A Major, pH-Induced Stereochemical Switch of Pairs of *trans*-Oriented Ligands in Complexes of *trans*-a_2Pt^{II} ($a = NH_3$, CH_3NH_2)

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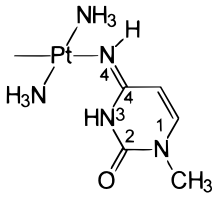
trans-$[Pt(CH_3NH_2)_2(1\text{-MeC-}N4)_2]X_2$ (**3a**, $X = NO_3^-$; **3b**, $X = ClO_4^-$), containing the model nucleobase 1-methylcytosine (1-MeC) platinated at N4 and protonated at N3, hence in its rare tautomeric form, has been prepared from the Pt^{IV} precursor *trans*,*trans*,*trans*-$[Pt(CH_3NH_2)_2(1\text{-MeC-}N4)_2(OH)_2](NO_3)_2 \cdot 2H_2O$ (**2**) upon reduction with H_2. Crystallization of **3a** from 1 M NaOH afforded *trans*-$[Pt(CH_3NH_2)_2(1\text{-MeC}^-\text{-}N4)_2] \cdot 4H_2O$ (**4a**) or, following lyophilization and deprotonation in CH_3OH by means of $(CH_3)_3CONa$, gave *trans*-$[Pt(CH_3NH_2)_2(1\text{-MeC}^-\text{-}N4)_2] \cdot 2CH_3OH$ (**4b**). While dihedral angles between the coplanar bases and the PtN_4 planes are large in the case of **2** (84.8(1)°) and **3b** (73.9(1)°), they become markedly smaller in **4a** (55.5(2)°) and **4b** (26.6(2)°) as a consequence of pairwise intramolecular H bonding between the NH protons of the CH_3NH_2 groups and the N3 positions of the cytosine nucleobases. DFT calculations for the corresponding NH_3 complex gave a dihedral angle of 22.3°. The switch of the mutually *trans*-oriented ligand pairs from approximately perpendicular to roughly coplanar appears to take place during the crystallization process, probably because of competition between intramolecular H bonding and intermolecular H bonding with the solvent. **2**: triclinic, $P\bar{1}$, $a = 5.937(1)$ Å, $b = 8.228(2)$ Å, $c = 12.470(2)$ Å, $\alpha = 80.36(3)°$, $\beta = 80.80(3)°$, $\gamma = 80.54(3)°$, $Z = 2$. **3b**, triclinic, $P\bar{1}$, $a = 7.392(1)$ Å, $b = 9.072(2)$ Å, $c = 10.047(2)$ Å, $\alpha = 112.40(3)°$, $\beta = 106.07(3)°$, $\gamma = 94.66(3)°$, $Z = 2$. **4a**, triclinic, $P\bar{1}$, $a = 7.104(1)$ Å, $b = 7.549(2)$ Å, $c = 9.209(2)$ Å, $\alpha = 87.74(3)°$, $\beta = 88.04(3)°$, $\gamma = 85.92(3)°$, $Z = 2$. **4b**, triclinic, $P\bar{1}$, $a = 7.045(1)$ Å, $b = 7.421(1)$ Å, $c = 9.966(2)$ Å, $\alpha = 109.25(3)°$, $\beta = 99.22(3)°$, $\gamma = 95.02(3)°$, $Z = 2$.

Introduction

Nucleobases bound to Pt entities can frequently be protonated or deprotonated.[1,2] In fact, the pH dependence of nucleobase proton resonances as measured by ^1H NMR spectroscopy,[3−5] potentiometry, or spectrophotometry[6] or obtained from kinetic data[7] has proved a good way in many cases to assign binding sites. Usually the protonation state has no major effect on the stereochemistry, viz. the dihedral angle between nucleobase and metal coordination plane. This is certainly true if the nucleobase is bound via an *endocyclic* donor atom to Pt.

We have recently reported on the formation, crystal structure and solution behavior of *trans*-$[Pt(NH_3)_2(1\text{-MeC-}N4)_2]^{2+}$, a nucleobase complex with Pt binding to an *exocyclic* group, N4.[8,9] In solution, the compound displays a high degree of rotational freedom about the Pt−N4 and N4−C4 bonds (Chart 1), as evident from the existence of at least four out of six possible rotamers in solution. It was also observed that deprotonation of the N(3)H position simplified the solution behavior (in $(CH_3)_2SO$-d_6) greatly, and we had proposed (on the basis of NMR data) that a switch of two *trans*-oriented ligands from an approximately perpendicular arrangement (with respect to the Pt coordination plane) to a roughly coplanar one had occurred.[9] The very poor solubility of *trans*-$[Pt(NH_3)_2(1\text{-MeC}^-\text{-}N4)_2]$ had prevented any verification or disproval of this hypothesis by X-ray crystallography. Therefore, we had decided to apply the density functional theory (DFT)[10] to this question and in addition to study a closely related compound, containing methylamine ligands at the Pt instead of ammine ligands, in the hope that insolubility may prove less a problem.

Chart 1



Experimental Section

Starting Compounds. *trans*-$[Pt(CH_3NH_2)_2(1\text{-MeC-}N3)_2](NO_3)_2$ was prepared as previously described.[11] $(CH_3)_3CONa$ (97% purity) was purchased from Aldrich. Methanol was dried over 3 Å molecular sieves prior to use. **Caution!** *Perchlorate salts of metal complexes with organic ligands are potentially explosive!*

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***trans,trans,trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC-*N3*)$_2$(OH)$_2$](NO$_3$)$_2$·2H$_2$O (1).** A sample of 1.054 g (1.669 mmol) of *trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC-*N3*)$_2$](NO$_3$)$_2$ was dissolved in H_2O (36 mL). After addition of H_2O_2 (36 mL, 10% in water) the solution was stirred at room temperature for 80 min, followed by heating to 70 °C for 60 min to decompose the surplus of H_2O_2. Slow evaporation of the solvent gave the yellowish compound **1** (297 mg, 0.423 mmol, 25%), which was filtered off, washed with water (1 mL), and dried (24 h, 40 °C). Anal. Calcd for $C_{12}H_{30}O_{12}N_{10}Pt$: C, 20.5; H, 4.3; N, 20.0. Found: C, 20.5; H, 4.2; N, 20.0. IR ($\tilde{\nu}$, cm^{-1}): 3474, 3284, 3075, 1637, 1392, 1337, 1076, 1060, 792, 769. ^{195}Pt NMR (D_2O, pD 4.3, δ, ppm): 1177. ^{1}H NMR (D_2O, pD 4.3, δ, ppm): 7.70 (d, H6), 5.97 (d, $^4J(^{195}Pt, ^1H) = 12.0$ Hz, H5), 3.44 (s, CH_3), 2.22 (s, $^3J(^{195}Pt, ^1H) = 27.1$ Hz, CH_3).

***trans,trans,trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC-*N4*)$_2$(OH)$_2$](NO$_3$)$_2$·2H$_2$O (2).** A 235 mg sample (0.335 mmol) of **1** was stirred in water (4 mL) for 48 h at 75 °C. The solution was then cooled to 4 °C for 3 h to complete the precipitation. The colorless compound was filtered off, washed with H_2O (1 mL), and dried (24 h, 40 °C) to yield 177 mg (0.253 mmol, 75%) of **2**. Colorless sticks of **2** could be obtained from the filtrate after 3 days at 4 °C. Anal. Calcd for $C_{12}H_{28}O_{11}N_{10}Pt$ (monohydrate): C, 21.1; H, 4.1; N, 20.5. Found: C, 21.2; H, 4.2; N, 20.4. IR ($\tilde{\nu}$, cm^{-1}): 3216, 1651, 1360, 1113, 823, 760, 602, 495. ^{195}Pt NMR (D_2O, pD 5.3, δ, ppm): 783. ^{1}H NMR (D_2O, pD 5.3, δ, ppm): 7.43 (d, $^5J(^{195}Pt, ^1H) = 4.9$ Hz, H6), 6.14 (d, H5), 3.37 (s, CH_3), 2.30 (s, $^3J(^{195}Pt, ^1H) = 28.6$ Hz, CH_3).

***trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC-*N4*)$_2$](ClO$_4$)$_2$ (3b).** Hydrogen was bubbled through a solution of **2** (70 mg, 0.10 mmol) in H_2O (20 mL) at 50 °C for 4.5 h in the reaction apparatus previously described.[9] Some finely dispersed Pt^0 (obtained by pyrolysis of Magnus Green Salt [Pt(NH$_3$)$_4$][PtCl$_4$]) had been added to accelerate the reaction. Slow evaporation to dryness in a N_2 flow resulted in a colorless, glassy residue of *trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC-*N4*)$_2$](NO$_3$)$_2$ **(3a)** which was dissolved in H_2O (5 mL). Colorless cubes precipitated after addition of a saturated solution of $NaClO_4$ in H_2O (5 mL). They were filtered off, washed with H_2O (1 mL) and dried (24 h, 40 °C) to yield 58 mg of **3b** (94 μmol, 94%). Anal. Calcd for $C_{12}H_{24}O_{10}N_8PtCl_2$: C, 20.4; H, 3.4; N, 15.9. Found: C, 20.3; H, 3.3; N, 16.2. IR (ν, cm^{-1}): 3289, 1708, 1650, 1333, 1310, 1072, 762, 621, 591. ^{195}Pt NMR (major rotamer, D_2O, pD 6.9, δ, ppm): −2674. ^{1}H NMR (major rotamer, D_2O, pD 6.9, δ, ppm): 7.15 (d, H6), 5.99 (d, H5), 3.33 (s, CH_3), 2.27 (s, $^3J(^{195}Pt, ^1H) = 12.8$ Hz, CH_3).

***trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC$^-$-*N4*)$_2$]·4H$_2$O (4a).** A 68 mg sample of **2** (97 μmol) was reduced with hydrogen for 6.5 h as described above. The completion of the reduction process was confirmed by ^{1}H NMR. After addition of 1 M NaOH (10 mL) the solution was kept in a weak N_2 flow for 4 d to yield colorless blocks. They were filtered off and washed with H_2O (1 mL). According to X-ray crystallography, **4a** crystallizes as a tetrahydrate. If dried (24 h, 40 °C), **4a** loses water and becomes yellowish (19 mg, 38 μmol, 39%). Anal. Calcd for $C_{12}H_{22}O_2N_8Pt$ (anhydrate): C, 28.5; H, 4.4; N, 22.2. Found: C, 28.3; H, 4.3; N, 22.2. IR ($\tilde{\nu}$, cm^{-1}): 3320, 3135, 1647, 1622, 1479, 1436, 1153, 858, 792, 515.

***trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC$^-$-*N4*)$_2$]·2CH$_3$OH (4b).** A 70 mg sample of **2** (0.10 mmol) was reduced with hydrogen for 4 h as described above, until the completion of the reduction process could be confirmed by ^{1}H NMR. The solution was lyophilized and dissolved in methanol (20 mL). A solution of $(CH_3)_3CONa$ (196 mg, 2.04 mmol) in methanol (10 mL) was added, and colorless crystals precipitated. They were filtered off and washed with CH_3OH (1 mL). According to X-ray crystallography, **4b** contains two methanol molecules per Pt. If dried (24 h, 40 °C), **4b** becomes likewise yellowish (31 mg, 61 μmol, 61%). According to ^{1}H NMR, IR and Raman spectroscopy, the solvent free compounds derived from **4a** and **4b** are identical.

Instrumentation. ^{1}H NMR measurements were carried out at ambient temperature on a Bruker AC 200 (D_2O, DMSO-d_6), a Bruker DPX 300 (D_2O) and a Bruker DRX 400 (90% H_2O, 10% D_2O) spectrometer. ^{195}Pt NMR spectra were recorded at 43 MHz on the AC 200 instrument. Chemical shifts are referenced to internal sodium 3-(trimethylsilyl)propanesulfonate (^{1}H, H_2O, D_2O), tetramethylsilane (^{1}H, DMSO-d_6) and external Na_2PtCl_6 (^{195}Pt). pD values were obtained by adding 0.4 to the pH meter (Metrohm 632) reading.[12] The pK_a values in H_2O were calculated from the pK_a* values in D_2O according to pK_a* = 1.015pK_a + 0.45.[13] The pK_a* values were determined ^{1}H NMR spectroscopically using the fitting functions for compounds displaying two pK_a values published by Sigel et al.[14] Elemental analyses were carried out on a LECO Elemental Analyzer CHNS-932 and a Carlo Strumentazione 1106 instrument. IR spectra were recorded on a Bruker FT-IR spectrometer (model IFS 28) with a He−Ne laser (λ = 633 nm). Raman spectra were recorded on a ISA Jobin Ivon T 64000 instrument with a Spectra Physics Ar^+−Laser at 514.5 nm.

X-ray Crystallography. Diffraction data for **2**, **3b**, **4a**, and **4b** were collected on an Enraf-Nonius Kappa CCD diffractometer[15,16] with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Data reduction and cell refinement were carried out using the programs DENZO and SCALEPACK.[17] Reflections which were partly measured on the previous and following frames were used to scale these frames to each other. This procedure in part eliminated absorption effects and also considered a crystal decay if present. No empirical absorption correction was applied. The structures were determined by standard Patterson methods[18] and refined with difference Fourier syntheses, using the SHELXTL-PLUS,[19] SHELXL-93[20] (**2**, **3b**), and SHELXL-97[21] (**4a**, **4b**) programs. For **2** and **3b**, hydrogen atoms at calculated positions were introduced in final cycles of refinement as fixed contributions, except those of water molecules. Crystal data and data collection parameters are summarized in Table 1.

Calculations. The calculations have been carried out by means of the Amsterdam Density Functional Program (ADF).[22] The molecular orbitals were expanded into a large, uncontracted set of Slater-type orbitals (STOs). The basis is of double-ζ quality for (n-1)s and (n-1)p orbitals, triple-ζ for (n-1)d and ns orbitals, and employs a single STO for np orbitals. The $1s^2$ core shell for carbon, oxygen and nitrogen and the core shells up to $4f^{14}$ level for platinum were treated by the frozen core approximation with relativistic effects included by scalar relativistic corrections (Darwin plus mass-velocity).[23] The numerical integration was done by means of the scheme developed by te Velde et al.[22] All calculations were carried out with the local-density approximation in the Vosko−Wilk−Nuasir parametrization[24] with nonlocal corrections for exchange and correlation (Perdew-Wang 91).[25] Geometries were optimized by means of the analytical gradient method implemented by Versluis and Ziegler.[26]

Results and Discussion

Syntheses of Compounds. The procedure of synthesizing compounds **1**−**4** followed previously described routes,[8,9,27,28] namely H_2O_2 oxidation of the known complex *trans*-[Pt(CH$_3$-

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Table 1. Crystallographic Data for Compounds **2**, **3b**, **4a**, and **4b**

	2	**3b**	**4a**	**4b**
empirical formula	$C_{12}H_{30}O_{12}N_{10}Pt$	$C_{12}H_{24}O_{10}N_8PtCl_2$	$C_{12}H_{30}O_6N_8Pt$	$C_{14}H_{30}O_4N_8Pt$
fw (g mol^{-1})	701.54	706.38	577.54	569.56
temperature (°C)	20	20	−137	−120
space group	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)
a (Å)	5.937(1)	7.392(1)	7.104(1)	7.045(1)
b (Å)	8.228(2)	9.072(2)	7.549(2)	7.421(1)
c (Å)	12.470(2)	10.047(2)	9.209(2)	9.966(2)
α (deg)	80.36(3)	112.40(3)	87.74(3)	109.25(3)
β (deg)	80.80(3)	106.07(3)	88.04(3)	99.22(3)
γ (deg)	80.54(3)	94.66(3)	85.92(3)	95.02(3)
V (Å^3)	586.9(2)	585.2(2)	492.0(2)	480.0(1)
Z	2	2	2	2
D_{calcd} (g cm^{-3})	1.985	2.004	1.949	1.970
μ (Mo Kα = 0.710 69 Å) (cm^{-1})	60.56	62.87	71.77	73.47
R_1 (obs. data)[a]	0.0232	0.0297	0.0199	0.0254
wR_2 (obs. data)[b]	0.0546	0.0600	0.0465	0.0499

[a] $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$.

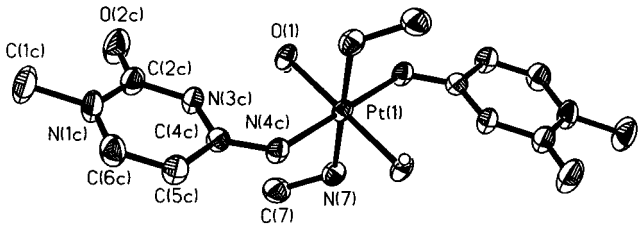


Figure 1. Cation of **2** with atom-numbering scheme.

$NH_2)_2$(1-MeC-*N3*)$_2$](NO$_3$)$_2$ to *trans,trans,trans*-[Pt(CH$_3$NH$_2$)$_2$-(1-MeC-*N3*)$_2$(OH)$_2$](NO$_3$)$_2$·2H$_2$O (**1**), isomerization to *trans,-trans,trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC-*N4*)$_2$(OH)$_2$](NO$_3$)$_2$·2H$_2$O (**2**), reduction to *trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC-*N4*)$_2$](NO$_3$)$_2$ (**3a**) and subsequent deprotonation of **3a** in H$_2$O or CH$_3$OH to give *trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC$^-$-*N4*)$_2$]·4H$_2$O **4a** and *trans*-[Pt(CH$_3$NH$_2$)$_2$-(1-MeC$^-$-*N4*)$_2$]·2CH$_3$OH **4b**, respectively. Upon filtration, **4a** and **4b** instantly changed their color from colorless to slightly yellow, accompanied by the loss of the crystallized solvent molecules. The dried products are identical according to IR, Raman and ^{1}H NMR spectroscopy. Addition of NaClO$_4$ to a solution of the glassy compound **3a** gave crystals of *trans*-[Pt-(CH$_3$NH$_2$)$_2$(1-MeC-*N4*)$_2$](ClO$_4$)$_2$ **3b**, which were suitable for X-ray crystallography.

X-ray Structure Analyses of 2 and 3b. Figure 1 depicts the cation of *trans,trans,trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC-*N4*)$_2$(OH)$_2$]-(NO$_3$)$_2$·2H$_2$O (**2**) with the atom-numbering scheme. The coordination geometry of Pt is octahedral, with angles about Pt and both Pt−N and Pt−O bond lengths in the normal range (Table 2). The nucleobases and the Pt−N$_4$ coordination plane are in an almost mutually perpendicular arrangement (χ = 84.8(1)°). The metal coordinates to the exocyclic N4 groups of the 1-methylcytosine ligands. The cation shows a short intramolecular hydrogen bond between N3c and O1 (2.645(4) Å, 151.2-(4)°), thus making the cytosine bases and the two hydroxo ligands approximately coplanar. This situation is analogous to that found in two modifications of the NH$_3$ complex,[28] where N3···HO separations of 2.662 and 2.601 Å are found. Neighboring complexes are connected via a hydrogen bond network involving the nitrate anions (N7−O11, 3.102(5) Å; 114.1(3)°; N4c−O11, 2.977 Å; 160(5)°). An additional hydrogen bond can be found between a hydroxo group and a nitrate oxygen of the next unit cell (O1−O13, 2.872(5) Å; 152(5)°). As expected, the structure of the cation of **2** is closely similar to that of the related compound *trans,trans,trans*-[Pt(NH$_3$)$_2$(1-MeC-*N4*)$_2$-(OH)$_2$](NO$_3$)$_2$·2H$_2$O with ammine instead of methylamine ligands.[28]

Table 2. Selected Structural Data of **2**, **3b**, **4a**, **4b**, and 1-MeC (Bond Lengths in Å, Angles in deg)

	2	**3b**	**4a**	**4b**	1-MeC[49]
Pt−N4	2.019(3)	1.993(3)	2.014(3)	2.017(3)	−
Pt−N$_{amine}$	2.061(3)	2.033(3)	2.052(3)	2.054(3)	−
C2−O2	1.219(5)	1.213(4)	1.268(4)	1.262(4)	1.234(2)
C2−N3	1.380(5)	1.385(4)	1.341(4)	1.342(5)	1.358(2)
N3−C4	1.359(4)	1.366(4)	1.375(4)	1.365(5)	1.332(2)
C4−N4	1.306(5)	1.305(4)	1.305(4)	1.324(5)	1.336(2)
N1−C2−O2	123.2(4)	123.2(3)	117.6(3)	117.6(3)	118.6(1)
N1−C2−N3	115.8(3)	115.2(3)	121.1(3)	120.9(3)	118.0(1)
C2−N3−C4	125.1(1)	125.9(3)	120.1(3)	120.3(3)	120.0(1)
N3−C4−C5	116.8(3)	115.8(3)	119.1(3)	119.7(3)	121.8(1)
N4−C4−C5	124.0(3)	124.6(3)	122.1(3)	120.8(3)	120.4(1)
N4−Pt−N$_{amine}$	91.3(1)	90.0(1)	92.7(1)	94.1(1)	−
χ[a]	84.8(1)	73.9(1)	55.5(2)	26.6(2)	−

[a] Angle χ between the nucleobase planes and the Pt coordination plane.

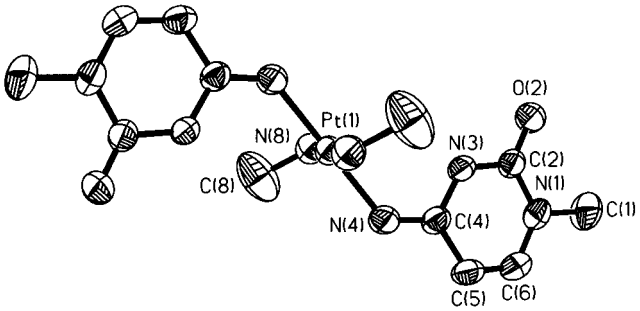


Figure 2. Cation of **3b** with atom-numbering scheme.

In Figure 2, the cation of *trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC-*N4*)$_2$]-(ClO$_4$)$_2$ **3b** is shown. The coordination geometry of Pt is square planar, with the nucleobases arranged in a *head−tail* fashion. Neighboring cations are interconnected via a H bonding system (N8−O2, 2.930(4) Å; 154.5(4)°). Furthermore, the perchlorate anions are involved in H bonding, too (N8−O13a, 3.00(1) Å; 163.2(6)°; N4−O12a, 3.00(2) Å; 163.3(6)°). Additional relevant angles and bond distances are given in Table 2. Again, structural details of the cation of **3b** and the two salts of the corresponding ammine complex *trans*-[Pt(NH$_3$)$_2$(1-MeC-*N4*)$_2$]$^{2+}$ do not differ significantly,[8,9] except that the angle χ (73.9(1)° in **2**) is smaller than in the case of the NH$_3$ analogues (88.4(5)° [8] and 79.0-(2)° [9]).

X-ray Structure Analyses of 4a and 4b. Figure 3 shows the X-ray structures of *trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC$^-$-*N4*)$_2$]·

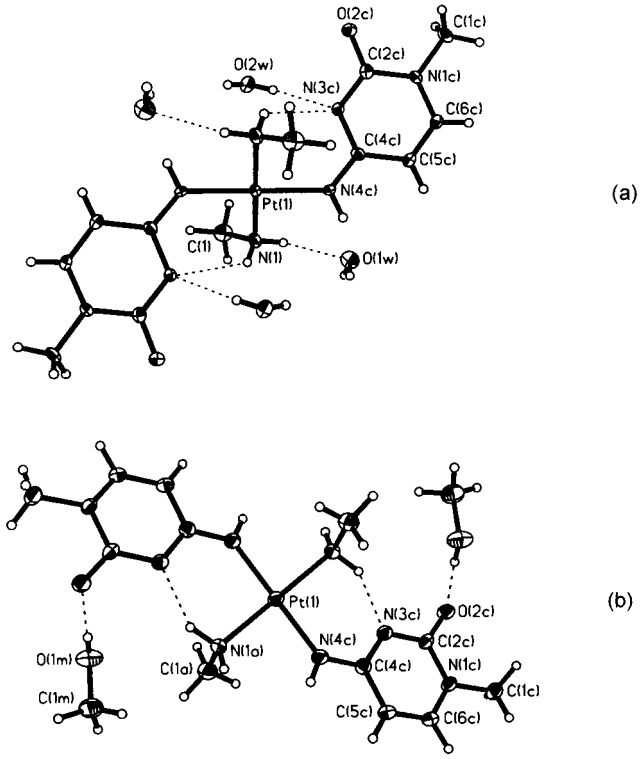
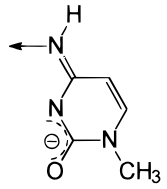


Figure 3. X-ray structures of **4a** (a) and **4b** (b) including H bonds.

Chart 2



$4H_2O$ (**4a**) and *trans*-$[Pt(CH_3NH_2)_2(1\text{-}MeC^-\text{-}N4)_2]\cdot 2CH_3OH$ (**4b**). In both complexes, the metal center has a square-planar coordination geometry, and the Pt−N bond lengths and angles about Pt are within the normal range (Table 2). A significant lengthening of the C2−O2 bond along with a shortening of the C2−N3 distance and a widening of the N1−C2−N3 angle points toward a delocalization of the negative charge at N3 along the N3−C2−O2 bonds (Chart 2). The angle χ between the nucleobase planes and the Pt coordination plane is 55.5(2)° (**4a**) and 26.6(2)° (**4b**), respectively. In **4a**, a water molecule connects the 1-MeC ligands and methylamine moieties of neighboring complexes through hydrogen bonds (O2w−N3c, 2.900(4) Å; 173(5)°; O2w−O2c, 2.878(4) Å; 173(5)°; N1−O2w, 3.066(4) Å; 152(5)°). The other water molecule forms hydrogen bonds with the methylamine group of the same unit cell (N1−O1w, 3.071(5) Å; 171(4)°). The distance between the methylamine nitrogen and the deprotonated N3 atom is in the upper range of a hydrogen bond (N1−N3c′, 3.168(5) Å; 127(5)°). On the other hand, **4b** displays a distinct intramolecular hydrogen bond between N1a and N3c (2.863(5) Å, 150(5)°). The proton involved in this hydrogen bond shows a slight elongation of the N−H bond as compared to the other proton at N1a. This difference (bond lengths 0.98(6) Å and 0.86(6) Å) is not significant, however. On the other hand, this effect is clearly reproduced in the DFT results on *trans*-$[Pt(NH_3)_2(1\text{-}MeC^-\text{-}N4)_2]$, where the ammine proton pointing toward N3c displays a 0.15 Å longer distance to its nitrogen than the other protons. Furthermore, in **4b** the solvent molecule does not undergo H bonding with N3c as seen in **4a,** yet with O2c (O1m−O2c, 2.825(5) Å; 176(6)°). Additional hydrogen bonds exist between neighboring complex molecules (N1a−O2c, 2.973(5) Å; 162(6)°; N4c−O2c, 3.002(5) Å; 154(4)°).

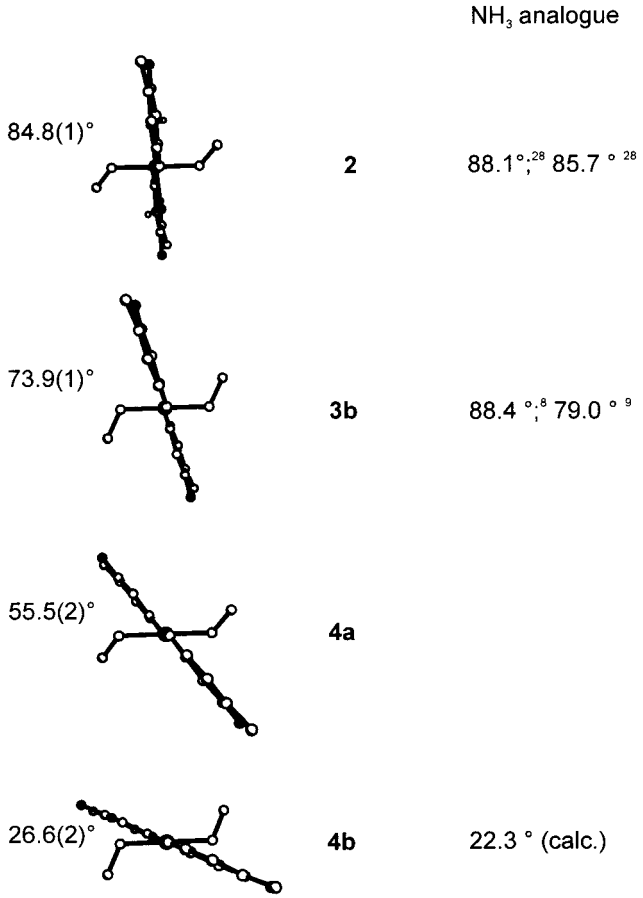
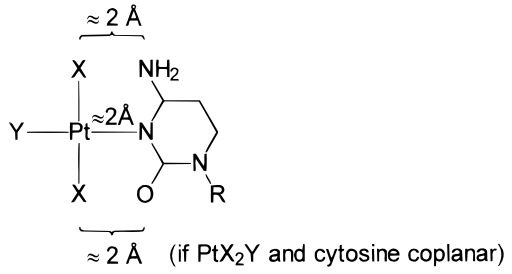


Figure 4. pH-induced switch of the 1-MeC ligands in complexes of the type *trans*-$[Pt(CH_3NH_2)_2L_2]$.

Concerning the bond lengths and angles of the coordinated nucleobase, the structures of **4a** and **4b** do not differ significantly except of the C4−N4 distance (1.305(4) and 1.324(5) Å) and the corresponding N4−C4−C5 angle (122.1(3)° and 120.8(3)°). This can easily be correlated with the formation of a shorter intramolecular H bond between N1a and N3c in **4b**. To reach the best possible orientation for such H bond, the N3c atom has to move away from the N1a nitrogen, which occurs by increasing the C4−N4 bond length, decreasing the N4−C4−C5 angle and increasing the N4c−Pt−N1a′ angle.

Comparison of 2−4a, 4b. A comparison of the angle χ between the nucleobase planes and the Pt coordination plane of compounds **2**, **3b**, **4a**, and **4b** is given in Figure 4. It can clearly be seen that the methylamine groups are moving into the nucleobase planes when going from **2** to **4b**. This is mainly the effect of the deprotonation of the endocyclic N3 nitrogen atoms of the coordinated methylcytosine ligands and, correlated with this, the formation of two intramolecular hydrogen bonds between the deprotonated N3 atoms and the methylamine ligands in **4b**. In **4a**, such intramolecular stabilization is less efficient due to the presence of water molecules which form H bonds with these sites, too. However, the trend toward a decreasing χ is clearly present in **4a** as well. The decrease in χ between **2** (84.8(1)°) and **3b** (73.9(1)°) is considered to be essentially a consequence of crystal packing, as judged from the χ angles in the analogous NH_3 compounds (88.4(5)°,[8] 79.0-

Chart 3



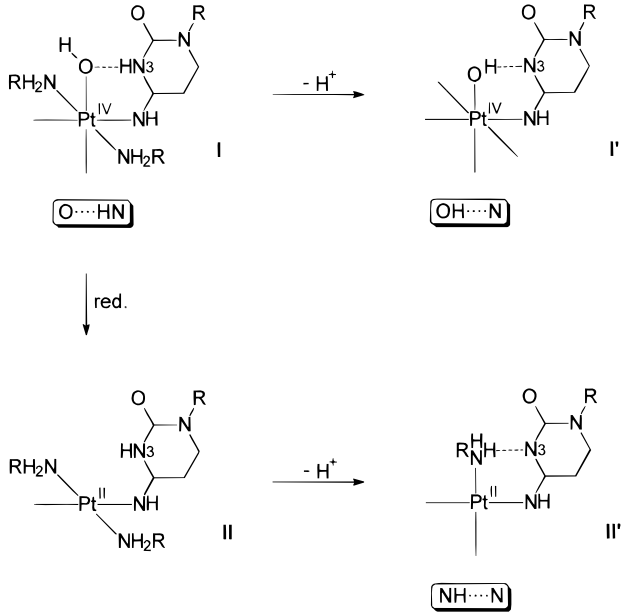
(2)°[9]) as well as in numerous Pt^{II} complexes containing nucleobases.[29]

DFT Calculations. The DFT calculations were carried out on the ammine complex *trans*-[$Pt(NH_3)_2$(1-MeC$^-$-*N4*)$_2$] instead of the methylamine one for the reason of saving computing time. The result should easily be transferable to the X-ray crystallographically determined structure of the methylamine compounds **4a** and **4b**, as the large similarities between the closely related compounds *trans*,*trans*,*trans*-[Pta_2(1-MeC-*N4*)$_2(OH)_2]^{2+}$ and *trans*-[Pta_2(1-MeC-*N4*)$_2]^{2+}$ suggest (vide supra). To obtain a suitable starting geometry, the coordinates of the X-ray structure analysis of the *trans*-[$Pt(NH_3)_2$(1-MeC-*N4*)$_2$](ClO_4)$_2$ complex[8] had been slightly modified: the anions and the proton at N3 had been removed, and the angle χ had been set to 45°. This geometry was subjected to an energy minimization, in the course of which χ decreased to a value of 22.3°. The length of the intramolecular H bond between N3 and NH_3 was calculated as 2.56 Å. All computed N−H and C−H bond lengths are about 0.2 Å longer than the X-ray crystallographically determined ones. This phenomenon is to be explained by the transfer of electron density toward the heavier atom which in X-ray single-crystal structure analysis leads to an apparent shortening of these bonds.

Significance of Nucleobase Switch. pH-induced stereochemical switches of cytosine nucleobases coordinated to Pt via the endocyclic N3 site are not expected to be dramatic. This is due to the fact that coplanarity of the base(s) and additional ligand(s) is difficult (or impossible) to be achieved as a consequence of a rather short (≈2 Å) separation between X groups and the exocyclic groups in such an arrangement and the resulting repulsion (Chart 3). Consistent with this view are numerous X-ray structural studies[29] which display large dihedral angles between the $Pt^{II}X_2Y$ and cytosine planes. This interpretation also holds for Pt^{IV} compounds of types *trans*,*trans*,*trans*-[$Pt(NH_3)_2$(1-MeC-*N3*)$_2(OH)_2]^{2+}$ and *trans*,*trans*,*trans*-[$Pt(NH_3)_2$(1-MeC-*N3*)$_2(H_2O)(OH)]^{2+}$, despite rotation of a 1-MeC base in the latter case from *head*−*tail* to *head*−*head*.[27]

The situation is very much different if Pt binding takes place through the exocyclic N4 group. Then the separation between X groups and the N3 sites of cytosine is sufficiently large to permit H bond formation between these positions (Chart 4). The flexibility in the Pt−N4−C4 angle further adds to such a possibility. The compounds reported here, as well as several NH_3 analogues previously described,[8,9,27,28,30] permit an instructive comparison and allow some tentative conclusions concerning the driving force of the nucleobase movement (Scheme 1). Thus the X-ray crystal structure data of **2** and those of two NH_3 analogues[28] reveal coplanarity of the OH ligands and the 1-methylcytosine bases (**I**), with rather short intracomplex H bonds between the oxygen atom of the OH ligands and the N(3)H position of around 2.60−2.66 Å. Deprotonation of this Pt^{IV} compound, as revealed for a NH_3 analogue,[30] leads to loss of the N3 proton, but the hydrogen bond and likewise coplanarity between the cytosinato nucleobase and the OH ligand (**I′**) are retained. The H bond is considerably longer now (2.75 Å), however. Reduction of **I** to the Pt^{II} species **II** leads to a situation without any possibility of intracomplex H bond formation. The flexibility of the compound is manifested by the existence of various rotamers in solution.[8,9,31] Finally, deprotonation of **II** gives **II′** (**4a**, **4b**), but only in **4b** is there a short intramolecular H bond of 2.86 Å. This H bond is by 0.1−0.2 Å longer than the H bonds in **I′** and **I**, where coplanarity between the X ligand (X = OH in **I**, **I′**) and the cytosine nucleobase is realized. From a purely geometric point of view there is no reason the N atom of the NH_2R ligand and the nucleobase should not be coplanar, unless the H bonding interaction between the two sites is markedly weaker than in **I** and **I′**. This is, however, apparently the case, and the H bonding distances O···HN (**I**) < OH···N (**I′**) < NH···N (**II′**) thus reflect these differences.[32] The situation in the Ru^{III} complex [Ru(NH_3)$_5$(1-MeC$^-$-*N4*)](PF_6)$_2$ is different in that there two neighboring NH_3 groups form H bonds of 2.91 Å each with the deprotonated N3 site, therefore avoiding coplanarity of the N atom of a H bonded ammonia ligand with the base.[36]

Scheme 1. Comparison of Different H Bonding Patterns. **I**: **2**, Two NH_3 Analogues;[28] **I′**: Deprotonated NH_3 Analogue;[30] **II**: **3b**, Two NH_3 Analogues;[8,9] **II′**: **4b**.



pH Titration. To determine the reaction pathway from **3b** with an almost perpendicular arrangement of the metal coordination plane and the nucleobase planes toward **4a** with a more

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(31) Of course, solvent molecules interacting between N(3)H and am(m)ine groups of the NH_2R ligands could be responsible for preferential rotamer formation.

(32) The number of examples of intramolecular H bonds between metal−OH, metal−OH_2, and metal−NH_3 groups with NH donor or N acceptor sites in heterocyclic ligands is rather limited. See, e.g. for HOH···N, refs 33 and 34; for RHNH···N, ref 35; for H_2NH···N, ref 36.

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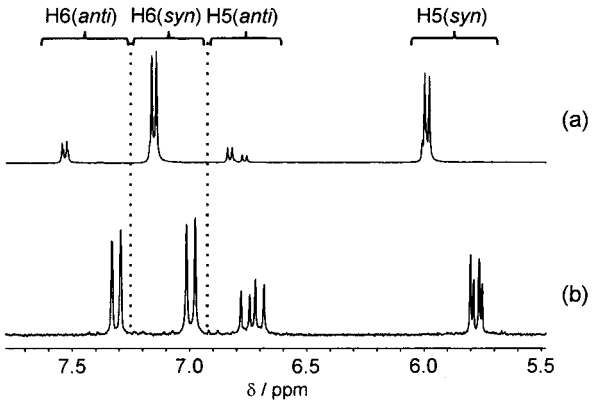


Figure 5. Aromatic region of the ^{1}H NMR spectra of (a) *trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC-*N4*)$_2$](ClO$_4$)$_2$ (**3b**; pD 7.1) and *trans*-[Pt(CH$_3$NH$_2$)$_2$(1-MeC$^-$-*N4*)$_2$] (**4a**; pD 10.7) showing the presence of four rotamers in different ratios.

tilted arrangement a pH titration was carried out and followed by ^{1}H NMR spectroscopy. Initially, one would expect to observe only one rotamer in alkaline solution and, as previously reported,[9] four rotamers in acidic medium. However, the titration reveals that even at pD 12.4 four rotamers (N3 syn with respect to Pt, N3 anti with respect to Pt; both orientations in head−head and head−tail arrangements) are present, although the rotameric ratio has significantly changed from approximately 4:1 (disregarding the differences in the populations of head−head and head−tail) to about 1.0:1.2:1.8:1.3 (Figure 5).[37] The former points out that the nucleobase planes still keep their perpendicular arrangement in aqueous solution and that the rotation into the platinum coordination plane occurs upon crystallization in the solid-state only. Furthermore, the latter confirms the postulation[9] that the initial rotamers are stabilized by H bonds involving the N(3)H protons of the nucleobases and solvent molecules. As with deprotonated N3 positions no such stabilization is feasible, the stabilities of the different rotamers are almost identical.

The pH titration reveals yet another interesting feature of the deprotonation process as three different pK_a values can be determined. The pK_a value for the first deprotonation step amounts to 7.46 ± 0.06 (3 σ) and is identical for all four rotamers. For the second step however, two different pK_a values are found. While the anti rotamers display a pK_a value of 8.7 ± 0.2, a much higher value of 9.6 ± 0.2 is determined for the syn rotamers. This can easily be explained by stabilization via H bonds as shown in Chart 5. During the second deprotonation step, an additional set of H5/H6 signals is detected in the chemical shift region of the syn rotamers, indicating the presence of three instead of two syn rotamers. This extra rotamer can only be observed between about pD 8.8 and 10.5 and may be attributed to a complex in which one nucleobase rotates into the platinum coordination plane forming a H bond with the methylamine ligand while the other methylcytosine ligand still keeps its perpendicular arrangement with respect to the metal coordination plane. However, this interpretation brings up the question why such rotation does not take place in the doubly deprotonated complex in solution.

(37) The suggestion by one referee that the four sets of ^{1}H NMR signals correspond to only three isomers (both nucleobases with N3 syn with respect to Pt, both nucleobases with N3 anti with respect to Pt, one nucleobase with N3 syn and the other with N3 anti with respect to Pt) as found in related compound (refs 38, 39) can be ruled out by the relative intensities of the NMR signals (Figure 5), as the last isomer having non equivalent nucleobases would give two sets of signals of equal intensity, which is not found.

Chart 4

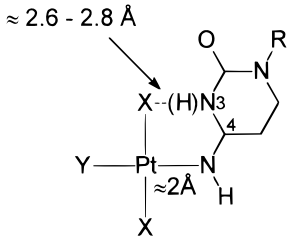
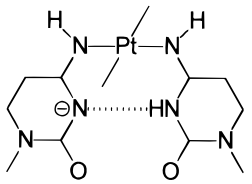


Chart 5



Summary

Examples of pH induced switches of metal complex geometries,[40,41] rotation of metal entities about intraligand bonds,[42] and rotation of ligands about metal−ligand bonds[27] have been documented, and these include also nucleobase complexes.[27,42] These switches are likely to be relevant to many other systems, but the lack of structures obtained at different pH values frequently prevents a direct proof. For example, the head−head orientation of two *trans*-oriented guanine-*N7* bases in a hexacoordinated Cu^{II} complex probably is due to the help of an aqua ligand which H bonds to the O6 sites,[43] and a similar situation is realized in a recently published Ru^{III} complex containing two *trans*-oriented triazolopyrimidine-*N9* ligands.[44] There is a good chance that at higher pH, with H_2O converted into a OH ligand, the orientation of the heterocyclic ligands might be head−tail. The near-coplanarity of the aliphatic amidato and the aqua ligands in *trans*-[Pt{HN=C(O)Bu^t}$_2$(H$_2$O)$_2$] is likewise brought about by two very short H bonds of 2.484(6) Å between a proton of the aqua ligands and the carbonyl oxygen atoms.[45] The example reported in this work adds to the list of compounds that display the phenomenon of behaving as a pH switch. There has been much excitement recently about pH dependent conformational changes in supramolecular devices such as logic gates and molecular shuttles.[46−48] It appears possible that metal

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entities undergoing pH dependent switches of ligands could also be exploited in this context.

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Supporting Information Available: pD-dependence data for **3b**; structural, energy convergence, and charge data on the calculated compound *trans*-[Pt(NH_3)$_2$(1-MeC$^-$-*N4*)$_2$]; and tables of X-ray structural data on compounds **2**, **3b**, **4a**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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