Crystal structure of (benzonitrile)chloro(*N*-phenylamidine-*N*-cyclohexylamine)platinum(II) chloride hydrate, [PtCl(C₇H₅N)(C₁₃H₁₉N₃)]Cl · 1.33H₂O

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Abstract

C₂₀H_{26.67}Cl₂N₄O_{1.33}Pt, trigonal, R3 (No. 146), *a* = 14.671(5) Å, *α* = 54.672°, *V* = 1955.6 Å³, *Z* = 3, *R*_{gt}(*F*) = 0.051, *wR*_{ref}(*F*²) = 0.121, *T* = 193 K.

Source of material

The title compound was prepared following similar procedure, which is normally applied for the synthesis of complexes of the general formula (L-L)MCl₂, (M = Pd and Pt; L-L: bidentate ligand) [1, 2]. A solution of (1*R*,2*R*)-(–)-1,2-diaminocyclohexane (0.76 g, 6.65 mmol) in CH₂Cl₂ (30 ml) was added to a solution of [(PhCN)₂PtCl₂] (3.0 g, 6.05 mmol) in the same solvent (30 ml). Upon addition, the color changed from yellow to orange. Stirring was continued for 12 hrs at room temperature, then the solution was filtered and concentrated. Upon addition of ether, a yellow precipitate was formed, which was filtered, washed with petroleum ether (50 ml), and dried under vacuum (yield: 2.5 g, 68%). Recrystallization was made from acetone.

Experimental details

Two water oxygen atoms, each at a special site with a site occupation factor of 0.5, have been refined isotropically. They do not take part of intermolecular hydrogen bonding system. The hydrogen atoms of water molecules were picked up from difference fourier map.

Discussion

Since the discovery of the activity *cis*-[(H₃N)₂PtCl₂] clinically called cisplatin, one of the most successful anticancer agents [3], many new platinum complexes have been synthesized and evaluated for their antitumor activity [4]. Carboplatin [(H₃N)₂Pt(C₆H₆O₄)], a second generation analogue of cisplatin has reduced toxic side effects for the same efficiency thanks to its much lower reactivity. The third generation drugs include compounds like oxaliplatin

(*trans*-1,1,2-diaminocyclohexane platinum(II) oxalate), which showed a colorectal antitumor activity, can be administrated orally and had positive preclinical evaluations for use in cisplatin resistant tumors. Investigation on this type of chiral complexes showed that *trans* isomer *trans*-1 (*trans*-(–)-1*R*,2*R*) is more efficient than the corresponding *trans*-*d* (*trans*-(+)-1*S*,2*S*) and the *cis*-isomer (1*R*,2*S*) [5]. According to an X-ray study carried out on the oxaliplatin complex [6], we found that although the complex was synthesized starting from the enantiomerically pure isomer *trans*-1 (*trans*-(–)-1*R*,2*R*) and the platinum salt K₂PtCl₄, the product does not only consist from the desired isomer, but from a mixture of both the *trans*-1 and *trans*-*d* isomers. No retention of optical isomerism was observed. Previously we described the synthesis of square-planar palladium(II) and platinum(II) complexes with bidentate heterodonor ligands [1,2,7] by displacement of the weakly coordinated ligands (benzonitrile) with a bidentate chelate.

The reaction of bidentate amine ligand, (1*R*,2*R*)-(–)-1,2-diaminocyclohexane, with [(PhCN)₂PtCl₂] proceeds via nucleophilic addition on the benzonitrile ligand, forming a seven-membered chelate ring, where there is a considerable electron delocalization in the ring, the bond N3—C7 (1.30(2) Å) and N2—C7 (1.30(2) Å) being of the same magnitude. The neighboring single bond N2—C2 (1.45(2) Å) is also shorter than typical N—C bond. The Pt atom of the cationic complex molecule is at the center of a nearly square-planar arrangement. The greatest deviations from the planarity are within 0.01 Å – 0.04 Å. Pt1—N1, Pt1—N3, Pt1—N4 and Pt1—Cl1 bond lengths are 2.03(1) Å, 2.00(1) Å, 1.97(1) Å and 2.310(4) Å, respectively. The bond angles around platinum vary from 88.9(3)° to 92.5(4)°. The bond N4—C14 is a typical triple bond, 1.14(2) Å, and the neighboring single bond C14—C15 (1.43(2) Å) shows a slight electron delocalization in the benzonitrile ligand. There is an extensive but weak H-bond network stabilizing the solid state structure. Three individual water molecules are present per one complex molecule, divided at different symmetry sites, one of them partially occupied, summing up to a total of 1.33H₂O.

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.17 × 0.20 × 0.25 mm
Wavelength:	Mo K _α radiation (0.71073 Å)
μ:	56.03 cm ^{–1}
Diffractometer, scan mode:	AFC7S, ω/2θ
2θ _{max} :	50.5°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	5283, 4697
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 3662
<i>N</i> (<i>param</i>) _{refined} :	257
Programs:	teXsan [8], SHELX-97 [9], ORTEP3 [10]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U _{iso}
H(1WA)	3b		0.8194	0.7253	0.1408	0.141
H(1WB)	3b		0.8233	0.7094	0.0468	0.141
O(2W)	1a	0.500	0.170(2)	x	x	0.22(3)
H(2WA)	1a	0.500	0.1489	x	x	0.264
H(2WB)	3b	0.167	0.1235	0.2187	0.2067	0.264
O(3W)	1a	0.500	0.348(2)	x	x	0.19(2)
H(3WA)	3b	0.167	0.3405	0.3103	0.3272	0.231
H(3WB)	3b	0.167	0.2988	0.4202	0.3364	0.231
H(1A)	3b		0.6093	0.7846	0.5372	0.075
H(1B)	3b		0.6020	0.7337	0.4800	0.075
H(2A)	3b		0.6734	0.7870	0.2086	0.080
H(3A)	3b		0.3531	0.8745	0.4088	0.087
H(1C)	3b		0.7632	0.7744	0.3500	0.073
H(2C)	3b		0.5810	0.9818	0.2590	0.075
H(3C)	3b		0.7242	0.9824	0.0710	0.086
H(3B)	3b		0.8214	0.8672	0.1290	0.086

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(4A)	3b		0.8518	1.0414	0.0644	0.097
H(4B)	3b		0.7142	1.1007	0.1405	0.097
H(5B)	3b		0.8305	1.0236	0.2470	0.098
H(5C)	3b		0.8910	0.8947	0.2393	0.098
H(6B)	3b		0.7433	0.8851	0.4322	0.083
H(6C)	3b		0.6438	0.9999	0.3767	0.083
H(9A)	3b		0.5698	0.8477	0.0911	0.108
H(10A)	3b		0.5230	0.7604	0.0325	0.133
H(11A)	3b		0.4171	0.6309	0.1836	0.149
H(12A)	3b		0.3624	0.5829	0.3796	0.136
H(13A)	3b		0.4037	0.6674	0.4405	0.110
H(16A)	3b		0.2574	1.1211	0.7821	0.127
H(17A)	3b		0.2708	1.1716	0.8985	0.148
H(18A)	3b		0.4576	1.0897	0.9118	0.143
H(19A)	3b		0.6201	0.9568	0.8243	0.121
H(20A)	3b		0.6083	0.9048	0.7076	0.116

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Pt(1)	3b	0.42153(5)	0.91780(6)	0.49605(5)	0.0647(3)	0.0690(3)	0.0597(3)	−0.0243(3)	−0.0181(2)	−0.0278(3)
Cl(1)	3b	0.2211(3)	1.0365(4)	0.5264(4)	0.062(2)	0.120(3)	0.131(3)	−0.011(2)	−0.022(2)	−0.076(3)
Cl(2)	1a	0.6876(1)	x	x	0.065(2)	0.065(2)	0.065(2)	−0.0242(9)	−0.0242(9)	−0.0242(9)
Cl(3)	1a	0.8513(3)	x	x	0.145(4)	0.145(4)	0.145(4)	−0.057(2)	−0.057(2)	−0.057(2)
Cl(4)	1a	0.5644(1)	x	x	0.069(2)	0.069(2)	0.069(2)	−0.026(1)	−0.026(1)	−0.026(1)
O(1W)	3b	0.822(1)	0.683(1)	0.116(1)	0.114(8)	0.14(1)	0.14(1)	−0.039(8)	−0.030(7)	−0.099(8)
N(1)	3b	0.5942(9)	0.8035(8)	0.4744(8)	0.081(6)	0.055(5)	0.055(6)	−0.031(5)	−0.030(5)	−0.010(4)
N(2)	3b	0.6173(9)	0.832(1)	0.252(1)	0.062(6)	0.077(7)	0.073(6)	−0.014(5)	−0.030(5)	−0.040(5)
N(3)	3b	0.4239(9)	0.867(1)	0.394(1)	0.058(6)	0.093(8)	0.076(7)	−0.018(6)	−0.028(6)	−0.041(6)
N(4)	3b	0.422(1)	0.962(1)	0.599(1)	0.087(8)	0.080(7)	0.062(7)	−0.042(6)	−0.016(6)	−0.029(6)
C(1)	3b	0.688(1)	0.847(1)	0.360(1)	0.047(6)	0.056(7)	0.063(7)	−0.014(5)	−0.025(5)	−0.014(6)
C(2)	3b	0.652(1)	0.906(1)	0.252(1)	0.063(7)	0.058(7)	0.061(7)	−0.023(6)	−0.025(6)	−0.016(5)
C(3)	3b	0.750(1)	0.941(1)	0.139(1)	0.073(8)	0.080(9)	0.050(7)	−0.029(7)	−0.022(6)	−0.017(6)
C(4)	3b	0.783(1)	1.024(1)	0.139(1)	0.090(9)	0.09(1)	0.062(8)	−0.049(8)	−0.032(7)	−0.008(7)
C(5)	3b	0.816(1)	0.966(1)	0.246(1)	0.083(9)	0.077(9)	0.077(9)	−0.043(7)	−0.024(7)	−0.016(7)
C(6)	3b	0.717(1)	0.928(1)	0.364(1)	0.075(8)	0.065(7)	0.080(8)	−0.024(7)	−0.037(7)	−0.025(6)
C(7)	3b	0.512(1)	0.824(1)	0.310(1)	0.060(7)	0.070(7)	0.066(7)	−0.011(6)	−0.031(6)	−0.033(6)
C(8)	3b	0.485(1)	0.768(1)	0.274(1)	0.075(8)	0.064(7)	0.09(1)	−0.009(7)	−0.046(7)	−0.036(7)
C(9)	3b	0.526(1)	0.796(2)	0.150(1)	0.10(1)	0.11(1)	0.08(1)	−0.034(9)	−0.035(8)	−0.047(8)
C(10)	3b	0.499(2)	0.743(2)	0.115(2)	0.12(1)	0.12(1)	0.14(2)	−0.02(1)	−0.06(1)	−0.08(1)
C(11)	3b	0.436(2)	0.665(2)	0.206(2)	0.14(2)	0.14(2)	0.14(2)	−0.05(1)	−0.07(2)	−0.05(2)
C(12)	3b	0.403(2)	0.638(2)	0.321(2)	0.14(2)	0.10(1)	0.13(2)	−0.05(1)	−0.08(1)	−0.01(1)
C(13)	3b	0.427(1)	0.688(2)	0.357(2)	0.10(1)	0.11(1)	0.11(1)	−0.051(9)	−0.047(9)	−0.04(1)
C(14)	3b	0.427(1)	0.986(1)	0.658(1)	0.09(1)	0.082(9)	0.056(7)	−0.049(8)	−0.014(7)	−0.021(7)
C(15)	3b	0.431(1)	1.014(1)	0.733(1)	0.082(9)	0.086(9)	0.068(8)	−0.039(8)	−0.020(7)	−0.030(7)
C(16)	3b	0.332(2)	1.089(2)	0.790(2)	0.10(1)	0.11(1)	0.13(1)	−0.03(1)	−0.05(1)	−0.06(1)
C(17)	3b	0.339(2)	1.119(2)	0.858(2)	0.13(2)	0.15(2)	0.14(2)	−0.02(1)	−0.05(1)	−0.11(2)
C(18)	3b	0.451(2)	1.068(2)	0.867(2)	0.16(2)	0.13(2)	0.13(2)	−0.05(1)	−0.09(1)	−0.05(1)
C(19)	3b	0.547(2)	0.991(2)	0.814(2)	0.11(1)	0.12(1)	0.10(1)	−0.05(1)	−0.04(1)	−0.04(1)
C(20)	3b	0.541(2)	0.960(2)	0.745(2)	0.10(1)	0.10(1)	0.10(1)	−0.04(1)	−0.024(9)	−0.045(9)

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