Crystal structure of bis(2-phenylpyridin-1-ium)hexabromidoplatinate(IV) dihydrate, $C_{22}H_{24}Br_6N_2O_2Pt$

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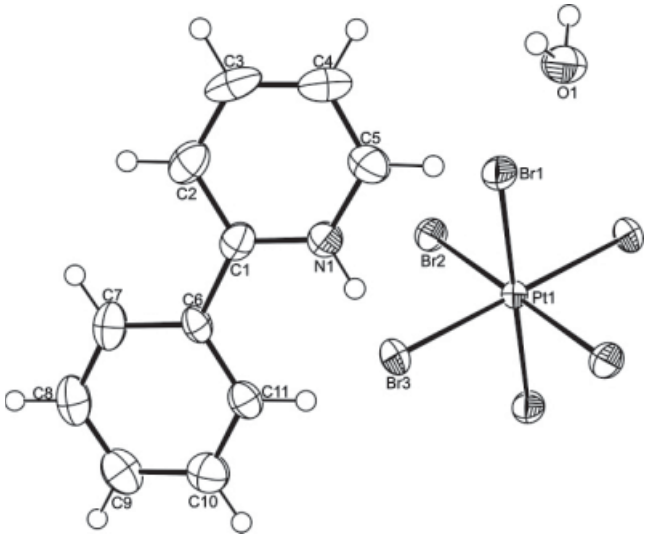

Abstract

$C_{22}H_{24}Br_6N_2O_2Pt$, triclinic, $P\bar{1}$ (no. 2), a = 7.711(1) Å, b = 9.078(2) Å, c = 11.018(2) Å, α = 69.643(4)°, β = 71.268(4)°, γ = 78.109(4)°, V = 680.9 Å^3, Z = 1, $R_{gt}(F)$ = 0.0317, $wR_{ref}(F^2)$ = 0.0718, T = 200 K.

Table 1. Data collection and handling.

Crystal:	red blocks, size 0.06×0.10×0.11 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	139.78 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ and ω
$2\theta_{max}$:	52.14°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4211, 2580
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2069
$N(param)_{refined}$:	154
Programs:	SHELX [5], ORTEP-3[6], PLATON [7]

Source of material

To a solution of K_2PtBr_6 (0.245 g, 0.325 mmol) in H_2O (30 ml) / EtOH (30 ml) was added 2-phenylpyridine (*ppy*; 0.129 g, 0.830 mmol) and stirred for 72 h at room temperature. After evaporation of the solvent, the residue was washed with H_2O and dried at 50 °C, to give an orange powder (0.245 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a CH_3CN solution.The crystallization water originating from the synthesis is still present.

Experimental details

Carbon-bound hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C–H) = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). Nitrogen-bound hydrogen atom was located from the difference Fourier map and then refined with U_{iso}(H) = 1.2U_{eq}(N). The H atoms of the solvent water molecule were located from the difference Fourier map and then allowed to ride on their parent O atom in the final cycles of refinement with d(O–H) = 0.84 Å and U_{iso}(H) = 1.5 U_{eq}(O). The highest peak (1.10 e·Å^{-3}) and the deepest hole (–1.03 e·Å^{-3}) in the difference Fourier map are located 1.09 Å and 1.11 Å from the atoms Br3 and Pt1, respectively.

Discussion

The asymmetric unit of the title crystal structure contains a protonated 2-phenylpyridine cation, one half of $[PtBr_6]^{2-}$ and a water molecule. The structure of the ionic compound is much different from that of the product of the analogous reaction of *ppy* with K_2PtCl_6, in which an anionic Pt(IV) complex $[PtCl_4(C_{11}H_8N)]^-$ with a 2-phenylpyridinium counter-cation was synthesized [1]. The octahedral dianionic complex $[PtBr_6]^{2-}$ is located on an inversion center. The distances d(Pt–Br) are nearly equivalent (2.4611(8) Å, 2.4662(8) Å and 2.4668(8) Å), and the *cis* ∠Br–Pt–Br bond angles lie in the range of 89.81(3)-90.19(3)°. These values are similar to those found in the complexes $K_2[PtBr_6]$ [2], $[Rh(NH_3)_5Cl][PtBr_6]$ [3] and $(C_{21}H_{19}N_2)_2[PtBr_6]$ [4]. In the crystal structure, the ions and the water molecules are linked by intermolecular O–H···Br hydrogen bonds with d(O···Br) = 3.512(5) Å, 3.513(5) Å and 3.630(5) Å, thereby forming a chain structure along [100]. Each water molecule, as an H-bond acceptor, is linked to the 2-phenylpyridinium N–H group with d(N···O) = 2.744(8) Å. In addition, the nearly planar cations are stacked in columns also along [100]. When viewed down [100], the successive cations are stacked in the opposite direction. In the columns, several intermolecular π-π interactions between adjacent six-membered rings are present. For Cg1 (the centroid of ring C6-C11) and Cg2^i (ring N1-C5, symmetry code i: -x,1-y,-z), the centroid-centroid distance is 3.967(5) Å and the dihedral angle between the ring planes is 1.9(4)°.

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

Atom	Site	x	y	z	U_{iso}
H(1N)	2*i*	0.115(9)	0.431(9)	0.257(8)	0.039
H(2)	2*i*	0.3599	0.7268	–0.0837	0.048
H(3)	2*i*	0.3784	0.8835	0.0391	0.056
H(4)	2*i*	0.2612	0.8086	0.2720	0.058
H(5)	2*i*	0.1354	0.5724	0.3794	0.049
H(7)	2*i*	0.3425	0.5773	–0.1774	0.048
H(8)	2*i*	0.3235	0.4076	–0.2892	0.054
H(9)	2*i*	0.2062	0.1680	–0.1709	0.051
H(10)	2*i*	0.0801	0.1048	0.0635	0.051
H(11)	2*i*	0.0936	0.2761	0.1746	0.037
H(1A)	2*i*	–0.0142	0.7848	0.5310	0.060
H(1B)	2*i*	0.1258	0.7246	0.5806	0.060

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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)	1*f*	½	0	½	0.0277(2)	0.0274(2)	0.0201(2)	–0.0081(2)	–0.0045(2)	–0.0069(2)
Br(1)	2*i*	0.4815(1)	0.28234(8)	0.47780(8)	0.0502(5)	0.0283(4)	0.0335(4)	–0.0095(3)	–0.0061(4)	–0.0100(4)
Br(2)	2*i*	0.81934(9)	0.00948(9)	0.35533(8)	0.0302(4)	0.0466(5)	0.0329(4)	–0.0119(3)	0.0012(3)	–0.0148(4)
Br(3)	2*i*	0.3857(1)	0.07260(9)	0.30017(8)	0.0443(4)	0.0443(5)	0.0265(4)	–0.0087(3)	–0.0157(4)	–0.0081(4)
N(1)	2*i*	0.1723(8)	0.5143(7)	0.2135(6)	0.038(4)	0.030(3)	0.028(4)	–0.007(3)	–0.005(3)	–0.011(3)
C(1)	2*i*	0.2360(9)	0.5523(8)	0.0798(7)	0.024(4)	0.034(4)	0.031(4)	–0.005(3)	–0.009(3)	–0.002(4)
C(2)	2*i*	0.314(1)	0.6945(8)	0.0116(9)	0.038(4)	0.030(4)	0.043(5)	–0.003(3)	–0.014(4)	0.001(4)
C(3)	2*i*	0.324(1)	0.7874(9)	0.085(1)	0.033(4)	0.027(4)	0.077(7)	–0.011(3)	–0.020(4)	–0.005(5)
C(4)	2*i*	0.256(1)	0.7435(9)	0.222(1)	0.045(5)	0.040(5)	0.066(7)	–0.015(4)	–0.014(5)	–0.020(5)
C(5)	2*i*	0.182(1)	0.6057(9)	0.2842(9)	0.047(5)	0.043(5)	0.040(5)	–0.009(4)	–0.009(4)	–0.020(4)
C(6)	2*i*	0.2217(9)	0.4438(8)	0.0103(7)	0.025(4)	0.036(4)	0.021(4)	0.000(3)	–0.004(3)	–0.013(3)
C(7)	2*i*	0.289(1)	0.4812(9)	–0.1275(8)	0.038(4)	0.046(5)	0.027(4)	0.001(4)	–0.003(4)	–0.007(4)
C(8)	2*i*	0.279(1)	0.379(1)	–0.1940(8)	0.043(5)	0.058(6)	0.028(5)	0.003(4)	–0.007(4)	–0.014(4)
C(9)	2*i*	0.207(1)	0.239(1)	–0.1248(9)	0.042(5)	0.048(5)	0.043(5)	0.009(4)	–0.014(4)	–0.025(5)
C(10)	2*i*	0.135(1)	0.2005(9)	0.0142(9)	0.043(5)	0.039(5)	0.047(5)	–0.002(4)	–0.018(4)	–0.013(4)
C(11)	2*i*	0.1429(9)	0.3028(8)	0.0797(8)	0.028(4)	0.036(4)	0.030(4)	0.001(3)	–0.013(3)	–0.011(4)
O(1)	2*i*	0.0345(7)	0.6974(6)	0.5710(5)	0.047(3)	0.036(3)	0.042(3)	–0.010(2)	–0.016(3)	–0.012(3)

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