Synthesis and Structure of the Di-5,6-dihydropyrimidino[5,4-*c*] Carbazole Hexachloroplatinate(IV) Monohydrate

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Abstract

The crystal structure of the di-5,6-dihydropyrimidino[5,4-*c*] carbazole hexachloroplatinate(IV) monohydrate has been determined by X-ray analysis. The compound crystallizes in the monoclinic space group $P2_1/m$ with cell dimensions a = 8.697(3), b = 22.895(5), c = 7.808(1) Å, β = 108.65(2)°, Z = 2. The structure was refined to R = 0.027 and R_w = 0.027 with use of 2302 independent reflections. The platinum and four (among the six) chlorine atoms which are bound to the metal and the water molecule lie in the mirror plane ($y = \pm\frac{1}{4}$). In the DPCH$^+$ cations, the cyclohexadiene ring remains in a skew-chair conformation.

In a previous paper [1], we described the synthesis and crystal structure of the tetra-5,6-dihydropyrimidino[5,4-c] carbazole dichloride hexachloroplatinate(IV) tetrahydrate. By modifying the experimental procedure, one new compound was synthesized corresponding to the formula $[C_{14}N_3H_{12}{}^+]_2$-$[PtCl_6]^{2-}\cdot H_2O$.

Experimental

The 5,6-dihydropyrimidino[5,6-*c*] carbazole called hereafter DPC was obtained as previously described [2]. DPC (5×10^{-4} mol) was dissolved in HCl 1 M solution (25 ml). To this solution was added K_2PtCl_4 (2.5×10^{-4} mol) dissolved in water (25 ml). A yellow precipitate was formed immediately and was partially dissolved in acetone. Single crystals were obtained by slow evaporation of this solution under ambient air pressure. The diffraction data were collected from a single crystal of dimensions 0.28 × 0.15 × 0.12 mm. Crystal data: $PtC_{28}H_{26}Cl_6N_6O$, M_r = 870.5, monoclinic, space group $P2_1/m$, a = 8.697(3), b = 22.895(5), c = 7.808(1) Å, β = 108.65(2)°, V = 1473.1(1) Å^3, D_m = 1.92(2), D_c = 1.96 g cm^{-3}, Z = 2, $F(000)$ = 848, μ(Mo Kα) = 53.32 cm^{-1}. Unit cell parameters were obtained from least-squares analysis of 25 reflexions ($14 < \theta < 15°$) on a Enraf-Nonius CAD-4 diffractometer. Intensity data were recorded on the same instrument using Mo Kα radiation (λ = 0.7107 Å, monochromatized graphite), in the ω–1.33θ scan mode with an ω scan width of 1.00 + 0.35 tan θ and ω scan speeds of 3.3–1.6 deg min^{-1}.

Collected intensities were corrected for Lorentz–polarization effects but not for absorption. Unit cell content: 4DPCH$^+$, $2[PtCl_6]^{2-}$; $2H_2O$ solvate molecules. The structure was solved by the heavy atom method and was refined by least-squares techniques using SHELX 76 program system [3], the final R value being 0.027 for 2302 reflections for which $F > 3\sigma(F)$. Atomic scattering factors were taken from the 'International Tables for X-ray Crystallography' and anomalous dispersion corrections were applied to the curves for platinum and chlorine [4]. The drawing was made with ORTEP II [5]. Atomic positional parameters are given in Table 1.

A brief summary of interatomic distances and angles is given in Table 2 (see also 'Supplementary Material').

Results and Discussion

The platinum atom, four chlorine among the six atoms surrounding the metal atom, and one water molecule are found in the mirror plane ($y = \frac{1}{4}$). The two remaining chlorine atoms are in apical position, thus forming a slightly distorted octahedron coordination around the Pt atom as found in one

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TABLE 1. Atomic positional parameters

Atom	x	y	z	B_{eq} (Å^2)
Pt	0.40157(4)	0.2500	0.16345(5)	2.899(8)
Cl(1)	0.6683(2)	0.2500	0.1648(3)	3.88(6)
Cl(2)	0.1330(3)	0.2500	0.1596(4)	5.84(9)
Cl(3)	0.4921(4)	0.2500	0.4750(4)	6.6(1)
Cl(4)	0.3079(3)	0.2500	−0.1494(4)	7.0(1)
Cl(5)	0.4046(2)	0.35058(6)	0.1707(3)	5.90(6)
O	0.914(1)	0.2500	0.620(1)	5.9(3)
N(1)	1.1437(5)	0.4231(2)	0.3897(7)	3.8(1)
C(2)	1.1241(8)	0.3717(3)	0.449(1)	4.9(2)
N(3)	0.9808(7)	0.3495(2)	0.4444(8)	4.8(2)
C(4)	0.8422(7)	0.3810(3)	0.3717(8)	4.1(2)
C(5)	0.7069(7)	0.4744(3)	0.241(1)	4.9(2)
C(6)	0.7141(6)	0.5190(3)	0.1037(8)	4.0(2)
N(7)	0.9252(5)	0.5923(2)	0.0845(6)	3.6(1)
C(8)	1.1902(8)	0.6420(3)	0.1152(9)	4.2(2)
C(9)	1.3557(8)	0.6369(3)	0.1973(9)	4.3(2)
C(10)	1.4221(7)	0.5891(3)	0.3028(8)	4.3(2)
C(11)	1.3272(6)	0.5428(3)	0.3264(7)	3.5(2)
C(12)	1.1592(6)	0.5475(2)	0.2476(7)	3.0(1)
C(13)	1.0219(6)	0.5113(2)	0.2449(6)	2.9(1)
C(14)	1.0082(6)	0.4558(2)	0.3149(7)	3.1(1)
C(15)	0.8508(6)	0.4342(3)	0.3047(7)	3.4(2)
C(16)	0.8836(6)	0.5413(3)	0.1454(7)	3.4(2)
C(17)	1.0946(6)	0.5971(3)	0.1445(7)	3.3(2)

previous compound [1]. In the DPCH$^+$ cations, the cyclohexadiene ring remains in a skew-chair conformation. The distances from the C(5) and C(6) atoms to the mean planes are found to be 0.326 and −0.149 Å respectively. The other rings (benzene, indole and pyrimidine) are as expected from previous X-ray studies.

The packing of the title compound (stereoscopic view) is shown in Fig. 1. The 'mean planes' of DPCH$^+$ cations which are related by a crystallographic inversion center are nearly parallel. The distance between these mean planes calculated from the homologous indole rings are 3.391 and 3.532 Å for the pairs I, I^{ii} and I, I^{iii} respectively (symmetry code ii: $2-x$, $1-y$, $1-z$; iii: $2-x$, $1-y$, $-z$). The molecular overlapping is rather larger than in compound I, involving the indole ring especially for the I, I^{iii} pair. In addition to the cation–anion charge interactions, there is an extensive hydrogen-bonding network stabilizing the crystal.

	Distance (Å)	Angles (°)
N(3)–H(N3)...O	2.814(9)	157(8)
N(7)–H(N7)...Cl(5)^{iii}	3.202(5)	151
O–Ha...Cl(3)	3.477(9)	166(15)
O–Hb...Cl(4)^{iv}	3.321(8)	161(11)

Symmetry code iv: $1+x, y, 1+z$.

TABLE 2. Interatomic distances (Å) and angles (°)

Distances (Å)			
Pt–Cl(1)	2.316(2)	Pt–Cl(4)	2.315(3)
Pt–Cl(2)	2.326(3)	Pt–Cl(5)	2.304(2)
Pt–Cl(3)	2.305(3)		
N(1)–C(2)	1.249(9)	C(8)–C(9)	1.381(9)
N(1)–C(14)	1.361(7)	C(8)–C(17)	1.387(9)
C(2)–N(3)	1.34(1)	C(9)–C(10)	1.380(9)
N(3)–C(4)	1.362(8)	C(10–C(11)	1.392(9)
C(4)–C(15)	1.338(9)	C(11)–C(12)	1.396(7)
C(5)–C(6)	1.49(1)	C(12)–C(13)	1.448(8)
C(5)–C(15)	1.505(8)	C(12)–C(17)	1.401(8)
C(6)–C(16)	1.494(8)	C(13)–C(14)	1.404(8)
N(7)–C(16)	1.351(8)	C(13)–C(16)	1.388(7)
N(7)–C(17)	1.401(6)	C(14)–C(15)	1.433(8)
Angles (°)			
Cl(1)–Pt–Cl(2)	179.6(3)	Cl(2)–Pt–Cl(5)	90.21(5)
Cl(1)–Pt–Cl(3)	89.5(1)	Cl(3)–Pt–Cl(4)	179.4(3)
Cl(1)–Pt–Cl(4)	91.1(1)	Cl(3)–Pt–Cl(5)	88.66(6)
Cl(1)–Pt–Cl(5)	89.80(5)	Cl(4)–Pt–Cl(5)	91.35(6)
Cl(2)–Pt–Cl(3)	90.9(1)	Cl(5)–Pt–Cl(5)^{i}	177.3(1)
Cl(2)–Pt–Cl(4)	88.5(1)		
C(2)–N(1)–C(14)	117.3(5)	C(16)–C(13)–C(12)	106.7(5)
N(1)–C(2)–N(3)	124.4(6)	C(14)–C(13)–C(12)	133.2(4)
C(2)–N(3)–C(4)	120.2(6)	N(1)–C(14)–C(13)	119.7(5)
N(3)–C(4)–C(15)	119.5(6)	N(1)–C(14)–C(15)	121.0(5)
C(15)–C(5)–C(6)	115.8(6)	C(13)–C(14)–C(15)	119.3(4)
C(16)–C(6)–C(5)	110.0(4)	C(4)–C(15)–C(14)	117.6(5)

(continued)

TABLE 2. *(continued)*

C(16)–N(7)–C(17)	108.8(4)	C(4)–C(15)–C(5)	122.9(6)
C(9)–C(8)–C(17)	116.8(6)	C(14)–C(15)–C(5)	119.1(5)
C(8)–C(9)–C(10)	121.3(6)	N(7)–C(16)–C(13)	110.0(5)
C(11)–C(10)–C(9)	122.1(6)	N(7)–C(16)–C(6)	125.1(5)
C(10)–C(11)–C(12)	117.6(5)	C(13)–C(16)–C(6)	124.8(5)
C(11)–C(12)–C(17)	119.1(5)	N(7)–C(17)–C(8)	128.7(5)
C(11)–C(12)–C(13)	134.7(5)	N(7)–C(17)–C(12)	108.3(5)
C(17)–C(12)–C(13)	106.2(4)	C(8)–C(17)–C(12)	123.0(5)
C(16)–C(13)–C(14)	120.0(5)		

Symmetry code i: $x, \frac{1}{2} - y, z$.

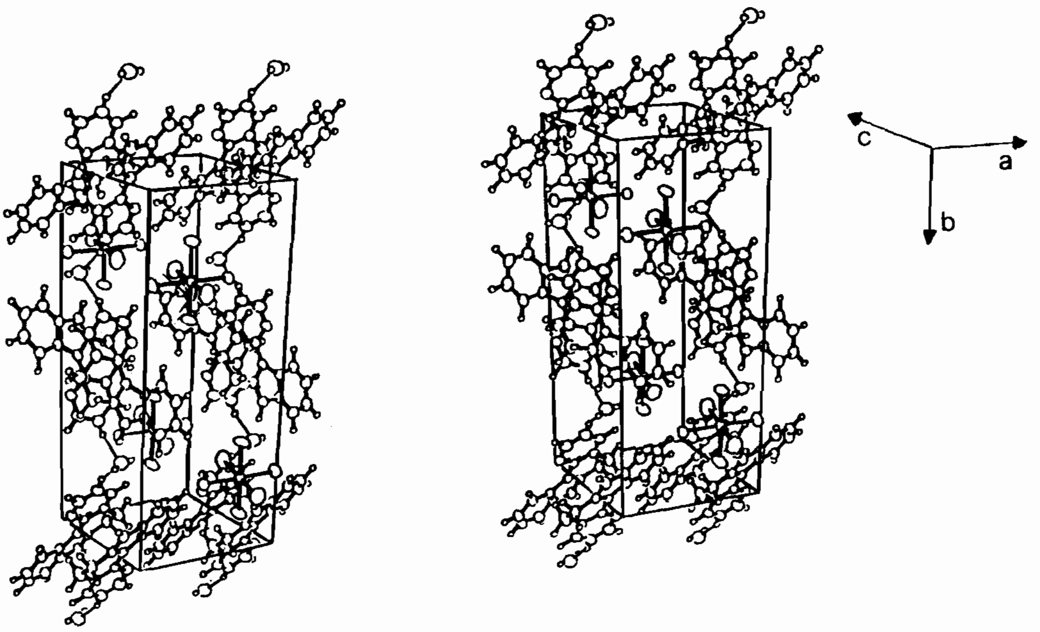

Fig. 1. Stereoscopic view of the title compound showing the overlapping between the DPCH$^+$ ions and the hydrogen bondings involved in the water molecule.

Thus, one water molecule is bonded to two DPCH$^+$ ions which are related by the mirror plane in which the water molecule lies.

Supplementary Material

Tables of hydrogen atomic coordinates, anisotropic temperature factors, 'mean planes', and a listing of observed and calculated structure factors are available from the authors on request.

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