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Synthesis and Structure of the Tetra-5,6-dihydropyrimidino[5,4-*c*]carbazole Dichloride Hexachloroplatinate(IV) Tetrahydrate

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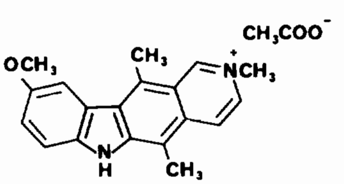
Abstract

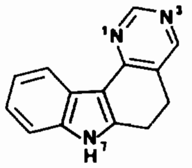
The crystal structure of tetra-5,6-dihydropyrimidino[5,4-*c*]carbazole dichloride hexachloroplatinate(IV) tetrahydrate has been determined by X-ray analysis. The complex crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions a = 8.222(3), b = 13.140(2), c = 14.753(2) Å, α = 114.81(1), β = 92.93(2), γ = 95.54(2)°, Z = 1. The Pt atom is in the inversion center. The structure was refined to R = 0.028 and R_w = 0.028 with use of 5044 independent reflections. The unit-cell contains two Cl^- anions, one $[PtCl_6]^{2-}$ anion, four $DPCH^+$ cations and four H_2O solvate molecules. The Pt atom exhibits a slightly distorted octahedron coordination. The Pt(IV)–Cl distances of 2.311(1), 2.320(2) and 2.325(1) Å and the Cl–Pt–Cl angle values very close to 90° agree well with those found in K_2PtCl_6. The two independent DPC molecules are protonated on the two homologous sp^2 N(3) and N(23) atoms. The $DPCH^+$ cations remain in a skew-chair conformation. In addition to the cation–anion charge interaction, there is an extensive hydrogen-bonding network stabilizing the crystal, via the $DPCH^+$, H_2O and Cl^- species.

Introduction

The derivatives of 5,6-dihydropyrimidino[5,4-*c*]-carbazole (called hereafter DPC) with antineoplastic intention and synthesized from the design of ellipticine showed activity in the course of preliminary study on mouse leukemia P388. In the light of the properties and crystal structure of $[ethidium]_2PtCl_4$ [1] and $[rhodamine\text{-}123]_2PtCl_4 \cdot H_2O$ [2], the first tetrachloroplatinate(II) with anticancer activity, we attempted to synthesize an analogous complex salt by replacing the rhodamine cation by the protonated DPC molecule ($DPCH^+$).



Ellipticinium acetate, an antitumoral agent



DPC

The DPC molecule is a tetraheterocycle in which the cyclohexadiene ring is in a skew-chair conformation. Moreover, it exhibits dimorphism, as revealed by X-ray crystallographic studies [3, 4].

Experimental

Synthesis

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 formed immediately. This precipitate was partially dissolved in 1 M HCl solution. Single crystals were obtained by slow evaporation of this solution under ambient air pressure. Under these conditions, there is a slow oxidation of Pt(II) to Pt(IV), as confirmed by X-ray study.

Crystallography

Data collection

Crystallographic measurements were made at room temperature using an Enraf–Nonius CAD-4 diffrac-

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tometer with graphite monochromatized Mo Kα radiation and a crystal with dimensions of 0.25 × 0.2 × 0.2 mm^3. Intensities of 5260 independent reflections were measured within $2° < 2\theta < 50°$, using the ω–0.66θ scan-mode with an ω scan-width of $0.90 + 0.34 \tan\theta$ and ω scan-speeds of 10–5.5 deg min^{-1}. Data were corrected for Lorentz and polarization effects but not for absorption. Unit-cell parameters and the orientation matrix were determined and refined using setting angles for 25 well-spaced reflections using $24 < 2\theta < 29°$.

Crystal data

The values found were: $a = 8.222(3)$, $b = 13.140(2)$, $c = 14.753(2)$ Å; $\alpha = 144.81(1)$, $\beta = 92.93(2)$, $\gamma = 95.54(2)°$), $V = 1433$ Å^3, $M_r = 1439.8$. $\rho_{obs} = 1.67$, $\rho_{calc} = 1.67$ g cm^{-3}. Space group: triclinic $P\bar{1}$. $Z = 1$. μ(Mo Kα) = 28.5 cm^{-1}. Unit-cell content: 1 [$PtCl_6^{2-}$]; 2 Cl^-; 4 H_2O solvate molecules; 4 $DPCH^+$ (*i.e.* two crystallographically independent cations). Formula: $[C_{14}N_3H_{12}^+]_4[PtCl_6^{2-}]2Cl^- \cdot 4H_2O$, $C_{56}H_{56}Cl_8N_{12}O_4Pt$.

Structure determination

The platinum atom is in the inversion center. The chloride ions were found from a three-dimensional Patterson synthesis and subsequent least-squares refinement and electron density difference syntheses revealed all the non-hydrogen atoms. Further refinement using a full-matrix least-squares and all non-hydrogen atoms with anisotropic temperature factors minimized $\Sigma w(|F_o| - |F_c|)^2$. The hydrogen atoms were inserted in idealized positions and those on water molecules were found from difference Fourier syntheses; 5044 intensities satisfying the criterion $F > 3\sigma(F)$ were retained; a final refinement with unit weights led to R and R_w of 0.028.

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 chloride [5]. The computations were carried out on a Gould Computer using SHELX 76 program system [6]. The drawings were made with ORTEP [7].

The fractional atomic coordinates and equivalent isotropic thermal parameters are listed in Table I. Bond lengths and bond angles are given in Table II.

Results and Discussion

Platinum Environment

The platinum(IV) atom in the inversion center exhibits a slightly distorted octahedron coordination. The Pt(IV)–Cl distances of 2.311(1), 2.320(2) and 2.325(1) Å, as well as the Cl–Pt–Cl angle values which are very close to 90° (the maximum deviation is less than 1.27(5)°), agree well with those found in K_2PtCl_6 [8]. As shown in Fig. 1 there is no evidence for coordination of $DPCH^+$ to platinum(IV): thus, there is salt formation, as indicated by the crystal structure.

TABLE I. Atomic Positional Parameters

	x	y	z	B_{eq} (Å^2)
Pt	0.5	0.5	0.5	2.382(7)
Cl(1)	0.7842(1)	0.5153(1)	0.52703(9)	3.53(4)
Cl(2)	0.5331(1)	0.5510(1)	0.36871(9)	3.98(4)
Cl(3)	0.5107(2)	0.6886(1)	0.6095(1)	4.02(4)
Cl(4)	0.3185(2)	0.8332(1)	0.8875(1)	4.81(5)
O(1)	0.1380(4)	0.6938(3)	0.6789(3)	3.9(1)
O(2)	0.3827(7)	0.0863(4)	0.9238(4)	6.6(2)
N(1)	0.8365(4)	0.5316(3)	0.1580(3)	3.2(1)
C(2)	0.8452(6)	0.4799(4)	0.2165(4)	3.5(2)
N(3)	0.9828(5)	0.4849(3)	0.2720(3)	3.4(1)
C(4)	1.1222(6)	0.5468(4)	0.2711(4)	3.3(2)
C(5)	1.2740(5)	0.6805(4)	0.2142(4)	3.4(2)
C(6)	1.2876(5)	0.6965(4)	0.1179(4)	3.4(2)
N(7)	1.0928(5)	0.7320(3)	0.0006(3)	3.2(1)
C(8)	0.8435(6)	0.7219(4)	−0.1096(4)	3.7(2)
C(9)	0.6788(7)	0.6817(5)	−0.1330(4)	4.1(2)
C(10)	0.5980(6)	0.6264(5)	−0.0812(4)	4.1(2)
C(11)	0.6813(5)	0.6101(4)	−0.0055(4)	3.4(2)
C(12)	0.8490(5)	0.6487(4)	0.0179(3)	2.8(1)
C(13)	0.9764(5)	0.6451(4)	0.0869(3)	2.7(1)
C(14)	0.9764(5)	0.5923(3)	0.1532(3)	2.6(1)
C(15)	1.1250(5)	0.6041(4)	0.2128(3)	2.8(1)
C(16)	1.1223(5)	0.6952(4)	0.0717(3)	2.7(1)
C(17)	0.9275(6)	0.7043(4)	−0.0343(3)	3.0(1)
N(21)	0.1560(5)	0.8562(4)	0.4530(3)	3.7(1)
C(22)	0.1573(7)	0.8127(5)	0.5186(4)	4.3(2)
N(23)	0.0218(6)	0.7740(4)	0.5469(3)	4.3(2)
C(24)	−0.1290(7)	0.7787(4)	0.5093(4)	4.0(2)
C(25)	−0.3061(6)	0.8386(5)	0.4019(4)	4.1(2)
C(26)	−0.3091(6)	0.8210(4)	0.2923(4)	3.9(2)
N(27)	−0.1362(6)	0.9193(3)	0.2095(3)	3.9(1)
C(28)	0.1038(8)	1.0107(5)	0.1588(4)	4.8(2)
C(29)	0.2672(9)	1.0447(5)	0.1798(5)	5.4(2)
C(30)	0.3568(8)	1.0338(4)	0.2574(3)	4.8(2)
C(31)	0.2826(6)	0.9880(4)	0.3156(4)	3.8(2)
C(32)	0.1153(6)	0.9518(4)	0.2963(3)	3.3(1)
C(33)	−0.0060(6)	0.9000(4)	0.3370(3)	3.0(1)
C(34)	0.0057(6)	0.8602(4)	0.4121(3)	3.1(1)
C(35)	−0.1419(6)	0.8222(4)	0.4416(4)	3.4(2)
C(36)	−0.1558(6)	0.8820(4)	0.2806(3)	3.2(1)
C(37)	0.0274(7)	0.9624(4)	0.2165(4)	3.6(2)

$DPCH^+$ Conformation

The two crystallographically independent $DPCH^+$ cations, called hereafter **I** and **II**, are labeled from N(1) to C(17) and N(21) to C(37) respectively.

In the $DPCH^+$ cations, the cyclohexadiene ring remains in a skew-chair conformation. The other rings (benzene, indole and pyrimidine) are as expected from previous X-ray studies.

It is noteworthy that the two independent DPC molecules are protonated on the two homologous sp^2

TABLE II. Bond Distances and Bond Angles

(a) Interatomic distances (Å)

Pt–Cl(1)	2.326(1)		
Pt–Cl(2)	2.320(2)		
Pt–Cl(3)	2.311(1)		
N(1)–C(2)	1.308(8)	N(21)–C(22)	1.314(9)
N(1)–C(14)	1.357(6)	N(21)–C(34)	1.363(6)
C(2)–N(3)	1.341(7)	C(22)–N(23)	1.338(8)
N(3)–C(4)	1.345(6)	N(23)–C(24)	1.350(7)
C(4)–C(15)	1.359(8)	C(24)–C(35)	1.347(9)
C(5)–C(6)	1.529(8)	C(25)–C(26)	1.533(8)
C(5)–C(15)	1.500(6)	C(25)–C(35)	1.514(8)
C(6)–C(16)	1.484(6)	C(26)–C(36)	1.484(7)
N(7)–C(16)	1.347(7)	N(27)–C(36)	1.342(8)
N(7)–C(17)	1.386(6)	N(27)–C(37)	1.390(7)
C(8)–C(9)	1.376(7)	C(28)–C(29)	1.351(9)
C(8)–C(17)	1.380(8)	C(28)–C(37)	1.397(9)
C(9)–C(10)	1.406(9)	C(29)–C(30)	1.394(10)
C(10)–C(11)	1.383(8)	C(30)–C(31)	1.374(9)
C(11)–C(12)	1.396(6)	C(31)–C(32)	1.386(7)
C(12)–C(13)	1.441(7)	C(32)–C(33)	1.446(8)
C(12)–C(17)	1.406(8)	C(32)–C(37)	1.413(8)
C(13)–C(14)	1.417(8)	C(33)–C(34)	1.414(8)
C(13)–C(16)	1.386(6)	C(33)–C(36)	1.392(7)
C(14)–C(15)	1.424(6)	C(34)–C(35)	1.425(7)

(b) Angles (deg)

Cl(3)–Pt–Cl(2)	89.68(5)		
Cl(3)–Pt–Cl(1)	89.56(4)		
Cl(2)–Pt–Cl(1)	88.73(5)		
C(2)–N(1)–C(14)	117.1(4)	C(22)–N(21)–C(34)	116.5(5)
N(1)–C(2)–N(3)	123.7(5)	N(21)–C(22)–N(23)	124.1(5)
C(2)–N(3)–C(4)	120.5(5)	C(22)–N(23)–C(24)	120.9(6)
N(3)–C(4)–C(15)	120.0(4)	N(23)–C(24)–C(35)	119.1(5)
C(15)–C(5)–C(6)	114.9(4)	C(35)–C(25)–C(26)	112.2(4)
C(16)–C(6)–C(5)	110.5(4)	C(36)–C(26)–C(25)	108.6(4)
C(16)–N(7)–C(17)	109.2(4)	C(36)–N(27)–C(37)	109.2(4)
C(9)–C(8)–C(17)	117.7(5)	C(29)–C(28)–C(37)	117.7(6)
C(8)–C(9)–C(10)	121.0(6)	C(28)–C(29)–C(30)	121.4(7)
C(11)–C(10)–C(9)	121.3(5)	C(31)–C(30)–C(29)	121.4(6)
C(10)–C(11)–C(12)	118.5(5)	C(30)–C(31)–C(32)	119.0(5)
C(11)–C(12)–C(17)	119.5(5)	C(31)–C(32)–C(37)	118.6(5)
C(11)–C(12)–C(13)	135.2(5)	C(31)–C(32)–C(33)	136.5(5)
C(17)–C(12)–C(13)	105.3(4)	C(37)–C(32)–C(33)	104.9(4)
C(16)–C(13)–C(14)	125.3(4)	C(36)–C(33)–C(34)	119.7(5)
C(16)–C(13)–C(12)	107.5(5)	C(36)–C(33)–C(32)	107.5(5)
C(14)–C(13)–C(12)	131.8(4)	C(34)–C(33)–C(32)	132.6(4)
N(1)–C(14)–C(13)	119.6(4)	N(21)–C(34)–C(33)	120.0(4)
N(1)–C(14)–C(15)	121.8(5)	N(21)–C(34)–C(35)	121.4(5)
C(13)–C(14)–C(15)	118.6(4)	C(33)–C(34)–C(35)	118.6(4)
C(4)–C(15)–C(14)	116.7(4)	C(24)–C(35)–C(24)	118.0(5)
C(4)–C(15)–C(5)	122.1(4)	C(24)–C(35)–C(25)	122.2(5)
C(14)–C(15)–C(5)	121.2(5)	C(34)–C(35)–C(25)	119.7(5)
N(7)–C(16)–C(13)	109.4(4)	N(27)–C(36)–C(33)	109.6(4)
N(7)–C(16)–C(6)	125.0(4)	N(27)–C(36)–C(26)	125.7(4)
C(13)–C(16)–C(6)	125.3(5)	C(33)–C(36)–C(26)	124.5(5)
N(7)–C(17)–C(8)	129.2(5)	N(27)–C(37)–C(28)	129.3(5)
N(7)–C(17)–C(12)	108.7(4)	N(27)–C(37)–C(32)	108.8(5)
C(8)–C(17)–C(12)	122.1(4)	C(28)–C(37)–C(32)	121.8(5)

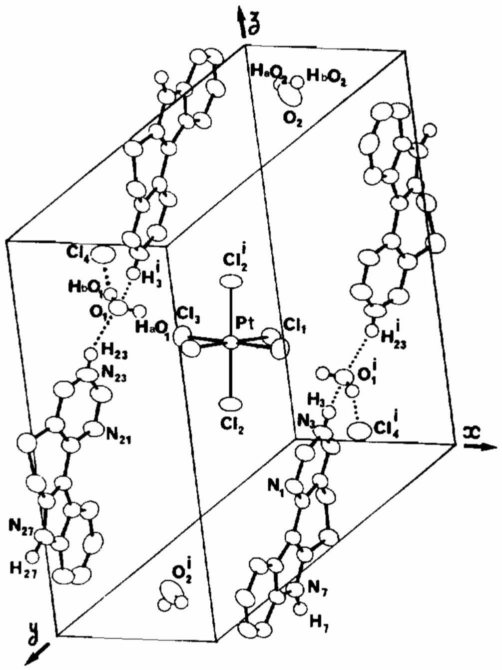

Fig. 1. The contents of one unit cell with atom labeling.

N(3) and N(23) atoms respectively. As a matter of fact, the lone-pair of the N(1) atom is a lesser donor than the homologous pair of the N(3) atom, as a consequence of the steric hindrance due to the neighborhood of the hydrogen atom bonded to the C(11) atom. The donor capacity of this N(3) or N(23) atom lone-pair was observed in the coordination complex between Co(NO$_3$)$_2$ and the DPC molecule, where a covalent Co(II)–N(3) bond was found [9].

Intermolecular Bonding

The packing of the title compound is shown in Fig. 1. The stereoscopic view (Fig. 2) shows that the 'mean-planes' of DPCH$^+$ cations, related by a crystallographic inversion center, are nearly parallel. Figure 3 is relative to one of the DPCH$^+$ cations, labelled **I**, and its centrosymmetric homolog **I**′. The distance between the 'mean planes', calculated from the homologous indole rings of each independent DPCH$^+$ cation, are 3.60 and 3.30 Å for the pairs **I**, **I**′ and **II** and **II**′ respectively, thus giving strong π–π interactions in the latter case. These values should be compared to those previously reported in the monoclinic form **I** of the DPC molecule (3.35 Å) in which the molecular overlapping is smaller [3]. In cation **I** of the hexachloroplatinate(IV) salt, the N(1), C(4), C(15), C(14), C(11), C(12), C(17), N(7) and C(8) atoms are involved, while in the cations **II**, the overlapping involves the N(21), C(22), N(23), C(32) and C(34) atoms only. In addition, another overlapping between cations **I** and **II** themselves (with a distance between the indole 'mean-planes' of about 3.40 Å) gives rise to a columnar packing, the axis of which is approximately parallel to [011]. Thus, in these infinite columns, the stacking sequence ···**I**′–**I**–**II**–**II**′··· is to be observed (Fig. 4).

In addition to the cation–anion charge interactions, there is an extensive hydrogen-bonding network stabilizing the crystal.

	Distance (Å)
Cl(4)····HB(O1)–O(1)	3.051(4)
Cl(4)····HB(O2^{ii})–O(2^{ii})	3.125(7)
Cl(4)····H(N7^{iii})–N(7^{iii})	3.115(5)
O(1)····H(N3^{i})–N(3^{i})	2.842(7)
O(1)····H(N23)–N(23)	2.745(7)
O(2)····H(N27^{iv})–N(27^{iv})	2.724(8)

i: $1-x, 1-y, 1-z$
ii: $x, 1+y, z$
iii: $-1+x, y, 1+z$
iv: $-x, 1-y, 1-z$

Thus, Cl(4) is bonded to the two H$_2$O molecules and one DPCH$^+$ via the N(7^{iii}) atom. Figure 2 shows that one DPCH$^+$ cation is linked by hydrogen bonding to a first DPCH$^+$ (crystallographically indepen-

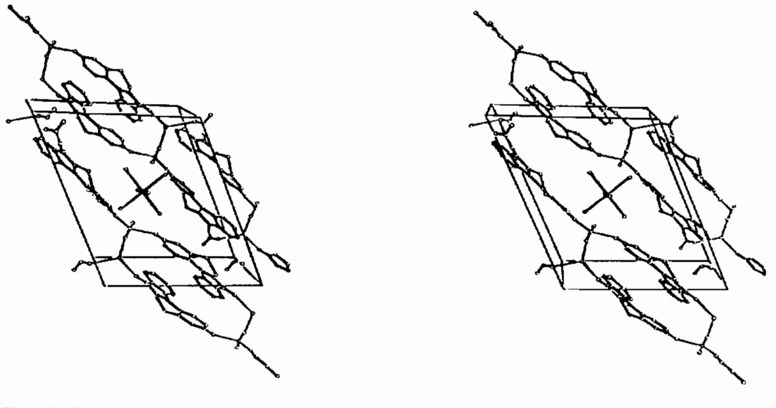

Fig. 2. Stereoscopic view of the title compound with hydrogen bonding.

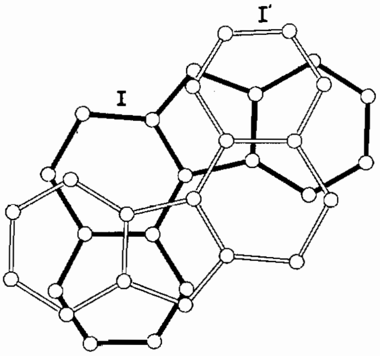

Fig. 3. Overlapping between the DPCH$^+$ ion (I) and its centrosymmetric homolog (I').

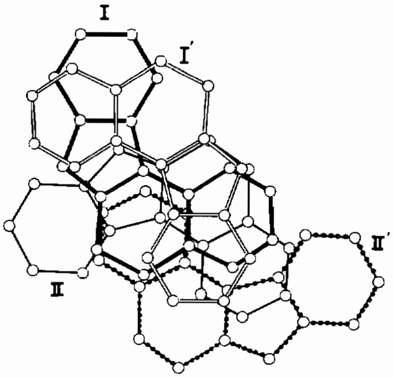

Fig. 4. Stacking sequence of the different DPCH$^+$ ions ···I'–I–II–II'···.

dent from the previous one) via the O(1) atom of $H_2O(1)$ and to a second DPCH$^+$ via the O(2) atom of $H_2O(2)$ and the Cl(4) ion, thus forming an infinite zig-zag chain. Two infinite chains related by a center of symmetry are bridged by O(1) and Cl(4) atoms, giving rise to a two-dimensional band-like network.

Work is in progress to further characterize the biological properties of this and related compounds.

Supplementary Material

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

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