Crystal structure of tetrachloro(metformin)platinum(IV)—dimethylformamide (1:2), $C_4N_5H_{11}PtCl_4 \cdot 2(CH_3)_2NCHO$

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Abstract

$C_{10}H_{25}Cl_4N_7O_2Pt$, triclinic, $P\bar{1}$ (No. 2), $a = 9.339(3)$ Å, $b = 9.589(5)$ Å, $c = 12.199(4)$ Å, $\alpha = 83.81(5)^\circ$, $\beta = 72.36(3)^\circ$, $\gamma = 80.86(4)^\circ$, $V = 1025.8$ Å³, $Z = 2$, $\rho_m = 1.97(2)$ g·cm⁻³, $R_{gt}(F) = 0.036$, $wR_{ref}(F^2) = 0.101$, $T = 293$ K.

Source of material

K_2PtCl_6 (4 mmol, 1.94 g) was dissolved in 100 mL of hot water. Metformin hydrochloride (8 mmol, 1.32 g) dissolved in 10 mL of water was added by stirring to this solution. The reaction mixture was stirred and kept at 343 K for 36 h. A yellow solid was obtained which was 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

Metformin (*N,N*-dimethylbiguanide) was introduced as an oral glucose-lowering agent to treat non-insulin dependent diabetes mellitus. Metformin combines with many elements of the transition series, especially copper(II) and platinum(II), to give highly colored chelate complexes, due to the presence of the two imine

groups in *cis* position thus acting as a chelating agent [1,2]. This prompted us to synthesize and characterize this complex of Pt(IV) by metformin.

The asymmetric unit consists of one molecule $PtCl_4(C_4H_{11}N_5)$ and two crystallographically independent DMF solvent molecules. Pt(IV) is coordinated to four Cl atoms and one metformin molecule which acts as a bidentate ligand through their N atoms in *cis* position, resulting in a distorted octahedron. The Pt atom is $-0.003(2)$ Å out of the best least-squares basal plane defined by Cl3, Cl4, N2 and N4 atoms [maximum deviation $0.005(2)$ Å for N2 and N4]. The axial sites are occupied by the Cl1 and Cl2 atoms which are out of this plane up to $-2.316(3)$ and $2.332(3)$ Å, respectively. The Pt—Cl and Pt—N bond lengths fall in the narrow ranges: $2.313(2)$ Å to $2.336(2)$ Å and $1.988(5)$ Å to $2.011(5)$ Å, respectively. The values of the bond angles at the Pt atom are in the range $88.1(2)^\circ - 92.76(7)^\circ$. These distances and angles are typical for Pt(IV) complexes that have six-membered rings with similar donor atoms [3–5]. The metal-ligand ring has a nearly planar geometry as a consequence of the *p* conjugation along the pseudoaromatic outline N2–C1–N3–C2–N4 [maximum deviation: $-0.066(4)$ Å for C1] whereas the platinum atom lies at $-0.602(8)$ Å from this plane. The two biguanide moieties (C1–N1–N2–N3) and (C2–N3–N4–N5) are each planar with C1 at $0.009(6)$ Å out of the N1, N2, N3 and C2 at $-0.003(7)$ Å out of N3, N4 and N5 plane. These two halves make a dihedral angle of $12.5(3)^\circ$ compared with $15(2)^\circ$ for the tetrachloro(metformin)-Pt(IV)dimethylsulfoxide solvate [6]. The crystal cohesion is ensured by four hydrogen bonds involving N1, N2, N3 and N4 from the metformin: two bonds with O10 [for N1–H1A...O10: $2.841(8)$ Å, 147° and for N2–H2...O10: $2.930(8)$ Å, 143°], one with O20 [for N3–H3...O20: $2.762(8)$ Å, 138°] and one with Cl4 [for N4–H4...Cl4ⁱ: $3.454(6)$ Å, 148° ; symmetry code *i*: $-x, 1-y, 1-z$]. There are several van der Waals contacts, the shortest being $3.200(5)$ Å.

Table 1. Data collection and handling.

Crystal:	yellow, parallelepipedic, size $0.125 \times 0.250 \times 0.350$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	73.79 cm ⁻¹
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	56.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4918, 4918
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3963
$N(param)_{refined}$:	217
Programs:	SIR92 [7], SHELXL-97 [8], CAMERON [9], WinGX [10]

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

Atom	Site	x	y	z	U _{iso}
H(1A)	2i	0.2032	-0.1689	0.3071	0.049
H(1B)	2i	0.0376	-0.1651	0.3250	0.049
H(3)	2i	-0.1147	0.0285	0.3385	0.038
H(21)	2i	-0.1130	0.1729	0.1477	0.086
H(22A)	2i	-0.3173	0.0711	-0.0610	0.143
H(22B)	2i	-0.3804	0.0229	0.0696	0.143
H(22C)	2i	-0.2280	-0.0555	-0.0062	0.143
H(23A)	2i	-0.2308	0.2675	-0.0948	0.137
H(23B)	2i	-0.0826	0.2733	-0.0613	0.137
H(23C)	2i	-0.2396	0.3416	0.0160	0.137
H(13A)	2i	0.8206	-0.4484	0.1241	0.170
H(13B)	2i	0.8057	-0.4095	0.249	0.170
H(13C)	2i	0.8536	-0.2995	0.1444	0.170

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(51A)	2i	-0.4704	0.1549	0.4695	0.065
H(51B)	2i	-0.3463	0.0503	0.5097	0.065
H(51C)	2i	-0.3413	0.0662	0.3794	0.065
H(2)	2i	0.2887	0.0376	0.3290	0.040
H(4)	2i	-0.0820	0.3652	0.4543	0.039
H(12A)	2i	0.6249	-0.4513	0.0807	0.156
H(12B)	2i	0.5277	-0.3036	0.0722	0.156
H(12C)	2i	0.4702	-0.4136	0.1750	0.156
H(11)	2i	0.6225	-0.1790	0.2946	0.069
H(52A)	2i	-0.4584	0.3677	0.4768	0.070
H(52B)	2i	-0.3211	0.4358	0.3919	0.070
H(52C)	2i	-0.3270	0.3996	0.5215	0.070

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	2i	0.18565(2)	0.29473(2)	0.33065(2)	0.0238(1)	0.0214(1)	0.0344(1)	-0.00147(8)	-0.00343(9)	-0.00414(8)
Cl(4)	2i	0.1604(2)	0.5389(2)	0.3329(2)	0.0474(9)	0.0210(7)	0.061(1)	-0.0041(6)	-0.0074(8)	-0.0059(6)
Cl(1)	2i	0.1357(2)	0.3179(2)	0.1546(2)	0.058(1)	0.051(1)	0.0375(8)	-0.0089(8)	-0.0119(8)	-0.0011(7)
Cl(2)	2i	0.2257(2)	0.2710(2)	0.5121(2)	0.0367(8)	0.0428(9)	0.0451(9)	-0.0043(7)	-0.0152(7)	-0.0051(7)
Cl(3)	2i	0.4436(2)	0.2779(2)	0.2394(2)	0.0255(8)	0.052(1)	0.065(1)	-0.0050(7)	0.0046(7)	-0.0061(9)
N(1)	2i	0.1136(6)	-0.1225(5)	0.3211(5)	0.033(3)	0.024(3)	0.064(4)	-0.003(2)	-0.009(3)	-0.011(2)
O(10)	2i	0.4345(7)	-0.1598(6)	0.2701(6)	0.042(3)	0.052(3)	0.093(5)	0.007(3)	-0.007(3)	-0.016(3)
N(3)	2i	-0.0551(6)	0.0766(5)	0.3557(5)	0.027(2)	0.021(2)	0.049(3)	0.001(2)	-0.014(2)	-0.006(2)
C(21)	2i	-0.160(1)	0.104(1)	0.1294(9)	0.059(6)	0.097(8)	0.066(6)	-0.011(5)	-0.022(5)	-0.026(6)
C(2)	2i	-0.1199(7)	0.2059(6)	0.3988(5)	0.027(3)	0.025(3)	0.032(3)	0.000(2)	-0.007(2)	-0.002(2)
N(5)	2i	-0.2706(6)	0.2295(6)	0.4289(5)	0.030(3)	0.028(3)	0.055(3)	0.001(2)	-0.010(2)	-0.008(2)
O(20)	2i	-0.1716(8)	-0.0071(8)	0.1942(6)	0.083(5)	0.078(5)	0.062(4)	-0.022(4)	-0.031(3)	-0.007(3)
N(10)	2i	0.6362(8)	-0.3183(8)	0.1911(6)	0.045(4)	0.054(4)	0.054(4)	0.006(3)	0.003(3)	-0.003(3)
N(20)	2i	-0.2087(8)	0.1300(8)	0.0367(6)	0.058(4)	0.070(5)	0.054(4)	-0.015(4)	-0.010(3)	-0.016(3)
C(22)	2i	-0.290(2)	0.035(1)	0.007(1)	0.13(1)	0.098(9)	0.086(8)	-0.026(8)	-0.058(8)	-0.014(7)
C(23)	2i	-0.189(2)	0.265(1)	-0.032(1)	0.12(1)	0.091(9)	0.077(7)	-0.049(8)	-0.033(7)	0.006(6)
C(13)	2i	0.792(1)	-0.373(2)	0.176(1)	0.064(7)	0.17(1)	0.069(7)	0.053(8)	0.000(5)	0.002(7)
C(51)	2i	-0.3654(8)	0.1153(8)	0.4486(7)	0.027(3)	0.044(4)	0.059(4)	-0.010(3)	-0.009(3)	-0.005(3)
N(2)	2i	0.2017(6)	0.0854(5)	0.3318(5)	0.025(2)	0.025(2)	0.049(3)	0.002(2)	-0.010(2)	-0.008(2)
N(4)	2i	-0.0375(5)	0.2977(6)	0.4097(4)	0.020(2)	0.039(3)	0.037(3)	-0.003(2)	-0.003(2)	-0.011(2)
C(1)	2i	0.0925(7)	0.0146(6)	0.3365(5)	0.029(3)	0.023(3)	0.025(3)	0.003(2)	-0.005(2)	-0.005(2)
C(12)	2i	0.558(1)	-0.377(1)	0.124(1)	0.085(8)	0.084(8)	0.13(1)	-0.027(7)	0.012(8)	-0.039(8)
C(11)	2i	0.567(1)	-0.215(1)	0.2553(7)	0.044(4)	0.064(5)	0.059(5)	-0.004(4)	-0.006(4)	-0.012(4)
C(52)	2i	-0.3512(8)	0.3701(7)	0.4572(7)	0.033(3)	0.029(3)	0.077(5)	0.002(3)	-0.013(3)	-0.015(3)

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