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# Mono- and Bis(1-methylcytosine) Complexes of Cisplatin: the Crystal Structures of *cis*-$[(NH_3)_2Pt(1\text{-}MeC)Cl]_2[Pt(CN)_4]$ and *cis*-$[(NH_3)_2Pt(1\text{-}MeC)_2][Pt(CN)_4]\cdot 2H_2O$

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## Abstract

The crystal structures are reported of two nucleobase complexes of Cisplatin, *cis*-$[(NH_3)_2Pt(1\text{-}MeC)Cl]_2[Pt(CN)_4]$ (**1**) and *cis*-$[(NH_3)_2Pt(1\text{-}MeC)_2][Pt(CN)_4]\cdot 2H_2O$ (**2**), with 1-MeC = 1-methylcytosine, $C_5H_7N_3O$. **1** crystallizes in space group $P2_1/n$ with $a = 17.576(7)$, $b = 10.916(5)$, $c = 6.846(3)$ Å, $\beta = 98.36(4)°$, $Z = 2$, **2** crystallizes in space group $P\bar{1}$ with $a = 12.368(4)$, $b = 11.219(4)$, $c = 10.526(3)$ Å, $\alpha = 109.12(4)°$, $\beta = 98.01(4)°$, $\gamma = 113.65(4)°$, $Z = 1$. The structures were refined to $R = 0.051$ (**1**), 0.077 (**2**), $R_w = 0.054$ (**1**), 0.077 (**2**). Pt coordination occurs in both complexes through the N3 position of the cytosine ring. In **2** the two nucleobases are oriented head-to-tail. The structures are compared with related compounds containing different counteranions.

## Introduction

The rather unexpected finding that cross-links of the antitumor agent Cisplatin, *cis*-$(NH_3)_2PtCl_2$, with double-stranded DNA are not completely reversed by an excess of $CN^-$ – *ca.* 5–10% of the bound Pt is not removed [1] – is intriguing both with regard to speculations concerning the mode of action of Pt antitumor drugs and from a mechanistic point of view. We have recently addressed this aspect by treating a large number of model nucleobase complexes of Pt with excess $CN^-$ at pH 8 and following the displacement of the nucleobase(s) by $^1H$ NMR spectroscopy [2]. As a result, we found that Pt bound to uracil or thymine nucleobases via the N3 position is extremely slow to react with $CN^-$, most likely due to kinetic reasons. In contrast, the nucleobases cytosine (N3 coordination), adenine (N7 coordination) and guanine (N7 coordination) are substituted relatively fast, unless they are present in complexes that contain uracil or thymine bases bound to Pt simultaneously. Another interesting result that emerged from this study was the finding that with low $CN^-$: Pt-ratios (e.g. 2:1), the mixed nucleobase (or $NH_3$) cyanide complexes are usually not formed, but rather the following reaction takes place:

$$[(NH_3)_2PtL_1L_2]^{n+} + 2CN^- \longrightarrow$$
$$0.5[(NH_3)_2PtL_1L_2]^{n+}[Pt(CN)_4]^{(0.5n)-} + NH_3 + 0.5L_1 + 0.5L_2$$

In several cases [2] the tetracyanoplatinate salts have been isolated in crystalline form and studied using X-ray analysis. We report here the crystal structures of two complexes obtained via the above route, *cis*-$[(NH_3)_2Pt(1\text{-}MeC)Cl]_2[Pt(CN)_4]$ (**1**) and *cis*-$[(NH_3)_2Pt(1\text{-}MeC)_2][Pt(CN)_4]\cdot 2H_2O$ (**2**).

## Experimental

Details of the preparation of the two title compounds **1** and **2** are reported elsewhere [2]. Crystal data and details of the data collection are summarized in Table I. The X-ray measurements were made on a Philips PW 1100 diffractometer at room temperature using graphite-monochromatized Mo K$\alpha$ radiation ($\lambda = 0.71069$ Å). Lp and, in a later stage, empirical absorption corrections (program of Walker and Stuart [3]) were applied. The coordinates of the Pt atoms in both compounds were obtained from Patterson maps. The other non-hydrogen atoms were located by subsequent $\Delta F$ syntheses. Hydrogen atoms were ignored at all stages. The Pt atoms were refined with anisotropic temperature factors. Scattering factors were taken from Cromer and Mann [4],

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TABLE I. Crystallographic Data of **1** and **2**

| Compound | 1 | 2 |
|---|---|---|
| Formula | $Pt_3O_2N_{14}C_{14}H_{26}Cl_2$ | $Pt_4O_8N_{24}C_{28}H_{48}$ |
| $M_r$ | 1078.6 | 1629.2 |
| Space group | $P2_1/n$ | $P\bar{1}$ |
| $Z$ | 2 | 1 |
| $a$ (Å) | 17.576(7)[a] | 12.368(4)[b] |
| $b$ (Å) | 10.916(5) | 11.219(4) |
| $c$ (Å) | 6.846(3) | 10.526(3) |
| $\alpha$ (deg) | 90 | 109.12(4) |
| $\beta$ (deg) | 98.36(4) | 98.01(4) |
| $\gamma$ (deg) | 90 | 113.65(4) |
| $U$ (Å$^3$) | 1299.5 | 1202.4 |
| Crystal size (mm) | 0.1, 0.2, 0.3 | 0.1, 0.1, 0.2 |
| $\mu$ (cm$^{-1}$) | 157.3 | 112.1 |
| $d_c$ (g cm$^{-1}$) | 2.757 | 2.250 |
| $d_m$ (g cm$^{-1}$) | 2.78 | 2.26 |
| $\theta_{max}$ (deg) | 23 | 24 |
| No. of unique reflections collected | 1804 | 3764 |
| No. used in refinement | 1384 ($F \geqslant 2\sigma(F)$) | 3533 ($F \geqslant 3\sigma F$) |
| $R(F)$ | 0.051 | 0.077 |
| $R_w(F)$ | 0.054 | 0.077 |

[a]At 20 °C; 15 reflections. [b]At 20 °C; 24 reflections.

TABLE II. Positional Parameters and Temperature Factors (Å) for **1**

| Atom | $x$ | $y$ | $z$ | $U_{11}$ |
|---|---|---|---|---|
| Pt1 | 0.5000(0) | 0.5000(0) | 0.5000(0) | 0.020(1) |
| Pt2 | 0.2504(1) | 0.5273(1) | −0.0019(1) | 0.017(1) |
| C1 | 0.4738(11) | 0.4214(20) | 0.7395(30) | 0.026(5) |
| N1 | 0.4533(9) | 0.3763(18) | 0.8797(27) | 0.036(4) |
| C2 | 0.6021(12) | 0.4238(22) | 0.5298(34) | 0.036(6) |
| N2 | 0.6608(9) | 0.3732(18) | 0.5345(26) | 0.034(4) |
| C11 | 0.1979(3) | 0.7197(6) | −0.0139(9) | 0.039(1) |
| N1a | 0.0328(7) | 0.3556(14) | −0.0653(21) | 0.015(3) |
| C1a′ | −0.0188(10) | 0.3001(20) | −0.2360(30) | 0.027(5) |
| C2a | 0.1013(10) | 0.4052(18) | −0.0991(27) | 0.018(4) |
| O2a′ | 0.1202(7) | 0.4016(14) | −0.2699(21) | 0.033(4) |
| N3a | 0.1512(8) | 0.4521(14) | 0.0562(23) | 0.016(4) |
| C4a | 0.1331(10) | 0.4503(19) | 0.2422(28) | 0.019(4) |
| N4a′ | 0.1813(9) | 0.4980(19) | 0.3894(26) | 0.032(4) |
| C5a | 0.0613(10) | 0.3951(19) | 0.2760(28) | 0.020(4) |
| C6a | 0.0120(11) | 0.3491(19) | 0.1158(31) | 0.027(5) |
| N10 | 0.2967(8) | 0.3493(16) | 0.0106(25) | 0.028(4) |
| N11 | 0.3512(9) | 0.6067(18) | −0.0530(25) | 0.030(4) |

and correction terms for anomalous scattering from Cromer and Libermann [5]. Final positional and thermal parameters are given in Tables II and III. The equivalent isotropic temperature factors for the Pt atoms were calculated from the $U_{ij}$ values by $U_{eq} = (1/3)\Sigma U_{ij} a_i^* a_j^* a_i a_j$ ($U_{ij}$ in Å$^2$). The highest peak in the final difference map was 1.9 e/Å$^3$ (1.4 Å away from Pt2) for **1** and 1.3 e/Å$^3$ (1.6 Å away from Pt1) for **2**. The SHELX program package [6] was used in the structure analyses.

## Results and Discussion

The crystal structures of **1** and **2** have been performed in order to unambiguously confirm the composition of the products isolated from solutions containing *cis*-$[(NH_3)_2Pt(1\text{-}MeC)Cl]Cl$ and *cis*-$[(NH_3)_2Pt(1\text{-}MeC)_2]Cl_2$, respectively, and cyanide. Our results indicate that $CN^-$ readily substitutes all ligands in mixed nucleobase, ammine, halide complexes of Pt(II) to give the tetracyanoplatinate(II) anion which then is capable of precipitating still-unreacted cation.

The molecular cation of *cis*-$[(NH_3)_2Pt(1\text{-}MeC)Cl]_2[Pt(CN)_4]$, (**1**), is shown in Fig. 1, and that of *cis*-$[(NH_3)_2Pt(1\text{-}MeC)_2][Pt(CN)_4]$, (**2**), in Fig. 2. Selected interatomic distances and angles are listed in Tables IV and V, and conformational details are given in Tables VI and VII.

The cation of **1** compares well with two crystalline forms of *cis*-$[(NH_3)_2Pt(1\text{-}MeC)Cl]NO_3$ previously reported by us [7] and, as far as the $(NH_3)_2Pt$(1-MeC)-moiety is concerned, also with the related aqua- and hydroxo complexes [8]. Pt coordination is through N3 of the cytosine ring, which is almost perpendicular to the Pt coordination plane (97° in **1** *vs.* 84° and 88° in the two $NO_3^-$ salts). The orientation of the 1-MeC ring appears to be determined by intermolecular hydrogen bonding inter-

TABLE III. Positional Parameters and Temperature Factors (Å) for 2

| Atom | $x$ | $y$ | $z$ | $U_{11}$ |
|---|---|---|---|---|
| Pt1 | 0.8302(1) | 0.5128(1) | 0.8568(1) | 0.020(1) |
| N11 | 0.9437(19) | 0.5602(22) | 0.7397(21) | 0.034(4) |
| N12 | 0.8648(17) | 0.3474(20) | 0.8451(20) | 0.028(4) |
| N1a | 0.6949(19) | 0.7596(22) | 0.7266(21) | 0.033(4) |
| C1a' | 0.6174(29) | 0.7327(33) | 0.5908(33) | 0.051(7) |
| C2a | 0.7159(21) | 0.6478(25) | 0.7338(24) | 0.028(5) |
| O2a' | 0.6647(17) | 0.5361(20) | 0.6298(20) | 0.046(4) |
| N3a | 0.7921(17) | 0.6743(20) | 0.8585(19) | 0.026(4) |
| C4a | 0.8502(22) | 0.8027(25) | 0.9695(25) | 0.030(5) |
| N4a' | 0.9209(21) | 0.8286(24) | 1.0901(23) | 0.042(5) |
| C5a | 0.8255(27) | 0.9179(32) | 0.9621(31) | 0.047(6) |
| C6a | 0.7511(26) | 0.8913(30) | 0.8384(30) | 0.043(6) |
| N1b | 0.6965(19) | 0.4597(22) | 1.1930(21) | 0.034(4) |
| C1b' | 0.7578(27) | 0.5002(32) | 1.3460(31) | 0.048(7) |
| C2b | 0.7716(19) | 0.5029(23) | 1.1157(22) | 0.022(4) |
| O2b' | 0.8837(13) | 0.5740(15) | 1.1669(15) | 0.023(3) |
| N3b | 0.7182(17) | 0.4630(19) | 0.9734(19) | 0.025(4) |
| C4b | 0.5890(21) | 0.3822(25) | 0.9140(25) | 0.029(5) |
| N4b' | 0.5426(20) | 0.3466(23) | 0.7772(22) | 0.038(5) |
| C5b | 0.5140(24) | 0.3435(28) | 0.9974(28) | 0.038(6) |
| C6b | 0.5692(24) | 0.3825(27) | 1.1336(27) | 0.036(5) |
| Pt2 | 0.0000(0) | 0.0000(0) | 0.5000(0) | 0.025(1) |
| C1 | 0.0210(22) | 1.1142(26) | 0.3905(26) | 0.032(5) |
| N1 | 0.0356(23) | 1.1816(26) | 0.3232(26) | 0.050(6) |
| C2 | −0.1740(23) | 0.8730(27) | 0.3787(26) | 0.034(5) |
| N2 | −0.2738(26) | 0.7965(30) | 0.3049(30) | 0.063(7) |
| Pt3 | 0.5000(0) | 0.0000(0) | 0.0000(0) | 0.030(1) |
| C3 | 0.6722(22) | 0.1362(25) | 0.0315(25) | 0.030(5) |
| N3 | 0.7730(22) | 0.2141(26) | 0.0494(25) | 0.047(5) |
| C4 | 0.5368(17) | 0.0390(20) | 0.1956(20) | 0.014(4) |
| N4 | 0.5657(24) | 0.0671(28) | 0.3145(27) | 0.053(6) |
| O1 | 0.8541(26) | 0.2917(31) | 0.4829(30) | 0.088(8) |
| O2 | 0.3428(28) | 0.9150(33) | 0.3826(32) | 0.096(8) |

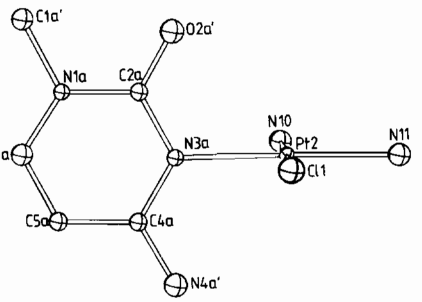

Fig. 1. Molecular cation of *cis*-$[(NH_3)_2Pt(1\text{-}MeC)Cl]_2[Pt(CN)_4]$ (1).

actions involving the exocyclic atoms O2a′ and N4a′ rather than any intramolecular interaction, unlike in complexes of unsubstituted uracil or thymine, where intramolecular hydrogen bonding leads to considerably smaller dihedral angles of 50°–56° [9]. The coordination geometry of Pt is normal as in related nucleobase complexes of *cis*-$Pt^{II}$ [7–10], although, as with *cis*-$(NH_3)_2Pt(1\text{-}MeT)Cl \cdot H_2O$ [11] (1-MeT = 1-methylthymine anion), there is a trend towards differences in $Pt-NH_3$ bond lengths ($Pt-NH_3$ *trans* to Cl longer than $Pt-NH_3$ *trans* to 1-MeC ring, 2.104(17) Å *vs.* 2.049(17) Å). Due to the relatively large errors in 1-MeC distances and angles, a comparison with the free ligand [12] is not meaningful.

TABLE IV. Selected Bond Distances (Å), Angles (deg) and Close Contacts (Å) in 1

| Distances | | Angles | |
|---|---|---|---|
| Pt1–C1 | 1.96(2) | C1–Pt1–C2 | 93(1) |
| Pt1–C2 | 1.96(2) | Cl1–Pt2–N10 | 179(1) |
| C1–N1 | 1.18(3) | Cl1–Pt2–N11 | 88(1) |
| C2–N2 | 1.17(3) | Cl1–Pt2–N3a | 92(1) |
| Pt2–Cl1 | 2.29(1) | N10–Pt2–N11 | 93(1) |
| Pt2–N10 | 2.10(2) | N10–Pt2–N3a | 88(1) |
| Pt2–N11 | 2.05(2) | N11–Pt2–N3a | 178(1) |
| Pt2–N3a | 2.02(2) | C6a–N1a–C2a | 123(2) |
| N1a–C1a′ | 1.50(2) | N1a–C2a–N3a | 119(2) |
| N1a–C2a | 1.40(2) | C2a–N3a–C4a | 122(2) |
| C2a–O2a′ | 1.25(2) | N3a–C4a–C5a | 119(2) |
| C2a–N3a | 1.36(2) | C4a–C5a–C6a | 119(2) |
| N3a–C4a | 1.36(3) | C5a–C6a–N1a | 119(2) |
| C4a–N4a′ | 1.32(2) | | |
| C4a–C5a | 1.45(3) | | |
| C5a–C6a | 1.39(3) | | |
| C6a–N1a | 1.34(3) | | |

Close contacts (<3.4 Å)

| | | | |
|---|---|---|---|
| N1–N10(i) | 3.03 | C1–N1–N10(i) | 133 |
| N1–N11(i) | 3.16 | C1–N1–N11(i) | 92 |
| N4a′–O2a′(i) | 2.90 | C1a–N4a′–O2a′(i) | 102 |
| N2–N11(ii) | 3.28 | C2–N2–N11(ii) | 91 |
| N2–N4a′(iii) | 3.09 | C2–N2–N4a′(iii) | 124 |

Symmetry operations:

(i) $x, y, 1 + z$
(ii) $1 - x, 1 - y, -z$
(iii) $1 - z, 1 - y, 1 - z$

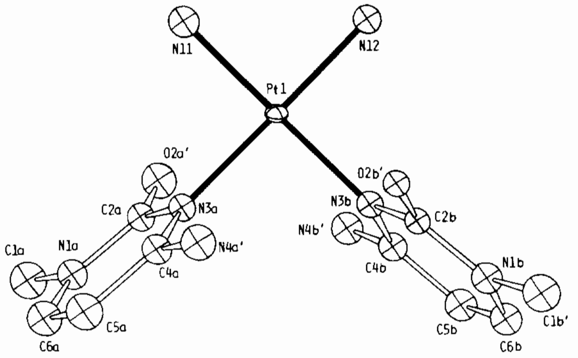

Fig. 2. Molecular cation of *cis*-$[(NH_3)_2Pt(1\text{-}MeC)_2][Pt(CN)_4] \cdot 2H_2O$ (2).

TABLE V. Selected Bond Distances (Å), Angles (deg) and Close Contacts (Å) in **2**

| Distances | | Angles | |
|---|---|---|---|
| Pt1–N11 | 2.02(2) | N11–Pt1–N12 | 89(1) |
| Pt1–N12 | 2.04(2) | N11–Pt1–N3a | 90(1) |
| Pt1–N3a | 2.04(2) | N11–Pt1–N3b | 179(1) |
| Pt1–N3b | 2.01(2) | N12–Pt1–N3a | 177(1) |
| Pt2–C1 | 1.96(3) | N12–Pt1–N3b | 90(1) |
| Pt2–C2 | 1.97(3) | N3a–Pt1–N3b | 91(1) |
| Pt3–C3 | 1.96(2) | C6a–N1a–C2a | 121(2) |
| Pt3–C4 | 1.90(2) | N1a–C2a–N3a | 118(2) |
| C1–N1 | 1.18(3) | C2a–N3a–C4a | 123(2) |
| C2–N2 | 1.15(4) | N3a–C4a–C5a | 119(2) |
| C3–N3 | 1.14(3) | C4a–C5a–C6a | 118(3) |
| C4–N4 | 1.15(3) | C5a–C6a–N1a | 122(3) |
| N1a–C1a′ | 1.47(4) | C6b–N1b–C2b | 121(2) |
| N1a–C2a | 1.40(3) | N1b–C2b–N3b | 119(2) |
| C2a–O2a′ | 1.20(3) | C2b–N3b–C4b | 119(2) |
| C2a–N3a | 1.37(3) | N3b–C4b–C5b | 121(2) |
| N3a–C4a | 1.34(3) | C4b–C5b–C6b | 118(2) |
| C4a–N4a′ | 1.31(3) | C5b–C6b–N1b | 122(2) |
| C4a–C5a | 1.47(4) | | |
| C5a–C6a | 1.35(4) | | |
| C6a–N1a | 1.36(3) | | |
| N1b–C1b′ | 1.51(4) | | |
| N1b–C2b | 1.37(3) | | |
| C2b–O2b′ | 1.22(3) | | |
| C2b–N3b | 1.39(3) | | |
| N3b–C4b | 1.40(3) | | |
| C4b–N4b′ | 1.33(3) | | |
| C4b–C5b | 1.41(4) | | |
| C5b–C6b | 1.34(4) | | |
| C6b–N1b | 1.39(3) | | |

Close contacts (<3.4 Å) in **2**

| | | | |
|---|---|---|---|
| N11–O1 | 2.96 | Pt1–N11–O1 | 107 |
| O2a′–N4b′ | 3.07 | C2a–O2a′–N4b′ | 96 |
| O2b′–N4a′ | 3.10 | C2b–O2b′–N4a′ | 99 |
| N4–O1 | 3.22 | C4–N4–O1 | 115 |
| N4–O2(i) | 2.94 | C4–N4–O2(i) | 108 |
| N3–N12(ii) | 3.09 | C3–N3–N12(ii) | 85 |
| N1–O1(iii) | 3.37 | C1–N1–O1(iii) | 83 |
| N2–N4b′(iv) | 2.90 | C2–N2–N4b′(iv) | 157 |
| N12–O2(v) | 2.93 | Pt1–N12–O2(v) | 107 |
| N4–O2(v) | 3.14 | C4–N4–O2(v) | 167 |

Symmetry operations:

(i) $= x, -1 + y, z$
(ii) $= x, y, -1 + z$
(iii) $= -1 + x, 1 + y, z$
(iv) $= -x, 1 - y, 1 - z$
(v) $= 1 - x, 1 - y, 1 - z$

TABLE VI. Best Planes and Deviations of Atoms from them in **1**[a]

(1) Pt1-coordination plane

| | | | | | |
|---|---|---|---|---|---|
| Pt1(*) | C1(*) | N1(*) | C2(*) | N2(*) | Pt2 |
| −0.02 | 0.01 | 0.00 | 0.04 | −0.03 | −2.96 |

(2) Pt2-coordination plane

| | | | | | |
|---|---|---|---|---|---|
| C11(*) | N3a(*) | N10(*) | N11(*) | Pt1 | Pt2 |
| −0.01 | 0.01 | −0.01 | 0.01 | 3.89 | −0.01 |

(3) 1-MeC plane

| | | | | | |
|---|---|---|---|---|---|
| N1a(*) | C2a(*) | N3a(*) | C4a(*) | C5a(*) | C6a(*) |
| 0.01 | −0.01 | 0.00 | 0.01 | −0.01 | 0.00 |
| C1a′ | O2a′ | N4a′ | Pt1 | Pt2 | |
| −0.05 | −0.08 | 0.03 | −2.39 | 0.03 | |

(4) Dihedral angles (deg)

| | |
|---|---|
| Pt2-coordination plane/1-MeC plane | 97 |

Equations

(1) $5.765x + 8.319y + 3.454z = 8.786$ Å
(2) $2.668x + 1.143y + 6.506z = 1.273$ Å
(3) $-7.465x + 9.752y - 0.569z = 3.249$ Å

[a] Deviations of atoms from planes are in Å. Atoms with an asterisk define the plane. The equations refer to the basis a, b, c.

TABLE VII. Best Planes and Deviations of Atoms from them in **2**[a]

(1) Pt1 coordinations plane

| | | | | |
|---|---|---|---|---|
| N11(*) | N12(*) | N3a(*) | N3b(*) | Pt1 |
| 0.02 | −0.02 | −0.02 | 0.02 | 0.02 |

(2) 1-MeCa plane

| | | | | | |
|---|---|---|---|---|---|
| N1a(*) | C2a(*) | N3a(*) | C4a(*) | C5a(*) | C6a(*) |
| 0.00 | 0.00 | −0.01 | 0.02 | −0.02 | 0.01 |
| C1a′ | O2a′ | N4a′ | Pt1 | | |
| 0.08 | 0.02 | −0.03 | 0.15 | | |

(3) 1-MeCb plane

| | | | | | |
|---|---|---|---|---|---|
| N1b(*) | C2b(*) | N3b(*) | C4b(*) | C5b(*) | C6b(*) |
| 0.01 | −0.01 | 0.00 | 0.01 | −0.01 | 0.00 |
| C1b′ | O2b′ | N4b′ | Pt1 | | |
| 0.05 | −0.03 | 0.02 | 0.12 | | |

(4) Dihedral angles (deg)

| | |
|---|---|
| Pt1 coordination plane/1-MeCa plane | 77 |
| Pt1 coordination plane/1-MeCb plane | 102 |
| 1-MeCa plane/1-MeCb plane | 84 |

Equations

(1) $5.679x + 1.024y + 5.904z = 10.278$ Å
(2) $9.968x + 1.389y - 6.527z = 3.242$ Å
(3) $6.400x - 10.753y + 0.533z = 0.136$ Å

[a] Deviations of atoms from planes are in Å. Atoms with an asterisk define the plane. The equations refer to the basis a, b, c.

There have been two independent crystal structure determinations [13, 14] of *cis*-$[(NH_3)_2Pt(1\text{-}MeC)_2](NO_3)_2 \cdot (1\text{-}MeC)$. In this compound, a free 1-MeC ring is co-stacked with one of the two platinated rings. This extra 1-methylcytosine is missing in the compound **2** described here, but the cation geometry is otherwise similar. In particular, as in the previously described compound, the two nucleobases are arranged head-to-tail. The dihedral angles between the Pt coordination plane and the 1-MeC rings in **2** are markedly different, however, 77° and 102°, while in the $NO_3^-$ salt they are virtually identical (101.3° and 102.4°). As a consequence, the base, base dihedral angle in both structures is different as well, 84° in **2** *vs.* 102° in the $NO_3^-$ salt, and instead of two intramolecular hydrogen bonds between the exocyclic O2 of one ring and N4 of the other in the $NO_3^-$ salt, there is just one (e.g. O2a′–N4b′, 3.07 Å) in **2**. Another difference refers to the perpendicular displacement of the Pt atom from the nucleobase: it is 0.15 Å (ring **a**) and 0.12 Å (ring **b**) in the tetracyanoplatinate(II), compared to 0.14 Å and 0.32 Å in the nitrate salt.

The geometry of the $[Pt(CN)_4]^{2-}$ anions is normal [15] in both structures. In **2** the tetracyanoplatinate(II) is distributed over two positions with occupancies of 0.5 each.

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