Crystal structure of dibromo(2,2′-bipyrimidine-κ^2N,N')platinum(II), $PtBr_2(C_8H_6N_4)$

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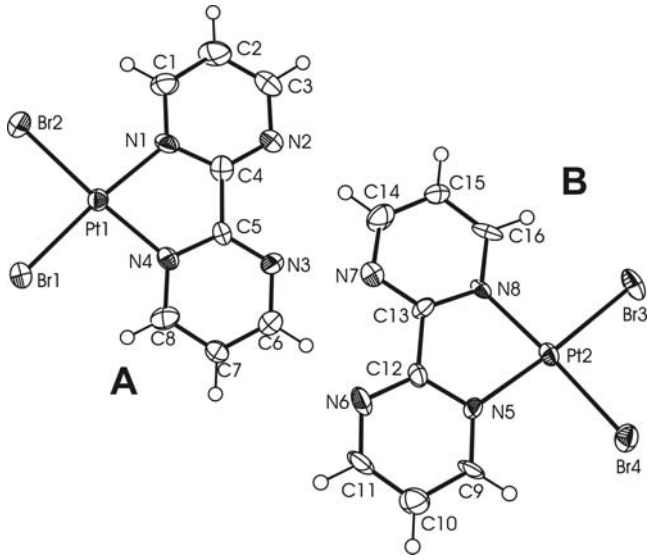

Abstract

$C_8H_6Br_2N_4Pt$, monoclinic, $P12_1/c1$ (no. 14), a = 15.214(1) Å, b = 21.326(2) Å, c = 6.9479(6) Å, β = 102.160(2)°, V = 2203.6 Å^3, Z = 8, $R_{gt}(F)$ = 0.043, $wR_{ref}(F^2)$ = 0.092, T = 200 K.

Source of material

To a solution of K_2PtBr_4 (0.3753 g, 0.633 mmol) in H_2O (30 ml) and MeOH (10 ml) was added 2,2′-bipyrimidine (bpym, 0.0503 g, 0.318 mmol), and the mixture was stirred for 3 h at room temparature. The precipitate was then separated by filtration, washed with H_2O and acetone, and dried under vacuum, to give a dark brown powder (0.1851 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a dimethyl sulfoxide solution at 80 °C.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å and U_{iso}(H) = 1.2 U_{eq}(C). The highest peak (2.43 e·Å^{-3}) and the deepest hole (–2.67 e·Å^{-3}) in the difference Fourier map are located 0.85 Å and 0.97 Å from the atoms Pt2 and Pt1, respectively.

Discussion

The title complex is isomorphous with the analogous Pt(II) complex [$PtCl_2$(bpym)] [1]. The asymmetric unit contains two crystallographically independent molecules with identical geometry within experimental errors. Each Pt(II) ion has a distorted square-planar environment defined by two N atoms of the chelating 2,2′-bipyrimidine ligand and two Br^- anions. The main contribution to the distortion is the tight N–Pt–N chelate angles (∠N1–Pt1–N4 = 80.0(4)° and ∠N5–Pt2–N8 = 81.0(3)°), which results in non-linear *trans* arrangements (∠Br1–Pt1–N1 = 174.8(3)°, ∠Br2–Pt1–N4 = 175.9(3)°, ∠Br3–Pt2–N5 = 175.9(3)° and ∠Br4–Pt2–N8 = 176.5(2)°). The Pt—N and Pt—Br bond lengths are almost equivalent, respectively (d(Pt1—N1/4) = 2.027(9) Å and 2.036(9) Å, d(Pt2—N5/8) = 2.022(9) Å and 2.032(9) Å; d(Pt1—Br1/2) = 2.420(1) Å and 2.430(1) Å, d(Pt2—Br3/4) = 2.416(1) Å and 2.420(1) Å). In the crystal structure, the two independent and nearly planar complexes are stacked in two different kinds of packing pattern along [001], and the complexes are not parallel with a dihedral angle of 12.95(6)°. The stacking aggregation is similar to that of [$PtCl_2$(bpym)] [1]. When viewed down the c axis, the successive complexes with the Pt1 atom (complex **A**) are rotated by about 117° with a Pt···Pt distance of 3.6070(7) Å. The successive complexes with the Pt2 atom (complex **B**), on the other hand, are stacked in the opposite direction with the Pt2···Pt2 distances of 3.4985(7) Å and 3.5700(7) Å. In the columns of the complexes **A** and **B**, numerous intermolecular π-π interactions between adjacent pyrimidine rings are present. The shortest distance between Cg1 (the centroid of ring N3-C6) and Cg1^i (symmetry code : x,½–y,–½+z) is 3.831(7) Å, and the dihedral angle between the ring planes is 1°. For Cg1 and Cg2 (ring N7-C14), the centroid-centroid distance is 5.067(7) Å and the dihedral angle between the ring planes is 14.9(6)°. The two independent complexes are connected by C–H···N interactions with d(C7···N6) = 3.40(2) Å. In addition, there are intramolecular C–H···Br hydrogen bonds with d(C–H···Br) = 3.33(1) - 3.39(1) Å and weak intermolecular C–H···Br hydrogen bonds with d(C–H···Br) = 3.60(1) - 3.82(1) Å.

Table 1. Data collection and handling.

Crystal:	brown rod, size 0.05 × 0.06 × 0.36 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	199.58 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	51.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13550, 4319
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2968
$N(param)_{refined}$:	271
Programs:	SHELXS-97, SHELXL-97 [2], ORTEP-III [3], PLATON [4]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.7058	0.1723	0.7692	0.043
H(2)	4*e*	0.7110	0.0635	0.7723	0.052
H(3)	4*e*	0.5772	0.0070	0.6709	0.041
H(6)	4*e*	0.2059	0.1622	0.3986	0.046
H(7)	4*e*	0.2144	0.2712	0.3932	0.038
H(8)	4*e*	0.3532	0.3207	0.5076	0.039
H(9)	4*e*	–0.1460	0.0958	0.6637	0.037
H(10)	4*e*	–0.1360	0.2062	0.6571	0.046
H(11)	4*e*	0.0085	0.2498	0.7250	0.042
H(14)	4*e*	0.3511	0.0657	0.8253	0.045
H(15)	4*e*	0.3280	–0.0421	0.8119	0.038
H(16)	4*e*	0.1798	–0.0788	0.7786	0.036

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	4*e*	0.55201(3)	0.27276(2)	0.64902(7)	0.0234(3)	0.0228(3)	0.0237(3)	–0.0023(2)	0.0049(2)	0.0010(2)
Br(1)	4*e*	0.51166(8)	0.38267(6)	0.6244(2)	0.0329(7)	0.0233(7)	0.0377(8)	–0.0032(5)	0.0064(6)	0.0001(6)
Br(2)	4*e*	0.70903(8)	0.30283(6)	0.7507(2)	0.0270(7)	0.0348(8)	0.0409(8)	–0.0071(6)	0.0019(6)	0.0007(6)
N(1)	4*e*	0.5737(6)	0.1790(4)	0.667(1)	0.030(6)	0.023(6)	0.023(6)	0.006(5)	0.000(5)	0.006(5)
N(2)	4*e*	0.4979(7)	0.0807(5)	0.612(2)	0.031(6)	0.023(7)	0.037(7)	0.003(5)	0.006(5)	0.002(5)
N(3)	4*e*	0.3379(6)	0.1480(5)	0.492(2)	0.022(6)	0.027(6)	0.045(7)	0.000(5)	–0.002(5)	–0.003(5)
N(4)	4*e*	0.4235(6)	0.2413(4)	0.560(1)	0.031(6)	0.022(6)	0.018(5)	0.000(5)	0.005(4)	0.005(4)
C(1)	4*e*	0.6520(8)	0.1488(6)	0.728(2)	0.025(7)	0.040(9)	0.042(8)	0.007(6)	0.007(6)	0.002(7)
C(2)	4*e*	0.6554(9)	0.0848(6)	0.730(2)	0.039(9)	0.04(1)	0.049(9)	0.018(7)	0.008(7)	–0.013(7)
C(3)	4*e*	0.5757(9)	0.0515(6)	0.670(2)	0.049(9)	0.025(8)	0.028(8)	0.009(7)	0.008(7)	0.002(6)
C(4)	4*e*	0.4995(8)	0.1422(6)	0.614(2)	0.032(8)	0.027(8)	0.028(7)	–0.001(6)	0.013(6)	–0.006(6)
C(5)	4*e*	0.4152(8)	0.1778(5)	0.550(2)	0.029(7)	0.017(7)	0.031(7)	–0.003(5)	0.006(6)	0.002(6)
C(6)	4*e*	0.2625(9)	0.1825(6)	0.437(2)	0.027(8)	0.037(9)	0.048(9)	–0.003(6)	0.002(6)	0.006(7)
C(7)	4*e*	0.2672(8)	0.2469(6)	0.438(2)	0.031(8)	0.027(8)	0.034(8)	0.001(6)	0.000(6)	0.012(6)
C(8)	4*e*	0.3494(8)	0.2762(6)	0.503(2)	0.030(8)	0.043(9)	0.021(7)	0.002(6)	–0.005(6)	–0.001(6)
Pt(2)	4*e*	–0.00858(3)	–0.01401(2)	0.74866(7)	0.0272(3)	0.0143(3)	0.0235(3)	–0.0013(2)	0.0043(2)	–0.0009(2)
Br(3)	4*e*	0.01229(9)	–0.12612(6)	0.7810(2)	0.0557(9)	0.0138(7)	0.0450(9)	–0.0007(6)	0.0142(7)	0.0008(6)
Br(4)	4*e*	–0.16844(8)	–0.03040(6)	0.7155(2)	0.0295(7)	0.0288(8)	0.0357(8)	–0.0069(6)	0.0066(6)	–0.0049(6)
N(5)	4*e*	–0.0163(6)	0.0804(4)	0.726(1)	0.017(5)	0.023(6)	0.029(6)	–0.006(4)	–0.005(4)	0.006(5)
N(6)	4*e*	0.0761(7)	0.1714(5)	0.754(2)	0.042(7)	0.015(6)	0.046(7)	–0.004(5)	0.004(6)	0.002(5)
N(7)	4*e*	0.2255(7)	0.0907(5)	0.802(2)	0.031(7)	0.023(6)	0.044(7)	0.000(5)	0.005(5)	0.001(5)
N(8)	4*e*	0.1243(6)	0.0056(4)	0.777(1)	0.026(5)	0.013(6)	0.010(5)	0.001(4)	–0.008(4)	0.001(4)
C(9)	4*e*	–0.0887(8)	0.1154(5)	0.689(2)	0.031(8)	0.017(7)	0.048(9)	0.015(6)	0.014(6)	0.009(6)
C(10)	4*e*	–0.0838(9)	0.1805(6)	0.684(2)	0.037(8)	0.032(9)	0.044(9)	0.005(7)	0.005(7)	–0.010(7)
C(11)	4*e*	0.0024(9)	0.2055(6)	0.722(2)	0.042(9)	0.014(7)	0.047(9)	0.011(6)	0.005(7)	0.003(6)
C(12)	4*e*	0.0657(8)	0.1091(5)	0.751(2)	0.027(7)	0.015(7)	0.024(7)	–0.003(5)	0.003(5)	–0.001(5)
C(13)	4*e*	0.1442(7)	0.0664(5)	0.782(2)	0.014(6)	0.025(8)	0.026(7)	–0.001(5)	0.002(5)	–0.009(6)
C(14)	4*e*	0.2917(8)	0.0500(7)	0.812(2)	0.024(7)	0.05(1)	0.044(9)	–0.002(7)	0.015(6)	0.003(7)
C(15)	4*e*	0.2790(8)	–0.0139(6)	0.804(2)	0.020(7)	0.028(8)	0.045(9)	0.006(6)	0.003(6)	0.001(6)
C(16)	4*e*	0.1919(8)	–0.0351(6)	0.786(2)	0.036(8)	0.025(8)	0.026(7)	0.019(6)	0.001(6)	0.005(6)

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