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Crystal structure of (*N*-benzylpropane-1,3-diamine- κ^2N, N')(2,2'-bipyridine- κ^2N, N') platinum(II) chloride, $C_{20}H_{24}Cl_2N_4Pt$

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Abstract

$C_{20}H_{24}Cl_2N_4Pt$, monoclinic, $P2_1/c$ (no. 14), $a = 13.1119(7)$ Å, $b = 13.5673(8)$ Å, $c = 11.7167(5)$ Å, $\beta = 99.714(7)^\circ$, $V = 2054.43(19)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0233$, $wR_{ref}(F^2) = 0.0516$, $T = 103$ K.

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The title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.50 × 0.30 × 0.20 mm
Wavelength:	Mo K α radiation (0.71075 Å)
μ :	7.08 mm ⁻¹
Diffractometer, scan mode:	Rigaku R-Axis RAPID, ω
θ_{max} , completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	19454, 4699, 0.053
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3983
$N(param)_{refined}$:	244
Programs:	Crystal Structure [1], SHELX [2], Mercury [3]

conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The 2,2'-bipyridine platinum(II) dichloride was synthesized according to the literature method with slightly modifications [4]. To a suspension of 2,2'-bipyridine platinum(II) dichloride (420 mg, 1.0 mmol) in water (20 mL), *N*-benzylpropane-1,3-diamine·2HCl (284 mg, 1.2 mmol), and sodium bicarbonate (159 mg, 1.5 mmol) were added. The mixture was stirred at 353 K for 2 h. The solution was filtered and the filtrate was concentrated under vacuum. Ethanol was added and white precipitate was removed by filtration. The filtrate was concentrated and then reprecipitated from ether/ethanol. Yield: 253 mg (43%). Single crystals suitable for crystal structure determination were obtained by vapor diffusion of diethyl ether into a ethanol solution of the product at 298 K. **Elemental analysis**, Found: C 41.13; H 4.11; N 9.47%. Calcd for $[C_{20}H_{24}Cl_2N_4Pt]$: C 40.96; H 4.13; N 9.55%. **¹H NMR** (D₂O) δ : 8.73 (d, 1H), 8.39 (t, 1H), 8.34 (d, 1H), 8.25 (d, 1H), 8.18 (t, 1H), 7.85 (m, 2H), 7.81 (t, 1H), 7.75 (d, 1H), 7.39 (t, 1H), 7.22 (m, 3H), 4.52 (d, 1H), 3.99 (d, 1H), 3.32 (m, 2H), 3.19 (d, 1H), 2.99 (t, 1H), 2.28 (m, 2H).

Experimental details

Absorption corrections were applied by using multi-scan program. Hydrogen atoms were placed in calculated positions and included in the refinement in the riding model approximation, with $U_{iso}(H)$ set to $1.2U_{eq}(C)$.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
Pt1	0.25871(2)	0.00560(2)	0.35292(2)	0.01391(5)
Cl1	0.08614(7)	0.02830(6)	0.68034(6)	0.02413(18)
Cl2	0.34219(7)	0.16495(5)	0.03469(6)	0.02164(17)
N1	0.3780(2)	−0.05265(17)	0.2848(2)	0.0161(5)
N2	0.3359(2)	−0.06574(17)	0.4950(2)	0.0179(6)
N4	0.1994(2)	0.08949(17)	0.2101(2)	0.0170(6)
H4A	0.254053	0.090198	0.160007	0.020*
N3	0.1381(2)	0.05643(17)	0.4266(2)	0.0178(6)
H3A	0.078509	0.031342	0.385935	0.021*
H3B	0.145161	0.031605	0.499703	0.021*
C13	0.1848(3)	0.1955(2)	0.2423(3)	0.0213(7)
H13B	0.251219	0.220640	0.285224	0.026*
H13A	0.167685	0.234622	0.170292	0.026*
C4	0.5437(3)	−0.1296(2)	0.3324(3)	0.0230(7)
H4	0.596124	−0.157862	0.388809	0.028*
C8	0.4674(3)	−0.1468(2)	0.6823(3)	0.0231(7)
H6	0.513171	−0.172700	0.746850	0.028*
C2	0.4787(3)	−0.0844(2)	0.1368(3)	0.0220(7)
H2	0.485003	−0.081851	0.057317	0.026*
C6	0.4285(3)	−0.1035(2)	0.4814(2)	0.0164(6)
C1	0.3902(3)	−0.0504(2)	0.1728(3)	0.0201(7)
H1	0.335915	−0.024471	0.116821	0.024*
C5	0.4528(3)	−0.0955(2)	0.3634(2)	0.0183(7)
C7	0.4950(3)	−0.1457(2)	0.5732(3)	0.0206(7)
H5	0.558856	−0.173584	0.561263	0.025*
C3	0.5576(3)	−0.1219(2)	0.2173(3)	0.0261(8)
H3	0.620593	−0.142375	0.194797	0.031*
C12	0.1021(3)	0.2121(2)	0.3146(3)	0.0226(7)
H12A	0.036024	0.184955	0.273164	0.027*
H12B	0.092673	0.283941	0.323570	0.027*
C9	0.3729(3)	−0.1098(2)	0.6950(3)	0.0237(7)
H7	0.351965	−0.111243	0.768737	0.028*
C10	0.3073(3)	−0.0702(2)	0.6005(2)	0.0217(7)
H8	0.241348	−0.045904	0.610161	0.026*
C14	0.1036(3)	0.0502(2)	0.1350(3)	0.0198(7)
H14B	0.078929	0.098379	0.073057	0.024*
H14A	0.048348	0.041702	0.182363	0.024*
C11	0.1259(3)	0.1655(2)	0.4337(3)	0.0216(7)
H11B	0.190396	0.194329	0.476884	0.026*
H11A	0.069137	0.180511	0.477053	0.026*
C15	0.1243(3)	−0.0479(2)	0.0809(3)	0.0190(7)
C20	0.1142(3)	−0.1357(2)	0.1383(3)	0.0237(7)
H20	0.095163	−0.134827	0.212981	0.028*
C16	0.1516(3)	−0.0504(2)	−0.0292(3)	0.0238(7)
H16	0.159338	0.009267	−0.069226	0.029*
C19	0.1320(3)	−0.2255(2)	0.0869(3)	0.0290(8)
H19	0.126167	−0.285373	0.127329	0.035*
C18	0.1581(3)	−0.2275(3)	−0.0224(3)	0.0309(8)
H18	0.169451	−0.288663	−0.057677	0.037*
C17	0.1675(3)	−0.1403(2)	−0.0800(3)	0.0272(8)
H17	0.185139	−0.141648	−0.155344	0.033*

Comment

Platinum complexes have been used for cancer chemotherapy [5, 6]. The target of platinum complexes are nucleotides [7–9]. However, platinum complexes also affect the activities of proteins [10, 11]. We have demonstrated that platinum complexes with an aromatic heterocycle and *N*-arylmethylpropane-1,3-diamine exhibited cytotoxicities and inhibitory activities against cancer-associated proteins [12, 13]. As part of our studies in this area, we have synthesized the title complex, [Pt(C₁₀H₈N₂)(C₁₀H₁₆N₂)]Cl₂. The synthesis and structure of an analogous (*N*-benzylethane-1,2-diamine)(2,2'-bipyridine) platinum(II) nitrate salt have been reported [14]. However, the title complex is a chloride salt and contains, in contrast to the literature known ones, a *N*-benzylpropane-1,3-diamine as ligand. It is known that a counter ion may affect structure and solubility of a complex salt. Also, solubility is important for clinical application. It is possible that the size of the Pt chelate ring also affects the structure of the platinum complex. Thus, we determined the structure of the title complex.

The asymmetric unit of the title structure consists of one dicationic platinum complex and two chloride counter anions (*cf.* the figure). The central platinum atom is chelated with *N*-benzylpropane-1,3-diamine and 2,2'-bipyridine. The centroid-centroid distance between the N1/C1–C5 ring and the C15–C20 ring is 4.657(2) Å. The Pt1–N4–C14–C15 torsion angle is −63.4(3)°. The C15–C20 aromatic ring is close to the N1/C1–C5 ring of 2,2'-bipyridine. The C15–C20 ring and the 2,2'-bipyridine ligand are not in the same plane, but are in a bowed configuration. Principally, platinum complexes have a square planar geometry [15, 16]. However, the title complex shows distortion from planarity. The r.m.s. deviation of the least-squares plane formed by Pt1, N1, N2, N3 and N4 is 0.075 Å. Furthermore, the propanediamine chain is tilted to 2,2'-bipyridine plane.

In the crystal, [Pt(C₁₀H₈N₂)(C₁₀H₁₆N₂)]²⁺ forms dimer through π–π interaction. Intermolecular π–π stacking interactions are observed between the 2,2'-bipyridine rings. The above mentioned dimer is composed of enantiomeric pair. The [Pt(C₁₀H₈N₂)(C₁₀H₁₆N₂)]²⁺ dimers are interlinked through a NH...Cl...HN hydrogen-bonding network.

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