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Crystal structure of bis[(*p*-chlorophenyl)isopropylbiguadinium] tetrachloroplatinate(II) bisdimethylformamide, $C_{14}H_{24}Cl_3N_6OPt_{0.5}$, and of bis[(*p*-chlorophenyl)isopropylbiguadinium] hexachloroplatinate(IV) bisdimethylformamide, $C_{28}H_{46}Cl_8N_{12}O_2Pt$

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Abstract

$C_{14}H_{24}Cl_3N_6OPt_{0.5}$, triclinic, $P\bar{1}$ (No. 2), $a = 9.347(2)$ Å, $b = 10.228(2)$ Å, $c = 11.503(3)$ Å, $\alpha = 72.46(2)°$, $\beta = 87.64(2)°$, $\gamma = 85.90(2)°$, $V = 1045.7$ Å^3, $Z = 2$, $\rho_m = 1.61$ g·cm^{-3}, $R_{gt}(F) = 0.031$, $wR_{ref}(F^2) = 0.069$, $T = 293$ K.

$C_{28}H_{46}Cl_8N_{12}O_2Pt$, monoclinic, $P12_1/n1$ (No. 14), $a = 10.604(2)$ Å, $b = 9.996(3)$ Å, $c = 21.103(7)$ Å, $\beta = 101.23(2)°$, $V = 2194$ Å^3, $Z = 2$, $\rho_m = 1.61$ g·cm^{-3}, $R_{gt}(F) = 0.038$, $wR_{ref}(F^2) = 0.119$, $T = 293$ K.

Source of material

For the synthesis of the complex of Pt(II), K_2PtCl_4 (4 mmol, 1.66 g) was dissolved in 20 mL of water, and proguanil hydrochloride (8 mmol, 2.32 g, dissolved in 200 mL of hot water) was added to this solution by stirring. The reaction mixture was stirred and kept at 343 K for 10 minutes. A precipitate was quickly obtained, separated by filtration, washed with water, methanol and ethyl ether and dried. The pink complex obtained is soluble in dimethylformamide. Single crystals were obtained by slow evaporation of this solution under ambient air pressure.

For the preparation of the complex(IV), K_2PtCl_6 (4 mmol, 1.94 g) was dissolved in 100 mL of hot water, and proguanil hydrochloride (8 mmol, 2.32 g, dissolved in 200 mL of water) was added to this solution by stirring. The reaction mixture was stirred and kept at 343 K for 36 h. A yellow solid was obtained, separated by filtration, washed with water, methanol and ethyl ether and dried. The complex obtained is soluble in hot dimethylformamide. Single crystals were obtained by slow evaporation of this solution under ambient air pressure.

Discussion

In the course of our attempts to synthesize complexes of Pt(II) or Pt(IV) by biguanide derivatives, we recently synthesized and characterized the tetrachloro(metformin) platinum(IV) bisdimethylformamide solvate [1]. In the present work, we describe the crystal structure of the (*p*-chlorophenyl) isopropylbiguanidium [proguanilium] cation with tetrachloroplatinate(II) (**1**) or hexachloroplatinate(IV) (**2**) as counteranion. Each salt structure consists of two proguanilium cations related by a crystallographic inversion centre and one $PtCl_4^{2-}$ (compound **1**) or $PtCl_6^{2-}$ (compound **2**) anion. In addition, two DMF solvate molecules complete each structure.

In **1**, the platinum(II) atom on the inversion centre exhibits a slightly distorted square planar coordination. The Pt(II)—Cl distances of 2.297(1) Å and 2.303(1) Å, as well as a Cl–Pt–Cl angle value which is very close to 90° (88.83(5)°) agree well with those found in pyrido[2,3-*h*]pyrrolo[1,2-*a*]quinoxalinium tetrachloroplatinate monohydrate [2]. In the proguanilium cation, distances and angles are as expected from proguanil hydrochloride [3]. The dihedral angle between mean-planes P(1) [N1, N2, N3] and P(2) [N3, N4, N5] is 49.9(2)°. Thus, the proguanilium cation is not planar. Moreover, C7 is 0.026(4) Å out of P(1) and C8 is 0.036(4) Å out of P(2). The N3 atom is not bonded to a hydrogen atom, correlatively with a double protonation level with N2 and N4 atoms, a situation which is similar to that found in the proguanil, hydrochloride [3]. The N—C bonds involving C7 and C8 atoms are in the narrow ranges: 1.315(5) Å to 1.356(5) Å as a consequence of the π conjugation along the outline N2–C7–N3–C8–N4 including also N1 and N5. The N2–C7–N1–C1 sequence exhibits a *trans* conformation as shown by the torsion angle value of 175.5(4) Å, while the N3–C8–N5–C9 sequence is in a *cis* conformation (torsion angle 10.4(6) Å). The packing is characterized by two intramolecular hydrogen bonds [N2–H22···N4: 2.973(5) Å, 107°, N4–H42···N2: 2.973(5) Å, 108°] and eight interactions that can be considered as hydrogen bonds, since they correspond to H···A contacts significantly shorter that the sum of van der Waals radii. These bonds involving N1, N2, N4 and N5 connect the proguanilium cation with $PtCl_4^{2-}$ and DMF, the shortest being N4–H42···O50 (2.869(5) Å, 160°).

In **2**, the platinum(IV) atom on the inversion centre exhibits a slightly distorted octahedron coordination. The Pt(IV)—Cl distances of 2.310(2) Å, 2.314(2) Å and 2.318(2) Å, as well as the Cl–Pt–Cl angle values which are very close to 90° (maximum deviation 0.86°) agree well with those found in K_2PtCl_6 [4]. In the proguanilium cation, distances and angles are as expected from **1**. Thus, the dihedral angle between mean-planes P(1)[N1, N2, N3] and P(2) [N3, N4, N5] is 40.9(3)° (proguanilium cation not planar); C7 is 0.026(7) Å out of P(1) and C8 is 0.027(7) Å out of P(2). The conformation is the same: *trans* for N2–C7–N1–C1 sequence [torsion angle 178.0(6)°] and *cis* for N3–C8–N5–C9 sequence [torsion angle −1(1)°]. The packing is characterized by two intramolecular hydrogen bonds N2–H22···N4 (2.884(9) Å, 111°), N4–H42···N2 (2.884(9) Å, 98°), and eight interactions that can be considered as hydrogen bonds, the shortest being N2—H22···O50 (2.874(9) Å, 148°).

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1. $C_{14}H_{24}Cl_3N_6OPt_{0.5}$

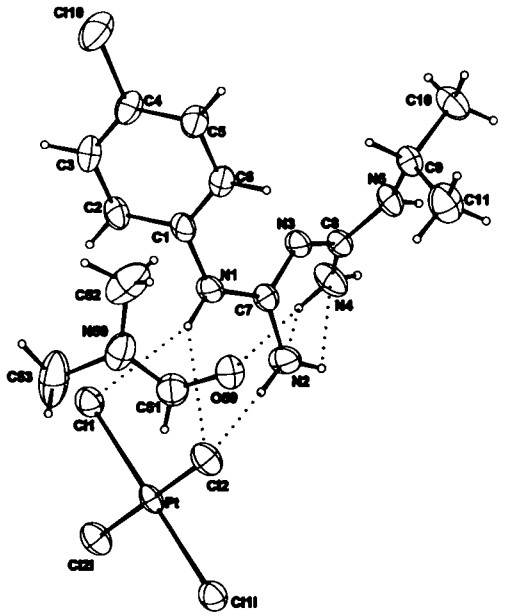

Table 1. Data collection and handling.

Crystal:	pink parallelepiped, size 0.180 x 0.200 x 0.225 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	37.79 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	51.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4036, 4036
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3740
$N(param)_{refined}$:	233
Programs:	SIR92 [5], SHELXL-97 [6],WinGX [7]

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

Atom	Site	x	y	z	U_{iso}
H(21)	2i	0.2850	0.9886	0.8593	0.107(4)
H(22)	2i	0.4404	1.0147	0.8507	0. 107
H(2)	2i	0.1704	0.5563	0.8821	0. 107
H(3)	2i	0.1710	0.3715	0.8065	0. 107
H(41)	2i	0.7394	0.8535	0.9673	0. 107
H(42)	2i	0.5816	0.8410	0.9847	0. 107
H(5)	2i	0.4096	0.5711	0.5204	0. 107
H(6)	2i	0.4100	0.7551	0.5976	0. 107
H(9)	2i	0.7148	0.7723	0.6250	0. 107
H(101)	2i	0.9593	0.7124	0.6586	0. 107
H(102)	2i	0.9930	0.8678	0.6117	0. 107
H(103)	2i	0.9359	0.7962	0.5215	0. 107
H(111)	2i	0.6301	1.0013	0.5732	0. 107
H(112)	2i	0.7304	0.9758	0.4685	0. 107
H(113)	2i	0.7879	1.0474	0.5586	0. 107
H(521)	2i	0.3291	0.4817	1.1522	0. 107
H(522)	2i	0.4747	0.5494	1.1503	0. 107
H(523)	2i	0.3606	0.6186	1.0506	0. 107
H(531)	2i	0.1713	0.5029	1.2828	0. 107
H(532)	2i	0.1062	0.6535	1.2625	0. 107
H(533)	2i	0.2095	0.5853	1.3711	0. 107
H(1)	2i	0.206(3)	0.816(6)	0.821(5)	0. 107
H(50)	2i	0.844(4)	0.864(6)	0.787(5)	0. 107
H(51)	2i	0.313(6)	0.806(6)	1.248(5)	0. 107

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)	1i	0.0	1.0	1.0	0.0217(1)	0.0611(2)	0.0477(1)	-0.00224(8)	-0.00090(7)	-0.0127(1)
Cl(1)	2i	0.0163(1)	0.7751(1)	0.9976(1)	0.0446(5)	0.0626(7)	0.0629(6)	-0.0011(5)	-0.0006(4)	-0.0156(5)
Cl(2)	2i	0.0221(1)	1.0684(1)	0.79105(9)	0.0518(6)	0.0793(8)	0.0484(6)	0.0011(5)	0.0005(4)	-0.0109(5)
Cl(10)	2i	0.2997(2)	0.3121(2)	0.6019(1)	0.135(1)	0.0689(9)	0.092(1)	-0.0361(9)	0.0003(9)	-0.0343(8)
N(1)	2i	0.2868(3)	0.7885(4)	0.7928(4)	0.027(2)	0.064(2)	0.084(3)	-0.005(2)	0.002(2)	-0.036(2)
C(1)	2i	0.2921(4)	0.6741(4)	0.7482(4)	0.027(2)	0.057(3)	0.057(2)	-0.005(2)	-0.004(2)	-0.017(2)
N(2)	2i	0.3722(4)	0.9655(4)	0.8437(4)	0.037(2)	0.070(3)	0.104(3)	0.002(2)	-0.006(2)	-0.045(2)
C(2)	2i	0.2198(4)	0.5590(5)	0.8097(4)	0.041(2)	0.073(3)	0.061(3)	-0.017(2)	0.003(2)	-0.021(2)
N(3)	2i	0.5297(3)	0.8085(4)	0.7823(3)	0.029(2)	0.060(2)	0.072(2)	-0.006(1)	0.001(1)	-0.030(2)
C(3)	2i	0.2201(5)	0.4483(5)	0.7649(4)	0.058(3)	0.058(3)	0.062(3)	-0.025(2)	-0.003(2)	-0.006(2)
N(4)	2i	0.6579(4)	0.8440(5)	0.9397(4)	0.032(2)	0.111(3)	0.070(3)	-0.004(2)	-0.002(2)	-0.040(2)
C(4)	2i	0.2937(5)	0.4525(5)	0.6583(4)	0.067(3)	0.053(3)	0.057(3)	-0.018(2)	-0.010(2)	-0.015(2)
N(5)	2i	0.7703(3)	0.8392(4)	0.7618(3)	0.028(2)	0.075(3)	0.061(2)	-0.010(2)	-0.001(1)	-0.021(2)
C(5)	2i	0.3629(5)	0.5675(5)	0.5942(4)	0.067(3)	0.059(3)	0.056(3)	-0.018(2)	0.003(2)	-0.017(2)
C(6)	2i	0.3623(4)	0.6777(4)	0.6402(4)	0.050(2)	0.046(3)	0.059(3)	-0.010(2)	-0.002(2)	-0.009(2)
C(7)	2i	0.4015(4)	0.8549(4)	0.8089(4)	0.031(2)	0.052(3)	0.060(2)	-0.003(2)	-0.002(2)	-0.018(2)
C(8)	2i	0.6497(4)	0.8341(4)	0.8281(4)	0.030(2)	0.051(2)	0.060(2)	-0.001(2)	-0.001(2)	-0.017(2)
C(9)	2i	0.7773(4)	0.8411(5)	0.6346(4)	0.038(2)	0.062(3)	0.058(3)	-0.009(2)	0.002(2)	-0.017(2)
C(10)	2i	0.9305(5)	0.8007(6)	0.6038(5)	0.044(2)	0.101(4)	0.078(3)	-0.005(2)	0.009(2)	-0.037(3)
C(11)	2i	0.7269(6)	0.9788(6)	0.5512(5)	0.074(3)	0.088(4)	0.077(4)	0.000(3)	0.002(3)	0.002(3)
O(50)	2i	0.4545(4)	0.8198(4)	1.1377(3)	0.062(2)	0.075(2)	0.096(3)	-0.019(2)	0.014(2)	-0.032(2)
N(50)	2i	0.3110(4)	0.6444(4)	1.2104(4)	0.058(2)	0.052(3)	0.103(3)	-0.005(2)	-0.021(2)	-0.002(2)
C(51)	2i	0.3561(6)	0.7651(6)	1.2021(5)	0.063(3)	0.063(4)	0.082(4)	0.001(3)	0.002(3)	-0.014(3)
C(52)	2i	0.3740(8)	0.5672(7)	1.1347(7)	0.113(5)	0.073(4)	0.156(7)	0.003(4)	-0.056(5)	-0.038(4)
C(53)	2i	0.1892(7)	0.5921(7)	1.2883(7)	0.099(5)	0.092(5)	0.139(6)	-0.032(4)	-0.027(4)	0.045(4)

2. $C_{28}H_{46}Cl_8N_{12}O_2Pt$

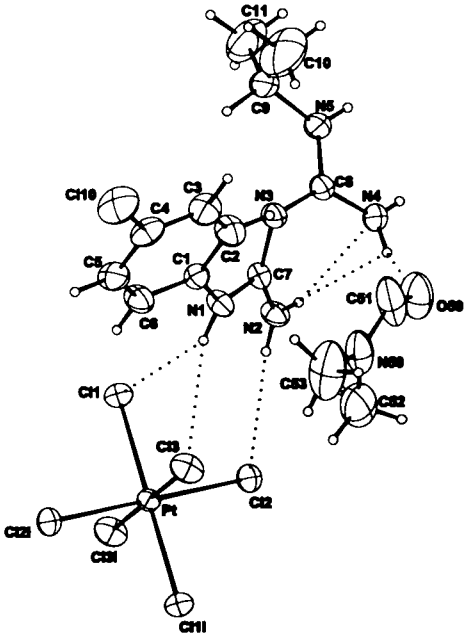

Table 4. Data collection and handling.

Crystal:	yellow parallelepiped, size 0.20 × 0.20 × 0.22 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	37.26 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	55.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5267, 5267
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2876
$N(param)_{refined}$:	251
Programs:	SIR92 [5], SHELXL-97 [6],WinGX [7]

Table 5. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.42(1)	0.31(1)	0.642(6)	0.16(1)
H(21)	4e	0.65(1)	0.33(1)	0.672(6)	0.16
H(22)	4e	0.72(1)	0.31(1)	0.731(6)	0.16
H(2)	4e	0.3442	0.0751	0.7478	0.16
H(3)	4e	0.1374	0.0135	0.7484	0.16
H(41)	4e	0.80(1)	0.12(1)	0.841(6)	0.16
H(42)	4e	0.75(1)	0.11(2)	0.779(6)	0.16
H(5)	4e	0.68(1)	0.18(1)	0.916(6)	0.16
H(50)	4e	0.0050	0.2953	0.6198	0.16
H(6)	4e	0.2147	0.3590	0.6183	0.16
H(9)	4e	0.4584	0.3085	0.8770	0.16
H(101)	4e	0.4156	0.0913	0.8919	0.16
H(102)	4e	0.3643	0.1810	0.9423	0.16
H(103)	4e	0.4915	0.0989	0.9635	0.16
H(111)	4e	0.6032	0.4223	0.9513	0.16
H(112)	4e	0.6081	0.3038	1.0004	0.16
H(113)	4e	0.4813	0.3868	0.9798	0.16
H(521)	4e	0.5149	0.0218	0.5516	0.16
H(522)	4e	0.6336	-0.0569	0.5897	0.16
H(523)	4e	0.5948	0.0808	0.6159	0.16
H(531)	4e	0.3572	-0.0472	0.5507	0.16
H(532)	4e	0.2943	-0.0549	0.6120	0.16
H(533)	4e	0.3469	-0.1850	0.5848	0.16

Table 6. 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)	2e	1/2	1/2	1/2	0.0368(2)	0.0359(2)	0.0357(1)	-0.0025(2)	0.0065(1)	0.0017(2)
Cl(1)	4e	0.4623(2)	0.5642(2)	0.60002(8)	0.061(1)	0.059(1)	0.0431(8)	0.0028(9)	0.0152(7)	-0.0036(8)
Cl(2)	4e	0.6887(2)	0.3976(2)	0.55107(8)	0.047(1)	0.069(1)	0.0534(9)	0.0154(9)	0.0050(7)	0.0053(8)
Cl(3)	4e	0.3895(2)	0.3036(2)	0.50810(9)	0.071(1)	0.050(1)	0.062(1)	-0.021(1)	0.0103(9)	0.0062(8)
N(1)	4e	0.4259(6)	0.2693(6)	0.6784(3)	0.044(3)	0.056(4)	0.049(3)	-0.001(3)	0.002(3)	0.014(3)
C(1)	4e	0.3003(6)	0.2265(7)	0.6833(3)	0.042(4)	0.048(4)	0.045(3)	-0.001(3)	0.007(3)	-0.001(3)
N(2)	4e	0.6402(6)	0.3080(7)	0.7050(3)	0.042(3)	0.061(4)	0.052(3)	-0.005(3)	0.012(3)	0.014(3)
C(2)	4e	0.2763(8)	0.1203(9)	0.7220(4)	0.060(5)	0.063(5)	0.077(5)	-0.009(4)	0.018(4)	0.016(4)
N(3)	4e	0.5265(5)	0.2249(6)	0.7823(3)	0.041(3)	0.066(4)	0.046(3)	0.009(3)	0.008(2)	0.010(3)
C(3)	4e	0.1532(9)	0.0833(9)	0.7219(4)	0.071(6)	0.060(5)	0.086(6)	-0.011(5)	0.030(5)	0.004(5)
N(4)	4e	0.7359(7)	0.1359(8)	0.8134(3)	0.052(4)	0.080(5)	0.056(4)	0.027(4)	0.012(3)	0.011(4)
C(4)	4e	0.0519(7)	0.1463(9)	0.6835(4)	0.042(4)	0.083(6)	0.077(5)	-0.014(4)	0.030(4)	-0.010(5)
N(5)	4e	0.6242(6)	0.2059(8)	0.8882(3)	0.060(4)	0.083(5)	0.041(3)	0.023(4)	0.005(3)	0.001(3)
C(5)	4e	0.0735(7)	0.251(1)	0.6453(4)	0.045(4)	0.102(7)	0.060(4)	0.002(5)	0.014(4)	0.004(5)
C(6)	4e	0.1992(7)	0.2893(9)	0.6450(4)	0.048(4)	0.081(6)	0.062(4)	0.004(4)	0.012(3)	0.019(4)
C(7)	4e	0.5354(6)	0.2640(7)	0.7245(3)	0.043(4)	0.041(4)	0.047(3)	0.004(3)	0.004(3)	0.006(3)
C(8)	4e	0.6302(6)	0.1910(7)	0.8274(3)	0.044(4)	0.051(4)	0.043(3)	0.006(3)	0.005(3)	0.006(3)
C(9)	4e	0.5125(9)	0.259(1)	0.9121(4)	0.066(6)	0.116(8)	0.057(5)	0.030(6)	0.019(4)	0.013(5)
Cl(10)	4e	-0.1032(2)	0.0922(3)	0.6825(1)	0.055(1)	0.132(2)	0.118(2)	-0.017(2)	0.036(1)	-0.006(2)
C(10)	4e	0.440(1)	0.149(2)	0.9288(9)	0.16(2)	0.19(2)	0.25(2)	0.03(1)	0.14(2)	0.03(2)
C(11)	4e	0.555(1)	0.351(2)	0.9655(6)	0.18(1)	0.19(2)	0.12(1)	0.08(1)	0.02(1)	-0.05(1)
O(50)	4e	0.6388(7)	-0.0739(9)	0.7137(4)	0.091(5)	0.113(6)	0.117(6)	0.026(5)	-0.034(4)	-0.024(5)
N(50)	4e	0.4790(9)	-0.0691(9)	0.6306(5)	0.093(7)	0.063(6)	0.102(7)	0.019(5)	-0.026(5)	-0.020(5)
C(51)	4e	0.526(1)	-0.106(1)	0.6880(6)	0.15(1)	0.075(7)	0.13(1)	0.041(8)	-0.052(9)	-0.016(7)
C(52)	4e	0.563(2)	0.000(1)	0.5938(7)	0.23(2)	0.11(1)	0.11(1)	0.08(1)	-0.01(1)	-0.033(9)
C(53)	4e	0.360(1)	-0.091(1)	0.5915(7)	0.093(9)	0.13(1)	0.19(1)	0.024(9)	-0.053(9)	-0.07(1)

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