Articles

Contribution from the Fachbereich Chemie, Universität Dortmund, 4600 Dortmund, FRG,
and Department of Chemistry, University of Helsinki, 00100 Helsinki, Finland

Palladium–1-Methylcytosine Chemistry: N3 and N3,N4 Metal Binding to 1-Methylcytosine and an Unexpected Trans → Cis Isomerization of Two $(NH_3)_2Pd^{II}$ Entities

Michael Krumm,[1a] Ilpo Mutikainen,[*,1b,c] and Bernhard Lippert[*,1a]

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A series of complexes of Pd(II) with the model nucleobase 1-methylcytosine (1-MeC) has been prepared and studied by spectroscopic (^{1}H NMR, IR, Raman) and X-ray methods: *trans*-$[Pd(NH_3)_2(1\text{-}MeC)_2]X_2{\cdot}nH_2O$ ($X = NO_3^-$ (**1a**); ClO_4^- (**1b**)), $[Pd(1\text{-}MeC)_4]X_2{\cdot}nH_2O$ ($X = NO_3^-$, $n = 2$ (**2a**)); $X = Cl^-$, $n = 7$ (**2b**)), *cis*-$[(NH_3)_2Pd(1\text{-}MeC^-)_2Pd(NH_3)_2](NO_3)_2{\cdot}2H_2O$ (**3**), $Pd(1\text{-}MeC^-)_2{\cdot}4H_2O$ (**4**), and $[Pd(NH_3)(1\text{-}MeC)_3](NO_3)_2$ (**5**). Metal binding in **1**, **2**, and **5** is through N(3) of 1-MeC, whereas N(3) and the deprotonated N(4) position are involved in metal binding in **3** and **4**. While **1**, **2**, and **5** are obtained in a planned and predictable fashion, formation of **3** and **4** is not readily rationalized. In particular, the reaction of **1a** with *trans*-$[Pd(NH_3)_2(H_2O)_2]^{2+}$, which gives **3** with *cis*-$(NH_3)_2Pd^{II}$ entities and head–tail arranged 1-methylcytosinato ligands, is unexpected. The behavior of **1**, **5** and *trans*-$[Pd(1\text{-}MeC)_2(D_2O)_2]^{2+}$ in D_2O at 40–45 °C is rather complex and points to extensive scrambling of all ligands. The structures of **1a**, **2a**, and **3** have been determined by X-ray crystallography. **1a**: monoclinic system, space group $P2_1/n$, $a = 6.804$ (2) Å, $b = 10.292$ (3) Å, $c = 12.952$ (3) Å, $\beta = 102.05$ (2)°, $V = 887.0$ (4) Å^3, $Z = 2$. **2a**: triclinic system, space group $P\bar{1}$, $a = 9.138$ (1) Å, $b = 12.670$ (3) Å, $c = 14.137$ (3) Å, $\alpha = 80.50$ (2)°, $\beta = 74.14$ (2)°, $\gamma = 87.89$ (1)°, $V = 1552.9$ (5) Å^3, $Z = 2$. **3**: monoclinic system, space group $P2_1/n$, $a = 10.015$ (2) Å, $b = 17.094$ (3) Å, $c = 14.216$ (2) Å, $\beta = 101.72$ (2)°, $V = 2383.0$ (9) Å^3, $Z = 4$. The structures were refined to $R = 0.022$ (**1a**), 0.058 (**2a**), and 0.059 (**3**) and $R_w = 0.024$ (**1a**), 0.060 (**2a**), and 0.061 (**3**). The Pd$\cdots$Pd distance in the dinuclear cation of **3** is 2.948 (1) Å.

Introduction

Palladium(II) amine complexes have widely been applied in studies concerned with the interactions of metal ions with nucleobases, the constituents of nucleic acids.[2-13] Compared to Pt(II),[14] the number of structurally characterized Pd(II) nucleobase complexes is rather limited, however.[15-20] A major advantage of Pd(II) over corresponding Pt(II) species are the considerably faster reaction kinetics of the former.[21] The chemistries of both d^8 metal ions are generally considered to be very similar or identical. While available evidence indeed suggests that the coordination chemistries of enM^{II} (M = Pt or Pd) are identical, there has been at least one recent report[4b] on the migration of dienPd^{II} from N3 to N4 in cytidine which lacks evidence for a similar reaction of dienPt^{II}.[22] Some of the results presented in this paper concerning the reactions of *trans*-$(NH_3)_2Pd^{II}$ strongly call for more scepticism in this respect. In fact, the here reported trans → cis isomerization of two $(NH_3)_2Pd^{II}$ entities is a rare case in d^8 metals coordination chemistry,[23,24] although we note that it has been observed for $Pd(NH_3)_2X_2$ species before.[23] Our results may also be of relevance with regard to attempts to prepare Pd analogues of Pt compounds displaying antitumor activity in that the structural similarities should not be overemphasized in designing Pd compounds with suspected activity.

Our initial goal was the preparation of *trans*-$[(NH_3)_2Pd(1\text{-}MeC)_2]^{2+}$ (1-MeC = model nucleobase 1-methylcytosine, $C_5H_7N_3O$) and the study of the behavior of the exocyclic groups of the palladated 1-MeC toward additional metal electrophiles. At an early stage, it became evident that reaction of *trans*-$(NH_3)_2PdCl_2$ with 2 equiv of 1-MeC is rather complex and by no means readily leads to the expected bis(1-methylcytosine) product. Rather, a complicated array of products is formed. While we are unable as yet to fully interpret the reaction products,

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(1) (a) University of Dortmund. (b) University of Helsinki. (c) Present address: Brookhaven National Laboratory, Department of Chemistry, Upton, NY.

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we wish to herewith give an intermediate report on some of our findings.

Experimental Section

Starting Materials. 1-Methylcytosine,[25] K_2PdCl_4,[26] *trans*-$Pd(NH_3)_2Cl_2$,[27] and *trans*-Pd(1-MeC)$_2$Cl$_2$[15] were prepared by published methods; *trans*-$[Pd(NH_3)_2(H_2O)_2](NO_3)_2$ was obtained via reaction of *trans*-$Pd(NH_3)_2Cl_2$ with 2 equiv of $AgNO_3$ (H_2O, 1 h 22 °C, in the dark) and filtration of AgCl.

trans-[Pd(NH$_3$)$_2$(1-MeC)$_2$](NO$_3$)$_2$ (1a). *trans*-$Pd(NH_3)_2Cl_2$ (4 mmol) was suspended in water (200 mL), and $AgNO_3$ (8 mmol) was added. After the mixture was stirred for 1 h at 22 °C in the dark, AgCl was removed by filtration and 1-MeC (8 mmol) was added to the yellow solution (pH 3.7) with stirring. After 18 h at 40 °C and cooling to room temperature, 141 mg of a reddish brown byproduct was filtered off, with the filtrate (pH 6.6) concentrated to 25 mL by rotary evaporation and allowed to evaporate. After 6 days, 1.33 g (63%) of yellow cubes of **1a** were isolated and dried in air. Anal. Calcd for $PdC_{10}H_{20}N_{10}O_8$: C, 22.93; H, 4.04; N, 26.74. Found: C, 23.10; H, 4.10; N, 26.40.

trans-[Pd(NH$_3$)$_2$(1-MeC)$_2$](ClO$_4$)$_2$ (1b). Reaction of *trans*-$Pd(NH_3)_2Cl_2$ with 2 equiv of 1-MeC in H_2O (30 min, 45 °C), evaporation to dryness and recrystallization from an aqueous solution of $NaClO_4$ (20-fold excess, evaporation at 4 °C) produced **1b** as a yellow, microcrystalline material in 23% yield. Anal. Calcd for $PdC_{10}H_{20}N_8O_{10}Cl_2$: C, 20.37; H, 3.42; N, 19.00. Found: C, 20.70; H, 3.30; N, 18.90. The identity of the cations of **1b** and **1a** was confirmed by IR analysis.

[Pd(1-MeC)$_4$](NO$_3$)$_2$·2H$_2$O (2a). To a solution of *trans*-Pd(1-MeC)$_2$Cl$_2$ (1 mmol) in water (100 mL) were each added 2 equiv of $AgNO_3$ and 1-MeC with stirring. The pH of the mixture was raised from 4.5 to 7.5 by means of 1 N NaOH and the mixture kept at 40 °C for 18 h with daylight excluded. The sample was then brought to 22 °C, AgCl filtered off and the yellow solution concentrated to a 15-mL volume by rotary evaporation. Yellow, transparent cubes of **2a** were harvested in 56% yield after 10 days of slow evaporation. The crystals, which according to X-ray analysis contain 2 water molecules per heavy metal, lose water when kept in air. Dehydrated samples analyze without water. Anal. Calcd for $C_{20}H_{28}N_{14}O_{10}Pd$: C, 32.91; H, 3.87; N, 26.86. Found: C, 32.50; H, 3.70; N, 26.75.

Attempts to obtain a tris(1-methylcytosine) compound by reaction of *trans*-Pd(1-MeC)$_2$Cl$_2$ with 1 equiv of $AgNO_3$ and 1 equiv of 1-MeC failed and instead produced **2a** and the starting compound.

[Pd(1-MeC)$_4$]Cl$_2$·7H$_2$O (2b). A mixture of K_2PdCl_4 (0.74 mmol) and 1-MeC (3.7 mmol) in water (15 mL) was stirred for 5 h at 22 °C, the cloudy mixture filtered, and the solution concentrated to a 5-mL volume. Evaporation at 22 °C gave large, yellow crystals of **2b**, which rapidly lose water of crystallization when brought into the air. Only the first batch obtained (after 3 days) was free of starting material 1-MeC. Anal. Calcd for $C_{20}H_{42}N_{12}O_{11}Cl_2Pd$: C, 29.87; H, 5.26; N, 20.90. Found:[28] C, 29.70; H, 4.55; N, 21.15.

cis-[(NH$_3$)$_2$Pd(1-MeC$^-$)$_2$Pd(NH$_3$)$_2$](NO$_3$)$_2$·2H$_2$O (3). *trans*-$Pd(NH_3)_2Cl_2$ (1 mmol) was converted to the diaqua species by addition of $AgNO_3$ (2 mmol) (40 mL H_2O, 1 h, 22 °C, daylight excluded), AgCl was filtered off, and a solution of **1a** in water (50 mL) was added. The pH (3.70) was adjusted to 8 by means of 1 N NaOH. After 5 h at 22 °C (pH 6.2) the orange-yellow solution was concentrated to 20 mL and allowed to evaporate. After 8 days reddish brown, transparent crystals of **3** were isolated in 32% yield and briefly dried in air. Anal. Calcd for $C_{10}H_{28}N_{12}O_{10}Pd_2$: C, 17.42; H, 4.09; N, 24.39. Found: C, 17.35; H, 4.15; N, 23.60.

Pd(1-MeC$^-$)$_2$·4H$_2$O (4). A poorly soluble, orange-brown to pink product of composition Pd(1-MeC$^-$)$_2$·4H$_2$O (**4**) was obtained on various occasions (cf. text). Anal. Calcd for $C_{10}H_{20}N_6O_6Pd$: C, 28.15; H, 4.72; N, 19.69. Found: C, 28.60; H, 4.50; N, 19.55. The structure of this compound is unclear at present. According to ^{1}H NMR spectroscopy (Me$_2$SO-d_6), **4** contains 1-MeC$^-$ ligands.

[Pd(NH$_3$)(1-MeC)$_3$](NO$_3$)$_2$ (5). A 0.95-mmol sample of **1a** and 1 mmol of 1-MeC were dissolved in water (100 mL) and the yellow solution (pH 6.6) was kept at 40 °C for 68 h. After filtration of some **4**, the solution (pH 7) was concentrated to 20 mL and allowed to crystallize. After 5 days at 22 °C, yellowish white needles of **5** were isolated in 26% yield and dried in air. Anal. Calcd for $C_{15}H_{24}N_{12}O_9Pd$: C, 28.93; H, 3.88; N, 26.99. Found: C, 28.80; H, 3.85; N, 27.00.

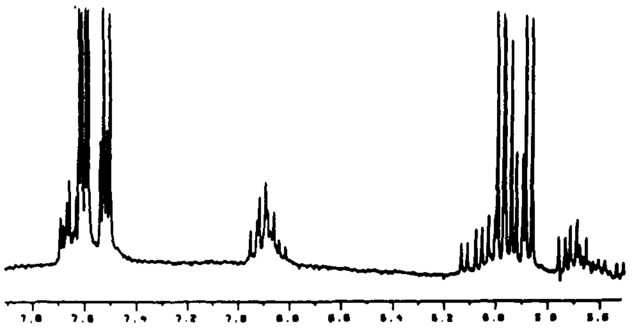

Figure 1. Low-field ^{1}H NMR spectrum (D_2O, pD 6.4) of products obtained from reaction of *trans*-$(NH_3)_2PdCl_2$ with 2 equiv of 1-MeC.

Instrumentation. ^{1}H NMR spectra were recorded on Bruker AM 300 and Bruker AC 200 FT NMR spectrometers. pD values were determined by use of a glass electrode and addition of 0.4 to the meter reading. IR spectra (KBr pellets) were taken on Perkin-Elmer 580 B and Bruker IFs 113v FT spectrometers, Raman spectra on a Coderg T 800 with argon (514.5 nm) or krypton laser (647.1 nm) excitation. The water content of **3** was established by thermogravimetry (Thermo 2000, Mettler).

X-ray Crystallography. The X-ray measurements of all compounds were carried out at room temperature on a Nicolet F3 single-crystal diffractometer using graphite-monochromated Mo Kα radiation. Crystal data and other parameters of data collections are given in Table I. The intensity data were corrected for Lorentz and polarization effects and for absorption by ψ-scan method (3). The structures were solved by Patterson method (SHELX-86)[29] and completed by Fourier techniques. The hydrogen atoms were located in difference maps. The non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were refined as isotropic in **1a**. In **2a** and **3**, the hydrogen atoms were riding with the non-hydrogen atom at a distance of 1.08 Å and constant U_{iso} = 0.05 Å^2. Both in **2a** and **3** one of the NO_3^- groups was partly disordered, with rotation about a N–O bond (**2a**) and the N atom (**3**), respectively. Attempts to find unique static disorder models for the disordered nitrates failed and gave unreasonable bond lengths and angles and poor contacts only. Anisotropic refinement was tried in every stage but did not produce reasonable results. Therefore the nitrates were refined as idealized rigid groups. In **3**, the hydrogen atoms of water molecule O8 could not be located. The SHELX-76[30] package was used for the calculations. Tables II–IV contain the atomic coordinates. The isotropic temperature factors were calculated according to $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*a_i a_j$. The scattering factors[31] for neutral atoms were used, and corrections for anomalous scattering[32] were applied to all atoms. The planes were calculated by using MPLN[33] and drawings were done by ORTEP[34] using a VAX 8650 computer.

Results and Discussion

Reaction of trans-(NH$_3$)$_2$PdCl$_2$ with 1-MeC. The reaction of *trans*-$(NH_3)_2PtCl_2$ with 1-MeC proceeds in a clean way, leading to both 1:1 and 2:1 compounds, viz. *trans*-[(NH$_3$)$_2$Pt(1-MeC)Cl]Cl and *trans*-[(NH$_3$)$_2$Pt(1-MeC)$_2$]Cl$_2$. ^{1}H NMR spectroscopic data for the two compounds (doublets for H5 and H6 in the case of the 1:1 complex, two doublets each of unequal intensities due to hindered rotation in the case of the 2:1 compound)[35] are consistent with expectation. In contrast, reaction of *trans*-$(NH_3)_2PdCl_2$ with 1-MeC (2 equiv, 40 °C, 18 h) is much more complex (Figure 1). In the aromatic region of the ^{1}H NMR spectrum (D_2O, pD 6.4) four groups of H5 and H6 resonances are to be distinguished which, from comparison with Pt(II)

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Table I. Crystal Data for **1a**, **2a**, and 3

	1a	**2a**	**3**
formula	$C_{10}H_{20}N_{10}O_8Pd$	$C_{20}H_{28}N_{14}O_{10}Pd{\cdot}2H_2O$	$C_{20}H_{24}N_{12}O_8Pd_2{\cdot}2H_2O$
fw	514.73	766.96	809.32
cryst size	0.30 × 0.20 × 0.12	0.3 × 0.15 × 0.10	0.4 × 0.3 × 0.15
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	6.804 (2)	9.138 (1)	10.015 (2)
b, Å	10.292 (2)	12.670 (3)	17.094 (3)
c, Å	12.952 (3)	14.137 (3)	14.216 (2)
α, deg	90	80.50 (2)	90
β, deg	102.05 (2)	74.15 (2)	101.72 (2)
γ, deg	90	87.89 (1)	90
V, Å^3	887.0 (4)	1552.9 (5)	2383.0 (9)
Z	2	2	4
d_{calc}, g cm^{-3}	1.84	1.50	1.91
d_{measd}, g cm^{-3}	1.89	...	1.92
μ(Mo Kα), cm^{-1}	11.0	6.9	16.8
F(000), e	488	716	1360
radiation	Mo Kα	Mo Kα	Mo Kα
λ, Å	0.71069	0.71069	0.71069
monochromator	graphite	graphite	graphite
scan	ω	ω	ω
scan width, deg	1	1	1
scan speed, deg min^{-1}	1.5–29.3	2.0–29.3	1.5–29.3
$2\theta_{max}$, deg	53	50	53
h,k,l range	+9,+13,±17	+11,±16,±17	+12,+21,±17
test reflcns	1,−2,−1 2,1,3 4,−3,−1	2,−1,2 3,−1,3 4,−1,2	1,−3,0 0,−5,5 −3,8,4
temp, °C	21	21	21
abs cor	none	none	empirical
rel transm	0.970–1.000	0.980–1.000	0.787–1.000
no. of reflcns measd	2112	6174	5409
no. of uniq. reflcns	1840	5388	5228
R_{int}	0.01	0.04	0.04
no. of obsd. reflcns ($I > 3\sigma(I)$)	1456	3682	2299
no. of params	173	502	291
R^a	0.022	0.058	0.059
$R_w{}^b$	0.024	0.059	0.061
$\Delta\rho_{fin}$(max/min), e Å^{-3}	+0.54/−0.35	+1.84/−0.84	+1.04/−0.99

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $R = [\sum w(||F_o| - |F_c||)^2/\sum wF_o{}^2]^{1/2}$ with $w = 1/\sigma^2(F_o)$.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) of **1a** with Esd's Given in Parentheses

atom	x/a	y/b	z/c	U_{eq}
Pd	0.0000 (0)	0.0000 (0)	0.0000 (0)	0.0270 (1)
N2	0.2374 (4)	0.0270 (2)	0.1233 (2)	0.037 (1)
N1	0.2548 (3)	0.2711 (2)	0.1727 (1)	0.028 (1)
C1	0.4082 (5)	0.2620 (3)	0.2369 (2)	0.041 (2)
C2	0.2170 (3)	0.1616 (2)	0.1188 (1)	0.027 (1)
O2	0.3157 (3)	0.0624 (1)	0.1194 (1)	0.040 (1)
N3	0.0622 (3)	0.1689 (1)	0.0656 (1)	0.025 (1)
C4	0.0431 (3)	0.2795 (2)	0.0636 (1)	0.030 (1)
N4	0.1944 (4)	0.2808 (3)	0.0133 (2)	0.045 (2)
C5	0.0040 (4)	0.3914 (2)	0.1158 (2)	0.036 (1)
C6	0.1506 (4)	0.3824 (2)	0.1704 (2)	0.033 (1)
N6	0.4002 (3)	0.3553 (2)	0.1337 (2)	0.042 (1)
O3	0.2687 (4)	0.3267 (2)	0.1812 (2)	0.071 (2)
O4	0.4734 (3)	0.2705 (2)	0.0878 (2)	0.064 (2)
O5	0.4522 (6)	0.4669 (3)	0.1331 (5)	0.146 (3)
H1	0.402 (5)	−0.343 (3)	−0.281 (3)	0.048 (10)
H2	0.373 (5)	−0.198 (4)	−0.288 (3)	0.053 (10)
H3	0.525 (6)	−0.245 (4)	−0.196 (3)	0.059 (11)
H4	−0.226 (5)	−0.213 (3)	0.011 (2)	0.034 (9)
H5	−0.259 (5)	−0.356 (4)	−0.017 (3)	0.048 (10)
H6	−0.063 (6)	−0.471 (3)	−0.115 (3)	0.048 (10)
H7	0.181 (5)	−0.458 (4)	−0.205 (3)	0.044 (9)
H8	0.218 (6)	0.012 (3)	0.177 (3)	0.050 (11)
H9	0.350 (9)	0.004 (4)	0.104 (5)	0.084 (17)
H10	0.237 (6)	−0.094 (4)	0.135 (3)	0.055 (13)

chemistry, are assigned to H6 of (1-MeC-*N*^{3})Pd (ca. 7.5–7.7 ppm), H5 of (1-MeC-*N*^{3})Pd (ca. 5.85–6.15 ppm), H6 of (1-MeC$^-$-*N*^{3},*N*^{4})Pd (ca. 6.8–7 ppm) and H5 of (1-MeC$^-$*N*^{3},*N*^{4})Pd (ca. 5.6–5.8 ppm). Resonances due to free 1-MeC are expected around 7.56 and 5.96 ppm, respectively, at the pD indicated. It was this complexity that initiated the work reported here. We assumed that loss or scrambling of ligands might occur and decided to study and characterize possible products.

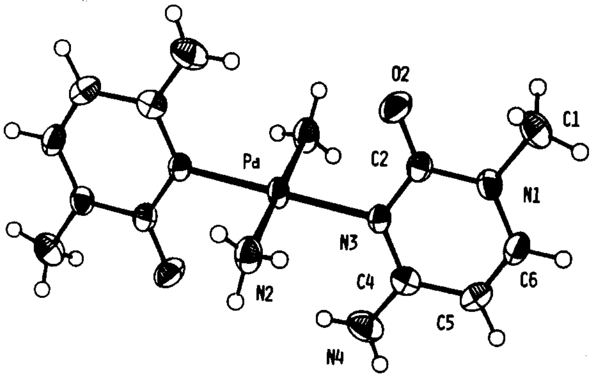

Figure 2. ORTEP diagram of the cation of *trans*-[Pd(NH$_3$)$_2$(1-MeC-*N*^{3})$_2$](NO$_3$)$_2$ (**1a**). The thermal ellipsoids for non-hydrogen atoms are drawn at the 50% probability level.

Characterization of *trans*-[Pd(NH$_3$)$_2$(1-MeC-*N*^{3})$_2$](NO$_3$)$_2$ (1a). Displacement of the Cl ligands of *trans*-Pd(NH$_3$)$_2$Cl$_2$ by water prior to reaction of 1-MeC permitted the isolation of **1a** in good yield. **1a** is isomorphous with the corresponding Pt compound.[36a] Figure 2 gives a view of the centrosymmetric cation. Selected

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(36) (a) Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *Inorg. Chem.* **1981**, *20*, 808. (b) Brown, B. E.; Lock, C. J. L. *Acta Cryst., Sect. C* **1988**, *C44*, 611.

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) (Except for Protons) for **2a**

atom	x/a	y/b	z/c	U_{eq}
Pd1	0.1673 (0)	0.3220 (0)	0.2811 (0)	0.0282 (3)
N31	0.3395 (7)	0.2636 (4)	0.3414 (4)	0.031 (3)
C41	0.4829 (9)	0.2450 (6)	0.2886 (6)	0.038 (5)
N41	0.5156 (8)	0.2596 (6)	0.1909 (5)	0.043 (4)
C51	0.5946 (10)	0.2100 (8)	0.3380 (6)	0.049 (5)
C61	0.5529 (11)	0.1943 (8)	0.4392 (7)	0.053 (5)
N11	0.4054 (8)	0.2112 (5)	0.4909 (5)	0.042 (4)
C11	0.3637 (12)	0.1874 (9)	0.5998 (6)	0.063 (7)
C21	0.2957 (9)	0.2435 (6)	0.4451 (5)	0.037 (4)
O21	0.1647 (6)	0.2567 (4)	0.4917 (4)	0.042 (3)
N32	0.1032 (7)	0.1699 (5)	0.2800 (4)	0.038 (4)
C42	0.0010 (9)	0.1105 (6)	0.3550 (6)	0.041 (5)
N42	−0.0665 (8)	0.1527 (6)	0.4359 (5)	0.049 (4)
C52	−0.0340 (11)	0.0065 (8)	0.3478 (8)	0.056 (6)
C62	0.0401 (13)	−0.0334 (8)	0.2650 (9)	0.068 (7)
N12	0.1433 (10)	0.0251 (6)	0.1891 (6)	0.060 (6)
C12	0.2247 (18)	−0.0177 (10)	0.1016 (9)	0.095 (10)
C22	0.1784 (11)	0.1309 (7)	0.1940 (7)	0.046 (5)
O22	0.2711 (7)	0.1840 (5)	0.1261 (4)	0.053 (4)
N33	−0.0166 (7)	0.3799 (5)	0.2344 (4)	0.039 (4)
C43	−0.0326 (10)	0.3882 (7)	0.1404 (6)	0.045 (5)
N43	0.0758 (10)	0.3498 (7)	0.0729 (5)	0.057 (5)
C53	−0.1654 (13)	0.4347 (8)	0.1192 (8)	0.060 (7)
C63	−0.2706 (14)	0.4710 (9)	0.1898 (10)	0.070 (8)
N13	−0.2556 (8)	0.4622 (6)	0.2837 (5)	0.050 (5)
C13	−0.3734 (13)	0.5025 (11)	0.3627 (10)	0.084 (10)
O23	−0.1183 (6)	0.4063 (4)	0.3947 (4)	0.045 (4)
C23	−0.1274 (9)	0.4166 (6)	0.3078 (6)	0.041 (5)
N34	0.2417 (7)	0.4743 (4)	0.2705 (4)	0.034 (4)
C44	0.2226 (8)	0.5302 (6)	0.3466 (6)	0.036 (4)
N44	0.1643 (8)	0.4811 (6)	0.4389 (4)	0.044 (4)
C54	0.2769 (11)	0.6440 (7)	0.3184 (5)	0.051 (6)
C64	0.3318 (11)	0.6794 (6)	0.2424 (6)	0.050 (5)
N14	0.3641 (8)	0.6259 (5)	0.1578 (4)	0.042 (4)
C14	0.4388 (14)	0.6743 (8)	0.0560 (7)	0.070 (7)
C24	0.3108 (9)	0.5220 (6)	0.1742 (6)	0.040 (4)
O24	0.3275 (7)	0.4713 (4)	0.1052 (4)	0.052 (4)
N1	0.3434 (9)	0.9644 (6)	0.3527 (6)	0.053 (5)
O1	0.3059 (8)	0.8702 (5)	0.3571 (5)	0.065 (5)
O2	0.2908 (8)	1.0086 (5)	0.4267 (5)	0.065 (5)
O3	0.4333 (9)	1.0123 (6)	0.2782 (5)	0.087 (6)
N2	0.9453 (9)	0.7153 (6)	0.1544 (6)	0.102 (4)
O4	1.0416 (12)	0.6675 (9)	0.0979 (7)	0.158 (5)
O5	0.9498 (15)	0.7114 (11)	0.2413 (7)	0.191 (6)
O6	0.8306 (14)	0.7494 (14)	0.1302 (11)	0.264 (10)
O7	0.2948 (16)	0.0441 (9)	0.8486 (8)	0.151 (9)
O8	0.8065 (10)	0.1652 (7)	0.1054 (7)	0.099 (6)
H1	0.173 (2)	0.055 (7)	0.867 (7)	
H2	0.283 (10)	0.129 (1)	0.829 (6)	
H3	0.771 (10)	0.083 (2)	0.117 (6)	
H4	0.846 (10)	0.200 (6)	0.028 (2)	
H11	0.410 (5)	0.263 (7)	0.170 (6)	
H21	0.614 (6)	0.220 (6)	0.151 (6)	
H31	0.708 (4)	0.188 (7)	0.300 (6)	
H41	0.607 (9)	0.176 (7)	0.500 (4)	
H51	0.457 (5)	0.223 (4)	0.618 (5)	
H61	0.342 (6)	0.108 (2)	0.642 (4)	
H71	0.263 (4)	0.235 (4)	0.620 (5)	
H12	−0.142 (8)	0.101 (6)	0.497 (4)	
H22	−0.070 (10)	0.237 (2)	0.406 (6)	
H32	−0.113 (8)	−0.033 (6)	0.415 (3)	
H42	0.049 (10)	−0.114 (3)	0.249 (6)	
H52	0.112 (3)	−0.021 (5)	0.092 (5)	
H62	0.267 (6)	−0.098 (2)	0.113 (5)	
H72	0.299 (5)	0.028 (4)	0.036 (3)	
H13	0.031 (9)	0.351 (7)	0.009 (4)	
H23	0.183 (5)	0.312 (6)	0.075 (7)	
H33	−0.183 (10)	0.434 (7)	0.047 (3)	
H43	−0.371 (6)	0.510 (6)	0.175 (6)	
H53	−0.452 (6)	0.513 (5)	0.317 (4)	
H63	−0.425 (7)	0.451 (4)	0.432 (2)	
H73	−0.349 (8)	0.580 (2)	0.379 (4)	
H14	0.149 (10)	0.529 (6)	0.497 (4)	
H24	0.146 (10)	0.399 (2)	0.432 (6)	
H34	0.254 (10)	0.658 (7)	0.394 (2)	
H44	0.550 (10)	0.716 (7)	0.122 (6)	
H54	0.538 (4)	0.633 (5)	0.019 (4)	
H64	0.475 (7)	0.744 (3)	0.079 (5)	
H74	0.371 (6)	0.700 (5)	0.005 (4)	

Table IV. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) (Except for Protons) for **3** with Esd's Given in Parentheses

atom	x/a	y/b	z/c	U_{eq}
Pd1	−0.1101 (1)	0.2157 (0)	0.1164 (0)	0.0342 (7)
Pd2	0.1143 (1)	0.2079 (0)	0.2862 (0)	0.0335 (6)
N1	−0.0629 (15)	0.3045 (8)	0.0316 (9)	0.057 (9)
N2	−0.2331 (14)	0.2919 (9)	0.1709 (8)	0.057 (9)
N3	0.2513 (14)	0.2720 (8)	0.2309 (8)	0.050 (8)
N4	0.0912 (13)	0.3032 (7)	0.3697 (9)	0.046 (8)
N31	0.0111 (11)	0.1408 (7)	0.0607 (7)	0.031 (6)
C41	0.1235 (14)	0.1028 (9)	0.1179 (9)	0.034 (6)
N41	0.1579 (13)	0.1183 (8)	0.2103 (8)	0.042 (8)
C51	0.1931 (14)	0.0471 (8)	0.0714 (10)	0.036 (8)
C61	0.1621 (15)	0.0381 (9)	−0.0234 (11)	0.042 (8)
N11	0.0600 (12)	0.0788 (7)	−0.0755 (7)	0.036 (9)
C11	0.0310 (20)	0.0732 (10)	−0.1810 (10)	0.056 (12)
C21	−0.0205 (16)	0.1292 (9)	−0.0334 (10)	0.042 (10)
O21	−0.1221 (11)	0.1596 (6)	−0.0831 (7)	0.047 (7)
N32	−0.0216 (11)	0.1437 (7)	0.3422 (8)	0.036 (8)
C42	−0.1385 (15)	0.1151 (9)	0.2856 (10)	0.036 (8)
N42	−0.1718 (12)	0.1314 (8)	0.1935 (8)	0.039 (7)
C52	−0.2284 (16)	0.0662 (10)	0.3278 (13)	0.052 (10)
C62	−0.2001 (18)	0.0585 (9)	0.4280 (11)	0.048 (10)
N12	−0.0837 (13)	0.0894 (7)	0.4806 (8)	0.039 (8)
C12	−0.0556 (17)	0.0864 (11)	0.5856 (9)	0.052 (10)
C22	0.0110 (16)	0.1273 (9)	0.4362 (9)	0.037 (9)
O22	0.1190 (11)	0.1521 (7)	0.4877 (6)	0.050 (7)
N5	0.2009 (20)	0.7268 (12)	0.5247 (12)	0.104 (7)
O1	0.2059 (17)	0.7032 (10)	0.6070 (11)	0.101 (5)
O2	0.2920 (19)	0.7667 (10)	0.5037 (14)	0.120 (6)
O3	0.1069 (22)	0.7084 (12)	0.4575 (15)	0.156 (8)
N6	0.0655 (14)	0.4726 (9)	0.1945 (8)	0.182 (13)
O4	−0.0235 (14)	0.4343 (9)	0.2202 (8)	0.205 (12)
O5	0.0689 (14)	0.5434 (9)	0.2050 (8)	0.170 (9)
O6	0.1520 (14)	0.4399 (9)	0.1593 (8)	0.233 (14)
O7	0.5454 (29)	0.2131 (13)	0.2940 (23)	0.185 (23)
O8	0.5518 (16)	0.0597 (13)	0.0763 (15)	0.145 (11)
H1	−0.0218 (15)	0.3031 (8)	−0.0329 (9)	
H2	−0.0262 (15)	0.3560 (8)	0.0729 (9)	
H3	−0.1729 (15)	0.3061 (8)	0.0126 (9)	
H4	−0.2105 (14)	0.3520 (9)	0.1917 (8)	
H5	−0.2595 (14)	0.2603 (9)	0.2303 (8)	
H6	−0.3176 (14)	0.2900 (9)	0.1102 (8)	
H7	0.1427 (14)	0.2813 (8)	0.2096 (8)	
H8	0.2939 (14)	0.2632 (8)	0.1677 (8)	
H9	0.2981 (14)	0.3226 (8)	0.2698 (8)	
H10	0.0658 (13)	0.2918 (7)	0.4387 (9)	
H11	0.0366 (13)	0.3543 (7)	0.3379 (9)	
H12	0.1995 (13)	0.3131 (7)	0.3789 (9)	
H13	0.220 (13)	0.071 (6)	0.246 (10)	
H14	0.2755 (0)	0.0124 (0)	0.1125 (0)	
H15	0.2154 (0)	0.0023 (0)	−0.0603 (0)	
H16	−0.0765 (20)	0.0649 (10)	−0.2092 (10)	
H17	0.0809 (20)	0.0170 (10)	−0.1699 (10)	
H18	0.0748 (20)	0.1068 (10)	−0.2315 (10)	
H19	−0.280 (3)	0.125 (9)	0.165 (10)	
H20	−0.3170 (0)	0.0362 (0)	0.2849 (0)	
H21	−0.2659 (0)	0.0277 (0)	0.4624 (0)	
H22	−0.0178 (17)	0.1181 (11)	0.6513 (9)	
H23	0.0060 (17)	0.0348 (11)	0.5834 (9)	
H24	−0.1601 (17)	0.0693 (11)	0.5829 (9)	
H25	0.448 (8)	0.242 (8)	0.273 (10)	
H26	0.518 (21)	0.170 (10)	0.293 (14)	

interatomic distances and angles are listed in Table V. The cation geometry is very similar to that of the corresponding Pt complex (NO_3^- salt,[36a] ClO_4^- salt[36b]) and, as far as the 1-MeC geometry is concerned, also to that of *trans*-$Pd(1\text{-}MeC)_2Cl_2$.[15] Dihedral angles between 1-MeC and the metal coordination plane in the three compounds are 78.4° (**1a**), 78.2° and 74.9° (Pt analogues), and 84.1° ($PdCl_2$ complex). The cytosine rings are coplanar. The packing (cf. supplementary material) of cations and nitrate anions in **1a** is similar to that of *trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2](NO_3)_2$[36a] in that nitrates are intercalated between 1-MeC planes of adjacent cations.

Table V. Selected Interatomic Distances (Å) and Angles (deg) in **1a** and **2a**

Compound 1a			
Pd1–N2	2.039 (3)	N2–Pd1–N3	90.6 (1)
Pd1–N3	2.019 (2)		
N1–C1	1.467 (3)	C2–N1–C6	121.9 (2)
N1–C2	1.377 (3)	N1–C2–N3	116.9 (2)
C2–O2	1.224 (3)	C2–N3–C4	121.4 (2)
C2–N3	1.376 (3)	N3–C4–C5	120.5 (2)
N3–C4	1.347 (3)	C4–C5–C6	117.8 (3)
C4–N4	1.328 (3)	C5–C6–N1	121.4 (3)
C4–C5	1.406 (4)	C2–N1–C1	117.7 (2)
C5–C6	1.340 (4)	C6–N1–C1	120.3 (2)
C6–N1	1.352 (3)	N1–C2–O2	121.3 (2)
		N3–C2–O2	121.8 (2)
		N3–C4–N4	119.2 (3)
		C5–C4–N4	120.3 (3)
Compound 2a			
Pd–N31	2.046 (7)	N31–Pd–N32	90.4 (3)
Pd–N32	2.035 (7)	N31–Pd–N33	174.5 (3)
Pd–N33	2.037 (7)	N31–Pd–N34	90.1 (3)
Pd–N34	2.040 (7)	N32–Pd–N33	89.7 (3)
		N32–Pd–N34	175.4 (3)
		N33–Pd–N34	90.2 (3)

	ring 1	ring 2	ring 3	ring 4
N1–C1	1.46 (1)	1.44 (2)	1.47 (2)	1.46 (1)
N1–C2	1.35 (1)	1.40 (1)	1.39 (1)	1.38 (1)
C2–O2	1.22 (1)	1.22 (1)	1.24 (1)	1.38 (1)
C2–N3	1.39 (1)	1.38 (1)	1.37 (1)	1.38 (1)
N3–C4	1.36 (1)	1.35 (1)	1.36 (1)	1.35 (1)
C4–N4	1.31 (1)	1.33 (1)	1.32 (1)	1.32 (1)
C4–C5	1.41 (1)	1.39 (1)	1.42 (2)	1.43 (1)
C5–C6	1.35 (1)	1.35 (2)	1.32 (2)	1.32 (1)
C6–N1	1.38 (1)	1.36 (1)	1.35 (2)	1.37 (1)
C2–N1–C6	122 (1)	120 (1)	121 (1)	120 (1)
N1–C2–N3	117 (1)	117 (1)	118 (1)	119 (1)
C2–N3–C4	122 (1)	122 (1)	120 (1)	121 (1)
N3–C4–C5	117 (1)	121 (1)	120 (1)	121 (1)
C4–C5–C6	118 (1)	118 (1)	120 (1)	118 (1)
C5–C6–N1	120(1)	123 (1)	121 (1)	122 (1)
C2–N1–C1	119 (1)	117 (1)	118 (1)	118 (1)
C6–N1–C1	119 (1)	121 (1)	121 (1)	121 (1)
N1–C2–O2	122 (2)	121 (1)	120 (2)	120 (2)
N3–C2–O2	121 (1)	122 (1)	122 (1)	121 (1)
N3–C4–N4	119 (1)	121 (1)	118 (1)	119 (1)
C5–C4–N4	121 (1)	121 (1)	122 (1)	120 (1)

IR and Raman spectra (solid state) of **1a** and the Pt(II) analogue show a high degree of similarity and are, over a wide range, virtually superimposable. Only in the low-frequency region (skeletal modes) are there minor differences. The established[37] patterns of IR and Raman bands of 1-MeC with Pt binding via N3 are confirmed in the case of the Pd compound **1a** (e.g. prominent Raman modes at 643, 795, 837, 1162, and 1250 cm^{-1}).

Solution Behavior of 1a. Recrystallization of **1a** from H_2O is accompanied by formation of several byproducts. Their formation is also evident from ^1H NMR spectra. Immediately after **1a** is dissolved in D_2O (pD 6.4), two sets of 1-MeC (H6, 7.62 and 7.65 ppm; H5, 5.97 and 6.03 ppm; CH_3, 3.42 and 3.45 ppm) and NH_3 resonances (3.06 and 3.10 ppm) of relative intensities 1:8 are observed which are assigned to two rotamers (head–head and head–tail) with the latter believed to be the preferred species. With time, and especially on slight warming (1 h, 40 °C), the spectrum changes and five sets of H5 and H6 1-MeC doublets are observed then (Figure 3). There is no indication for any N3, N4-bridged 1-MeC$^-$ species in solution, but a poorly soluble orange-pink product **4** of composition Pd(1-MeC$^-$)$_2$ precipitates from solution, which, according to elemental analysis, has lost the ammonia ligands completely. The slight rise in pD (0.4 units) is consistent with release of NH_3. Resonances due to free 1-MeC are not unambiguously identified. This suggests that the multiplicity of resonances could arise from species formed by loss and addition of NH_3 as well as trans → cis isomerization reactions. Different rotamers could give rise to additional resonances.

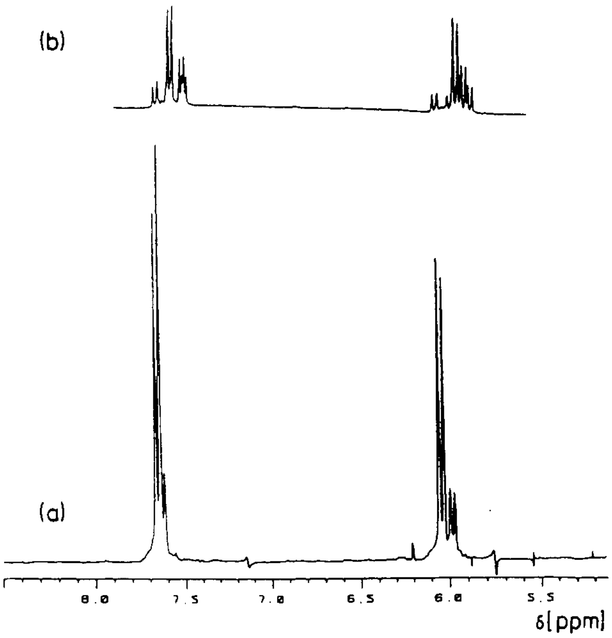

Figure 3. Low-field sections of ^1H NMR spectra of **1a** (a) immediately after dissolving it in D_2O (pD 6.4) and (b) after 1 h at 40 °C (pD 6.25).

Deprotonation of the exocyclic $NH_2(4)$ groups of the 1-MeC ligands of **1a** does not occur up to pH 14. However, addition of acid (DNO_3, pD 1) causes rapid cleavage of the Pd–(1-MeC) bond and appearance of resonances due to protonated 1-MeC.

[Pd(NH$_3$)(1-MeC)$_3$](NO$_3$)$_2$ (5). A yellowish white, crystalline compound of composition $[Pd(NH_3)(1\text{-}MeC)_3](NO_3)_2$ (**5**) was isolated from a solution containing **1a** and 1-MeC. Unlike the corresponding Pt complex,[38] which is inert and displays two sets of 1-MeC resonances in a 2:1 ratio in the ^1H NMR spectrum corresponding to the two rings trans to each other and the ring trans to NH_3, the ^1H NMR spectrum of **5** is considerably more complex. Immediately after the compound is dissolved the spectrum displays four H6 and five H5 1-MeC doublets. There is a further change with time that involves no free 1-MeC, however. It appears that initially there is formation of **1a** and **2a** according to

$$2\,\mathbf{5} \rightarrow \mathbf{1a} + \mathbf{2a}$$

as concluded from the appearance of resonances due to **2a**. This process could account for five signal sets. Since **1a** further changes (cf. above), the complexity of the spectrum could be explained in principle.

[Pd(1-MeC-*N*^{3})$_4$](NO$_3$)$_2$·2H$_2$O (2a) was prepared in good yield from *trans*-$[Pd(1\text{-}MeC\text{-}N^3)_2(H_2O)_2]^{2+}$ and 1-MeC. Alternatively, it was also obtained from *trans*-$[Pd(NH_3)_2(H_2O)_2]^{2+}$ and excess 1-MeC in low yield (20%) along with **1a**. Reaction of K_2PdCl_4 with an excess of 1-MeC gave the corresponding chloride salt **2b**. The tetrakis(1-methylcytosine) complex represents one of the few examples of d^8 metal ions carrying four nucleobases simultaneously.[9,11,39] One of these, a Pd(II) complex with four cytidine ligands,[9] has been observed to form on recrystallization of $[Pd(mit)_2(cyd)_2]Cl_2$ (mit = 1-methylimidazole-2-thiol, cyd = cytidine) from an ethanol solution on addition of diethyl ether.

Figure 4 provides a view of the cation of **2a**. Selected bond lengths and angles are included in Table V. As with **1a**, binding of the 1-MeC ligands is through N3. The four bases are arranged in a way that adjacent ones are oriented head-to-tail with respect to each other. As a consequence, the space above and below the Pd is shielded by two O2 oxygens, which are trans to each other and by two $NH_2(4)$ groups, which are trans to each other as well.

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[37] Faggiani, R.; Lippert, B.; Lock, C. J. L. *Inorg. Chem.* **1982**, *21*, 3210.

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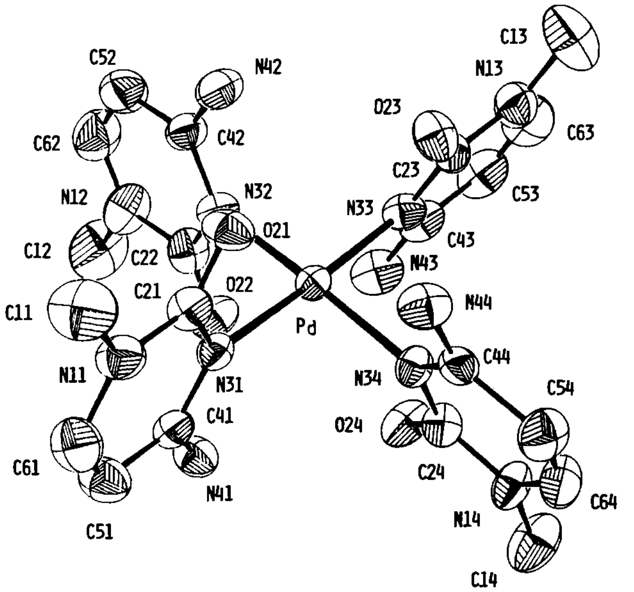

Figure 4. ORTEP diagram of the cation of $[Pd(1\text{-}MeC\text{-}N^3)_4](NO_3)_2{\cdot}2H_2O$ (**2a**).

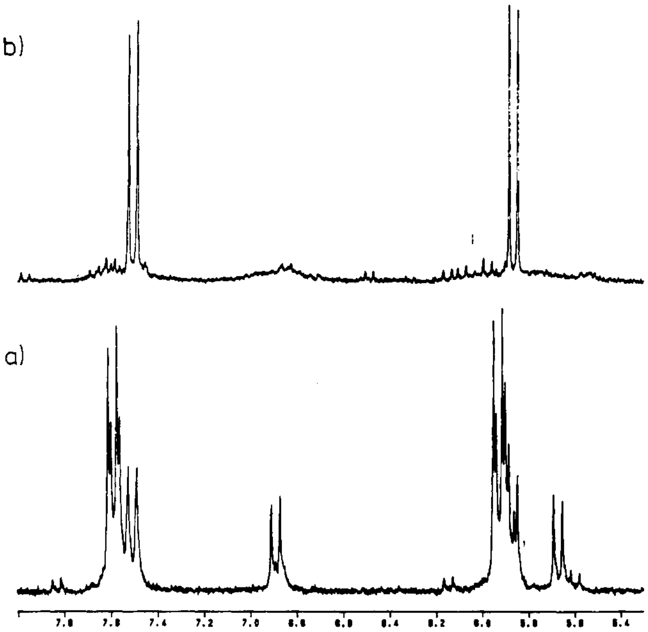

Figure 5. Low-field sections of ^1H NMR spectra of (a) *trans*-$[Pd(1\text{-}MeC)_2(D_2O)_2]^{2+}$ (D_2O, pD 2.3) immediately after filtration of AgCl and (b) the solution used for spectrum a after addition of NaOD (pD 5.3).

The 1-MeC rings form large dihedral angles with the PdN_4 coordination plane (85.7–103.8°, cf. supplementary material). There are no unusual structural features in the 1-MeC rings. The packing diagram is given in the supplementary material.

In the Raman spectrum (solid state) of **2a**, some of the ring modes are split (e.g. intense ring stretch at 1252 and 1275 cm^{-1}). This is probably due to vibrational coupling because it is not observed in solution (e.g. single band at 1263 cm^{-1}).

In D_2O, **2a** appears to be inert at neutral pH. There is no indication of deprotonation of $NH_2(4)$ groups up to pH 13. In DNO_3 acidic solution (pD 1–3.5), partial decomposition occurs with formation of $1\text{-}MeCD^+$.

Figure 6. IR absorptions (KBr) of **1a** (top) and of **3** (bottom) in the double-bond stretching region.

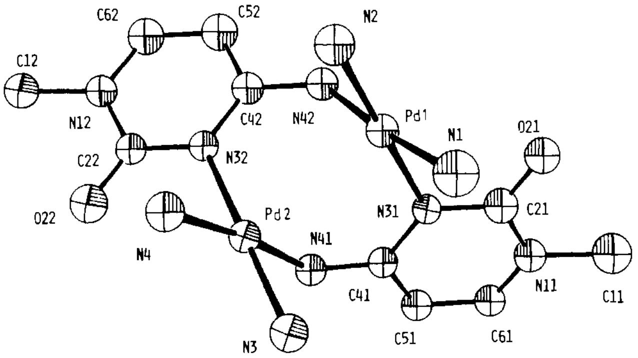

Figure 7. ORTEP diagram of the dinuclear cation of *cis*-$[(NH_3)_2Pd(1\text{-}MeC\text{-}N^3,N^4)_2Pd(NH_3)_2](NO_3)_2{\cdot}2H_2O$ (**3**).

***trans*-$[Pd(1\text{-}MeC)_2(H_2O)_2]^{2+}$.** Removal of the Cl ligands from *trans*-$Pd(1\text{-}MeC\text{-}N^3)_2Cl_2$ by $AgNO_3$ treatment yields the aqua species and its hydroxo derivatives, respectively. The ^1H NMR spectrum of the product (D_2O, pD 2.3) displays seven sets of 1-MeC resonances, four of which are due to N3-bound ligand. In addition, two sets of resonances due to anionic $1\text{-}MeC^-$ carrying Pd at both N3 and N4 are detected as well as a set of free $1\text{-}MeCH^+$ resonances (Figure 5). The spectrum simplifies greatly when the pD is raised to 5.3. The major species present then is **2a** as confirmed by isolating the product on a preparative scale. Formation of the tetrakis (1-methylcytosine) complex **2a** obviously is according to

$$trans\text{-}[Pd(1\text{-}MeC)_2(H_2O)_2]^{2+} \rightarrow \underset{\mathbf{2a}}{\tfrac{1}{2}[Pd(1\text{-}MeC)_4]^{2+}} + \tfrac{1}{2}[Pd(H_2O)_4]^{2+}$$

but we are presently unable to unambiguously rationalize the behavior of *trans*-$[Pd(1\text{-}MeC)_2(H_2O)_2]^{2+}$ in moderately acidic solution.

When the pH of an aqueous solution of *trans*-$[Pd(1\text{-}MeC)_2(H_2O)_2]^{2+}$ is raised to ca. 12, there is almost quantitative formation of $Pd(1\text{-}MeC^-)_2$ (**4**).

Formation and Characterization of *cis*-$[Pd_2(NH_3)_4(1\text{-}MeC^-\text{-}N^3,N^4)_2](NO_3)_2{\cdot}2H_2O$ (3). Reaction of **1a** with *trans*-$[Pd(NH_3)_2(H_2O)_2](NO_3)_2$ yielded a crystalline compound of analytical composition $Pd(NH_3)_2(1\text{-}MeC^-)NO_3{\cdot}H_2O$. The IR spectrum of this compound **3** was virtually superimposable with that of the previously described dinuclear complex *cis*-$[(NH_3)_2Pt(1\text{-}MeC^-\text{-}N^3,N^4)_2Pt(NH_3)_2](NO_3)_2$[40] with two head–tail oriented anionic cytosine ligands. In particular, the double-bond stretching region of the IR (Figure 6) was very useful in differentiating between N3-bound 1-MeC and N3,N4-bridging $1\text{-}MeC^-$.[41] In the Raman spectrum (solid state) intense ring modes occur at 808 and 1248 cm^{-1}. The ^1H NMR spectrum (D_2O, pD 6.5) of **3** unambiguously confirmed N3,N4-bridging $1\text{-}MeC^-$ with doublets at 6.91 (H6) and 5.71 ppm (H5), $^3J = 7.5$ Hz, and a singlet (CH_3) at 3.28 ppm. The crystal structure analysis of **3** established that the two $1\text{-}MeC^-$ ligands indeed are head-to-tail

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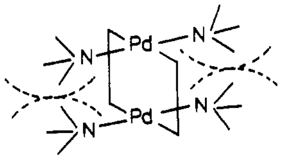
Table VI. Selected Interatomic Distances (Å) and Angles (deg) in 3

Pd1-Pd2	2.948 (1)	N1-Pd1-N2	88.8 (6)
Pd1-N1	2.052 (13)	N1-Pd1-N31	90.6 (5)
Pd1-N2	2.050 (13)	N2-Pd1-N31	179.3 (5)
Pd1-N31	2.033 (11)	N1-Pd1-N42	175.3 (5)
Pd1-N42	1.984 (13)	N2-Pd1-N42	92.0 (5)
		N31-Pd1-N42	92.0 (5)
		C21-N31-Pd1	117 (1)
		C41-N31-Pd1	122 (1)
Pd2-N3	2.035 (13)	N3-Pd2-N4	87.7 (5)
Pd2-N4	2.056 (11)	N3-Pd2-N32	179.6 (3)
Pd2-N32	2.032 (12)	N4-Pd2-N4	92.2 (5)
Pd2-N41	1.972 (13)	N3-Pd2-N41	88.0 (5)
		N4-Pd2-N41	173.8 (5)
		N32-Pd2-N41	92.0 (5)
		C22-N32-Pd2	117 (1)
		C42-N32-Pd2	122 (1)

	ring 1	ring 2		ring 1	ring 2
N1-C1	1.47 (2)	1.46 (2)	C2-N1-C6	122 (1)	121 (1)
N1-C2	1.39 (2)	1.40 (2)	N1-C2-N3	119 (1)	120 (1)
C2-O2	1.23 (2)	1.25 (2)	C2-N3-C4	121 (1)	121 (1)
C2-N3	1.33 (2)	1.34 (2)	N3-C4-C5	117 (1)	120 (1)
N3-C4	1.41 (2)	1.37 (2)	C4-C5-C6	121 (1)	118 (2)
C4-N4	1.32 (2)	1.31 (2)	C5-C6-N1	120 (1)	120 (2)
C4-C5	1.42 (2)	1.45 (2)	C2-N1-C1	118 (2)	118 (1)
C5-C6	1.33 (2)	1.40 (2)	C6-N1-C1	120 (1)	120 (1)
C6-N1	1.33 (2)	1.36 (2)	N1-C2-O2	121 (2)	119 (1)
			N3-C2-O2	120 (1)	121 (1)
			N3-C4-N4	120 (1)	122 (1)
			C5-C4-N4	123 (1)	119 (1)

and that the ammonia ligands are arranged cis. Figure 7 illustrates the dinuclear cation. Bond lengths and angles of the cation are listed in Table VI, the packing diagram is deposited as supplementary material. 3 is isomorphous with the Pt complex.[40] The geometry of the cation of 3 is very similar to that of the corresponding Pt(II) complex, which has been described in detail.[40] Differences refer, for example, to the metal–metal separation within the cation, which is significantly shorter in the case of Pd(II) (2.950 (2) Å vs 2.981 (2) Å) and to the dihedral angle between the metal planes (31.5° in 3 vs 34° in the Pt compound). Unlike the Pt(II) complex, which can be oxidized to the diplatinum(III) derivative, oxidation of 3 by means of Ce(IV) is not accomplished. This finding thus parallels previous observations.[19,42]

Trans → Cis Isomerization Leading to 3. Certainly *the* most unusual feature about 3 is its formation from two *trans*-$(NH_3)_2Pd^{II}$ entities. While from model building it is evident that a dinuclear complex with two *trans*-$(NH_3)_2Pd^{II}$ moieties is unlikely to be formed for steric reasons (structure I), there is no immediate explanation why the head–tail dinuclear complex is formed rather than a head–head isomer. Another important aspect of the formation of 3 is that N4 deprotonation, despite the high pK_a of ca. 16.7[43] of the amino group of the free ligand, takes place rather easily at pH 8. It again supports previous comments[14] on this topic.



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Conclusion. *trans*-$Pd(NH_3)_2Cl_2$ and its hydrolysis products interact with the model nucleobase 1-MeC in a complicated and rather unpredictable way. The multiplicity of species formed (cf. Figure 1) is not fully accounted for by the compounds prepared and described in this paper. While the compounds formed in solution are inert on the NMR time scale, the system as a whole is quite labile, certainly much more so than the Pt(II) system. It is also evident that several products with N3,N4-bridged 1-MeC$^-$ are possible and formed, not just the isolated *head–tail* dinuclear complex 3.

Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft (DFG) and by the Fonds der Chemischen Industrie. We thank O. Renn for the ^{1}H NMR spectra.

Supplementary Material Available: Listings of thermal parameters and least-squares planes and deviations of atoms and figures showing packing diagrams and Raman spectra of **2a** (12 pages); listings of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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