Mixed Nucleobase, Amino Acid Complexes of Pt(II). Preparation and X-ray Structure of *trans*-$[(CH_3NH_2)_2Pt(1\text{-}MeC\text{-}N^3)(gly\text{-}N)]NO_3\cdot 2H_2O$ and its Precursor *trans*-$[(CH_3NH_2)_2Pt(1\text{-}MeC\text{-}N^3)Cl]Cl\cdot H_2O$

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Abstract

The preparation and crystal structures of two Pt(II) complexes are reported. *trans*-$[(NH_2CH_3)_2Pt(1\text{-}MeC)Cl]Cl\cdot H_2O$ (**1**) and *trans*-$[(NH_2CH_3)_2Pt(1\text{-}MeC)(gly)]NO_3\cdot 2H_2O$ (**2**) with 1-MeC = 1-methylcytosine and gly = glycine anion are considered a precursor (**1**) and a product (**2**) of a hypothetical cross-linking reaction of a *trans*-diamineplatinum(II) moiety with a nucleic acid and the amino terminus of a protein, peptide, or amino acid. Compound **1** crystallizes in the space group $P\bar{1}$ and has cell dimensions $a = 7.749(1)$, $b = 9.854(2)$, $c = 10.100(1)$ Å; $\alpha = 101.45(1)$, $\beta = 103.81(1)$, $\gamma = 95.46(1)°$, $Z = 2$. Compound **2** crystallizes in the space group $P\bar{1}$ as well, cell dimensions being $a = 8.790(2)$, $b = 9.839(3)$, $c = 11.580(4)$ Å; $\alpha = 75.42(2)$, $\beta = 71.64(2)$, $\gamma = 86.92(2)°$, $Z = 2$. pH-dependent ^1H NMR spectra of **2** in D_2O have been recorded in the range $0.4 < pH^* < 13.5$ and are indicative of two acid/base equilibria, viz.

$$[(NH_2CH_3)_2Pt(1\text{-}MeC)(glyH)]^{2+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} 2 \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} (NH_2CH_3)_2Pt(1\text{-}MeC^-)(gly)$$

with pK_a values of 2.5 and *c.* 12.5.

Introduction

Interest in ternary complexes of Pt(II) and Pd(II) with amino acids (peptides) and nucleobases (nucleic acids) has led to several preparative and solution studies in recent years [1–4]. Structural studies, on the other hand, appear to be very rare. In fact, there seems to be only a single example, a Pd(II) complex containing gly-L-tyr and cytidine [5]. As part of a systematic study on mixed nucleobase, amino acid complexes of *cis*- and *trans*-diamineplatinum(II), which could serve as models for cross-linking reactions with nucleic acids and proteins [6], *trans*-$[(NH_2CH_3)_2Pt(1\text{-}MeC\text{-}N^3)(gly\text{-}N)]NO_3\cdot 2H_2O$ (1-MeC = 1-methylcytosine, gly = glycine anion) has been prepared and its crystal structure determined. The title compound was obtained via the precursor *trans*-$[(NH_3CH_3)_2Pt(1\text{-}MeC\text{-}N^3)Cl]Cl\cdot H_2O$, the crystal structure of which is reported as well.

Experimental

1-MeC [7] and *trans*-$(NH_2CH_3)_2PtCl_2$ [8] were prepared as previously published; gly was obtained from Sigma. *trans*-$[(NH_2CH_3)_2Pt(1\text{-}MeC)Cl]Cl\cdot H_2O$ (**1**) was obtained as follows: 1 mmol *trans*-$(NH_2CH_3)_2PtCl_2$, 1 mmol 1-MeC and 3 mmol NaCl were stirred in 30 ml H_2O for 60 h at 40 °C. The resulting slightly yellow solution was evaporated to dryness by rotary evaporation. The residue was briefly treated with 5 ml of water and then filtered from unreacted *trans*-$(NH_2CH_3)_2PtCl_2$. The resulting colorless solution was allowed to evaporate at 4 °C. The product formed was recrystallized from water, giving 283 mg of colorless cubes. *Anal.* Calc. for $[(NH_2CH_3)_2Pt(C_5H_7N_3O)Cl]Cl\cdot H_2O$: C, 17.8; H, 4.1; N, 14.9. Found: C, 17.7; H, 4.0; N, 14.8%.

trans-$[(NH_2CH_3)_2Pt(1\text{-}MeC)(gly)]NO_3\cdot 2H_2O$, (**2**) was prepared in the following way: 0.35 mmol of **1**, 0.7 mmol $AgNO_3$ and 0.7 mmol gly were stirred in 2 ml H_2O for 72 h at 60 °C (stoppered test tube), filtered from AgCl and slowly allowed to evaporate at 4 °C. The product formed was recrystallized from water, giving 143 mg of colorless cubes. *Anal.* Calc. for *trans*-$[(NH_2CH_3)_2Pt(C_5H_7N_3O)(C_2H_4NO_2)](NO_3)\cdot 2H_2O$: C, 19.5; H, 4.6; N, 17.7. Found: C, 19.4; H, 4.1; N, 18.1%.

Details concerning the X-ray data collection and structure determinations are as follows. Crystal size 0.50 × 0.20 × 0.30 mm (**1**), 0.30 × 0.15 × 0.08 mm (**2**), triclinic space group $P\bar{1}$, $a = 7.749(1)$, $b = 9.854(2)$, $c = 10.100(1)$ Å, $\alpha = 101.45(1)$, $\beta =$

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103.81(1), $\gamma = 95.46(1)^\circ$, $U = 725.7(2)$ Å^3, $Z = 2$, $D_c = 2.147$ g cm^{-3} (**1**); triclinic space group $P\bar{1}$, $a = 8.790(2)$, $b = 9.839(3)$, $c = 11.580(4)$ Å, $\alpha = 75.42(2)$, $\beta = 71.64(2)$, $\gamma = 86.92(2)^\circ$, $U = 919.6(5)$ Å^3, $Z = 2$, $D_c = 2.002$ g cm^{-3} (**2**). A total of 5315 reflections were collected ($\omega/2\theta$ scans, $\theta_{max} = 25^\circ$, whole sphere in reciprocal space). After averaging ($R_{int} = 0.022$) 2583 independent reflections were obtained. For the final structure refinement 2553 reflections with $F \geq 3.0\sigma(F)$ were used (**1**). In the case of **2** a total of 9146 reflections were collected ($3.0^\circ \leq 2\theta \leq 55.0^\circ$, whole sphere in reciprocal space). After averaging ($R_{int} = 0.069$) 4272 independent reflections were obtained. For the final refinement 4083 reflections with $F \geq 3.0\sigma(F)$ were used. Lp and empirical absorption corrections via ψ-scans were applied for **1** and **2** and in the case of **2** a decay correction up to 10%.

The position of the Pt atom was determined by direct methods (SHELXTL PLUS) [9]. The other non-hydrogen atoms were located by subsequent ΔF-syntheses. H atoms were arbitrarily placed in geometrically calculated positions (C–H, N–H 0.96 Å). All non-H atoms were refined with anisotropic thermal parameters and H atoms with a common isotropic temperature factor. The final values for R and R_w are 0.037 and 0.042 (**1**) and 0.025 and 0.026 (**2**) respectively ($w^{-1} = \sigma^2(F) + 0.0015F^2$ (**1**); $w^{-1} = \sigma^2(F) + 0.00043F^2$) (**2**). In Tables 1 and 2 the atomic coordinates and equivalent isotropic temperature factors (calculated by $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$) are listed. Complex scattering factors were taken from ref. 10. Other programs used are given in refs. 11–14.

TABLE 1. Atomic coordinates and equivalent isotropic displacement parameters (Å$^2 \times 10^4$) for **1**

	x	y	z	U_{eq}/U [a]
Pt(1)	0.00312(2)	−0.26680(2)	−0.07392(2)	243
Cl(1)	−0.0398(3)	−0.3027(2)	0.1339(2)	443
Cl(2)	0.5749(2)	0.4199(2)	0.2950(2)	494
O(1)	0.528(1)	0.2791(7)	0.5546(8)	769
O(2)	0.2545(7)	−0.0444(5)	−0.1410(5)	394
N(1)	0.1828(7)	−0.0966(5)	−0.3812(5)	293
N(3)	0.0406(8)	−0.2347(6)	−0.2588(5)	244
N(4)	−0.1650(8)	−0.4305(6)	−0.3837(6)	372
N(5)	−0.2285(8)	−0.1748(7)	−0.0966(7)	366
N(6)	0.2290(9)	−0.3638(7)	−0.0454(7)	368
C(1)	0.306(1)	0.0240(9)	−0.3767(9)	521
C(2)	0.1668(8)	−0.1215(7)	−0.2523(6)	287
C(4)	−0.0473(9)	−0.3216(7)	−0.3806(7)	311
C(5)	−0.0254(9)	−0.2937(7)	−0.5114(6)	342
C(6)	0.0901(9)	−0.1843(8)	−0.5038(7)	359
C(11)	−0.252(1)	−0.0727(9)	−0.1914(9)	500
C(12)	0.387(1)	−0.286(1)	0.0694(8)	534

[a] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

TABLE 2. Atomic coordinates and equivalent isotropic displacement parameters (Å$^2 \times 10^4$) for **2**

	x	y	z	U_{eq}/U [a]
Pt(1)	0.21522(2)	0.23675(1)	0.15017(1)	272
O(2b)	0.3211(5)	0.1178(3)	0.3811(3)	558
O(21a)	−0.0455(6)	0.1836(4)	−0.1939(4)	660
O(22a)	0.1193(4)	0.0193(3)	−0.1416(3)	411
O(71)	0.7954(6)	0.4131(5)	0.0975(4)	786
O(72)	0.7186(7)	0.4463(6)	0.2816(5)	978
O(73)	0.5593(5)	0.4856(5)	0.1708(5)	721
O(8)	0.7654(4)	0.1227(4)	0.6792(3)	534
O(9)	0.4986(4)	0.2394(4)	0.8044(3)	559
N(1a)	0.2015(4)	0.1524(3)	0.0078(3)	316
N(1b)	0.3042(5)	0.2991(4)	0.4714(3)	474
N(3b)	0.2312(4)	0.3237(3)	0.2889(3)	338
N(4b)	0.1494(5)	0.5382(4)	0.1938(4)	508
N(5)	−0.0262(4)	0.1959(4)	0.2359(3)	367
N(6)	0.4575(4)	0.2735(4)	0.0628(3)	367
N(7)	0.6898(5)	0.4465(4)	0.1855(4)	449
C(1a)	0.0954(5)	0.2240(4)	−0.0631(4)	348
C(1b)	0.3746(9)	0.2112(7)	0.5638(6)	754
C(2a)	0.0553(5)	0.1343(4)	−0.1410(4)	358
C(2b)	0.2876(5)	0.2400(5)	0.3803(4)	398
C(4b)	0.1931(5)	0.4601(4)	0.2881(4)	388
C(5)	−0.0872(6)	0.1516(6)	0.3739(5)	563
C(5b)	0.2029(6)	0.5145(5)	0.3878(4)	466
C(6)	0.5591(6)	0.1509(5)	0.0881(6)	586
C(6b)	0.2585(6)	0.4329(6)	0.4750(4)	496

[a] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

^{1}H NMR spectra were recorded in D_2O (TSP internal reference) on a 300-MHz Bruker AM 300 spectrometer. pD values were determined by means of a glass electrode and addition of 0.4 to the pH meter reading. For the determination of pK_a values the uncorrected (pH*) values were taken. NaOD and DNO_3 were applied to get the desired acidity (basicity).

Results and Discussion

X-ray Structures

Figure 1 depicts *trans*-$[(NH_2CH_3)_2Pt(1\text{-MeC})Cl]\text{-}Cl\cdot H_2O$ (**1**) and Fig. 2 gives a stereoscopic view of the unit cell. Bond lengths and angles are given in Table 3. Pt displays a square-planar coordination sphere with slight deviations of two of the angles from 90°. The Pt1–Cl1 distance is not significantly different from that in *trans*-$(NH_2CH_3)_2PtCl_2$ [8], and the Pt–$NH_2(CH_3)$ entities in **1** display similar orientations as in the former. The 1-MeC ligand, which is coordinated to Pt1 via N3, forms a large dihedral angle of 81.54° with the Pt1,Cl1,N6,N5 coordination plane. Its orientation relative to the Pt coordination plane is not a consequence of intracomplex hydrogen bond formation.

The geometry of the 1-MeC ligand, which is essentially planar (largest deviations O2, 0.05 Å; C1, 0.025 Å), is normal and compares well with a large number of Pt(II) complexes of the 1-MeC [15], including *trans*-$[(NH_3)_2Pt(1\text{-MeC})Cl]Cl\cdot 1.5H_2O$ [16].

Intermolecular hydrogen bonding in **1** includes a pair of H bonds between N5 and O2 of two centrosymmetrically related cations (2.95(1) Å) as well as several contacts between amine protons of the CH_3NH_2 ligands and both coordinated and ionic chloride (Table 4).

Compound **2** and its atom numbering scheme are shown in Fig. 3 and bond lengths and angles are listed in Table 5. Pt1 is coordinated by two $NH_2(CH_3)$ groups in *trans*-orientation, a 1-MeC ring and a deprotonated glycine. Binding to the nucleobase is through N3 and to the glycinate anion via the amino

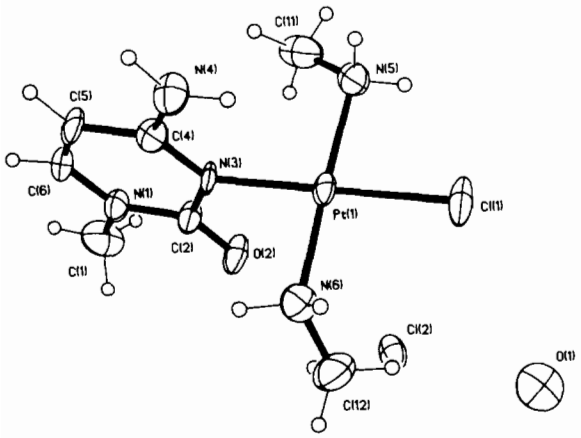

Fig. 1. View and atom numbering scheme of *trans*-$[(CH_3NH_2)_2Pt(1\text{-MeC})Cl]Cl\cdot H_2O$ (**1**).

TABLE 3. Bond distances (Å) and angles (°) for 1

Pt(1)–Cl(1)	2.290(2)
Pt(1)–N(3)	2.037(6)
Pt(1)–N(5)	2.072(7)
Pt(1)–N(6)	2.061(7)
O(2)–C(2)	1.224(6)
N(1)–C(1)	1.44(1)
N(1)–C(2)	1.403(9)
N(1)–C(6)	1.352(7)
N(3)–C(2)	1.392(9)
N(3)–C(4)	1.334(7)
N(4)–C(4)	1.331(9)
N(5)–C(11)	1.52(1)
N(6)–C(12)	1.491(9)
C(4)–C(5)	1.45(1)
C(5)–C(6)	1.31(1)
N(5)–Pt(1)–N(6)	177.3(3)
N(3)–Pt(1)–N(6)	89.6(3)
N(3)–Pt(1)–N(5)	92.9(3)
Cl(1)–Pt(1)–N(6)	90.6(2)
Cl(1)–Pt(1)–N(5)	87.0(2)
Cl(1)–Pt(1)–N(3)	179.8(2)
C(2)–N(1)–C(6)	121.4(6)
C(1)–N(1)–C(6)	121.6(6)
C(1)–N(1)–C(2)	117.0(6)
Pt(1)–N(3)–C(4)	121.4(5)
Pt(1)–N(3)–C(2)	117.2(4)
C(2)–N(3)–C(4)	121.4(6)
Pt(1)–N(5)–C(11)	117.4(5)
Pt(1)–N(6)–C(12)	115.9(5)
N(1)–C(2)–N(3)	116.1(5)
O(2)–C(2)–N(3)	122.3(5)
O(2)–C(2)–N(1)	121.5(6)
N(3)–C(4)–N(4)	120.2(6)
N(4)–C(4)–C(5)	119.0(6)
N(3)–C(4)–C(5)	120.6(6)
C(4)–C(5)–C(6)	117.1(6)
N(1)–C(6)–C(5)	123.1(6)

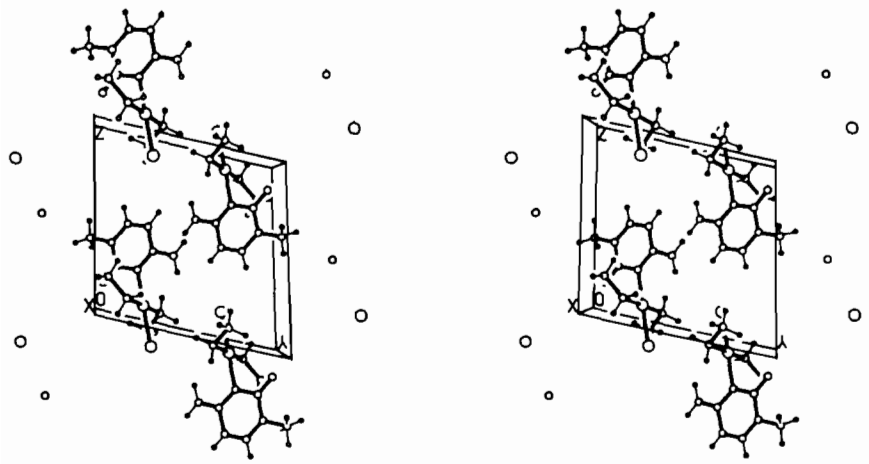

Fig. 2. Stereoview of the unit cell of **1**.

TABLE 4. Hydrogen bonding distances (Å) and angles (°) in 1 and 2[a, b]

Compound 1			
N(5)...O(2)[1]	2.953(8)	N(5)–H(5)...O(2)	155.3(7)
N(5)...Cl(2)[1]	3.366(6)	N(5)–H(5B)...Cl(2)	161.8(7)
N(6)...Cl(2)[2]	3.226(8)	N(6)–H(6A)...Cl(2)	163.7(7)
N(6)...Cl(1)[3]	3.322(7)	N(6)–H(6B)...Cl(1)	143.7(7)
Compound 2			
N(6)...O(73)[0]	2.990(7)	N(6)–H(61)...O(73)	172.8(4)
N(5)...O(22A)[1]	2.874(6)	N(5)–H(51)...O(22A)	178.5(4)
N(1A)...O(22A)[1]	3.106(4)	N(1A)–H(11A)...O(22A)	124.9(4)
N(1A)...O(9)[2]	2.907(4)	N(1A)–H(12A)...O(9)	156.4(4)
N(6)...O(9)[2]	3.001(6)	N(6)–H(62)...O(9)	146.2(4)
N(6)...O(73)[3]	3.152(6)	N(6)–H(62)...O(73)	136.1(4)
N(5)...O(71)[4]	3.015(6)	N(5)–H(52)...O(71)	153.6(4)
N(5)...O(72)[4]	3.270(7)	N(5)–H(52)...O(72)	145.6(4)

[a]Symmetry operations for 1: [1] $-x, -y, -z$; [2] $-x+1, -y, -z$; [3] $-x, -y-1, -z$. Symmetry operations for 2: [0] x, y, z; [1] $-x, -y, -z$; [2] $x, y, z-1$; [3] $-x+1, -y+1, -z$; [4] $x-1, y, z$. [b]The H atoms were placed in calculated positions and the estimated standard deviations of the positional coordinates of the atoms to which the H atoms are bound were attributed to the positional coordinates of the H atoms. Therefore the estimated standard deviations of the angles at the H atoms are too low.

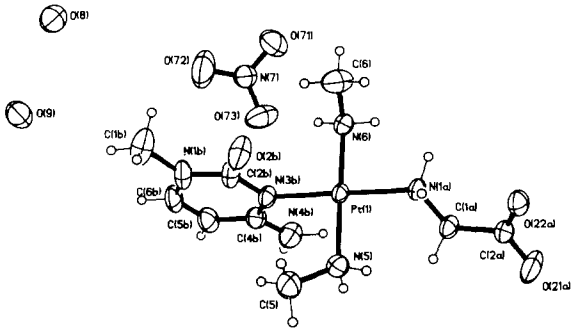

Fig. 3. View and atom numbering scheme of *trans*-$[(CH_3NH_2)_2Pt(1\text{-MeC})(gly\text{-}N)]NO_3 \cdot 2H_2O$ (2).

group. The arrangement of the monodentate glycinate ligand is such that, unlike in glycinate or thioglycinate chelates [17], the carboxylate group has undergone rotation about the NH_2–CH_2 bond leading to an extended structure with the COO^- group pointing away from the metal. A similar situation is envisaged in a recently described alanine complex of Pt(II), *trans*-$Cl_2Pt(ala)_2$ [18]. As a consequence, there are no short intracomplex distances between the nucleobase and the amino acid in 2, and the 1-MeC ring adopts an orientation relative to the Pt coordination plane that is not too different from that observed in 1 (dihedral angle 80.35°). The only major difference of the *trans*-$(NH_2CH_3)_2Pt(1\text{-MeC})$ entities in 1 and 2 refers to the relative orientation of the two methyl groups. Since no immediate effect of the gly ligand on this difference can be seen, we suggest that it is essentially a consequence of packing. In fact, the CH_3 groups of both methylamine ligands in 2 have close contacts with nitrate oxygens (*c.* 3.39 Å), whereas in 1 only one of the methyl groups

TABLE 5. Bond distances (Å) and angles (°) in 2

Pt(1)–N(1a)	2.061(4)
Pt(1)–N(3b)	2.045(4)
Pt(1)–N(5)	2.053(3)
Pt(1)–N(6)	2.057(3)
O(2b)–C(2b)	1.221(6)
O(21a)–C(2a)	1.242(7)
O(22a)–C(2a)	1.236(5)
O(71)–N(7)	1.244(6)
O(72)–N(7)	1.216(8)
O(73)–N(7)	1.240(6)
N(1a)–C(1a)	1.469(6)
N(1b)–C(1b)	1.473(8)
N(1b)–C(2b)	1.373(7)
N(1b)–C(6b)	1.363(7)
N(3b)–C(2b)	1.375(6)
N(3b)–C(4b)	1.364(6)
N(4b)–C(4b)	1.319(7)
N(5)–C(5)	1.472(6)
N(6)–C(6)	1.487(6)
C(1a)–C(2a)	1.533(7)
(C4b)–C(5b)	1.416(8)
C(5b)–C(6b)	1.328(7)
N(5)–Pt(1)–N(6)	178.7(2)
N(3b)–Pt(1)–N(6)	89.4(2)
N(3b)–Pt(1)–N(5)	91.7(2)
N(1a)–Pt(1)–N(6)	89.9(2)
N(1a)–Pt(1)–N(5)	89.0(2)
N(1a)–Pt(1)–N(3b)	178.9(2)
Pt(1)–N(1a)–C(1a)	115.7(3)
C(2b)–N(1b)–C(6b)	121.3(4)
C(1b)–N(1b)–C(6b)	122.0(5)
C(1b)–N(1b)–C(2b)	116.8(5)
Pt(1)–N(3b)–C(4b)	121.4(3)
Pt(1)–N(3b)–C(2b)	116.9(3)

(continued)

TABLE 5. *(continued)*

C(2b)–N(3b)–C(4b)	121.6(4)
Pt(1)–N(5)–C(5)	118.8(3)
Pt(1)–N(6)–C(6)	115.0(3)
O(72)–N(7)–O(73)	121.3(5)
O(71)–N(7)–O(73)	118.8(5)
O(71)–N(7)–O(72)	119.8(5)
N(1a)–C(1a)–C(2a)	112.3(4)
O(22a)–C(2a)–C(1a)	118.4(4)
O(21a)–C(2a)–C(1a)	115.4(4)
O(21a)–C(2a)–O(22a)	126.2(5)
N(1b)–C(2b)–N(3b)	117.4(4)
O(2b)–C(2b)–N(3b)	121.5(4)
O(2b)–C(2b)–N(1b)	121.1(4)
N(3b)–C(4b)–N(4b)	119.0(4)
N(4b)–C(4b)–C(5b)	121.8(4)
N(3b)–C(4b)–C(5b)	119.2(4)
C(4b)–C(5b)–C(6b)	118.4(5)
N(1b)–C(6b)–C(5b)	121.9(5)

(C11) displays a similar contact (to O2 of the 1-MeC rings). With *cis*-$(NH_2CH_3)_2PtCl_2$, two crystalline modifications, differing in the relative orientations of the methyl groups, have been observed as well [19]. A stereoview of the unit cell is given in Fig. 4 and short contacts are listed in Table 4. As can be seen, extensive hydrogen bonding exists between the amino protons of the CH_3NH_2 ligands and the glycine and nitrate, water, and carboxylate oxygens.

^1H NMR Spectra

The ^1H NMR spectrum of **1** is normal with two doublets for H5 and H6 of the 1-MeC ring,(6.059 ppm, 7.652 ppm, $^3J = 7.4$ Hz) and a singlet (3.441 ppm) for the N–CH_3 group. The CH_2 resonance of the gly ligand does not display any ^{195}Pt coupling (300 MHz) and, unlike with the related *cis*-$[(NH_3)_2$-Pt(1-MeC)(gly-*N*)$]^+$ compound [3], no temporary coupling between the amino group of gly and CH_2 of gly was observed. However, the CH_3 resonances of the amine ligands in both **1** and **2** show this phenomenon. In acidic medium, the CH_3 signals of freshly prepared samples display triplet structure (1:2:1, $J \simeq 6.3$ Hz) which slowly, and in neutral or alkaline solution quickly is lost and simplifies to a singlet. This process is accompanied by the loss of the broad NH_2 resonance of the amine ligand at *c.* 4.6 ppm, indicating that ^3J coupling between NH and CH protons is taking place as long as isotopic NH → ND exchange is not substantial. The resulting singlet shows signs of ^{195}Pt coupling (broad, ill-resolved satellites, $^3J \simeq 40$ Hz). The ^1H resonances of the non-exchangeable protons of **2** undergo pH* dependent chemical shifts (Fig. 5), indicative of the following equilibria:

$$[a_2Pt(1\text{-MeC})(\text{glyH-}N)]^{2+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}}$$

$$[a_2Pt(1\text{-MeC})(\text{gly-}N)]^{+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} a_2Pt(1\text{-MeC}^-)(\text{gly-}N)$$

pK_a values are 2.5 and *c.* 12.5 respectively, very similar to those of the *cis*-compound. Again we note the considerable acidification of glyH on Pt binding via the amino group [3] and the astonishing increase in NH_2 acidity of the 1-MeC ligand. In the case of the *cis*-compound, we have tentatively attributed this to the possibility of intracomplex hydrogen bond formation between the carboxylate group and $NH_2(4)$ of 1-MeC. In our ternary compound, a similar H bond could occur, although we estimate from model building that an intracomplex H bond should be around 3 Å or slightly longer in the case of a *trans*-geometry. While this interpretation indeed is not wholly satisfactory, we definitely feel that the

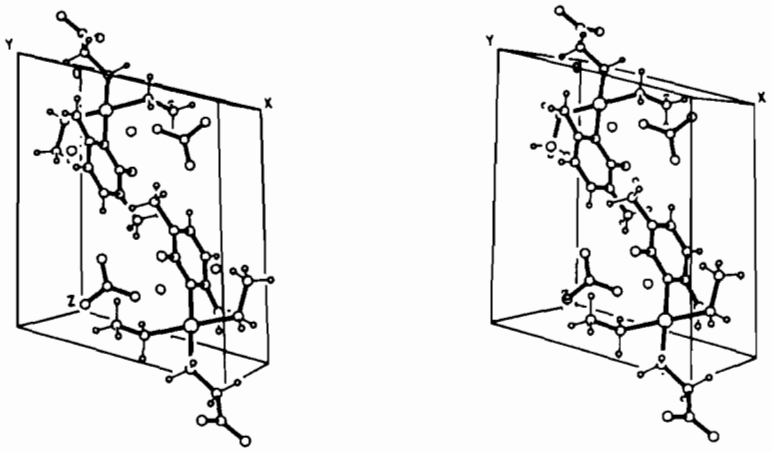

Fig. 4. Stereoview of the unit cell of **2**.

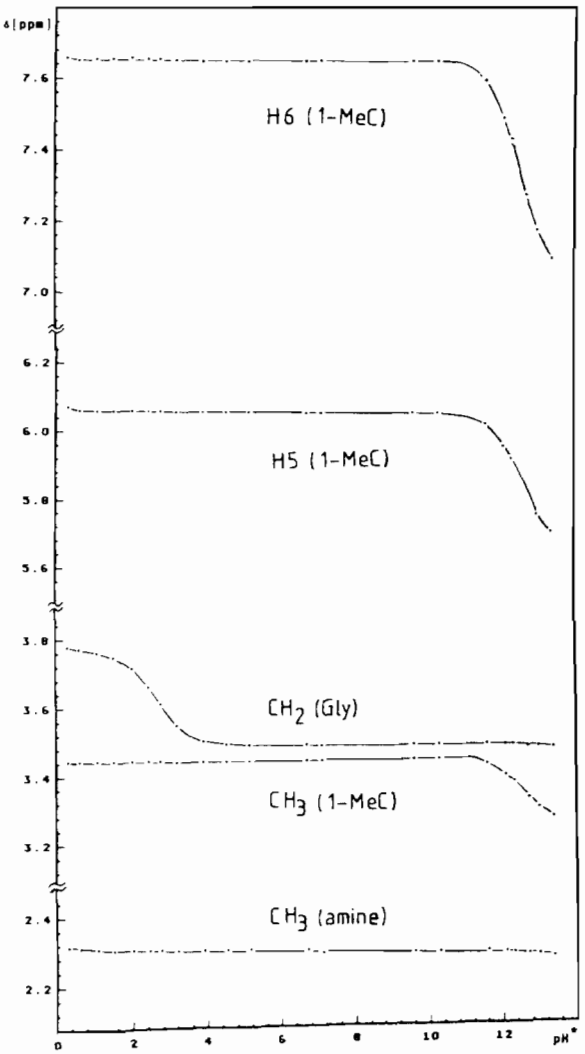

Fig. 5. pH* dependence of ^{1}H NMR chemical shifts of resonances of **2**.

cytosine-NH_2 acidity should not be attributed to the charge (+1) of the complex. In *cis*-$[(NH_3)_2Pt(1\text{-MeC})(1\text{-MeU})]^+$ (1-MeU = 1-methyluracil anion), the charge is identical, yet 1-MeC deprotonation does not even start at pD 13–14 [20].

Supplementary Material

Positional parameters and anisotropic temperature factors of **1**, short contacts and a listing of observed and calculated structure factors can be obtained from the Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2 under CSD 53879 on request. Requests should be accompanied by the complete literature citation.

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References

1 P. I. Vestues and R. B. Martin, *Inorg. Chim. Acta, 55* (1981) 99.
2 (a) A. Garoufis, R. Haran, M. Pasdeloup, J. P. Laussac and N. Hadjiliadis, *J. Inorg. Biochem., 31* (1987) 65; (b) S. Kasselouri, A. Garoufis and N. Hadjiliadis, *Inorg. Chim. Acta, 135* (1987) L23.
3 F. Schwarz, B. Lippert, A. Iakovidis and N. Hadjiliadis, *Inorg. Chim. Acta, 168* (1990) 275.
4 (a) B. T. Khan, G. N. Goud and S. V. Kumari, *Inorg. Chim. Acta, 80* (1983) 145; (b) B. T. Khan, S. V. Kumari and G. N. Goud, *J. Coord. Chem., 12* (1982) 19.
5 M. Sabat, K. A. Satyshur and M. Sundaralingam, *J. Am. Chem. Soc., 105* (1983) 976.
6 (a) S. J. Lippard and J. D. Hoeschele, *Proc. Natl. Acid. Sci. U.S.A., 76* (1979) 6091; (b) J. Filipski, K. W. Kohn and W. M. Bonner, *FEBS Lett., 152* (1983) 105; (c) Z. M. Banjar, L. S. Hnilica, R. C. Briggs, J. Stein and G. Stein, *Biochemistry, 23* (1984) 1921.
7 T. J. Kistenmacher, M. Rossi, J. P. Caradonna and L. G. Marzilli, *Adv. Mol. Relax. Interact. Processes, 15* (1979) 119.
8 J. Arpalathi, B. Lippert, H. Schöllhorn and U. Thewalt, *Inorg. Chim. Acta, 153* (1988) 45.
9 G. M. Sheldrick, *SHELXTL PLUS,* (Release 3.4) for Nicolet R 3 m/V Crystallographic Systems, University of Göttingen, Göttingen, F.R.G., 1987.
10 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, 1974.
11 M. Nardelli, *Comput. Chem., 7* (1983) 95.
12 D. E. Williams, *PCK 83,* QCPE Program, No. 481, University of Louisville, Louisville, KY, 1984.
13 A. L. Spek, in D. Sayre (ed.), *Computational Crystallography,* Clarendon Press, Oxford, 1982, p. 528.
14 Y. Le Page, *J. Appl. Crystallogr., 20* (1987) 264.
15 (a) R. Beyerle-Pfnür, B. Brown, R. Faggiani, B. Lippert and C. J. L. Lock, *Inorg. Chem., 24* (1985) 4001; (b) H. Schöllhorn, U. Thewalt, G. Raudaschl-Sieber and B. Lippert, *Inorg. Chim. Acta, 124* (1986) 207, and refs. therein.
16 J. F. Britten, *Ph.D. Thesis,* McMaster University, Hamilton, Ont., Canada, 1984.
17 (a) A. Iakovidis, N. Hadjiliadis, H. Schöllhorn, U. Thewalt and G. Trötscher, *Inorg. Chim. Acta, 164* (1989) 221; (b) H. C. Freeman and M. L. Golomb, *Acta Crystallogr., Sect. B, 25* (1969) 1203; (c) I. Zahn, K. Polborn and W. Beck, *Chem. Ber., 122* (1989) 53.
18 V. Pavone, A. Lombardi, B. Di Blasio, E. Benedetti and C. Pedone, *Inorg. Chim. Acta, 153* (1988) 171.
19 S. Wimmer, F. Wimmer, J. Jaud, N. P. Johnson and P. Castan, *Inorg. Chim. Acta, 144* (1988) 25.
20 B. Lippert, U. Thewalt, H. Schöllhorn, D. M. L. Goodgame and R. W. Rollins, *Inorg. Chem., 23* (1984) 2807.