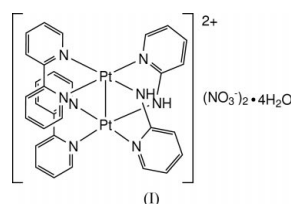
We report here the synthesis and crystal structure of (I) as the first example of a platinum complex involving ampy as a bridging ligand, even though two complexes with bridging ampy ligands have been reported for Ru (Chakravarty *et al.*, 1984) and Rh (Kanematsu *et al.*, 1999). It should be noted here that ampy is isoelectronic with the α-pyridonate ligand which was used to determine the first crystal structure for the so-called 'platinum blues', $[Pt^{2.25+}_2(NH_3)_4(\mu\text{-}\alpha\text{-pyridonato})_2]_2\text{-}(NO_3)_5\cdot H_2O$ (Barton *et al.*, 1979).
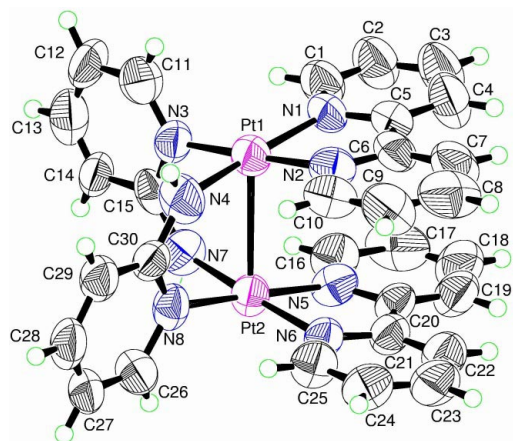
Figure 1
The structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level.
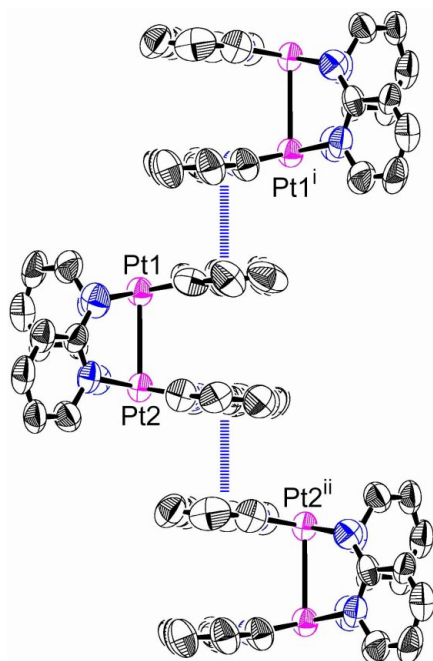

Figure 2
A view showing two crystallographically independent dimer–dimer associations. H atoms have been omitted for clarity. [Symmetry codes: (i) $2 - x, 2 - y, -z$; (ii) $1 - x, 2 - y, -z$.]

The asymmetric unit of (I) involves a diplatinum(II) cation and two nitrate anions. Although the elemental analysis indicated (I) to be a tetrahydrate product, only two of the water molecules could be located in this study (see *Experimental*). The nitrate geometries suffer from disorder phenomena, which are considered as the main cause for the relatively large displacement parameters for the main diplatinum cation.

Two Pt(bpy) units are bridged by two ampy ligands in a head-to-tail fashion (Fig. 1). The mean-plane calculations performed for the four coordinated atoms reveal that the two Pt coordination arrangements are planar, where the four-atom r.m.s. deviation is 0.011 Å for the N1/N2/N3/N4 plane and 0.006 Å for the N5/N6/N7/N8 plane. The dihedral angle
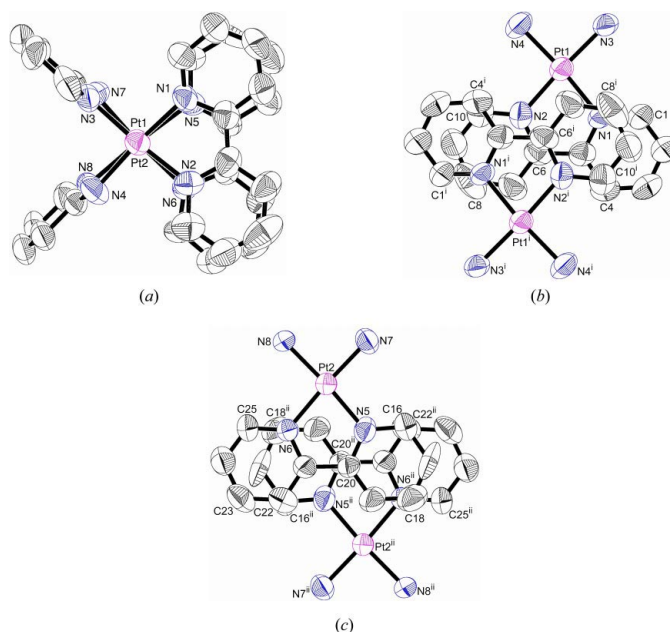

Figure 3
Views showing three different stacking interactions within the one-dimensional column: (*a*) an intradimer association, (*b*) an interdimer association through $(1,1,0)$, and (*c*) an interdimer association through $(\frac{1}{2},1,0)$. H atoms have been omitted for clarity.[Symmetry codes: (i) $2 - x, 2 - y, -z$; (ii) $1 - x, 2 - y, -z$.]

between the two Pt coordination planes within the dimeric unit (τ) and the average torsional twist of them about the Pt—Pt axis (ω) are estimated as $\tau = 22.0 (2)°$ and $\omega = 6.5 (5)°$ (see also Table 1), where $\omega = 0°$ denotes that the two Pt coordination planes stack in an eclipsed fashion. The two bpy ligands are also found to be planar, where the 12-atom r.m.s. deviations are 0.015 Å for the plane defined by N1/N2/C1–C10 and 0.012 Å for that defined by N5/N6/C16–C25. Within the dimer unit, the tilt angle between the two bpy planes [$7.90 (9)°$] is $14.1 (3)°$ smaller than that between the two Pt coordination planes, indicating that a relatively strong π-stacking interaction is achieved within the unit (see Figs. 2 and 3*a*), where the interplanar spacing between these bpy planes is 3.60 (14) Å (some short contacts are listed in Table 2). Atom Pt2 is shifted out of the coordination plane by 0.013 (5) Å towards the outside of the dimeric unit, while the shift of atom Pt1 from the coordination plane [0.001 (5) Å] is negligible. The intradimer Pt—Pt distance [Pt1—Pt2 = 2.8724 (6) Å] is quite similar to those observed for several analogs in a head-to-tail isomers; 2.899 (2) Å for HT-[Pt₂(bpy)₂(μ-α-pyrrolidinonato)₂](ClO₄)₂ (Matsumoto *et al.*, 1992), and 2.89 Å for HT-[Pt₂(bpy)₂(μ-pivalamidato)₂]²⁺ (Sakai *et al.*, 1993). However, the intradimer Pt—Pt distance in (I) is slightly longer than the value of 2.8489 (17) Å reported for HH-[Pt₂(phen)₂(μ-pivalamidato)₂](NO₃)₂·2H₂O (Sakai, Kurashima *et al.*, 2003), revealing that the π–π stacking interaction between the equatorial ligands within the dimeric unit is weaker in the bpy system than in the 1,10-phenanthroline system.

As shown in Figs. 2 and 4, the dimer cations stack along the *a* axis to give one-dimensional stacks of bpy units. The interdimer Pt···Pt distances are much too long to consider any
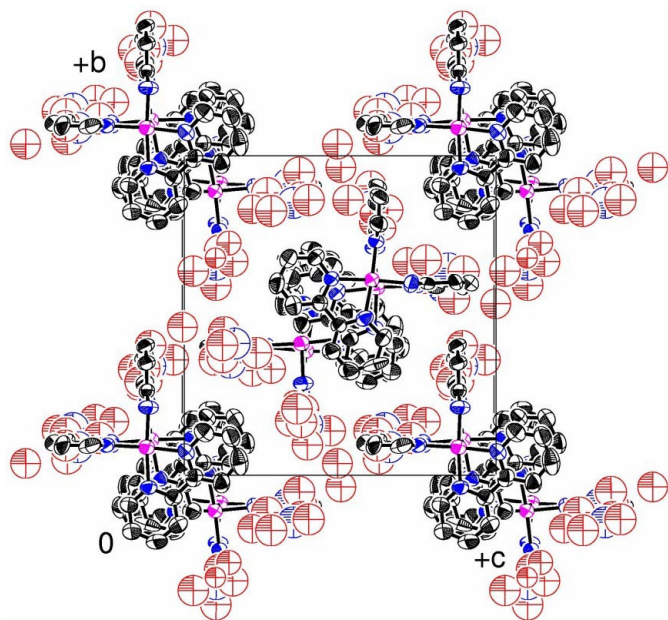
Figure 4
A crystal packing view along the *a* axis, showing one-dimensional stacks of bpy units. H atoms have been omitted for clarity.

metal–metal interactions (see Table 1). A quite similar type of one-dimensional array of dimers can be found in the crystal structure reported for HT-[Pt₂(bpy)₂(μ-α-pyrrolidinonato)₂](ClO₄)₂ (Matsumoto *et al.*, 1992). Two crystallographically independent dimer–dimer associations occur, as shown in Figs. 2, 3(*b*) and 3(*c*). In each case, two neighboring dimer cations are correlated through an inversion center. The interplanar spacing between the stacked bpy planes is 3.44 (2) Å for the stack Pt1···Pt1^i [symmetry code: (i) $2 - x$, $2 - y$, $-z$] (Fig. 3*b*), and is 3.45 (1) Å for the stack Pt2···Pt2^{ii} [symmetry code: (ii) $1 - x$, $2 - y$, $-z$] (Fig. 3*c*).

Efforts to achieve a triplatinum chain structure are still in progress in our laboratory.

Experimental

A solution of [Pt(bpy)(ampyH)₂](NO₃)₂·2H₂O (0.10 mmol, 0.07 g; Sakai *et al.*, 2003*a*) in water (10 ml) was sealed in a pressure-resistant vial and was heated at 413 K for 6 h. After cooling to room temperature, the solution was evaporated to a total volume of about 5 ml until a small amount of red precipitate started to deposit. Leaving the solution to stand in air at room temperature overnight afforded (I) as red needles (yield: 20%). Analysis calculated for C₃₀H₃₄N₁₀O₁₀Pt₂: C 33.22, H 3.16, N 12.91%; found: C 33.17; H 2.73, N 12.72%. IR (KBr): 3414 (*w*, *br*), 1623 (*m*), 1558 (*w*), 1506 (*m*), 1449 (*w*), 1384 (*s*, *br*), 1267 (*w*), 1160 (*w*), 1018 (*w*), 768 (*m*), 723 (*w*), 669 (*w*) cm⁻¹. UV–visible absorption (in H₂O, 293 K): λ_{max} = 248 nm (ε = 47300 $M^{-1}cm^{-1}$), λ_{max} = 303 nm (ε = 23700 $M^{-1}cm^{-1}$), λ_{sh} = 350 nm (ε = 5920 $M^{-1}cm^{-1}$), λ_{max} = 485 nm (ε = 2290 $M^{-1}cm^{-1}$; this band is assigned as a so-called metal–metal-to-ligand charge transfer transition and is responsible for the red color of the complex). The compound shows an emission centered at 670 nm (uncorrected data recorded on a Shimadzu RF-5300PC spectrofluorometer equipped with a Hamamatsu R928 photomultiplier tube) upon excitation at 425 nm, at room temperature, in the solid state. The crystals of (I) are

quite stable in air at room temperature and do not lose their luster. The number of water molecules has been determined as four based on the results of elemental analysis. However, only two could be located.

Crystal data

[Pt₂(C₁₀H₈N₂)₂(C₅H₅N₂)₂](NO₃)₂·4H₂O	D_x = 1.977 Mg m⁻³
M_r = 1048.82	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 5776
a = 14.1356 (8) Å	reflections
b = 16.0180 (9) Å	θ = 2.3–20.2°
c = 16.4055 (9) Å	μ = 7.99 mm⁻¹
β = 108.411 (1)°	T = 296 (2) K
V = 3524.5 (3) Å³	Needle, red
Z = 4	0.23 × 0.07 × 0.04 mm

Data collection

Bruker SMART APEX CCD-detector diffractometer	7197 independent reflections
ω scans	4146 reflections with $I > 2\sigma(I)$
Absorption correction: Gaussian (*XPREP* in *SAINT*; Bruker, 2001)	R_{int} = 0.095
	θ_{max} = 26.4°
	$h = -17 \rightarrow 17$
T_{min} = 0.298, T_{max} = 0.735	$k = -20 \rightarrow 20$
40126 measured reflections	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.051	$w = 1/[\sigma^2(F_o^2) + (0.0718P)^2]$
$wR(F^2)$ = 0.135	where $P = (F_o^2 + 2F_c^2)/3$
S = 0.90	$(\Delta/\sigma)_{max}$ = 0.001
7197 reflections	$\Delta\rho_{max}$ = 2.02 e Å⁻³
427 parameters	$\Delta\rho_{min}$ = −0.73 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Pt1—N1	2.028 (8)	Pt2—N6	2.024 (8)
Pt1—N2	2.017 (9)	Pt2—N7	1.985 (9)
Pt1—N3	2.043 (9)	Pt2—N8	2.020 (8)
Pt1—N4	2.001 (9)	Pt1—Pt2	2.8724 (6)
Pt2—N5	2.017 (8)		
N4—Pt1—N2	94.6 (4)	N7—Pt2—N5	96.3 (4)
N4—Pt1—N1	174.8 (4)	N7—Pt2—N8	88.0 (3)
N2—Pt1—N1	80.2 (4)	N5—Pt2—N8	175.6 (3)
N4—Pt1—N3	89.0 (3)	N7—Pt2—N6	176.3 (3)
N2—Pt1—N3	176.3 (3)	N5—Pt2—N6	80.1 (3)
N1—Pt1—N3	96.2 (3)	N8—Pt2—N6	95.6 (3)
N3—Pt1—Pt2—N7	6.2 (3)	N4—Pt1—Pt2—N8	7.2 (4)
N1—Pt1—Pt2—N5	6.4 (4)	N2—Pt1—Pt2—N6	6.2 (3)

Table 2
Contact distances (Å).

Pt1···Pt1^i	6.2077 (9)	C8···C1^i	3.56 (2)
Pt2···Pt2^{ii}	6.4875 (9)	C6···C6^i	3.58 (2)
N1···N5	3.491 (12)	C9···C1^i	3.471 (19)
N2···N6	3.440 (12)	N2···C5^i	3.513 (14)
C1···C16	3.552 (17)	N2···C6^i	3.590 (13)
C9···C24	3.605 (19)	N5···C21^{ii}	3.582 (13)
C10···C25	3.418 (16)	N6···C18^{ii}	3.509 (16)
C9···N1^i	3.630 (17)	C16···C22^{ii}	3.431 (17)
C10···C4^i	3.525 (19)	C18···C25^{ii}	3.602 (18)
C10···C5^i	3.562 (15)	C20···C20^{ii}	3.48 (2)
C8···N1^i	3.530 (17)		

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

The two nitrate ions involved in the asymmetric unit were both assumed to be disordered over two sites. Within each set of disordered atoms, all were assumed to have the same isotropic displacement parameter, and their occupation factors were assumed as 50%. The N—O distances were restrained at 1.22 (1) Å, the three O···O distances in each disordered nitrate were restrained as equal, and each nitrate was restrained to be planar. Only two of the four water molecules, which were believed to be involved could be located and both were treated as being disordered over two sites with 50% population each. All H atoms, except for those of water molecules, were placed in idealized positions [C—H(aromatic) = 0.93 Å and N—H = 0.86 Å], and included in the refinement in 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, four residual peaks in the range 1.06–2.02 e Å^{-3} were observed not only within 0.97 Å of the Pt atoms but also near atoms N10A and N5. The deepest hole was located 0.31 Å from O11A.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *KENX* (Sakai, 2002); software used to prepare material for publication: *SHELXL*97, *TEXSAN* (Molecular Structure Corporation, 2001) and *ORTEP*II (Johnson, 1976), *KENX*.

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