Crystal structure of bromido(2,2':6',2"-terpyridine-κ^3N,N',N'')platinum(II) tribromido(dimethyl sulfoxide-κS)platinate(II), $C_{17}H_{17}Br_4N_3OPt_2S$

Kwang Ha*

Chonnam National University, School of Applied Chemical Engineering, Research Institute of Catalysis, Gwangju 500-757, Republic of Korea

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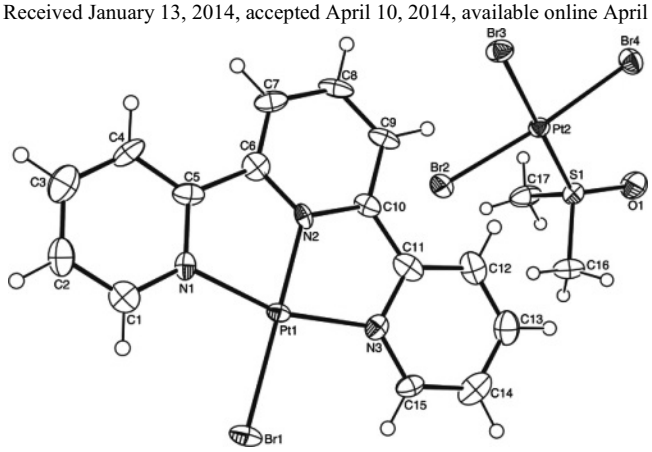

Abstract

$C_{17}H_{17}Br_4N_3OPt_2S$, monoclinic, $P2_1/c$ (no. 14), a = 6.7647(4) Å, b = 10.8048(6) Å, c = 31.196(2) Å, β = 95.544(1)°, V = 2269.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.0463, $wR_{ref}(F^2)$ = 0.1072, T = 200 K.

Table 1. Data collection and handling.

Crystal:	red plates, size 0.01×0.03×0.18 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	194.63 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ and ω
$2\theta_{max}$:	52.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	24344, 4450
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3661
$N(param)_{refined}$:	255
Programs:	SHELX [5], ORTEP-3 [6], PLATON [7]

Source of material

To a solution of K_2PtBr_4 (0.295 g, 0.50 mmol) in H_2O (20 ml) was added 2,2':6',2"-terpyridine (*terpy*; 0.117 g, 0.50 mmol) in acetone (20 ml) and stirred for 3 h at room temperature. The formed precipitate was separated by filtration, washed with H_2O and acetone, and dried at 50 °C, to give a yellow powder (0.224 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a dimethyl sulfoxide (DMSO) solution at 90 °C.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C–H) = 0.95 Å (aromatic) or 0.98 Å (CH_3) and U_{iso}(H) = 1.2Ueq(C) or 1.5U_{eq}(methyl C). The highest peak (1.74 e·Å^{-3}) and the deepest hole (–1.39 e·Å^{-3}) in the difference Fourier map are located 1.15 Å and 1.00 Å from the atoms Pt2 and Pt1, respectively.

Discussion

This contribution is part of my continuing interest on bromido platinum complexes [1, 2]. Single crystals of the title compound [PtBr(*terpy*)]- [$PtBr_3$(DMSO)] were unexpectedly obtained during crystallization from a dimethyl sulfoxide solution of the reaction product prepared by the reaction of K_2PtBr_4 and *terpy*. The complex is isomorphous with the previously reported chlorido-Pt(II) complex [PtCl(*terpy*)][$PtCl_3$(DMSO)] [3]. The crystal structure of the related bromido-Pt(II) complex [PtBr(*terpy*)]Br·2H_2O has been investigated previously [4]. The title compound consists of a cationic Pt(II) and an anionic Pt(II) complexes. In the cationic complex, the Pt(II) ion is four-coordinated in a distorted square-planar environment by three N atoms from the tridentate *terpy* ligand and a bromido ligand. The main contribution to the distortion is the tight N–Pt–N chelate angles (<N1–Pt1–N2 = 80.9(4)° and <N2–Pt1–N3 = 81.3(4)°), which results in non-linear *trans* arrangement of the N1–Pt1–N3 bond (<N1–Pt1–N3 = 162.2(4)°), whereas the N2–Pt1–Br1 bond is almost linear (<N2–Pt1–Br1 = 179.3(3)°). In the crystal, the nearly planar cationic complexes are stacked in columns along [100]. When viewed down the *a* axis, the successive complexes are stacked in the opposite direction with the Pt···Pt distances of 3.3679(6) Å and 3.4131(6) Å. In the columns, numerous intermolecular π-π interactions between adjacent pyridine rings are present. The shortest distance between Cg1 (the centroid of ring N1-C5) and Cg2^{i} (the centroid of ring N3-C15; symmetry code i: –*x*,–*y*,–*z*) is 3.664(7) Å, and the dihedral angle between the ring planes is 1.7(6)°. In the anionic complex, the central Pt(II) ion has a slightly distorted square-planar coordination geometry defined by three bromido ligands and one S atom of the DMSO molecule. The three Pt–Br bond lengths are almost equal with d(Pt–Br) = 2.4358(14) - 2.4546(14) Å. In the crystal structure, the cationic and anionic complexes are linked by intermolecular C–H···O and C–H···Br hydrogen bonds with d(C···O) = 3.192(18) Å and d(C···Br) = 3.596(13) - 3.794(15) Å, forming a three-dimensional network.

* e-mail: hakwang@chonnam.ac.kr

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	0.1828	–0.1211	–0.0872	0.046
H(2)	4*e*	0.1103	–0.0532	–0.1579	0.049
H(3)	4*e*	0.0791	0.1572	–0.1720	0.057
H(4)	4*e*	0.1257	0.2979	–0.1144	0.049
H(7)	4*e*	0.1991	0.4218	–0.0534	0.042
H(8)	4*e*	0.2543	0.5198	0.0137	0.045
H(9)	4*e*	0.2945	0.4043	0.0767	0.041
H(12)	4*e*	0.3365	0.2563	0.1333	0.046
H(13)	4*e*	0.4041	0.1006	0.1846	0.053
H(14)	4*e*	0.3985	–0.1087	0.1609	0.054
H(15)	4*e*	0.3342	–0.1502	0.0877	0.036
H(16A)	4*e*	1.0118	0.2559	0.2366	0.065
H(16B)	4*e*	0.8324	0.2612	0.1992	0.065
H(16C)	4*e*	0.7887	0.2737	0.2486	0.065
H(17A)	4*e*	1.1779	0.5563	0.2026	0.073
H(17B)	4*e*	1.1516	0.4241	0.1796	0.073
H(17C)	4*e*	1.2459	0.4334	0.2286	0.073

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*	0.25322(6)	0.00431(4)	0.00347(2)	0.0181(2)	0.0155(2)	0.0278(3)	–0.0007(2)	0.0027(2)	–0.0005(2)
Br(1)	4*e*	0.2594(2)	–0.2204(1)	–0.00168(5)	0.0261(7)	0.0172(6)	0.0537(9)	–0.0006(5)	0.0059(6)	–0.0017(6)
N(1)	4*e*	0.198(1)	0.0441(9)	–0.0600(3)	0.015(5)	0.036(6)	0.020(5)	–0.001(4)	0.000(4)	–0.003(4)
N(2)	4*e*	0.246(1)	0.1844(9)	0.0071(3)	0.011(5)	0.026(5)	0.022(5)	–0.004(4)	0.007(4)	–0.009(4)
N(3)	4*e*	0.308(1)	0.0225(9)	0.0682(3)	0.016(5)	0.033(6)	0.028(6)	0.000(4)	0.005(4)	0.004(5)
C(1)	4*e*	0.171(2)	–0.035(1)	–0.0928(5)	0.028(7)	0.042(8)	0.044(9)	–0.004(6)	0.000(6)	–0.004(7)
C(2)	4*e*	0.128(2)	0.005(2)	–0.1351(5)	0.028(7)	0.06(1)	0.032(8)	–0.010(7)	0.001(6)	–0.010(7)
C(3)	4*e*	0.110(2)	0.128(2)	–0.1434(5)	0.035(8)	0.07(1)	0.039(9)	–0.007(8)	0.005(7)	0.010(8)
C(4)	4*e*	0.138(2)	0.212(1)	–0.1091(5)	0.045(9)	0.040(8)	0.036(9)	–0.007(7)	0.002(7)	0.022(7)
C(5)	4*e*	0.182(2)	0.169(1)	–0.0675(5)	0.022(7)	0.022(6)	0.050(9)	–0.002(5)	0.009(6)	0.006(6)
C(6)	4*e*	0.215(2)	0.250(1)	–0.0292(4)	0.015(6)	0.035(7)	0.039(8)	–0.010(5)	0.007(5)	–0.001(6)
C(7)	4*e*	0.218(2)	0.374(1)	–0.0277(5)	0.025(7)	0.029(7)	0.048(9)	0.005(5)	–0.006(6)	0.012(6)
C(8)	4*e*	0.250(2)	0.432(1)	0.0122(5)	0.037(8)	0.013(6)	0.06(1)	0.001(5)	–0.006(7)	–0.004(6)
C(9)	4*e*	0.277(2)	0.364(1)	0.0495(5)	0.033(7)	0.016(6)	0.05(1)	0.000(5)	0.004(6)	–0.007(6)
C(10)	4*e*	0.276(2)	0.234(1)	0.0468(4)	0.020(6)	0.023(6)	0.034(7)	–0.001(5)	–0.007(5)	–0.007(5)
C(11)	4*e*	0.311(2)	0.144(1)	0.0814(5)	0.011(6)	0.032(7)	0.054(9)	–0.005(5)	0.006(6)	–0.009(6)
C(12)	4*e*	0.341(2)	0.172(1)	0.1245(5)	0.028(7)	0.044(8)	0.043(9)	–0.017(6)	0.007(6)	–0.016(7)
C(13)	4*e*	0.378(2)	0.081(2)	0.1550(5)	0.038(9)	0.06(1)	0.037(9)	–0.007(7)	0.009(7)	–0.006(8)
C(14)	4*e*	0.375(2)	–0.043(2)	0.1408(5)	0.028(8)	0.06(1)	0.05(1)	–0.012(7)	–0.005(7)	0.018(8)
C(15)	4*e*	0.338(2)	–0.067(1)	0.0972(4)	0.024(7)	0.028(7)	0.037(8)	0.003(5)	0.003(6)	0.010(6)
Pt(2)	4*e*	0.68139(7)	0.53208(4)	0.17589(2)	0.0275(3)	0.0214(2)	0.0254(3)	–0.0025(2)	0.0014(2)	0.0008(2)
Br(2)	4*e*	0.7787(2)	0.3871(1)	0.12158(5)	0.0553(9)	0.0312(7)	0.0337(8)	0.0038(6)	0.0036(7)	–0.0059(6)
Br(3)	4*e*	0.4208(2)	0.6118(1)	0.12283(4)	0.0416(8)	0.0275(7)	0.0337(8)	–0.0007(6)	–0.0085(6)	0.0013(5)
Br(4)	4*e*	0.5877(2)	0.6908(1)	0.22556(4)	0.0371(8)	0.0391(8)	0.0340(8)	0.0033(6)	0.0006(6)	–0.0073(6)
S(1)	4*e*	0.9101(5)	0.4552(3)	0.2244(1)	0.030(2)	0.030(2)	0.028(2)	–0.001(1)	0.003(1)	0.003(1)
O(1)	4*e*	0.923(2)	0.504(1)	0.2684(3)	0.062(7)	0.055(7)	0.032(6)	0.009(5)	–0.010(5)	0.003(5)
C(16)	4*e*	0.883(2)	0.294(1)	0.2276(5)	0.043(9)	0.028(7)	0.06(1)	0.004(6)	–0.001(7)	0.010(7)
C(17)	4*e*	1.148(2)	0.469(1)	0.2069(6)	0.037(8)	0.038(8)	0.07(1)	0.000(7)	0.014(8)	0.022(8)

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