Discussion

It seems likely that when a solution containing the equilibrium mixture $[RhCl(COCH_3)L_3]^+ \rightleftarrows [RhCl(CH_3)(CO)L_3]^+$ is exposed to air, the dimethylphenylphosphine ligand trans to methyl dissociates and is oxidized irreversibly (Scheme I). The five-coordinate cation $[RhCl(CH_3)(CO)L_2]^+$ so formed might reasonably be expected to dimerize to give a dicationic di-μ-chloro complex containing six-coordinate rhodium(III), and this in turn could undergo methyl migration to give a dinuclear acetyl complex **2** containing five-coordinate rhodium(III). The observed tri-μ-chloro complex **1** presumably is formed by addition of Cl^- to **2**, the chloride ion probably being derived either from that eliminated on reaction of $RhCl_2(COCH_3)L_3$ with NH_4PF_6 or from the dichloromethane solvent. The latter source is a possibility in view of the unexpected finding of 1,2-dichloroethane in crystals of **1** (R = CH_3) grown from dichloromethane/methanol. Although we have not been able to isolate the di-μ-chloro complex **2**, Clark and Reimer[26] have reported the formation of the analogous di-μ-bromo complex $[Rh_2Br_2(COCH_3)_2L_4](PF_6)_2$ by treatment of 1 mol of $RhBr_2(CH_3)(CO)L_2$ with 1 mol of $AgPF_6$. However, the reported IR (C=O) and ^1H NMR data are sufficiently similar to those for our tri-μ-chloro complex as to suggest that the compound may in fact be the corresponding tri-μ-bromo complex, formed by the reaction

$$2RhBr_2(CH_3)(CO)L_3 + AgPF_6 \rightarrow [Rh_2Br_3(COCH_3)_2L_4]PF_6 + AgBr$$

Acknowledgment. We thank Dr P. A. Tucker for helpful discussion.

Registry No. **1**·$0.5C_2H_4Cl_2$, 75149-77-8; **2**, 75149-79-0; $RhCl_2(COCH_3)L_3$, 22605-70-5; $RhCl_2(COC_2H_5)L_3$, 22605-71-6; $[RhCl(C_2H_4)_2]_2$, 12081-16-2; acetyl chloride, 75-36-5.

Supplementary Material Available: Listings of details of data collection (Table I), calculated phenyl hydrogen atom coordinates and isotropic thermal parameters (Table II), structure factor amplitudes (Table III), and bond distances and interbond angles of the phenyl rings (Table IV) (23 pages). Ordering information is given on any current masthead page.

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[26] Clark, H. C.; Reimer, K. J. *Inorg. Chem.* **1975**, *14*, 2133–2139.

Contribution from the Institute for Materials Research, McMaster University, Hamilton, Ontario, L8S 4M1, Canada, and the Institute for Inorganic Chemistry, Technical University of Munich, 8046 Garching, Federal Republic of Germany

Crystal Structures of Two Crystalline Forms of Chloro-*cis*-diammine(1-methylcytosine-N^3)platinum(II) Nitrate, $[PtCl(NH_3)_2(C_5H_7N_3O)](NO_3)$, and Their ^1H NMR, IR, and Raman Spectra

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Chloro-*cis*-diammine(1-methylcytosine-N^3)platinum(II) nitrate, $[PtCl(NH_3)_2(C_5H_7N_3O)](NO_3)$, can be obtained in two monoclinic crystal forms: $P2_1/c$, a = 8.143 (2) Å, b = 6.899 (1) Å, c = 21.434 (3) Å, β = 91.27 (2)°, Z = 4; $C2/c$, a = 13.155 (6) Å, b = 9.754 (5) Å, c = 19.097 (7) Å, β = 99.70 (3)°, Z = 8. Data were collected for both crystals with use of Mo Kα radiation and a Syntex $P2_1$ diffractometer. The crystal structures were determined by standard methods; that of the $P2_1/c$ crystal was refined to R_1 = 0.035 and R_2 = 0.040 on the basis of 3018 reflections and that of the $C2/c$ crystal to R_1 = 0.047 and R_2 = 0.064 on the basis of 1700 reflections. The cation, in both crystals, has a normal structure and bond lengths (Pt–N(ammonia) = 2.04 (1)–2.053 (8) Å; Pt–N(3) = 2.026 (6), 2.06 (1) Å; Pt–Cl = 2.299 (2), 2.300 (2) Å). Both crystals contain a unit composed of two cations and two nitrate ions, both cations being hydrogen bonded to the same oxygen atom of a nitrate group through a proton on 4-NH_2 of the cytosine ring. Thus both nitrate ions can be considered as bridging the two cations. The principal difference in the crystal packing is that in the $P2_1/c$ structure this two cation–two anion unit is essentially planar, whereas in the $C2/c$ structure it is bent about the nitrate–nitrate axis. ^1H NMR spectra of the two compounds in D_2O reveal a fast exchange of the C(5) proton of the 1-methylcytosine ligand with deuterium ion upon heating. The corresponding C(5) deuterated 1-methylcytosine complexes have been isolated and studied by infrared spectroscopy.

Introduction

cis-Dichlorodiammineplatinum(II) is a useful anticancer agent[2–4] and is used in the treatment of testicular cancer.[4,5] The drug's mode of action has been postulated to involve cross-linking of the two strands of DNA, thus interfering with replication, and there is experimental evidence that, in vivo, the ability of *cis*-dichlorodiammineplatinum(II) to cross-link DNA is very much greater than that of *trans*-dichlorodiammineplatinum(II), which has no anticancer activity.[6]

We have been studying the interaction of *cis*-dichlorodiammineplatinum(II) with various DNA bases in order to investigate the stereochemistry of the interactions, and we routinely use X-ray crystallography to characterize the products. It has been shown that, in vitro, the platinum complex interacts preferentially with the guanine- plus cytosine-rich areas of DNA,[7] and we have obtained and examined a crystalline product of the type $[Pt(NH_3)_2(9\text{-ethylguanine})(1\text{-methylcytosine})](ClO_4)_2$.[8] In order to make these mixed complexes, it is necessary to make products in which one chlorine ion of *cis*-$PtCl_2(NH_3)_2$ has been replaced by a DNA base. Few, if any, of these complexes had been adequately characterized although products in which one chloride ion of K_2PtCl_4 had been replaced by a DNA base have been described.[9,10] In addition, complexes with one base attached

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[1] (a) Technical University of Munich. (b) McMaster University.

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0020-1669/81/1320-0335$01.00/0

to the *trans*-dichloro(organic sulfoxide-*S*)platinum(II) moiety have been described.[11-13] In preparing the guanine–cytosine complex referred to above,[8] we have prepared and characterized chloro-*cis*-diammine(1-methylcytosine-N^3)platinum(II) nitrate. It exists in two different crystal forms with different space groups but, as expected, in a single form in solution. In D_2O solution the C(5) proton of the coordinated 1-methylcytosine ligand is exchanged against a deuterium ion when the complex is heated. We describe the work here.

Experimental Section

Chloro-*cis*-diammine(1-methylcytosine-N^3)platinum(II) nitrate, *cis*-$[PtCl(NH_3)_2(C_5H_7N_3O)]NO_3$, was prepared in two ways described subsequently. Usually a mixture of forms A (needles, space group $P2_1/c$) and B (roughly cubic parallelepipeds, space group $C2/c$) was obtained and the crystals were separated by hand. It appeared that temperature and slowness of the crystallization process were the important parameters in deciding which product was formed predominantly. Rapid cooling and fast evaporation at room temperature (large surface) yielded predominantly or even exclusively the A product, whereas slow evaporation at +4–+7 °C gave B as the major product. Addition of crystals of either A or B to a concentrated solution of the compound and subsequent cooling yielded the desired product in high yield.

Ways of Preparation. (a) *cis*-$Pt(NH_3)_2Cl_2$ (0.6 g) was reacted with 1 equiv of $AgNO_3$ in water (0.338 g, 30 mL). The precipitated silver chloride was removed by filtration, and the resulting solution was reacted with 1-methylcytosine (0.25 g) in water for 24 h at 45 °C. The resultant solution was then concentrated to 10-mL volume by rotary evaporation and cooled to +4 °C. After 2 days, a small amount of *cis*-$Pt(NH_3)_2Cl_2$ (~5 mg) was filtered off. After 12 days, a large amount of precipitate was collected from the brownish purple solution. It consisted of 300 mg of the $C2/c$ product, small amounts of *cis*-$Pt(NH_3)_2Cl_2$, and two other unidentified compounds (together ~30 mg). *cis*-$Pt(NH_3)_2Cl_2$ was removed by extraction with dimethylformamide and the product recrystallized from water. Depending upon the conditions of crystallization, either A or B as major products were obtained.

(b) This procedure involved the preparation of *cis*-$[PtCl(NH_3)_2(C_5H_7N_3O)]Cl\cdot H_2O$[14] from *cis*-$Pt(NH_3)_2Cl_2$ and 1-methylcytosine (3 g of *cis*-$Pt(NH_3)_2Cl_2$, 1.25 g of 1-methylcytosine, 500 mL of H_2O, 36 h, 40 °C, stoppered flask, concentration to 50-mL volume, filtration of unreacted *cis*-$Pt(NH_3)_2Cl_2$, slow evaporation at 22 °C; yield 1.6 g plus other products; recrystallization from H_2O) and subsequent reaction of the isolated crystalline product (0.333 g, 10 mL of H_2O) with $AgNO_3$ (0.127 g, 10 mL of H_2O). Silver chloride was removed by filtration and the product crystallized at 22 °C: main product A, yield 90%. Recrystallization from water yielded A or B as major products depending on the conditions of crystallization.

Anal. Calcd for A: C, 13.3; H, 2.9; N, 18.6; Pt, 43.2; O, 14.2. Found: C, 13.4; H, 3.0; N, 18.7; Pt, 43.6; O, 14.9. Calcd for B: C, 13.3; H, 2.9; N, 18.6; Pt, 43.2; O, 14.2. Found: C, 13.4; H, 2.9; N, 18.0; Pt, 43.1.

Prolonged heating of chloro-*cis*-diammine(1-methylcytosine-N^3)-platinum(II) nitrate in water (>0.5 h, 80–90 °C, 100 mg, 5 mL, stoppered or open flask) led to formation of a purple or blue solution. During this process, the pH was dropping (from ~5 to ~3 after 2 h at 90 °C). From the concentrated solution, the starting material was recovered in 60–70% yield. The crystals were blue, but two cautious recrystallizations from water (22 °C) yielded almost colorless crystals of the starting compound(s).

Deuterated Compounds. 1-Methylcytosine (ND_2) was prepared by heating for 0.5 h at 90 °C 1-methylcytosine in D_2O (250 mg, 5 mL) and crystallization at 22 °C.

The "fully" deuterated analogues (ND_2, $(ND_3)_2$, C(5)D) of A and B were obtained by heating *cis*-$[PtCl(NH_3)_2(C_5H_7N_3O)]NO_3$ (200 mg, 4 mL of D_2O) in a stoppered flask for 3 h in a 90 °C water bath and appropriate crystallization of the resulting blue solution (cf. preceding section). The partially deuterated compounds ($(ND_3)_2$, C(5)D) were obtained by dissolving the fully deuterated compounds in H_2O at room temperature and subsequent crystallization. The partially deuterated compounds (C(5)D) were obtained by three cycles of brief warming (60 °C, 25 min) of the fully deuterated compounds in H_2O and subsequent crystallization.

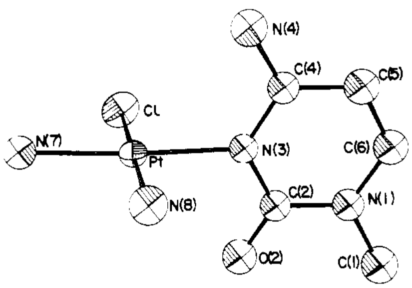

Figure 1. The molecular cation $[Pt(NH_3)_2(C_5H_7N_3O)Cl]^+$ ($P2_1/c$ structure).

Apparatus. ^1H NMR spectra were recorded on a Varian EM360 spectrometer at 60 MHz. Tetramethylsilane was used as external reference. Infrared spectra were recorded on a Perkin-Elmer 580 grating spectrometer as Nujol mulls with CsI windows and as KBr disks. No differences were observed between KBr and Nujol spectra. The reported frequencies were measured on an expanded scale with 1.3-cm^{-1} maximum resolution, calibration against polystyrene. IR intensities: vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, b = broad. Raman spectra of solid samples were recorded on a Coderg PH1 spectrometer with a krypton laser (647.1-nm excitation), calibration against indene. Both compounds A and B showed severe decomposition in the laser beam. This required fast scanning and consequently larger slit width (6 cm^{-1}).

Collection of the X-ray Data. Crystals of the two compounds were selected after examination under the polarizing microscope for homogeneity. Precession photographs showed both crystals were monoclinic, one with the systematic absences of $P2_1/c$ and the other with those of $C2/c$ or Cc. For the second crystal the space group $C2/c$ was assumed and justified by the satisfactory solution of the structure. Unit cell parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 reflections for each compound in the range $20° < 2\theta < 35°$ recorded on a Syntex $P2_1$ diffractometer using Mo Kα radiation $\lambda = 0.71069$ Å at 22 °C. Crystal data and other numbers related to data collection are summarized in Table I. Densities were obtained by flotation in a diiodomethane–chloroform mixture. Intensity data were also recorded on the Syntex $P2_1$ diffractometer using a coupled θ(crystal)–2θ(counter)scan. The methods of selection of scan rates and initial data treatment have been described.[15,16] Corrections were made for Lorentz–polarization effects and absorption.

Solution of the Structure. Both structures were solved in the same way. The coordinates of the platinum atom were found from a three-dimensional Patterson synthesis, and a series of full-matrix least-squares refinements followed by three-dimensional electron density difference syntheses revealed all the nonhydrogen atoms. At this stage the temperature factors of the platinum and chlorine atoms, which were previously isotropic, were made anisotropic. Tests were made at each stage to show the use of the increased parameters was significant.[17] Further refinement using full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ was terminated when the maximum shift/error was about 0.05. Cruickshank weighting schemes were used and corrections were made for secondary extinction with use of the method of Larson.[18] Throughout the refinement, the scattering curves were taken from ref 19 and anomalous dispersion corrections from ref 20 were applied to the curves for platinum and chlorine. The atom parameters for nonhydrogen atoms are listed in Tables II and III.[21]

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Table I

compd	$C_5H_{13}ClN_6O_4Pt$	$C_5H_{13}ClN_6O_4Pt$
fw	451.6	451.6
cryst size	cylinder, $r = 0.075$ mm, $l = 0.40$ mm	polyhedron with faces: {010}, 0.10 mm apart; $1\underline{1}0$ and $\overline{1}\overline{1}0$, 0.11 mm apart; $1\overline{1}0$ and $\overline{1}10$, 0.10 mm apart
systematic absences	$0k0, k = 2n + 1; h0l, l = 2n + 1$	$hkl, h + k = 2n + 1; h0l, l = 2n + 1$
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
unit cell parameters	$a = 8.143$ (2) Å, $b = 6.899$ (1) Å, $c = 21.434$ (3) Å, $\beta = 91.27$ (2)°	$a = 13.155$ (6) Å, $b = 9.754$ (5) Å, $c = 19.097$ (7) Å, $\beta = 99.70$ (3)°
V	1203.8 (9) Å^3	2415 (2) Å^3
Z	4	8
ρ_{calcd}	2.492 g cm^{-3}	2.484 g cm^{-3}
ρ_{obsd}	2.47 (2) g cm^{-3}	2.47 (2) g cm^{-3}
linear abs coeff	123.0 cm^{-1}	123.0 cm^{-1}
transmission coeff limits	4.03–4.33	1.93–3.96
max 2θ; quadrant	55°; $h,k,\pm l$	45°; $h,k,\pm l$
std reflctns	(1) 106; (2) 2,−1,6	(1) 317; (2) 006; (3) 204
overall esd	(1) 1.16%; (2) 1.12%	(1) 1.96%; (2) 1.93%; (3) 2.08%
temp	22 °C	22 °C
no. of independent reflctns	3018	1700
no. with $I > 3\sigma(I)$	2168	1344
$3\sigma(I) > I > \sigma(I)$ where $F_c > F_o$	135	61
$3\sigma(I) > I > \sigma(I)$ where $F_c < F_o$	187	81
$I < \sigma(I)$, rejected	528	214
final R_1[a]	0.0349	0.0467
final R_2[a]	0.0396	0.0641
final shift in esd: max (av)	0.035 (0.006)	0.057 (0.006)
g (secondary extinction)	2.23×10^{-7}	7.32×10^{-8}
final difference map		
highest peak; location	1.35 e/Å^3; 0.40, −0.08, 0.16	1.47 e/Å^3; 0.20, 0.30, 0.26
lowest valley; location	−1.11 e/Å^3; 0.20, 0.10, 0.31	−1.85 e/Å^3; 0.15, 0.12, 0.27
weighting	$1/w = 10.7 - 0.154\lvert F_o\rvert + 0.001\,05\lvert F_o\rvert^2$	$1/w = 34.6 - 0.293\lvert F_o\rvert + 0.003\,39\lvert F_o\rvert^2$

[a] $R_1 = (\Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\Sigma\lvert F_o\rvert; R_2 = [(\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2)/\Sigma w F_o^2]^{1/2}$.

Table II. Atom Parameters and Temperature Factors (Å^2) for Chloro-*cis*-diammine(1-methylcytosine-N^3)platinum(II) Nitrate (×10^3), Space Group $P2_1/c$

	x	y	z	U
Pt	182.07 (3)	230.01 (4)	315.68 (1)	*a*
Cl	286.6 (3)	−75.8 (3)	331.9 (1)	*a*
N(7)	336.2 (9)	267 (1)	242.5 (3)	37 (1)
N(8)	81 (1)	502 (1)	299.8 (4)	44 (2)
N(1)	−213.7 (9)	114 (1)	434.6 (3)	38 (2)
C(1)	−379 (1)	35 (1)	426.1 (5)	51 (2)
C(2)	−112 (1)	121 (1)	384.4 (4)	33 (2)
O(2)	−160.2 (8)	57 (1)	332.8 (3)	45 (1)
N(3)	39.6 (8)	203.0 (9)	391.4 (3)	30 (1)
C(4)	94 (1)	267 (1)	447.8 (4)	34 (2)
N(4)	243 (1)	344 (1)	452.8 (4)	43 (2)
C(5)	−9 (1)	258 (1)	499.8 (4)	41 (2)
C(6)	−161 (1)	181 (1)	491.5 (4)	42 (2)
N(9)	364.2 (9)	11 (1)	112.1 (4)	41 (2)
O(10)	422 (1)	12 (1)	59.3 (4)	63 (2)
O(11)	221 (1)	68 (1)	119.0 (4)	60 (2)
O(12)	452 (1)	−42 (1)	156.6 (4)	72 (2)

[a] Anisotropic temperature U_{ij}'s were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$, where β_{ij}'s occur as a temperature effect of the form $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$ and b_i and b_j are the reciprocal lattice vectors. For Pt, $U_{11} = 25.8$ (1), $U_{22} = 27.2$ (2), $U_{12} = -2.3$ (1), $U_{13} = -1.08$ (9), and $U_{23} = -1.9$ (1); for Cl, $U_{11} = 47$ (1), $U_{22} = 34$ (1), $U_{33} = 64$ (1), $U_{12} = -6.0$ (9), $U_{13} = 1$ (1), and $U_{23} = 1$ (1).

Table III. Atom Parameters and Temperature Factors (Å^2) for Chloro-*cis*-diammine(1-methylcytosine-N^3)platinum(II) Nitrate (×10^3), Space Group $C2/c$

	x	y	z	U
Pt	141.85 (4)	226.08 (5)	266.48 (2)	*a*
Cl	150.9 (3)	442.5 (4)	314.8 (2)	*a*
N(7)	82.6 (9)	312 (1)	171.0 (6)	39 (3)
N(8)	124.4 (8)	34 (1)	222.4 (6)	37 (3)
N(1)	203.0 (9)	55 (1)	473.6 (6)	45 (3)
C(1)	139 (1)	0 (2)	523.4 (9)	61 (5)
C(2)	152 (1)	100 (1)	408.4 (7)	35 (3)
O(2)	59.1 (7)	98 (1)	394.6 (5)	46 (2)
N(3)	213.2 (8)	146 (1)	361.9 (6)	36 (3)
C(4)	316 (1)	150 (1)	377.3 (7)	36 (3)
N(4)	371.7 (9)	193 (1)	330.1 (6)	43 (3)
C(5)	366 (1)	104 (2)	445.3 (8)	46 (4)
C(6)	307 (1)	57 (2)	491.5 (9)	55 (4)
N(9)	636 (1)	266 (1)	371.7 (8)	49 (3)
O(11)	592 (1)	303 (2)	315 (1)	68 (3)
O(10)	586 (1)	212 (1)	411.4 (7)	104 (5)
O(12)	729 (2)	284 (2)	389 (1)	112 (6)

[a] Anisotropic temperature U_{ij}'s were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$, where β_{ij}'s occur as a temperature effect of the form $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$ and b_i and b_j are the reciprocal lattice vectors. For Pt, $U_{11} = 32.8$ (4), $U_{22} = 34.8$ (5), $U_{33} = 24.5$ (4), $U_{12} = -0.5$ (2), $U_{13} = 6.3$ (2), and $U_{23} = 2.9$ (2); for Cl, $U_{11} = 55$ (2), $U_{22} = 39$ (2), $U_{33} = 49$ (2), $U_{12} = -6$ (2), $U_{13} = 7$ (2), and $U_{23} = -1$ (2).

Results and Discussion

1. Structure. The cation of the $P2_1/c$ structure is pictured in Figure 1, and selected interatomic distances and angles are given in Table IV. The two molecular cations are very similar, and only Cl–Pt–N(8) and N(8)–Pt–N(3) differ by more than 3σ ($\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$). The plane of the cytosine ring is almost at 90° to the square plane of the ligand ($P2_1/c$, 88°; $C2/c$, 84°) and there is no intramolecular hydrogen bonding between O(2) or N(4) and the N(8) ammonia group as we observed previously for related complexes of thymine and uracil.[22] The bond lengths and angles are normal and agree well with values we have obtained previously in similar com-

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(21) All calculations were carried out on a CDC-6400 computer. The programs DATCO3, ABSORB, and DATRDN from the X-RAY 76 program were used for preliminary data treatment. The full-matrix least-squares program, CUDLS, Fourier program, SYMFOU, and least-squares planes program, PALS, were written locally by J. S. Stephens, J. S. Rutherford, and P. G. Ashmore, respectively. Diagrams were prepared by use of the program ORTEP-II: Johnson, C. K. U.S. Atomic Energy Commission Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, Tenn. 1976.

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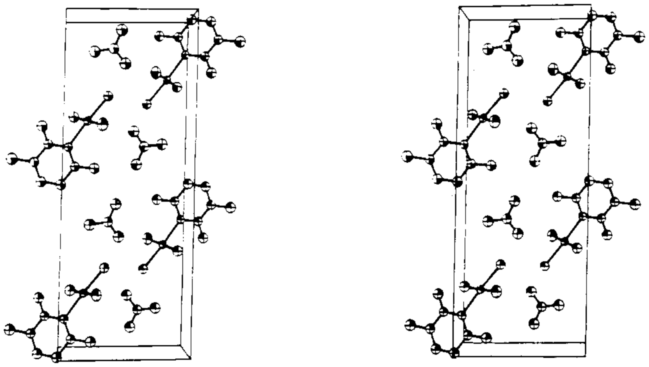

Figure 2. Packing of the title compound in the unit cell ($P2_1/c$) (c and a^* are parallel to the side and bottom of the page; the view is down b).

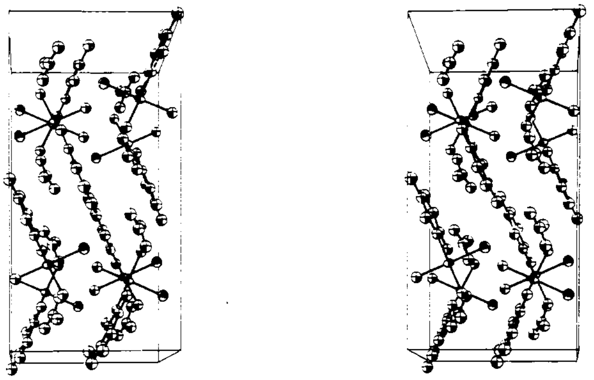

Figure 3. Packing of the title compound in the unit cell ($C2/c$) (b and c are parallel to the bottom and side of the page; the view is down a^*).

pounds;[11,22,23] the 1-methylcytosine parameters agree well with values given by Voet and Rich.[24]

The packing of the $P2_1/c$ structure is shown in Figure 2. The structure contains a large, essentially planar, basic unit comprising two nitrate ions and the pyrimidine rings of two cations, the whole being hydrogen bonded through O(10) and hydrogen atoms attached to N(4). These units are centered about the $z = {}^1/_2$ planes being canted so that the planes stack like tiles on a roof along the a direction. The displacement is such that the nitrate ions of one unit lie above and below the pyrimidine rings on the adjacent units. Thus in the b direction the units are interleaved. Apart from van der Waals forces, the only interaction between units in the b direction is a hydrogen bond between N(7) and O(11). In the c direction there are extensive hydrogen-bonding interactions between the stacks at $z = 0$ and $z = {}^1/_2$. This network is important in providing bonding both in the c direction and also in the b direction. Hydrogen bonding is between N(8)–Cl, N(8)–O(11), N(7)–O(2), and N(7)–O(12).

The packing in the $C2/c$ structure is shown in Figure 3. The basic unit of the two nitrate ions hydrogen bonded to the pyrimidine rings of two cations by N(4)–O(10) hydrogen bonds, which was identified in the $P2_1/c$ crystal, exists in the $C2/c$ structure, but it is no longer planar. It is bent about the nitrate–nitrate axis, the dihedral angle between the two pyrimidine rings being 103.7°. This leads to completely different packing in the $C2/c$ crystal.

The basic packing in the $P2_1/c$ cell can be transformed into that of the $C2/c$ cell if one considers one of the "tiles on the roof". The next tile would have to be displaced about one-fifth of the way along the [120] direction. The net effect of this is to give pyrimidine–pyrimidine overlap rather than pyrimidine–nitrate overlap. At the same time the groups in the pyrimidine nitrates–pyrimidine unit bend about the nitrate–nitrate axis. The effect of this bending and translation is to make the $Pt(NH_3)_2Cl$ groups, which in the $P2_1/c$ cell are at a large angle to one another in adjacent molecules related by the 2_1 axis at $x = 0$, $z = {}^1/_4, {}^3/_4$ (46.2°), nearly parallel to each other in the $C2/c$ cell (11.4°). The $Pt(NH_3)_2Cl$ planes are then relatively close to each other (Pt–Pt = 3.68 Å) and in the eclipsed conformation as can be seen in Figure 3.

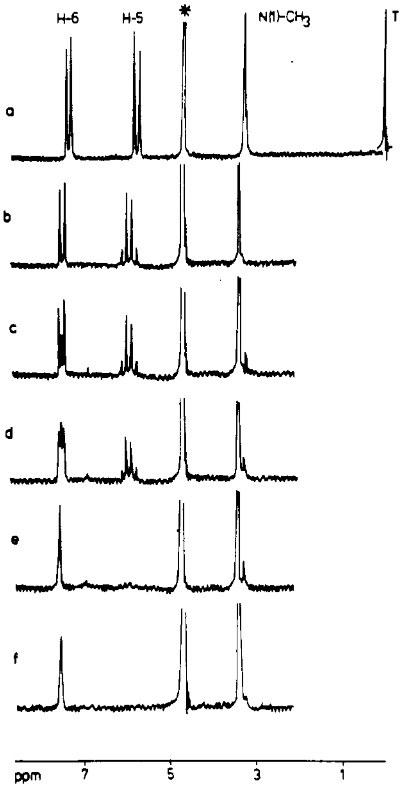

Figure 4. ^1H NMR spectra (D_2O, C_{Pt} = 0.2 M, σ scale, external Me_4Si): (a) 1-methylcytosine; (b) *cis*-$[PtCl(NH_3)_2(C_5H_7N_3O)]NO_3$ (A, B) after dissolving; (c) A and B after 15 min at 90 °C (pD 5.0); (d) A and B after 1 h at 90 °C; (e) A and B after 2 h at 90 °C (pD 3.2); (f) isolated A and B after 2 h at 90 °C in D_2O and two recrystallizations from H_2O (22 °C). (* is a solvent peak.)

Along the c direction at $z = 0$, ${}^1/_2$, contact is between interleaved pyrimidine and nitrate groups, whereas at $z = {}^1/_4$ the PtX_4 planes are interleaved. There is hydrogen bonding in the a direction between N(7) and Cl and N(8) and Cl. There is an extensive hydrogen-bonding network in this area. Up b the molecules are also bound by the N(8)–Cl interaction and the N(7)–O(2) interaction.

2. Spectroscopy. ^1H NMR Spectroscopy. As expected, compounds A and B are identical in solution. In Figure 4 the ^1H NMR spectrum of *cis*-$[PtCl(NH_3)_2(C_5H_7N_3O)]NO_3$ in D_2O (0.2 M, pD 5[25]) is shown together with the spectrum of 1-methylcytosine in the same solvent. There is a slight downfield shift of both H(6) and H(5) signals in the platinum complex compared to that of the free ligand as observed before the N(3)-platinated cytosine.[26,27] There is also a slight downfield shift of the N–CH_3 signal in the Pt complex. The H(5) signal shows side bands caused by coupling to the ^{195}Pt isotope with spin ${}^1/_2$. The coupling constant is $^4J_{^{195}Pt-^1H(5)}$ =

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[23] Faggiani, R.; Lippert, B.; Lock, C. J. L.; Rosenberg, B. *Inorg. Chem.* **1978**, *17*, 1941 and references therein.

[24] Voet, D.; Rich, A. *Prog. Nucleic Acid Res. Mol. Biol.* **1970**, *10*, 183.

[25] pD determination according to: Glasoe, P. K.; Long, F. A. *J. Phys. Chem.* **1960**, *64*, 188.

[26] (a) Kong, P.-C.; Theophanides, T. *Inorg. Chem.* **1974**, *13*, 1981. (b) Kong, P.-C.; Theophanides, T. *Bioinorg. Chem.* **1975**, *5*, 51.

[27] Chu, G. Y. H.; Duncan, R. E.; Tobias, R. S. *Inorg. Chem.* **1977**, *16*, 2625.

Table IV. Selected Interatomic Distances (Å) and Angles (Deg) for Chloro-*cis*-diammine(1-methylcytosine-N^3)platinum(II) Nitrate: $P2_1/c$, A; $C2/c$, B[a]

Nonhydrogen Bond Distances

	dist			dist			dist	
atoms	A	B	atoms	A	B	atoms	A	B
Pt–Cl	2.299 (2)	2.300 (4)	Pt–N(7)	2.047 (7)	2.04 (1)	Pt–N(8)	2.053 (8)	2.05 (1)
Pt–N(3)	2.026 (6)	2.06 (1)	N(1)–C(1)	1.46 (1)	1.48 (2)	N(1)–C(2)	1.37 (1)	1.38 (2)
C(2)–O(2)	1.24 (1)	1.21 (2)	C(2)–N(3)	1.37 (1)	1.37 (1)	N(3)–C(4)	1.35 (1)	1.33 (2)
C(4)–N(4)	1.33 (1)	1.32 (2)	C(4)–C(5)	1.41 (1)	1.43 (2)	C(5)–C(6)	1.35 (1)	1.35 (2)
C(6)–N(1)	1.36 (1)	1.36 (2)	N(9)–O(10)	1.24 (1)	1.20 (2)	N(9)–O(11)	1.24 (1)	1.21 (2)
N(9)–O(12)	1.24 (1)	1.22 (2)	O(10)–O(10)	2.87 (1)	3.15 (2)	N(8)–O(2)	2.96 (1)	3.07 (1)

Possible Hydrogen Bond Distances

A Form

N(8)–Cl^{i}	3.44 (1)	N(7)–O(11)	3.11 (1)	N(7)–O(12)	2.98 (1)
N(7)–O(2)^{ii}	2.93 (1)	N(7)–O(12)^{iii}	3.04 (1)	N(8)–O(11)^{ii}	3.08 (1)
N(4)–O(10)^{iv}	2.86 (1)	N(4)–O(10)^{iii}	2.98 (1)		

B Form

N(8)–Cl^{v}	3.28 (1)	N(7)–Cl^{vi}	3.38 (1)	N(7)–O(2)^{vi}	2.93 (2)
N(8)–O(10)^{vii}	2.93 (2)	N(4)–O(10)^{viii}	3.08 (2)	N(4)–O(11)	2.99 (2)
N(4)–O(10)	3.15 (2)	N(7)–O(12)^{viii}	2.91 (3)		

Nonhydrogen Bond Angles

	angle			angle			angle	
atoms	A	B	atoms	A	B	atoms	A	B
Cl–Pt–N(7)	89.9 (2)	88.2 (4)	Cl–Pt–N(8)	177.8 (2)	176.6 (3)	Cl–Pt–N(3)	90.6 (2)	90.3 (3)
N(7)–Pt–N(8)	90.7 (3)	90.5 (5)	N(7)–Pt–N(3)	176.4 (3)	175.2 (4)	N(8)–Pt–N(3)	88.9 (3)	91.2 (4)
Pt–N(3)–C(12)	118.8 (5)	118.1 (8)	Pt–N(3)–C(4)	120.2 (5)	118.7 (9)	C(1)–N(1)–C(2)	119.0 (7)	117 (1)
C(1)–N(1)–C(6)	120.7 (8)	120 (1)	C(6)–N(1)–C(2)	120.3 (7)	122 (1)	N(1)–C(2)–O(2)	120.1 (7)	120 (1)
N(1)–C(2)–N(3)	119.1 (7)	116 (1)	O(2)–C(2)–N(3)	120.8 (8)	123 (1)	C(2)–N(3)–C(4)	121.0 (7)	123 (1)
N(3)–C(4)–N(4)	119.1 (7)	121 (1)	N(3)–C(4)–C(5)	119.9 (7)	119 (1)	N(4)–C(4)–C(5)	121.0 (8)	119 (1)
C(4)–C(5)–C(6)	118.2 (8)	118 (8)	O(10)–N(9)–O(11)	119.1 (8)	118 (1)	O(11)–N(9)–O(12)	121.9 (9)	121 (2)
O(10)–N(9)–O(12)	118.9 (8)	121 (2)	Pt–N(8)–O(2)	100.8 (3)	97.5 (4)	C(2)–O(2)–N(8)	146.2 (6)	144 (1)

Possible Hydrogen Bond Angles

A Form

Pt^{i}–Cl^{i}–N(8)	125.1 (2)	Pt–N(8)–Cl^{i}	122.9 (3)	Pt–N(7)–O(11)	114.8 (3)
N(9)–O(11)–N(7)	88.6 (6)	Pt–N(7)–O(12)	126.2 (4)	N(9)–O(12)–O(7)	94.5 (6)
Pt–N(7)–O(2)^{ii}	102.0 (3)	C(2)^{ii}–O(2)^{ii}–N(7)	150.7 (6)	Pt–N(7)–O(12)^{iii}	81.8 (3)
N(9)^{iii}–O(12)^{iii}–N(7)	171.6 (7)	Pt–N(8)–O(11)^{ii}	111.7 (4)	N(9)^{ii}–O(11)^{ii}–N(8)	141.3 (6)
C(4)–N(4)–O(10)^{iv}	130.8 (6)	N(9)^{iv}–O(10)^{iv}–N(4)	122.3 (6)	C(4)–N(4)–O(10)^{iii}	170.3 (6)
N(9)^{iii}–O(10)^{iii}–N(4)	116.5 (6)	O(10)^{iii}–N(4)–O(10)^{iv}	58.9 (3)	N(4)^{ix}–O(10)–N(4)^{x}	121.1 (4)
O(11)–N(7)–O(12)	41.6 (3)	O(11)–N(7)–O(2)^{ii}	72.4 (3)	O(11)–N(7)–O(12)^{iii}	162.5 (4)
O(12)–N(7)–O(2)^{ii}	107.9 (3)	O(12)–N(7)–O(12)^{iii}	124.5 (3)	O(2)^{ii}–N(7)–O(12)^{iii}	111.1 (3)
O(2)–N(8)–O(11)^{ii}	135.7 (3)	N(7)–O(12)–N(7)^{x}	93.0 (3)	O(2)–N(8)–Cl^{i}	87.6 (2)
O(11)^{ii}–N(8)–Cl^{i}	98.3 (3)	N(7)–O(11)–N(8)^{xi}	79.4 (3)		

B Form

Pt–N(8)–Cl^{v}	107.1 (4)	Pt^{v}–Cl^{v}–N(8)	98.6 (2)	Pt–N(7)–Cl^{vi}	85.9 (3)
Pt^{vi}–Cl^{vi}–N(7)	72.5 (2)	Pt–N(7)–O(2)^{vi}	102.2 (5)	C(2)^{vi}–O(2)^{vi}–N(7)	129 (1)
Pt–N(8)–O(10)^{vii}	118.2 (6)	N(9)^{vii}–O(10)^{vii}–N(8)	138 (1)	C(4)–N(4)–O(10)^{viii}	155.7 (9)
N(9)^{viii}–O(10)^{viii}–N(4)	97 (1)	C(4)–N(4)–O(11)	104.4 (8)	N(9)–O(11)–N(4)	106 (1)
C(4)–N(4)–O(10)	142.8 (9)	N(9)–O(10)–N(4)	126 (1)	O(10)^{viii}–N(4)–O(11)	99.8 (6)
O(10)^{viii}–N(4)–O(10)	60.8 (5)	O(11)–N(14)–O(10)^{viii}	39.2 (5)	N(4)–O(10)–N(4)^{viii}	104.5 (6)
Pt–N(7)–O(12)^{viii}	95.3 (6)	N(9)^{viii}–O(12)^{viii}–N(7)	142 (4)	Cl^{v}–N(8)–O(2)	121.7 (4)
Cl^{v}–N(8)–O(10)^{vii}	98.6 (5)	O(2)–N(8)–O(10)^{vii}	114.8 (5)	Cl^{vi}–N(7)–O(2)^{vi}	77.3 (3)
Cl^{vi}–N(7)–O(12)^{viii}	155.7 (6)	O(2)^{vi}–N(7)–O(12)^{viii}	106.7 (6)	N(7)^{vi}–Cl–N(8)^{v}	170.1 (3)

[a] Atoms are related to those given in Tables II and III as follows: (i) $x, 1 + y, z$; (ii) $-x, {}^1/_2 + y, {}^1/_2 - z$; (iii) $1 - x, {}^1/_2 + y, {}^1/_2 - z$; (iv) $x, {}^1/_2 - y, {}^1/_2 + z$; (v) ${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$; (vi) $-x, y, {}^1/_2 - z$; (vii) $x - {}^1/_2, y - {}^1/_2, z$; (vii) $1 - x, y, {}^1/_2 - z$; (ix) $x, {}^1/_2 - y, z - {}^1/_2$; (x) $1 - x, y - {}^1/_2, {}^1/_2 - z$; (xi) $-x, y - {}^1/_2, {}^1/_2 - z$.

22 Hz. After the sample is heated to 90 °C in a water bath (stoppered tube), the solution turns purple within 10 min and blue within 1 h. This color change is accompanied by a drop in pD (3.2 after 2 h at 90 °C) and by changes in the ^{1}H NMR spectrum. The H(5) signal around 6.2 ppm decreases in intensity and eventually disappears. The H(6) doublet decreases in intensity as well, but at the same time a new singlet appears in the center of the H(6) doublet. There are also weak peaks occurring around 7 ppm and close to the N–CH$_3$ peak.

The spectral changes indicate an exchange of the proton at C(5) by a deuterium ion upon heating. This process makes the H(5) signal disappear and the H(6) doublet collapse to a singlet. Though the ^{2}H nucleus has a spin of 1 and therefore triplet splitting of the C(6) proton signal might be expected, the small magnetic moment and the possibility of quadrupole relaxation of the deuterium nucleus can account for the fact that it is not observed.[28] The chemical shifts of the H(6) proton signal and of the N–CH$_3$ signal are not affected by this isotopic change at C(5). The weak peaks at 3.3 and around

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[28] Pople, J. A. *Mol. Phys.* **1958**, *1*, 168.

7 ppm are assigned to an unidentified compound.[29]

Upon concentration and cooling of the blue solution, crystals of the starting compound can be isolated in 60–70% yield as well as several byproducts.[30] Depending upon the procedure of crystallization, crystals of either type A or type B are obtained (cf. Experimental Section). In any case, the crystals are blue, but the blue color originates from inclusions of small quantities of a blue product. Two to three recrystallizations (22 °C) of the blue crystals from D_2O or H_2O yield almost colorless crystals with a very slight bluish tint only. There are no IR spectroscopic differences between the blue crystals obtained from D_2O and the almost colorless crystals obtained after cautious recrystallization from D_2O. In Figure 4f the ^1H NMR spectrum of an isolated crystalline sample after two recrystallizations from H_2O is shown. As can be seen, the H(5) deuterium ion has not reexchanged under the mild conditions of the recrystallization procedures from H_2O. This opens up the possibility of preparing Pt–cytosine complexes that are specifically deuterated (or tritiated) at the C(5) position.

As to the possible mechanism of the H exchange at the C(5) position, two statements can be made at this stage. First, this process requires the solvolysis of the coordinated chloride ligand. If *cis*-$[PtCl(NH_3)_2(C_5H_7N_3O)]NO_3$ is heated together with an excess of NaCl in D_2O, the solution becomes slightly gray within 2 h at 90 °C. There is no spectroscopic evidence for a proton exchange at C(5) under these experimental conditions. Second, Pt attack at the exocyclic amine group of 1-methylcytosine appears not to be a sufficient condition for the proton exchange at C(5). In a dimeric Pt complex with simultaneous coordination through N(3) and the deprotonated amine group of 1-methylcytosine, bis(μ-(1-methylcytosinato-N^3,N^4))-bis(*cis*-diammineplatinum(II)) dinitrate dihydrate,[31] no C(5)H exchange can be observed under identical experimental conditions.

Vibrational Spectra. There are a number of differences in the IR and Raman spectra of the two forms of chloro-*cis*-diammine(1-methylcytosine-N^3)platinum(II) nitrate which, logically, should be interpreted as arising from differences in hydrogen bonding and packing, respectively. These include vibrations of the NH_3 groups, the exocyclic amine group of the cytosine ligand, the cytosine ring itself, and the PtN_2Cl(Cyto) skeleton. The minor differences in angles between the cytosine ring and the platinum coordination plane are considered too small to have a marked influence on vibrational frequencies of the ring.

(a) Ligand Modes. The identification of vibrations of the NH_3 groups and the NH_2 group of 1-methylcytosine was based on deuteration experiments and comparison with NH_3 vibrations of related *cis*-diammineplatinum(II) complexes[32] and published data on cytosine[33,34] and substituted cytosines.[35] Nevertheless, it was not possible to identify all expected modes because of simultaneous deuteration of the C(5) position of the cytosine ring and coupling. On the other hand, a differentiation between NH_3 and NH_2 vibrations in some cases was eased by the fact that protons of the cytosine NH_2 group exchanged faster than protons of the NH_3 groups. For example, the fully deuterated compound (C(5)D, ND_2, $(ND_3)_2$) exchanged the ND_2 deuterium ions completely upon recrystallizing the sample from H_2O at room temperature, whereas the exchange of ND_3 vs. NH_3 under these conditions is partial only and requires brief warming to be complete (cf. Experimental Section).

Two NH_2 modes, the stretching and wagging vibrations, were identified unambiguously. They do show differences in their positions in A and B. In A the NH_2 out-of-phase stretching vibration is observed at 3325 cm^{-1} (s), and in B this band is split into two components at 3355 (s) and 3325 cm^{-1} (s). Upon deuteration, two NH_2 stretching modes (out of phase and in phase) are observed at 2530 and 2370 cm^{-1} for A and at 2520, 2480, and 2360 cm^{-1} for B. The NH_2 wagging mode at 655 cm^{-1} (s) in A and 625 cm^{-1} (s) in B, which is readily recognized because of its high intensity and its broad band shape in the IR, is shifted upon deuteration to 486 cm^{-1} (A) and 496 cm^{-1} (B), respectively. Since, with increasing hydrogen bonding, the stretching modes are shifted to lower frequencies whereas deformation modes are shifted in the opposite direction, the observed differences can be interpreted in terms of a more strongly hydrogen-bonded NH_2 group in A compared with that in B. These findings are in agreement with the X-ray structure results (cf. Table IV). The NH_2 bending and rocking modes, expected around 1600–1700 and 1150–950 cm^{-1}[34–36] in the IR spectra, cannot be identified unambiguously. The former are not observed in the nondeuterated compounds since they are buried under the strong C=O and C=C stretching bands or possibly coupled to these modes. The broad band at 1165 cm^{-1} in the IR spectrum of the fully deuterated samples of A and B is tentatively assigned to the ND_2 bending mode. The IR range between 1250 and 950 cm^{-1} is strongly affected by deuteration at the C(5) position. With one exception (980-cm^{-1} band), all bands are shifted. Since, at the same time, ND_3 and ND_2 modes absorb in this range, we cannot assign the NH_2/ND_2 rocking modes. It appears possible—and the observed band shifts upon C(5) deuteration in this range support this—that the NH_2 rocking mode is strongly coupled to other modes as in the case of cytosine.[34]

Absorptions of the individual NH_3 groups, although differing slightly in A and B, do not permit any definite conclusions concerning differences in hydrogen-bond strength in the two compounds. NH_3 stretching modes are observed at 3275–3120 cm^{-1} (vs) in A (2455, 2340 (vs), 2300 cm^{-1} (s) deuterated A) and at 3280–3120 cm^{-1} (vs) in B (2450, 2350, 2300 cm^{-1} (vs) deuterated B). The degenerate deformation modes of the NH_3 groups, expected around 1600 cm^{-1}, are of too low intensity to be observed or identified in the spectra of the deuterated forms. The symmetric deformation modes are observed at 1345 and 1315 cm^{-1} (s) in A (1028, 1018 cm^{-1} (s) deuterated A) and at 1350 and 1330 cm^{-1} (s) in B (1040, 1030, 1025 cm^{-1} (s) deuterated B). The NH_3 rocking modes are found at 890 (s) and 760 cm^{-1} (m, sh) in A (670 (w), 590 cm^{-1} (m, sh) deuterated A) and at 890 (s), 845 (?) (m), and 750 cm^{-1} (m) in B (670 (m), 609 (m), 540 cm^{-1} (s, sh) deuterated B).

The effect of platination at N(3) of cytosine rings has been investigated by Tobias and co-workers.[27] They showed that platination has an effect on ring vibrations similar to that of protonation, although the shifts are smaller for the Pt elec-

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[29] Relative amount of this product: 2% of A and B.

[30] These products include at least a microcrystalline compound with a bright green metallic luster and a highly water-soluble purple product.

[31] Faggiani, R.; Lippert, B.; Lock, C. J. L.; Speranzini, R. A., *J. Am. Chem. Soc.*, in press.

[32] Faggiani, R.; Lippert, B.; Lock, C. J. L.; Rosenberg, B. *J. Am. Chem. Soc.* **1977**, *99*, 777.

[33] Angell, C. L. *J. Chem. Soc.* **1961**, 504.

[34] Susi, H.; Ard, J. S.; Purcell, J. M. *Spectrochim. Acta, Part A* **1973**, *29A*, 725.

[35] Lord, R. C.; Thomas, G. T., Jr. *Spectrochim. Acta, Part A* **1967**, *23A*, 2551.

[36] We have some reservations concerning the assignment of the NH_2 rocking mode of 1-methylcytosine by Lord and Thomas.[35] They assigned the 1125-cm^{-1} band (IR) to this mode and the 882-cm^{-1} band to the corresponding ND_2 mode. Even though there is a weak band at 885 cm^{-1} in the IR spectrum of 1-methylcytosine (ND_2), we feel that the broad band of medium intensity that is centered around 1000 cm^{-1} could be assigned to this mode as well. Provided this were correct, the NH_2 rocking mode might be expected at higher energy than the proposed 1125 cm^{-1}.

Table V

Least-Squares Planes through Part of the Molecules $[PtCl(NH_3)_2(C_5H_2N_3O)]NO_3$

plane	atoms in plane	dist of atom from plane, Å
		P2_1/*c*
1	N(1), C(2), N(3), C(4), C(5), C(6), C(1)*, O(2)*, N(4)*, Pt*	N(1) 0.01, C(2) −0.02, N(3) 0.02, C(4) −0.01, C(5) 0.00, C(6) 0.00, C(1) 0.04, O(2) −0.04, N(4) 0.01, Pt 0.12
2	N(7), N(8), N(3), Cl, Pt*	N(7) 0.05, N(8) −0.05, N(3) 0.05, Cl −0.05, Pt −0.01
3	O(10), O(11), O(12), N(9)*	N(9) −0.01
4	1^b	
5	2^b	
6	3^b	
		*C*2/*c*
7	N(1), C(2), N(3), C(4), C(5), C(6), C(1)*, O(2)*, N(4)*, Pt*	N(1) 0.00, C(2) 0.00, N(3) 0.00, C(4) 0.00, C(5) 0.00, C(6) 0.00, C(1) −0.05, O(2) 0.02, N(4) −0.03, Pt 0.13
8	N(7), N(8), N(3), Cl, Pt*	N(7) 0.07, N(8) −0.71, N(3) 0.07, Cl −0.07, Pt −0.01
9	O(10), O(11), O(12), N(9)*	N(9) 0.00
10	$7*^a$	
11	$8*^a$	
12	$9*^b$	

Interplanar Angles, Deg

1–2, 4–5	88.1	2–5	46.2	7–11, 8–10	73.3
1–3, 4–6	45.6	2–6, 3–5	86.5	7–12, 9–10	48.9
1–4	50.5	3–6	41.0	8–9, 11–12	76.3
1–5, 2–4	42.0	7–8, 10–11	84.0	8–11	11.4
1–6, 3–4	5.9	7–9, 10–12	7.8	8–12, 9–11	65.5
2–3, 5–6	47.6	7–10	76.3	9–12	53.9

[a] Atoms marked with an asterisk are given no weight in the refinement; other atoms are given unit weight. [b] Atoms in this plane are related to those in plane 1 by the 2_1 axis.

trophile. With regard to the two most intense Raman bands of 1-methylcytosine, the ring-stretching mode at 1261 cm^{-1} and the ring-breathing mode at 771 cm^{-1}, only the latter is substantially shifted in A and B (792 cm^{-1}). The former is shifted only little (1259 cm^{-1} in A, 1251 cm^{-1} in B) to lower energy. Another 1-methylcytosine mode, absorbing at 627 cm^{-1} and very intense in both the infrared and Raman, is shifted to 647 cm^{-1} in A and B, and the intense Raman band at 1524 cm^{-1} in 1-methylcytosine is shifted to 1533 cm^{-1} in A and B. Shifts of several other cytosine modes below 600 cm^{-1} are listed in Table V.

The positions of corresponding cytosine bands in the Raman spectra differ only slightly for A and B. Usually they are observed within ±3 cm^{-1}, the deviation of the ring-stretching mode, mentioned above, at 1250 cm^{-1} being the exception. Differences of this order of magnitude appear to be normal for corresponding vibrations of heterocycles that exhibit different hydrogen-bonding patterns.[37]

Deuteration of the N(3)-platinated 1-methylcytosine at the C(5) position, observed in the ^1H NMR spectra, is expressed in the IR spectra as well. A comparison of the IR spectra of A and B before deuteration, after deuteration, and after cautious recrystallization from H_2O clearly shows differences in the spectra. Changes are observed in particular in the 1250–950-cm^{-1} range and around 800 cm^{-1}, whereas the skeletal modes are practically unaffected. Simultaneously performed studies in H_2O instead of D_2O, which gave the starting material(s) without any change in the IR spectra, clearly demonstrated that only a proton/deuterium ion exchange was responsible for the observed ^1H NMR and IR spectroscopic changes but not for any other change at the cytosine ring.[38] In Figure 5 sections of the IR spectra of the *P*2_1/*c* product (A) prior and after C(5) deuteration as well as after three recrystallizations of the C(5) deuterated form from H_2O are shown.[39] It depicts the deuteration shift of the original 815-cm^{-1} band. This band disappears upon heating A in D_2O (Figure 5b) and is still missing in the product with the *cis*-diammine ligands and the 4-amino group of cytosine in the ^1H form (Figure 5c). Instead of this band, two new bands are observed at 605 and 551 cm^{-1} in Figure 5b and 591 and 563 cm^{-1} in Figure 5c. It is suggested that these two bands are caused by coupled vibrations of the original 580-cm^{-1} mode, and the shifted 815-cm^{-1} band is (essentially) a CH mode, e.g., out-of-plane deformation; one expects a deuteration shift to approximately 570 cm^{-1}. This is very close to the original 580-cm^{-1} band and close to the center of the two bands that are assumed to be coupled. From comparison of the spectra in Figure 5a,c, it is evident that the intense 650-cm^{-1} band is sensitive upon deuteration at C(5) and shifted to 640 cm^{-1} whereas the other cytosine and skeletal modes below 550 cm^{-1} are practically not affected by this isotopic change.

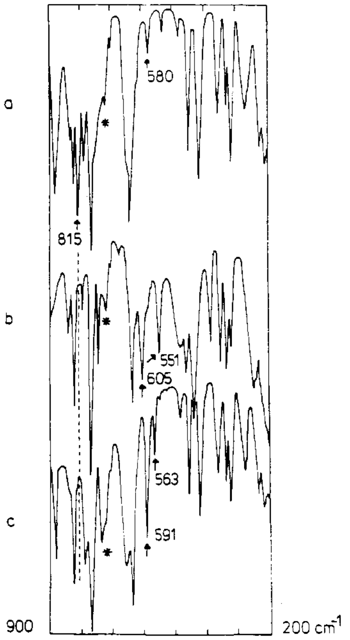

Figure 5. IR spectra (Nujol, CsI windows): (a) *cis*-$[PtCl(NH_3)_2(C_5H_7N_3O)]NO_3$, form A; (b) A after 2 h 90 °C in D_2O, isolation, and two recrystallizations at 22 °C from D_2O (ND_2, $(ND_3)_2$, C(5)D product); (c) A, fully deuterated, after three recrystallizations (25 min, 60 °C each) from H_2O (C(5)D product). (* is a Nujol band.)

The C(5)D stretching mode is observed as a weak, sharp band in the partially deuterated sample (NH_2, $(NH_3)_2$, C(5)D) at 2310 cm^{-1}; the C(6)H stretching mode, at 3060 cm^{-1} in the fully deuterated sample (ND_2, $(ND_3)_2$, C(5)D).

(b) Skeletal Modes. In the region between 600 and 150 cm^{-1} both platinum–ligand vibrations and vibrations of the cytosine ring are observed. In Table V the observed IR and Raman bands between 600 and 200 cm^{-1} are listed. The two Pt–NH_3 stretching modes around 513–540 cm^{-1} are recognized by their strong Raman intensities. In both compounds A and B the higher frequency band is assigned to the Pt–NH_3 stretching mode with the NH_3 group trans to the cytosine ligand; the lower frequency band, to the Pt–NH_3 stretch with NH_3 trans

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(37) Lippert, B., unpublished results.

(38) This refers to the isolated crystalline product but not necessarily to the coproducts of the reaction, e.g., the purple material (cf. Experimental Section).

(39) For the *C*2/*c* form, the observed changes are very similar.

to the chloride ligand. This assignment is based on the assumption that the Pt–1-methylcytosine interaction is essentially occurring through a σ bond. Therefore, the trans influence of the cytosine ligand should be comparable with those of other nitrogen donors, that is, stronger than that of chloride but weaker than that of oxygen donors: trans influence Cl > N $\sim$ Cyto(N^3) > O. A comparison of the ν(Pt–NH$_3$) frequencies in *cis*-$Pt(NH_3)_2(ONO_2)_2$ (562, 558 cm^{-1}),[16] *cis*-$[Pt(NH_3)_2$(1-methylcytosine)$_2]Cl_2$ (538, 529 cm^{-1}),[14] and *cis*-$Pt(NH_3)_2Cl_2$ (510 cm^{-1})[40] agrees with this assumption. In the IR spectra of the deuterated compounds the Pt–NH$_3$ stretching modes are shifted to lower energy. Only one mode—ND$_3$-*trans*-1-methylcytosine—is observed (504 cm^{-1} in A, 490 cm^{-1} in B) in each case, whereas the second band is buried under the intense ND$_2$ wagging mode of the cytosine ligand. The isotopic shifts (1.072 in A, 1.084 in B) for the ND$_3$ groups are close to the theoretical values for "free" ND$_3$ point masses vibrating against the large Pt mass.

Two bands are observed between 320 and 340 cm^{-1}, the range in which Pt–chloride (terminal) vibrations usually absorb. Since in both A and B the band at higher wavenumber is sensitive to deuteration, the bands at lower wavenumbers (321 (A) and 320 cm^{-1} (B)) are assigned to the Pt–Cl stretching vibrations.

Using the reduced point masses of the 1-methylcytosine/Pt and the NH$_3$/Pt pairs, respectively, and assuming similar force constants for both bonds, one can expect, in a first approximation, the Pt–1-methylcytosine stretching mode to absorb around 240 cm^{-1}. For Pt–pyridine complexes the stretching modes are usually observed between 250 and 300 cm^{-1},[41] which is in fair agreement with what one might expect when using this simplified model. In the same range also the Pt–NH$_3$ in-plane deformation modes can be expected, whereas Pt–NH$_3$ out-of-plane deformation modes and Pt–Cl deformation modes usually absorb below 200 cm^{-1}.[42] At least one band in the 300–200-cm^{-1} range is caused by a cytosine ligand mode. Since all IR bands between 300 and 200 cm^{-1} are shifted upon deuteration, it is not possible to assign them. In the Raman spectrum of A, an intense band is observed at 259 cm^{-1}. The corresponding band of B could not be observed because of experimental problems (cf. Experimental Section). However, this band is also observed in the Raman spectra of *cis*-$[PtCl(NH_3)_2$(1-methylcytosine)$]Cl\cdot H_2O$[14] and *cis*-$[Pt(NH_3)_2$(1-methylcytosine)$_2]Cl_2$.[14] In these compounds this band is shifted only insignificantly (2–4 cm^{-1}) to lower energy upon deuteration. Therefore the 259-cm^{-1} band is tentatively assigned to the Pt–1-methylcytosine stretching vibration.

(c) Anion Vibrations. The symmetry of ionic nitrate (D_{3h}) is lowered to C_1 in both compounds A and B. As a consequence, all four fundamentals become both IR and Raman active. The expected splitting of the two degenerate modes is not observed in all cases. NO$_3^-$ bands are observed for A at 708 (w) (IR), 706, 721 (w) (Ra), 830 (s) (IR), 836 (w) (Ra), 1050 (vw) (IR), 1051 (vs) (Ra), and 1380 (vs) (IR) and for B at 700 (vw), 720 (w) (IR), 705, 718 (w) (Ra), 828 (s) (IR), 823 (w) (Ra), 1050 (vw) (IR), 1051 (vs) (Ra), 1385 (vs) (IR), and 1391 (vw) (Ra).

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Registry No. *cis*-$[PtCl(NH_3)_2(C_5H_7N_3O)]NO_3$, 75659-39-1; *cis*-$[PtCl(NH_3)_2(C_5H_7N_3O)]NO_3$ (C(5)D), 75659-41-5; *cis*-$[PtCl(NH_3)_2(C_5H_7N_3O)]NO_3$ (ND$_2$, (ND$_3$)$_2$, C(5)D), 75659-43-7; *cis*-$[PtCl(NH_3)_2(C_5H_7N_3O)]NO_3$ ((ND$_3$)$_2$, C(5)D), 75659-45-9; *cis*-$[PtCl(NH_3)_2(C_5H_7N_3O)]Cl$, 75659-46-0; *cis*-$Pt(NH_3)_2Cl_2$, 15663-27-1.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes for the $P2_1/c$ crystal and the $C2/c$ crystal (18 pages). Ordering information is given on any current masthead page.

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[42] See, e.g.: Hiraishi, J.; Nakagawa, I.; Shimanouchi, T. *Spectrochim. Acta, Part A* **1968**, *24A*, 819.