$(NH_3)_2(MeCyt)_2](NO_3)_2 \cdot MeCyt$ which was observed in the spectrum of the deuterated compound as well (1037 (7), 1060 (8) cm^{-1}). The two bands may arise from the two different nitrate ions, but it is also possible that the splitting arose from Fermi resonance between the weak 1-methylcytosine mode at 1052 cm^{-1} and the intense NO_3 vibration usually observed around 1045 cm^{-1} in nitrate salts.

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Supplementary Material Available: Tables of temperature factors, least-squares planes and dihedral angles, Raman frequencies, and the moduli of observed and calculated structure factors and Figures A, Raman spectra in the ring-breathing mode region, and B, low-frequency Raman spectra (29 pages). Ordering information is given on any current masthead page.

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Model Complexes of Possible Cross-Linking Products of *cis*-$Pt(NH_3)_2^{2+}$ with Cytosine and Guanine Bases of DNA: X-ray Structures of Three Mixed-Ligand Complexes of *cis*-Diammineplatinum(II) with 1-Methylcytosine and Neutral and Anionic 9-Ethylguanine

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Three different mixed-ligand complexes of *cis*-$Pt(NH_3)_2^{2+}$ with 1-methylcytosine, C, and 9-ethylguanine, G, have been synthesized and studied by X-ray crystallography. *cis*-$[Pt(NH_3)_2GC](ClO_4)_2$ (I) has the space group $P2_1/n$ with $a = 20.117$ (7) Å, $b = 27.017$ (5) Å, $c = 8.727$ (2) Å, and $\beta = 105.13$ (2)° and has eight formula units in the unit cell. *cis*-$[Pt(NH_3)_2(G\text{-}H)C]ClO_4 \cdot 4H_2O$ (II) has the space group $P2_1/c$ with $a = 12.344$ (4) Å, $b = 16.103$ (5) Å, $c = 12.517$ (4) Å, and $\beta = 90.36$ (3)° and has four formula units in the unit cell. *cis*-$[Pt(NH_3)_2GC][Pt(NH_3)_2(G\text{-}H)C](ClO_4)_3$ (III) has the space group $C2/c$ with $a = 23.467$ (16) Å, $b = 11.960$ (3) Å, $c = 16.093$ (4) Å, and $\beta = 106.56$ (4)° and has four formula units in the unit cell. Data for all three compounds were collected with use of Mo Kα radiation and a Syntex $P2_1$ diffractometer. The crystal structures were determined by standard methods and refined to $R_1 = 0.0552$ (I), 0.0473 (II), and 0.0484 (III) and $R_2 = 0.0662$ (I), 0.0668 (II), and 0.0667 (III), on the basis of 3875 (I), 3749 (II), and 3279 (III) independent reflections. III crystallizes in a structure containing a novel hydrogen-bonding scheme between a neutral and an anionic guanine ligand which involves $N(2)H_2$, N(1), and O(6) of both G ligands. The acidity of the 9-ethylguanine ligand in I has been found to increase by 1.6 pK units as a consequence of platinum binding to the N1 position. This means that at a pH corresponding to the physiological pH, I and II are distributed approximately 85:15. Infrared and Raman spectra of the three compounds are presented. The effect of guanine deprotonation on the vibrational modes is studied. The conclusions on the nature of the short hydrogen bond between the N1 positions in III, drawn from IR and Raman spectra, are critically examined.

Introduction

There is substantial evidence pointing to DNA as the principal target of platinum antitumor drugs,[2] and to their ability to block DNA replication.[3] A preferential binding of platinum to DNA rich in guanine and cytosine content has been observed,[4] and several hypotheses have been forwarded to explain these findings. The two most popular theories presently discussed are those of intrastrand cross-linking of two guanine bases[5] and N7, O6 chelation of guanine by *cis*-diamineplatinum(II) complexes.[6] Though both models might explain the activity of cis complexes compared to that of the respective trans complexes, there are serious arguments against the N7, O6 proposal on stereochemical grounds.[7] In any case, strong binding of platinum to guanine is generally assumed. It is not certain whether the effect is kinetic in origin[8] or whether it is thermodynamically controlled,[9a] since the claim that equilibrium constants for 1:1 complexes of cis Pt(II) with guanosine, adenosine, and cytidine are nearly identical has been disputed.[9b] The consensus is that the effect is kinetic.[9b] Interestingly, results on the reaction of cis Pt(II) with G, C dinucleosides are controversial, supporting both preferential binding to G[10] and to C.[11]

We have recently started to systematically synthesize nucleobase model complexes of cis Pt(II) containing a single base,[12] two identical bases,[13] and two different bases. As a

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first example of mixed-nucleobase complexes of *cis*-diammineplatinum(II), we herewith report on three complexes that contain the 9-ethylguanine ligand, G, bound through N7 and the 1-methylcytosine ligand, C, bound through N3. Compound I, *cis*-$[Pt(NH_3)_2GC](ClO_4)_2$, contains G and C in their neutral forms, compound II, *cis*-$[Pt(NH_3)_2(G\text{-}H)C]ClO_4\cdot 4H_2O$, obtained from I after addition of 1 equiv of NaOH, contains a neutral C ligand and an anionic (N^1 deprotonated) guanine ligand, G-H. If deprotonation of the G ligand is incomplete, a compound III, *cis*-$[Pt(NH_3)_2GC][Pt(NH_3)_2(G\text{-}H)C](ClO_4)_3$, is obtained that contains I and II hydrogen bonded through the two guanine ligands. Such a hydrogen-bonding pattern between neutral and anionic guanine has not been observed before and represents an interesting alternative to the common G + C base-pairing scheme.[14]

The hydrogen-bonding behavior of 9-ethylguanine in solution is drastically changed when the N7 position becomes platinated. (We use the nomenclature N7 etc. when we talk generally about a position in a purine or pyrimidine; N(7), N(7A), etc. are used for specific atoms in the compounds.) Simultaneous deprotonation at N1 leads to an even more dramatic change in its hydrogen-bonding pattern. A detailed ^1H NMR study on this subject has been undertaken and will be published.[15]

Experimental Section

Preparation of the Compounds. *cis*-$[Pt(NH_3)_2GC](ClO_4)_2$ (I). Reaction of *cis*-$Pt(NH_3)_2Cl_2$ with C gave *cis*-$[Pt(NH_3)_2ClC]Cl\cdot H_2O$.[16] Reaction of this compound with 2 equiv of $AgClO_4\cdot H_2O$ and 1 equiv of G (c = 0.03 M (Pt), H_2O, 24 h, 40 °C), filtration of AgCl, and slow evaporation gave I. Recrystallization was from H_2O; yield 80–90%. The transparent crystals rapidly lose water and transparency when kept in air. An air-dried sample was analyzed as the hemihydrate. Anal. Calcd: C, 19.44; H, 3.13; N, 18.90; O, 22.66; Pt, 26.31. Found: C, 19.70; H, 2.96; N, 18.85; O, 23.06; Pt, 26.0. However, the sample studied by X-ray crystallography contained no water.

***cis*-$[Pt(NH_3)_2(G\text{-}H)C]ClO_4\cdot 4H_2O$ (II).** Titration of I with 1 equiv of NaOH under N_2 and subsequent concentration to a small volume gave colorless, transparent crystals of II. The solution (pH ~10–11) tended to oversaturate, which sometimes led to an instantaneous crystallization of the product; yield 80–85%. The elemental analysis depended upon pretreatment of the sample. Anal. Calcd for a freshly prepared sample (tetrahydrate): C, 20.45; H, 4.16; N, 19.90. Found: C, 20.79; H, 4.34; N, 19.62. Calcd for a sample dried for 20 h at high vacuum (monohydrate): C, 22.17; H, 3.57; N, 21.55; Pt, 30.01. Found: C, 22.26; H, 3.60; N, 21.82; Pt, 29.6.

***cis*-$[Pt(NH_3)_2GC][Pt(NH_3)_2(G\text{-}H)C](ClO_4)_3$ (III).** Titration of I with 0.5 equiv of NaOH under N_2 and subsequent concentration of the solution (pH 8.2) gave compound III as colorless, transparent crystals. Recrystallization was from hot water; yield 65%. Anal. Calcd (monohydrate): C, 20.87; H, 3.29; N, 20.28; O, 19.69; Pt, 28.24. Calcd (dihydrate): C, 20.60; H, 3.39; N, 20.02; O, 20.58; Pt, 27.88. Found: C, 21.11; H, 3.23; N, 20.16; O, 20.26; Pt, 27.7. Elemental analysis did not distinguish between the mono- and dihydrate. IR spectroscopy clearly shows the presence of water (ν(HOH) at 3620 (m) cm^{-1}), even though no water was found in the compound examined crystallographically. Compound III was prepared in its deuterated form (ND_3, ND_2 (C); ND_2, ND, C(8)D (G)) by 1-h heating in D_2O at 80 °C and subsequent crystallization. Deuteration of the C(8) position was evident from ^1H NMR spectroscopy. Deuterated I was obtained by 1-h treatment in D_2O at 70 °C and subsequent evaporation to dryness (ND_3, ND_2(C); ND_2, ND (G)). Compunds I, II, and III were also prepared as nitrate salts in an analogous way and identified by elemental analysis and by comparison of the IR spectra with those of the corresponding perchlorate compounds.

p*K* Determination. The pK_a of the equilibrium I + H_2O ⇄ II + H_3O^+ was determined in aqueous 0.1 M $NaClO_4$ solution by titration of I with 0.2 N NaOH. It was obtained from the titration curve according to the method described by Albert and Serjeant.[17] The average value obtained from several titrations was 8.2 ± 0.05 at 20 °C.

A p*K* determination for the equilibrium G + H_2O ⇄ $(G\text{-}H)^-$ + H_3O^+ with G = 9-ethylguanine in aqueous 0.1 M $NaClO_4$ at 20 °C gave p*K* = 9.75 ± 0.1, which is in good agreement with data reported for 9-methylguanine (9.8).[18]

Apparatus. Infrared spectra were recorded at room temperature on a Perkin-Elmer 580 grating spectrometer as Nujol mulls (CsI windows) and KBr pellets and calibrated against polystyrene. Reported frequencies were taken from spectra recorded on an extended scale with a maximum resolution of 1.3 cm^{-1}. Raman spectra were recorded at room temperature on a Coderg PH1 with krypton ion laser excitation (647.1 nm) and 200–400-mW power. Spectral slit widths were 4–6 cm^{-1} for the solid-state spectra. The spectra were calibrated against indene. Reported intensities refer to signal heights and were relative to the indicated signal.

Collection of the X-ray Data. Crystals of the three compounds were selected after examination under a polarizing microscope for homogeneity. Compounds I and III were mounted normally on fibers but II decomposed in the X-ray beam even when sealed in a Lindemann capillary. Satisfactory results were obtained with a crystal sealed in a capillary in which a drop of water was also present. Precession photographs revealed the symmetry of the crystals, and 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, the radiation being graphite-monochromated Mo Kα (λ = 0.710 69 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–iodoethane mixture. Intensity data were also recorded on the Syntex $P2_1$ diffractometer with use of a coupled θ (crystal)–2θ (counter) scan. The methods of selection of scan rates and initial data treatment have been described.[19,20] Corrections were made for Lorentz–polarization effects and absorption.

Solution of the Structure. All three structures were solved by the heavy-atom method. Coordinates of the platinum atoms were found from three-dimensional Patterson syntheses, and a series of full-matrix least-squares refinements followed by three-dimensional electron density syntheses revealed all the non-hydrogen atoms. After refinement, 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 more parameters was justified.[21] Further refinement using full-matrix least-squares minimizing $\sum w(|F_o| - |F_c|)^2$ was terminated when the maximum shift/error reached the limits in Table I. No attempt was made to locate the hydrogen atoms. Corrections were made for secondary extinction with the method of Larson.[22] The second perchlorate group in III (the one on the twofold axis) was clearly disordered, and several attempts were made with different orientations and occupancies. The present results are based on refining a constrained ClO_4^- group (Cl–O = 1.430 Å, O–Cl–O = 109.5°) and, while still poor, represent the best refinement. Throughout the refinement, scattering curves were taken from ref 23 and anomalous dispersion corrections from ref 24 were applied to the curves for platinum and chlorine. The atom parameters for non-hydrogen atoms are listed in Tables II–IV.

Results and Discussion

Formation of I, II, and III and the Acidification of G upon N7 Platination. Compound I was prepared by reacting *cis*-

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Table I. Crystal Data

	I	II	III
compd	$C_{12}H_{22}Cl_2N_{10}O_{10}Pt$	$C_{12}H_{29}ClN_{10}O_{10}Pt$	$C_{24}H_{43}Cl_3N_{20}O_{16}Pt_2$
fw	732.36	703.97	1364.27
cryst size, mm	cylinder, $r = 0.087$, $l = 0.40$	cylinder, $r = 0.133$, $l = 0.46$	cylinder, $r = 0.075$, $l = 0.25$
systematic absences	$0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$	$0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$	hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$
space group	$P2_1/n$[a]	$P2_1/c$	$C2/c$
unit cell parameters			
a, Å	20.117 (7)	12.344 (4)	23.467 (16)
b, Å	27.017 (5)	16.103 (5)	11.960 (3)
c, Å	8.727 (2)	12.517 (4)	16.093 (4)
β, deg	105.13 (2)	90.26 (3)	106.56 (4)
V, Å^3	4602 (2)	2488 (1)	4330 (3)
Z	8	4	4
ρ(calcd) g cm^{-3}	2.11	1.88	2.09
ρ(obsd), g cm^{-3}	2.10 (2)	1.90 (2)	
linear abs coeff, cm^{-1}	67.2	61.1	70.7
abs coeff limits	2.64–2.69	3.57–3.70	2.25–2.29
max 2θ, reflctns collected	45°; $h,k,\pm l$	45°; $h,k,\pm l$	55°; $h,k,\pm l$
std reflctns (esd)	−4,0,−2 (1.44%); −1,−1,−2 (1.77%)	5,−3,3 (2.00%); 3,−2,2 (1.61%)	−1,1,−3 (0.40%); 3,3,−3 (1.74%)
temp, °C	22	22	22
no. of independent reflctns	3875	3279	3749
no. with $I > 3\sigma(I)$	2815	2384	2507
no. with $3\sigma(I) > I > 0$	315	614	641
no. with $I < 0$, rejected	5	281	591
final R_1, R_2[b]	0.0552, 0.0662	0.0484, 0.0667	0.0473, 0.0668
final shift/error max (av)	0.023 (0.007)	0.038 (0.019)	0.154 (0.068)
g (secondary extinction)	3.84×10^{-8}	1.35×10^{-8}	1.82×10^{-8}
final difference map			
highest peak, e Å^{-3}; location	1.83; −0.06, 0.23, 0.65	0.92; 0.05, 0.70, 0.60	1.45; 0.25, 0.40, 0.95
lowest peak, e Å^{-3}; location	−0.89; 0.74, 0.10, 0.50	−0.70; 0.25, 0.15, 0.40	−1.13; 0.45, 0.00, 0.70
weighting scheme	$w = (99.51 - 0.8942\lvert F_o\rvert + 0.00385\lvert F_o\rvert^2)^{-1}$	$w = (\sigma^2 + (0.05F_o)^2)^{-1}$	$w = (\sigma^2 + (0.06F_o)^2)^{-1}$
error in an observn of unit wt	0.996	1.092	0.900

[a] This cell can be transformed to the $P2_1/c$ cell with $a = 8.727$ (2) Å, $b = 27.017$ (5) Å, $c = 19.728$ (7) Å, and $\beta = 100.15$ (2)° by the matrix (0,0,−1/010/101). [b] $R_1 = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$; $R_2 = (\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^2)^{1/2}$.

[aquo(1-methylcytosine-N^3)diammineplatinum(II)] perchlorate with 9-ethylguanine and isolated from slightly acidic solution (pH 4–5). Upon treatment with 1 equiv of NaOH, compound II was obtained from the strongly basic medium (pH 10–11). Treatment of I with 0.5 equiv of NaOH, corresponding to a titration of I up to pH = pK_a of the reaction

$$\mathrm{I} \underset{+\mathrm{H}^+}{\overset{-\mathrm{H}^+}{\rightleftharpoons}} \mathrm{II}$$

resulted in the formation of III in high yield.

Mixtures of III with I and II, respectively, were obtained over the range $4 \lesssim \mathrm{pH} \lesssim 10.5$. Therefore the two equilibria between I, II, and III can be formulated as

$$\mathrm{I} + H_2O \rightleftarrows \mathrm{II} + H_3O^+ \qquad \mathrm{p}K = 8.2 \pm 0.05$$

$$\mathrm{I} + \mathrm{II} \rightleftarrows \mathrm{III}$$

At pH 7.4 (physiological pH), the distribution between I and II in diluted aqueous solution is roughly 85:15. With increasing concentration the amount of III is growing at the expense of II and I.

In compound I the acidity of the N1 proton of the 9-ethylguanine ligand is changed by approximately 1.6 pK units compared to that of the free ligand. The observed acidification as a consequence of the inductive effect of platinum at the N7 position lies in the range observed for similar complexes of Cu and Zn[25] and Ru[26] as well as platinum complexes of G containing dinucleotides.[10,27] Only a slight increase in acidity (0.3 and 0.6 pK unit, respectively) of GMP in the 2:1 complexes of cis and trans Pt(II) has been reported by Tobias and co-workers, but greater acidity changes were found for the 1:1 complexes of the same ligand (Δ(pK) = 1 and 2.8).[7]

Structures. The molecular cations are illustrated in Figure 1, and selected interatomic distances and angles are given in Table V. The two independent molecules in I have a structural arrangement such that O(2A) and O(6)[3] and O(2C) and O(6B) are on the same side of the square plane and there is no internal hydrogen bonding in the cations. This results in large ring–ring and ring–square-plane dihedral angles (see Table VI; ring–ring 104 (1), 103 (1)°; G–square plane 84 (1), 88 (1)°; C–square plane 87 (1), 88 (1)°). In II and III, however, the cytosine ring is flipped over such that O(2A) and O(6) are on opposite sides of the square plane and so that internal hydrogen bonding occurs between N(4A) and O(6). This causes a significant change in the ring–square-plane dihedral angles (G–square plane for II 74 (1)°, for III 74 (1)°; C–square plane for II 78 (1)°, for III 65 (1)°), although the ring–ring angles are not much changed (for II 97 (1)°, for III 99 (1)°). Pt–N bond lengths lie within the range we have observed previously.[12,28,29] The errors do not allow differentiation of pairs of bond lengths, but Pt–NH$_3$ bond distances average about 2.06 Å and Pt–N(base) distances average 2.02 Å. N–Pt–N angles do not differ significantly from the ideal square-planar 90 and 180°. Because of the relatively large errors, bond lengths and angles within the bases do not differ significantly nor do they differ from values reported by Voet and Rich.[30] In particular, it is not possible to see any angular change at N(1) or adjacent C(6) or C(2) associated with the

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Table II. Atom Positional Parameters (×10^3) for *cis*-Diammine(1-methylcytosine-N^3)(9-ethylguanine-N^7)-platinum(II) Diperchlorate (I), $C_{12}H_{22}Cl_2N_{10}O_{10}Pt$

	x	*y*	*z*
Pt(1)	271.35 (4)	161.32 (3)	942.07 (9)
N(11)	204.3 (9)	200.1 (6)	1039 (2)
N(12)	351.6 (9)	174.3 (6)	1137 (2)
N(1)	149.8 (8)	232.9 (6)	417 (2)
C(2)	103 (1)	202.5 (8)	321 (2)
N(2)	74 (1)	218.3 (7)	167 (2)
N(3)	84.1 (9)	159.1 (6)	366 (2)
C(4)	120 (1)	146.6 (7)	510 (2)
C(5)	169.3 (9)	172.5 (6)	618 (2)
C(6)	183 (1)	220.8 (7)	587 (3)
O(6)	219.3 (7)	253.7 (5)	658 (1)
N(7)	193.6 (8)	145.7 (6)	750 (2)
C(8)	159 (1)	102.1 (8)	738 (2)
N(9)	114.3 (9)	102.5 (6)	584 (2)
C(9)	72 (2)	58 (1)	502 (4)
C(10)	2 (2)	69 (1)	465 (4)
N(1A)	404 (1)	123.4 (7)	663 (2)
C(1A)	438 (1)	152 (1)	554 (3)
C(2A)	366 (1)	149.1 (8)	748 (2)
O(2A)	366.2 (7)	194.0 (6)	748 (2)
N(3A)	335.4 (8)	121.9 (6)	843 (2)
C(4A)	340 (1)	71.3 (8)	850 (2)
N(4A)	308.8 (9)	47.4 (6)	939 (2)
C(5A)	379 (1)	46.5 (8)	759 (3)
C(6A)	409 (1)	74 (1)	666 (3)
Pt(2)	739.66 (4)	152.18 (3)	517.66 (9)
N(21)	804.9 (9)	189.7 (6)	410 (2)
N(22)	657.8 (9)	165.1 (6)	321 (2)
N(1B)	858.3 (9)	224.2 (6)	1040 (2)
C(2B)	907 (1)	194.0 (7)	1130 (2)
N(2B)	935 (1)	210.8 (7)	1285 (2)
N(3B)	931.5 (9)	153.5 (6)	1088 (3)
C(4B)	894 (1)	140.1 (8)	941 (2)
C(5B)	842 (1)	166.1 (7)	840 (2)
C(6B)	825 (1)	212.9 (7)	881 (2)
O(6B)	784.4 (7)	243.7 (5)	802 (1)
N(7B)	820.1 (8)	137.3 (6)	704 (2)
C(8B)	858 (1)	96.5 (8)	719 (2)
N(9B)	904.4 (9)	97.9 (6)	866 (2)
C(9B)	956 (1)	57.9 (9)	931 (3)
C(10B)	1032 (1)	78 (1)	952 (3)
N(1C)	607 (1)	115.8 (7)	803 (2)
C(1C)	575 (1)	146.8 (9)	902 (3)
C(2C)	643 (1)	141.0 (8)	708 (2)
O(2C)	642.0 (8)	186.2 (6)	708 (2)
N(3C)	677.9 (9)	112.9 (6)	625 (2)
C(4C)	674 (1)	62.9 (8)	625 (2)
N(4C)	706.6 (9)	38.5 (7)	537 (2)
C(5C)	635 (1)	38.5 (9)	714 (3)
C(6C)	605 (1)	65 (1)	803 (3)
Cl(1)	508.2 (3)	74.2 (2)	241.1 (8)
O(11)	476 (3)	35 (2)	129 (7)
O(12)	498 (2)	43 (1)	354 (4)
O(13)	466 (2)	107 (1)	159 (4)
O(14)	571 (1)	71 (1)	198 (3)
Cl(2)	246.4 (3)	91.7 (2)	320.4 (8)
O(21)	195 (1)	84.0 (8)	178 (3)
O(22)	252 (1)	143.2 (7)	357 (2)
O(23)	309 (1)	75.9 (7)	293 (1)
O(24)	235 (1)	65.4 (7)	450 (2)
Cl(3)	785.3 (5)	69.5 (3)	177 (1)
O(31)	826 (2)	68 (1)	330 (4)
O(32)	718 (1)	56.3 (8)	177 (2)
O(33)	809 (1)	38 (1)	77 (3)
O(34)	782 (1)	119 (1)	127 (3)
Cl(4)	4.7 (3)	232.7 (2)	726.4 (7)
O(41)	−27 (1)	249 (1)	845 (3)
O(42)	4 (2)	185 (2)	710 (5)
O(43)	18 (2)	261 (1)	601 (5)
O(44)	68 (3)	243 (2)	810 (6)

Table III. Atomic Positional Parameters (×10^4) for *cis*-Diammine(1-methylcytosine-N^3)(9-ethylguaninato-N^7)-platinum(II) Perchlorate Tetrahydrate (II), $C_{12}H_{29}ClN_{10}O_{10}Pt$

	x	*y*	*z*
Pt	2532.9 (4)	8164.5 (3)	980.3 (3)
N(11)	971 (9)	7755 (7)	744 (9)
N(12)	3023 (9)	6963 (6)	1294 (9)
N(1)	1351 (8)	9778 (6)	−2179 (7)
C(2)	909 (10)	10516 (8)	−1951 (10)
N(2)	518 (10)	10957 (8)	−2804 (9)
N(3)	825 (8)	10895 (6)	−1001 (8)
C(4)	1246 (9)	10386 (7)	−214 (9)
C(5)	1677 (9)	9631 (7)	−359 (8)
C(6)	1773 (9)	9292 (7)	−1406 (9)
O(6)	2212 (7)	8595 (5)	−1617 (7)
N(7)	2026 (8)	9327 (6)	647 (7)
C(8)	1794 (10)	9923 (8)	1321 (10)
N(9)	1336 (8)	10587 (6)	850 (7)
C(9)	1005 (11)	11377 (9)	1350 (11)
C(10)	1749 (16)	12107 (12)	976 (15)
N(1A)	5517 (10)	8869 (8)	2374 (10)
C(1A)	5921 (8)	8913 (8)	3525 (10)
C(2A)	4461 (11)	8626 (9)	2216 (10)
O(2A)	3867 (9)	8434 (7)	2971 (9)
N(3A)	4064 (8)	8551 (6)	1175 (7)
C(4A)	4736 (11)	8703 (8)	350 (10)
N(4A)	4438 (10)	8630 (8)	−634 (9)
C(5A)	5821 (13)	8997 (10)	551 (13)
C(6A)	6179 (14)	9076 (11)	1553 (13)
Cl	3969 (4)	1223 (4)	3224 (4)
O(11)	4544 (25)	866 (20)	3983 (25)
O(12)	2848 (31)	1448 (22)	3487 (28)
O(13)	3922 (17)	720 (12)	2285 (16)
O(14)	4471 (20)	1931 (14)	2938 (19)
O(W1)	691 (9)	5967 (7)	968 (8)
O(W2)	1081 (9)	7163 (7)	−1528 (9)
O(W3)	1364 (12)	4314 (9)	9808 (11)
O(W4)	2410 (12)	5880	−698 (12)

deprotonation. There appears to be an increase in Pt–N(7)–C(8) (~5°) and Pt–N(3A)–C(2A) (~4°) on deprotonation, and we assume this is caused by the structural change associated with the internal hydrogen bonding.

The packing of the compounds is shown in Figures 2–4. For I (Figure 2) the structure is made up of zigzag chains of cations along the *c* direction centered roughly at $x = {}^1/_4, {}^3/_4$, and $y = {}^1/_4, {}^3/_4$. Within the chains adjacent molecules are hydrogen bonded together in two ways, both of which are clearly shown in the diagram. In mode 1 (lower left) the molecules are pseudocentrosymmetrically joined by N(1)–O(2C), N(2)–O(2C) and N(1B)–O(2A), N(2B)–O(2A) hydrogen bonds. In mode 2 (lower right) the molecules are again pseudocentrosymmetrically joined by N(11)–O(6B) and N(21)–O(6) hydrogen bonds and much weaker hydrogen bonds N(12)–O(6B) and N(22)–O(6). In addition, there are possibly further weak N(11)–N(2) and N(21)–N(2B) hydrogen bonds.

There is almost no direct interaction between the chains which are effectively separated by the perchlorate groups. The remaining interactions are ionic and van der Waals interactions aided by some very weak hydrogen bonds between nitrogen atoms and the perchlorate ions. Indeed, the perchlorate ions seem to be positioned so as to maximize the interaction with the π systems of the two ring systems.

For II (Figure 3) the structure comprises chains of cations hydrogen bonded together, running along the *c* direction, centered roughly at $x = {}^1/_4$, $y = {}^3/_4$ and $x = {}^3/_4$, $y = {}^1/_4$. There is direct hydrogen bonding through N(12)–O(6) and water-mediated hydrogen bonding through O(2A)–O(W4) (strong), O(W4)–N(12) (weak) and N(11)–O(W1) (medium), O(W1)–O(6) (strong). There is significant interaction between the chains, with a partial cytosine–cytosine overlap near the center of the cell and guanine–guanine overlap, maximizing π–π interactions, at $x = 0$. This is aided by further hydrogen bonding involving O(W1) (see above) through O(W1)–N(2) and O(W1)–N(1) and also N(11)–N(3). The water molecules are concentrated near the $x = 0$ face

Table IV. Atomic Positional Parameters ($\times 10^4$) for *cis*-Diammine(1-methylcytosine-N^3)(9-ethylguanine-N^7)-platinum(II) *cis*-Diammine(1-methylcytosine-N^3)-(9-ethylguaninato-N^7)platinum(II) Triperchlorate (III), $C_{24}H_{43}Cl_3N_{20}O_{16}Pt_2$

	x	y	z
Pt	1534.9 (2)	2385.2 (3)	467.0 (3)
N(11)	1775 (5)	777 (9)	839 (7)
N(12)	2393 (5)	2874 (9)	1081 (7)
N(1)	−103 (5)	1289 (9)	1621 (7)
C(2)	−629 (5)	985 (9)	1006 (7)
N(3)	−720 (5)	963 (8)	163 (7)
C(4)	−242 (5)	1324 (8)	−79 (7)
C(5)	305 (5)	1640 (9)	454 (7)
C(6)	380 (6)	1641 (10)	1363 (8)
N(7)	668 (4)	1900 (8)	−49 (6)
C(8)	348 (5)	1789 (10)	−874 (8)
N(9)	−198 (5)	1402 (8)	−895 (6)
N(2)	−1066 (6)	713 (10)	1360 (8)
O(6)	859 (4)	1868 (8)	1933 (6)
C(9)	−670 (6)	1157 (11)	−1729 (9)
C(10)	−1182 (8)	2000 (15)	−1895 (11)
N(1A)	1379 (5)	5525 (9)	−785 (8)
C(2A)	945 (6)	4599 (10)	441 (8)
N(3A)	1317 (5)	3979 (8)	111 (6)
C(4A)	1569 (6)	4489 (10)	−505 (8)
C(5A)	746 (6)	5690 (11)	114 (9)
C(6A)	967 (7)	6090 (13)	−523 (10)
C(1A)	1644 (9)	6046 (16)	−1456 (12)
O(2A)	1954 (4)	3996 (7)	−725 (6)
N(4A)	766 (5)	4141 (9)	1089 (7)
Cl(1)	2501 (2)	4156 (3)	6745 (3)
O(11)	2966 (8)	4849 (14)	7312 (11)
O(12)	2550 (7)	4361 (14)	5921 (11)
O(13)	2657 (8)	3076 (15)	7078 (11)
O(14)	1958 (8)	4569 (14)	6801 (11)
Cl(2)	0	4395 (20)	7500
O(21)[a]	53 (30)	4066 (20)	8375 (20)
O(22)[a]	−87 (30)	4425 (20)	7583 (20)
O(23)[a]	531 (30)	4098 (20)	7284 (20)
O(24)[a]	−497 (30)	3833 (20)	6926 (20)

[a] Atoms with half-occupancy. The Cl(2) perchlorate ion was refined as a group with tetrahedral geometry and Cl–O = 1.430 (2) Å. Errors in positional coordinates are derived from the bond length error.

and in addition to the hydrogen bonds mentioned above provide further cross-linking and stabilization of the structure through hydrogen bonds to each other and one relatively strong hydrogen bond to the perchlorate group (O(W3)–O(12)). The perchlorate groups lie close to the $x = {}^1/_2$ plane and fill the space between cytosine rings, interacting mainly by ionic and van der Waals forces, although there are two very weak hydrogen bonds to the cation (N(12)–O(14) and N(4A)–O(13)).

The structure of III is shown in Figure 4 and comprises stacks of pairs of cations along the *b* direction. The pairs of cations (center of diagram) are arranged so as to maximize the π–π overlap of the guanine molecules. In addition there are very weak N(11)–N(3) hydrogen bonds between the two molecules. The stacks are separated by a lattice of layers of perchlorate ions lying along the $x = {}^1/_4, {}^3/_4$ and $z = {}^1/_4, {}^3/_4$ planes. Nevertheless there is interaction between neighboring cation stacks through hydrogen bonding, and this shows one of the most interesting features of the structure. In the *c* direction there is hydrogen bonding between the N(1) positions of a G and G-H molecule (2.73 (1) Å) and consequent N(2)–O(6) (2.99 (1) Å) hydrogen bonds giving rise to a novel G–G⁻ base pair akin to the more normal G–C pair. The G and G-H molecules are related by a twofold axis, and we assume, therefore, that the hydrogen atom is disordered about the axis. We have commented on the consequences of this previously.[14] It should be noticed, however, that the two hydrogen-bonded guanine molecules are not coplanar. There is a rotation about the N(1)–N(1) axis, giving an interplanar dihedral angle of 39 (1)°, which accounts for the N(2)–O(6) distances being considerably longer than N(1)–N(1). In the *a* direction the stacks are bonded through N(11)–O(2) and N(12)–O(2A) hydrogen bonds. Except for N(21)–O(21) (2.96 (2) Å), hydrogen bonds to the perchlorate ions are relatively weak. The perchlorate ions seem only to act as space fillers and are involved primarily in ionic and van der Waals interactions, which probably accounts for the high temperature factors and disorders.

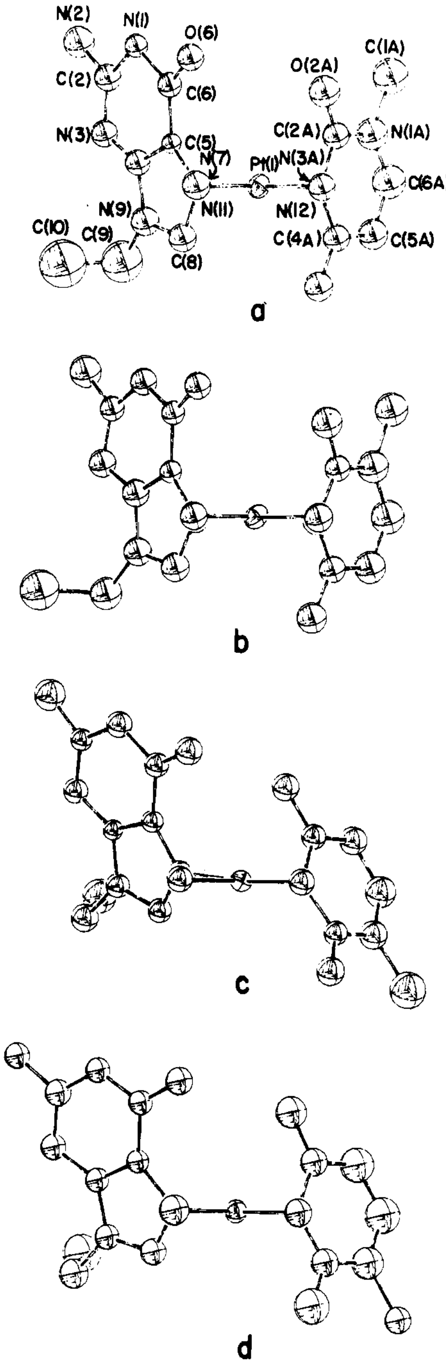

Figure 1. The molecular cations in (a) $[Pt(NH_3)_2CG](ClO_4)_2$ (I) cation 1, (b) $[Pt(NH_3)_2CG](ClO_4)_2$ (I), cation 2, (c) $[Pt(NH_3)_2CG][Pt(NH_3)_2C(G\text{-}H)](ClO_4)_3$ (III), and (d) $[Pt(NH_3)_2C(G\text{-}H)]ClO_4 \cdot 4H_2O$ (II). The labeling in c and d is the same as in a with allowance for the rotation of the cytosine molecule. In b the labeling can be obtained from a by the equivalences N(1) etc. = N(1B) etc., N(1A) etc. = N(1C) etc., Pt(1) = Pt(2), and N(11, 12) = N(21,22). All molecules are viewed along the axis from the midpoint of N(11) and N(12) to platinum.

Raman Solution Spectra (Me$_2$SO). In Table VI, Raman frequencies and relative intensities of I, II, and III in dimethyl

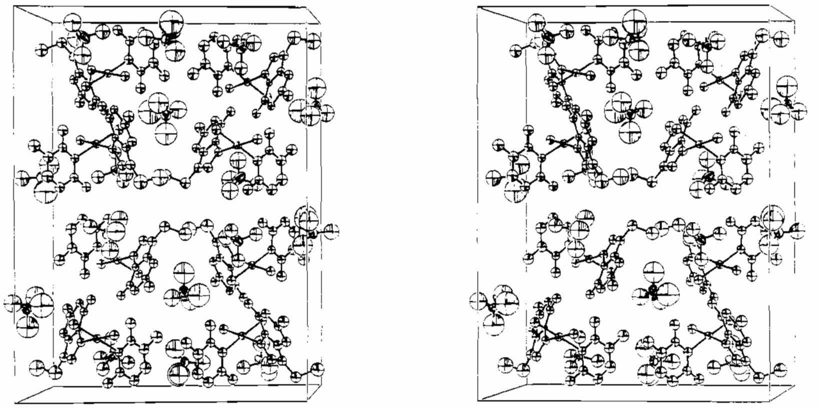

Figure 2. Packing in the unit cell of $[Pt(NH_3)_2CG](ClO_4)_2$ (I). *a* and *b* are parallel to the bottom and side of the page, respectively, and the view is down *c**.

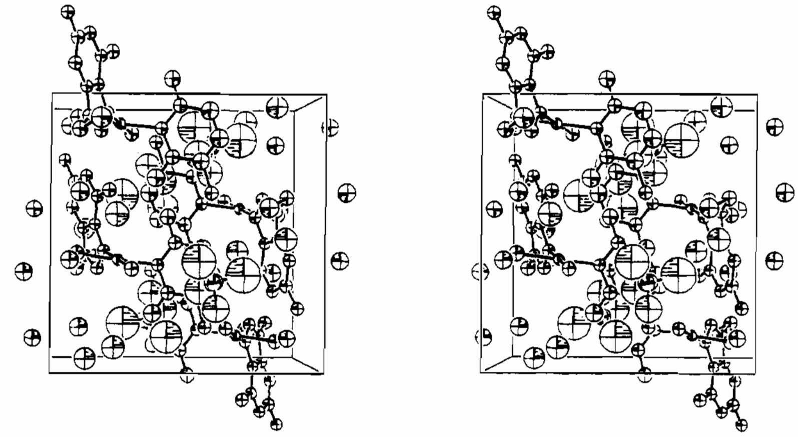

Figure 3. Packing in the unit cell of $[Pt(NH_3)_2C(G\text{-}H)](ClO_4)\cdot 4H_2O$ (II). *a* and *c** are parallel to the bottom and side of the page, respectively, and the view is down *b*.

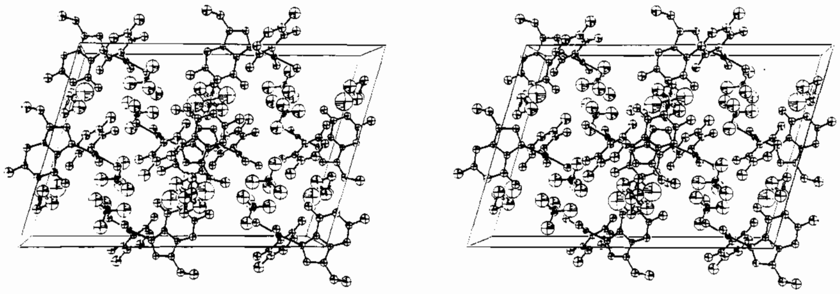

Figure 4. Packing in the unit cell of $[Pt(NH_3)_2CG][Pt(NH_3)_2C(G\text{-}H)](ClO_4)_3$. *a* and *c** are parallel to the bottom and side of the page, respectively, and the view is down *b*.

sulfoxide, Me_2SO, between 400 and 1700 cm^{-1} are listed. Me_2SO was used because it represents a destacking solvent and favors hydrogen bonding between the halves of III. At the concentration applied (0.25 M Pt) the Raman spectrum of III is a good superposition of the individual spectra of I and II. Minor differences probably are a consequence of hydrogen bonding between I and II in compound III.

A single set of signals for G and C resonances of III is observed in the ^1H NMR spectrum of III in the same solvent at room temperature.[15] This clearly indicates that proton exchange (N1H) between the halves of III is occurring. Because of the slow time scale of the NMR experiment, an average spectrum between I and II is observed, whereas the fast time scale of the Raman spectrum permits detection of all species in solution.

1-Methylcytosine bands in I, II, and III are identified by comparison with a great number of related complexes with N3 coordination of this ligand to the *cis*-diammineplatinum(II) moiety[11,12c,15] and bands of the 9-ethylguanine ligand (neutral and anionic) by comparison with *cis*-$[Pt(NH_3)_2G_2]^{2+}$ [15] and *cis*-$[Pt(NH_3)_2(G\text{-}H)_2]$.[31] The positions of cytosine bands in I and II differ only slightly (≤ 2 cm^{-1}). This is not unexpected, since the donor atom of 1-methylcytosine (N3) is identical in both compounds and any changes in the ligand sphere of platinum should not affect the cytosine modes strongly. In contrast, a series of bands attributable to the guanine ligand show distinct differences in I and II, reflecting the deprotonation of this ligand in II. This is seen particularly well in the 1500–1700-cm^{-1} range. In this range, which contains modes that are primarily C=O, C=C, and C=N stretching motions,[32] shifts of at least three of the G bands are observed.

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(31) Faggiani, R.; Lippert, B.; Lock, C. J. L., manuscript in preparation.

(32) Approximate descriptions of these modes have been given. See, e.g.: (a) Lord, R. C.; Thomas, G. J., Jr. *Spectrochim. Acta, Part A* **1967**, *23A*, 2551. (b) Small, E. W.; Peticolas, W. L. *Biopolymers* **1971**, *10*, 1377. (c) Rice, J.; Lafleur, L.; Medeiros, G. C.; Thomas, G. J., Jr. *J. Raman Spectrosc.* **1973**, *1*, 207. (d) Lane, M. J.; Thomas, G. J., Jr. *Biochemistry* **1979**, *18*, 3838.

Table V. Selected Interatomic Distances (Å) and Angles (Deg)

	IA	IB	II	III		IA	IB	II	III
Pt-N(11)	2.06 (2)	2.06 (2)	2.06 (1)	2.05 (1)	Pt-N(12)	2.05 (1)	2.07 (1)	2.06 (1)	2.06 (1)
Pt-N(3A)	2.03 (2)	2.04 (2)	2.00 (1)	2.01 (1)	Pt-N(7)	2.01 (1)	2.01 (1)	2.016 (9)	2.05 (1)
N(1)-C(2)	1.36 (2)	1.36 (2)	1.34 (2)	1.39 (2)	C(2)-N(3)	1.32 (3)	1.29 (3)	1.34 (2)	1.31 (2)
N(3)-C(4)	1.33 (2)	1.35 (3)	1.38 (2)	1.36 (2)	C(4)-C(5)	1.36 (2)	1.37 (3)	1.34 (2)	1.38 (1)
C(5)-C(6)	1.40 (3)	1.39 (3)	1.43 (3)	1.42 (2)	C(6)-N(1)	1.43 (2)	1.41 (2)	1.35 (2)	1.38 (2)
C(5)-N(7)	1.34 (2)	1.39 (2)	1.42 (1)	1.37 (2)	N(7)-C(8)	1.35 (3)	1.33 (2)	1.31 (2)	1.33 (1)
C(8)-N(9)	1.35 (2)	1.38 (3)	1.35 (2)	1.36 (2)	N(9)-C(4)	1.37 (3)	1.36 (3)	1.37 (1)	1.35 (2)
C(2)-N(2)	1.38 (3)	1.40 (3)	1.37 (2)	1.35 (2)	C(6)-O(6)	1.24 (2)	1.24 (2)	1.28 (1)	1.26 (1)
N(9)-C(9)	1.54 (4)	1.51 (3)	1.48 (2)	1.51 (2)	C(9)-C(10)	1.41 (5)	1.58 (4)	1.56 (2)	1.53 (2)
N(1A)-C(2A)	1.39 (3)	1.39 (3)	1.37 (2)	1.35 (2)	C(2A)-N(3A)	1.37 (3)	1.37 (3)	1.40 (2)	1.43 (2)
N(3A)-C(4A)	1.37 (3)	1.35 (3)	1.35 (2)	1.36 (2)	C(4A)-C(5A)	1.42 (3)	1.40 (4)	1.44 (2)	1.44 (2)
C(5A)-C(6A)	1.36 (4)	1.31 (4)	1.33 (2)	1.36 (2)	C(6A)-N(1A)	1.33 (3)	1.38 (3)	1.36 (2)	1.34 (2)
N(1A)-C(1A)	1.51 (4)	1.48 (4)	1.52 (2)	1.52 (3)	C(2A)-O(2A)	1.21 (3)	1.22 (3)	1.24 (2)	1.21 (2)
C(4A)-N(4A)	1.33 (2)	1.31 (3)	1.33 (2)	1.35 (2)	Cl(1)-O(11)	1.47 (2)	1.37 (2)	1.32 (3)	1.46 (2)
Cl(1)-O(12)	1.35 (2)	1.40 (2)	1.47 (4)	1.39 (2)	Cl(1)-O(13)	1.30 (2)	1.40 (2)	1.43 (2)	1.41 (2)
Cl(1)-O(14)	1.41 (2)	1.40 (2)	1.35 (2)	1.39 (2)	Cl(2)-O(21)	1.41 (2)	1.42 (2)		1.43^a
Cl(2)-O(22)	1.43 (2)	1.30^a		1.43^a	Cl(2)-O(23)	1.41 (2)	1.42 (3)		1.43^a
Cl(2)-O(24)	1.40 (2)	1.32^a		1.43^a					
N(11)-Pt-N(12)	91.7 (7)	90.3 (7)	90.0 (5)	88.7 (4)	N(11)-Pt-N(3A)	178.5 (7)	177.8 (7)	178.6 (4)	178.8 (4)
N(11)-Pt-N(7)	89.9 (7)	89.6 (7)	88.7 (4)	90.6 (4)	N(12)-Pt-N(3A)	89.6 (7)	91.0 (7)	89.6 (4)	90.1 (4)
N(12)-Pt-N(7)	177.7 (6)	177.8 (2)	178.5 (4)	175.4 (5)	N(3A)-Pt-N(7)	88.8 (6)	89.0 (7)	91.6 (4)	90.6 (4)
Pt-N(7)-C(5)	129 (1)	126 (1)	126.8 (7)	122.6 (9)	Pt-N(7)-C(8)	124 (1)	124 (1)	127.9 (8)	130 (1)
C(6)-N(1)-C(2)	123 (2)	122 (2)	121 (1)	120 (1)	N(1)-C(2)-N(3)	124 (2)	128 (2)	129 (1)	126 (2)
C(2)-N(3)-C(4)	112 (2)	110 (2)	109 (1)	113 (1)	N(3)-C(4)-C(5)	130 (2)	128 (2)	126 (1)	127 (1)
C(4)-C(5)-C(6)	117 (2)	120 (2)	120 (1)	117 (2)	C(5)-C(6)-N(1)	113 (2)	111 (1)	114 (1)	116 (1)
C(4)-C(5)-N(7)	110 (2)	106 (2)	108.3 (9)	109 (1)	C(5)-N(7)-C(8)	107 (1)	109 (2)	104.6 (9)	107 (1)
N(7)-C(8)-N(9)	109 (2)	107 (2)	113 (1)	109 (2)	C(8)-N(9)-C(4)	109 (2)	109 (2)	106 (1)	109 (1)
N(9)-C(4)-C(5)	105 (2)	108 (2)	108 (1)	106 (1)	N(1)-C(2)-N(2)	117 (2)	114 (2)	116 (1)	113 (1)
N(3)-C(2)-N(2)	119 (2)	118 (2)	115 (1)	121 (1)	N(3)-C(4)-N(9)	125 (2)	124 (2)	125 (1)	127 (1)
C(6)-C(5)-N(7)	132 (2)	133 (2)	131 (1)	134 (1)	C(5)-C(6)-O(6)	130 (2)	130 (2)	124 (1)	125 (2)
N(1)-C(6)-O(6)	117 (2)	119 (2)	122 (1)	119 (2)	C(8)-N(9)-C(9)	125 (2)	124 (2)	128 (1)	123 (1)
C(4)-N(9)-C(9)	125 (2)	127 (2)	126 (1)	128 (2)	N(9)-C(9)-C(10)	109 (3)	111 (2)	111 (1)	112 (2)
C(6A)-N(1A)-C(2A)	122 (2)	121 (2)	122 (1)	124 (2)	N(1A)-C(2A)-N(3A)	117 (2)	117 (2)	119 (1)	117 (2)
C(2A)-N(3A)-C(4A)	119 (2)	121 (2)	119 (1)	118 (3)	N(3A)-C(4A)-C(5A)	119 (2)	120 (2)	120 (1)	122 (2)
C(4A)-C(5A)-C(6A)	118 (2)	119 (2)	120 (1)	116 (2)	C(5A)-C(6A)-N(1A)	121 (3)	121 (3)	119 (2)	122 (2)
C(2A)-N(1A)-C(1A)	118 (2)	116 (2)	117 (1)	117 (2)	C(6A)-N(1A)-C(1A)	122 (2)	123 (2)	121 (1)	119 (2)
N(1A)-C(2A)-O(2A)	120 (2)	119 (2)	122 (1)	123 (2)	N(3A)-C(2A)-O(2A)	122 (2)	124 (2)	119 (1)	119 (1)
N(3A)-C(4A)-N(4A)	119 (2)	118 (2)	118 (1)	117 (1)	C(5A)-C(4A)-N(4A)	122 (2)	121 (2)	122 (1)	121 (2)
Pt-N(3A)-C(2A)	114 (1)	115 (1)	117.9 (8)	119 (1)	Pt-N(3A)-C(4A)	123 (2)	124 (2)	123.1 (8)	123 (1)
O(11)-Cl(1)-O(12)	85 (2)	109 (2)	117 (2)	104 (1)	O(11)-Cl(1)-O(13)	91 (2)	109 (2)	111 (2)	102 (1)
O(11)-Cl(1)-O(14)	93 (2)	107 (2)	108 (2)	107 (1)	O(12)-Cl(1)-O(13)	129 (2)	110 (2)	107 (2)	116 (1)
O(12)-Cl(1)-O(14)	118 (2)	106 (2)	107 (2)	109 (1)	O(13)-Cl(1)-O(14)	113 (12)	113 (12)	106 (1)	116 (1)
O(21)-Cl(2)-O(22)	110 (2)	113 (2)		109.5^a	O(21)-Cl(2)-O(23)	107 (2)	127 (2)		109.5^a
O(21)-Cl(2)-O(24)	114 (2)	95 (2)		109.5^a	O(22)-Cl(2)-O(23)	108 (22)	117 (2)		109.5^a
O(22)-Cl(2)-O(24)	109 (2)	104 (2)		109.5^a	O(23)-Cl(2)-O(24)	109 (2)	88 (2)		109.5^a

It is known that protonation of a ring atom of a heterocyclic ring (for 9-ethylguanine at N7) leads to a localization of double bonds, resulting in a general shift of these bands to higher frequencies.[32a] On the other hand, deprotonation leads to a migration of the π electrons and consequently to a diminution of the double-bond character.[32a,33,34] This is reflected in a shift of these bands to lower energy. N7 platination has an effect similar to similar protonation, although to a lesser extent.[7]

With regard to the complexes described here, the two most intense bands of 9-ethylguanine (in Me_2SO) at 1484 and 1562 cm^{-1} are shifted to 1500 and 1584 cm^{-1} in *cis*-$[Pt(NH_3)_2GC]^{2+}$ and 1503 and 1583 cm^{-1} in *cis*-$[Pt(NH_3)_2G_2]^{2+}$. Of the weaker bands in the double-bond stretching region, the G band at 1542 cm^{-1} is also shifted to higher energy upon platination (1564 cm^{-1} in I and 1557 cm^{-1} in *cis*-$[Pt(NH_3)_2G_2]^{2+}$), whereas the guanine mode at 1695 cm^{-1}, which has a strong ν(C=O) contribution,[32] does not shift much (1691 cm^{-1} in I and 1694 cm^{-1} in the bis(9-ethylguanine) complex). Two weak bands at 1608 and 1650 cm^{-1} in the guanine spectrum give a rather broad band centered at 1642 cm^{-1} in both platinum compounds with neutral G.

In compound II, *cis*-$[Pt(NH_3)_2(G\text{-}H)C]ClO_4$, contrary effects of platination and deprotonation on the ring double-bond vibrations might be expected. For the intense mode of 9-ethylguanine at 1484 cm^{-1}, the two effects apparently cancel each other, since this mode absorbs in II at nearly the same frequency (1482 cm^{-1}). In contrast, there is a definite shift of the 1691-cm^{-1} band of I to lower frequency in compound II, although the new position of this mode in the spectrum of II is unclear. In any case, the shift to lower wavenumbers indicates a very much reduced double-bond character of the C(6)–O(6) bond and a substantial contribution of an iminolate resonance structure to the overall electronic structure of the deprotonated G ligand. The X-ray results are not definitive; the mean C–O length is longer in the ions containing the G-H molecule, but the errors preclude a definite conclusion. Surprisingly, however, the intense G mode of I at 1584 cm^{-1} appears to be shifted to higher wavenumber in compound II with the deprotonated G ligand (1598 cm^{-1}). On the other hand, the slight asymmetry of this band in the solution spectrum and the presence of two strong bands around 1580 and 1590 cm^{-1} in the solid-state spectra of II and *cis*-$[Pt(NH_3)_2(G\text{-}H)_2]$ might be a hint that there is no actual shift of this G mode but only an apparent one because of insufficient resolution of an overlap with another shifted mode. There is a good possibility this shifted mode is the C(6)–O(6) stretching mode, since in the solid-state spectrum of *cis*-$[Pt(NH_3)_2$(G-

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Table VI. Raman Frequencies of I, II, and III in Me_2SO between 400 and 1700 cm^{-1} in Regions without Solvent Absorptions[a]

I	III	II	assignt
428 (0.6)	424 (0.1)	427 (0.5)	C
458 (1.9)	456 (2.6)	458 (1.3)	$\nu_2(ClO_4)$
478 (3.5)	477 (4.2)	478 (4.0)	C
514 (1.9)	514 (2.0)		G
534 (1.9)	~530 (3.9)	520 (2.3)	ν(Pt-NH_3)
542 (3.2)	541 (3.9)	540 (3.6)	
583 (1.5)	582 (1.9)	585 (2.7)	C
626 (5.2)	625 (4.2)	633 (3.3)	G, $\nu_4(ClO_4)$
645 (4.3)	639 (4.1)	643 (3.9)	C
solvent			
789 (10)	789 (10)	789 (10)	C
828 (1.1)	829 (1.0)	828 (1.2)	C
897 (0.1)	885 (1.0)	887 (0.6)	
solvent			
931 (11.4)	930 (~12)	931 (~10)	$\nu_1(ClO_4)$
solvent			
1163 (0.9)	1164 (0.9)	1163 (0.9)	C
1199 (0.6)	1201 (0.7)	1201 (0.8)	
1221 (0.6)	1224 (0.7)	1231 (1.6)	
1249 (7.1)	1247 (9.2)	1250 (7.9)	C
solvent			
1351 (0.7)	1348 (0.7)		G
	1331 (0.7)	1328 (1.0)	
1384 (3.1)	1384 (4.3)	1381 (3.6)	G
solvent			
	1475 (0.3)	1482 (1.6)	G
1500 (3.8)	1500 (2.9)		
1539 (1.5)	1538 (1.4)	1537 (1.4)	C
	1595 (2.4)	1598 (4.2)	G
1584 (5.7)	1586 (5.8)		
1642 (0.9)	1639 (1.0)	1642 (1.3)	
1678 (0.7)	1686 (1.5)	~1670 (~2.0)[b]	
1691 (1.8)			G

[a] Intensities (given in parentheses) are relative to that of the strongest C band at 789 cm^{-1} with arbitrary intensity 10. The slit width is 4 cm^{-1}, and the concentration of Pt is 0.25 M.
[b] Center of a very broad band, possibly superposition of two bands (~1656, ~1677 cm^{-1}) or even three bands.

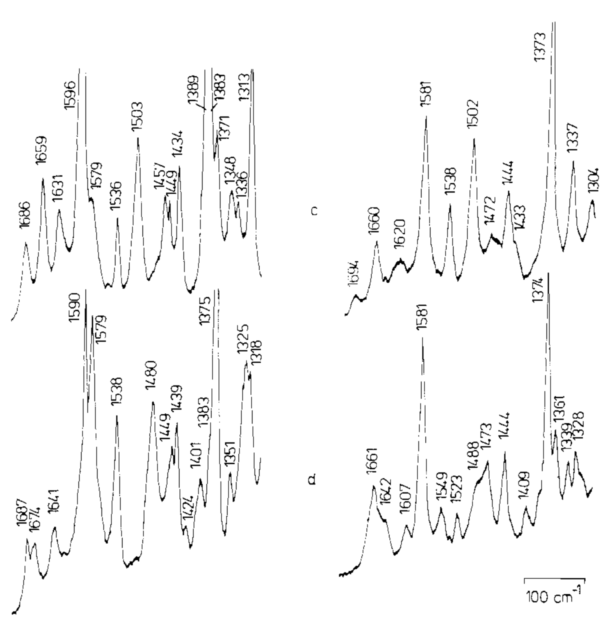

Figure 5. Solid-state Raman spectra between 1700 and 1300 cm^{-1}: (a) I; (b) II; (c) III; (d) deuterated III (ND_3, ND_2 (C); ND_2, ND, C(8)D (G)). The slit width is 4 cm^{-1} in all spectra.

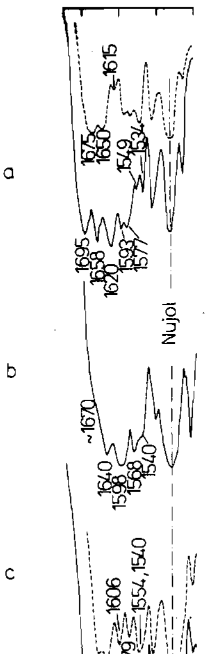

Figure 6. Solid-state infrared spectra (Nujol) between 1750 and 1400 cm^{-1}: (a) I (solid line), deuterated (ND_3, ND_2, ND) I (broken line); (b) II; (c) III (solid line), deuterated (ND_3, ND_2, ND, C(8)D) III (broken line). Indicated wavenumbers were taken from spectra recorded at an extended scale with maximum resolution of 1.3 cm^{-1}.

$H)_2$] there is no band in the 1600–1750-cm^{-1} region.[35]

A Raman spectroscopic change between I and II is also observed for one of the two Pt–NH_3 stretching modes. In I bands at 534 and 542 cm^{-1} are observed, whereas in II one band is shifted to 520 cm^{-1} while the second one remains almost unchanged (540 cm^{-1}). We assign the 534- and 520-cm^{-1} bands to the Pt–NH_3 stretching vibration of the NH_3 group trans to 9-ethylguanine and the deprotonated ligand. The 542- and 540-cm^{-1} bands are thus assigned to the Pt–NH_3 stretching vibration of the NH_3 trans to the 1-methylcytosine ligand. This assignment is consistent with our previous findings on a number of *cis*-diammineplatinum(II) complexes of 1-methylcytosine.[11,12,15]

Solid-State Raman and Infrared Spectra and the NHN Hydrogen Bond in III. It is not possible to say from the crystallographic results whether the hydrogen atom between the N1 positions on the two guanine ligands in III is on the twofold axis or disordered about the axis, although the bond length (2.73 (1) Å) is typical of noncentered hydrogen bonds.[36,37] Noncentered bonds appear to be more common than centered hydrogen bonds.[36,38,39] The potential for noncentered hydrogen bonds can vary from a system with a well-defined barrier[40] to a shallow double-minimum approaching the single-minimum case.[41] We have examined the solid-state vibrational spectra of I, II, and III (Table VII) to see whether the theory of Wood[42] could be applied to the

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(35) Because of very low solubility in Me_2SO, a solution spectrum of *cis*-$Pt(NH_3)_2(G\text{-}H)_2$ could not be obtained.

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Table VII. Raman Frequencies of I, II, and III between 300 and 1700 cm^{-1} in the Solid State[a]

I	III	II
326, 330 (1.6) G	336 (1.5)	331 (1.9) G
360 (1.2) G	375 (2.0)	379 (0.5) G
394 (1.3)	401 (1.2)	408 (2.2)
413 (1.6)	419 (1.4)	427 (0.7)
458 (3.9) C, $\nu_2(ClO_4)$	447 (0.6)	448, 453, 462 (2.0) C, $\nu_2(ClO_4)$
	461 (3.1)	
478 (3.8) C	480 (4.8)	477 (5.6) C
519 (1.8) 528 (3.9) 537 (4.7) } $\nu(Pt-NH_3)$, G	516 (3.4) 530 (5.5)	518 (3.7) 533 (2.2) } $\nu(Pt-NH_3)$, G (?)
		560 (1.2) G (?)
579 (2.3) C	580 (2.3)	583 (1.2) C
627 (11.1) 644 (7.6) } G, C, $\nu_4(ClO_4)$	625, 632 (5.7) 648 (5.7)	624 (0.8) 632 (8.8) 642 (6.7) } G, C, $\nu_4(ClO_4)$
		692 (0.6)
721 (1.3) G, C	734 (0.8)	722 (0.7) G
	771 (0.4)	770 (0.5)
791 (10.0) C	794 (10.0)	792 (10.0) C
833 (1.5) C	836 (1.5)	829 (2.1) C
886 (0.9) G	881 (0.4)	885 (0.6) G
911 (2.4)	914 (1.0)	912 (0.4)
930 (18.9) $\nu_1(ClO_4)$	924, 931 (13.9)	928 (2.8) 934, 939 (6.5) 948 (0.7) } $\nu_1(ClO_4)$ + ?
978 (1.1) C, G(?)	980 (1.0)	977 (1.0) C, G
		992 (0.4)
1030 (0.7) G	1023 (1.3)	1018 (1.3) G
1055 (0.3)		
1075 (1.4) G	1079 (0.7)	1081 (0.9) G
1098 (0.9) G	1099 (0.7)	
		1108 (0.9) C
1117 (1.0) G, C	1115 (0.4)	1124 (0.9)
1168 (1.1) C	1156 (1.4)	1158 (0.9) C
1186 (0.7)	1171 (0.4)	
1211 (0.4) C	1200 (0.8)	1201 (1.1) C
1229 (0.4)	1224 (0.8)	1225 (2.0) G
1243 (0.4)		
1265 (10.0) C	1253 (11.2)	1246 (8.7) C
		1278 (0.8)
		1295 (1.5) G
1313 (4.5) G	1304 (1.5)	1318, 1325 (2.6) G
1336 (1.8) 1348 (1.9) } G, C	1337 (2.6)	1351 (1.0) C
1371 (1.6) 1383, 1389 (8.0) } G	1373 (11.8)	1375, 1383 (8.3) G
		1401 (1.0) G
1433 (2.2) G, C	1433 (0.4)	1424 (0.4), 1439 (1.9)
1449, 1457 (1.7) G	1444 (2.4)	1449 (1.6) G
	1472 (1.0)	
1503 (2.7) G	1502 (3.8)	1480 (2.3) G
1536 (1.3) C	1538 (1.9)	1538 (2.1) C
1579 (1.6) G	1581 (4.2)	1579 (3.9) G
1596 (7.4) G		1590 (3.7) G
1631 (1.1) C	1620 (0.6)	1641 (0.6) C
1659 (2.0)	1660 (1.5)	1674 (0.6) C
1686 (1.0)	1694 (0.5)	1687 (0.8)

[a] Intensities (given in parentheses) are relative to that of the C band around 790 cm^{-1} with arbitrary intensity 10. The slit width is 2-4 cm^{-1}. Partial assignments were made from comparison with *cis*-$[Pt(NH_3)_2C_2]^{2+}$, *cis*-$[Pt(NH_3)_2G_2]^{2+}$, and *cis*-$Pt(NH_3)_2(G-H)_2$.

number of observed modes to give a definitive answer. Single noncoincident bands in the Raman and infrared spectra are expected for a single minimum, whereas doubling of internal modes in both infrared and Raman spectra is expected for a double minimum with a high barrier. If the barrier is low, a quartet of bands may result from interaction of proton tunneling with vibrations localized in the rings. Although there are marked differences in the hydrogen-bonding region of the spectra of III compared to those of I and II, one cannot use this region because unambiguous identification of all the modes present is not possible, even on deuteration, since one cannot selectively deuterate the N(1)-H···N(1) bond (Figures 5 and 6). In all cases, even under very mild conditions (solution in D_2O at room temperature, immediate evaporation at 10 °C), more than 90% deuteration of NH, NH_2 (G), NH_2 (C), and NH_3 and a partial deuteration of the C(8) position of G was achieved. A detailed analysis of the spectral region for the internal modes of these molecules also does not allow a definitive answer. The spectra of III are very "simple"; there is little evidence of band splitting (see Figure 7). The presence of bands in which IR and Raman frequencies do not coincide suggests a strict centering and a centered hydrogen bond, as for example: 375 (Ra), 368 (IR); 734 (Ra), 742 (IR); 1502 (Ra), 1514 (IR); 1581 (Ra), 1574 (IR); deuterated, 1226 (Ra), 1220 (IR); 1523 (Ra), 1516 (IR); 1549 (Ra), 1554, 1540 (IR) cm^{-1}. Several more bands with $\Delta\nu_{IR-RA} \approx$ 3-4 cm^{-1} are present. Nevertheless, band doubling does occur in the deuterated complex, e.g., the shifted 1502-cm^{-1} guanine mode at 1488 and 1473 cm^{-1} in the deuterated compound. Problems in using vibrational spectroscopy to study hydrogen bonding have been found before for the $(py)_2H^+$ cation. Until more work has been done on correlating vibrational spectra with hydrogen bonds of accurately known geometry, spectroscopic studies are unlikely to give a definitive answer.

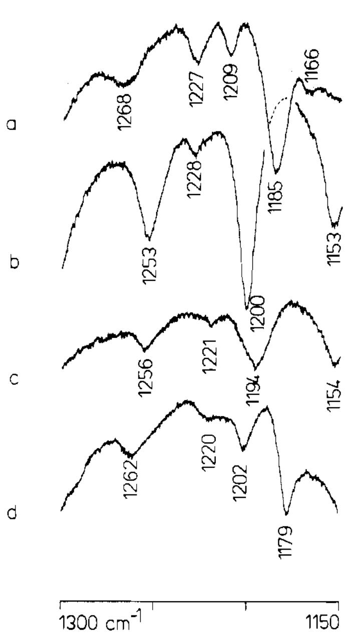

Figure 7. Solid-state infrared spectra (Nujol) between 1300 and 1150 cm^{-1}: (a) I; (b) II; (c) III; (d) deuterated III.

In conclusion, when considering spectroscopic and X-ray data, one is left with conflicting evidence on the actual nature of the NHN hydrogen bond in III, but probably it is a noncentered one with a low potential barrier.

Possible Relevance of $(G_2-H)^-$ Formation. It is possible that the observed hydrogen bonding between a neutral and an anionic 9-ethylguanine represents a general binding pattern of guanine residues in weakly alkaline media. Though we have not been able so far to isolate a crystalline $(G_2-H)^-$ salt, we feel that this was only because of the inappropriate solvents used. If solvents are used in which either G or G-H is very poorly soluble, rapid precipitation of the insoluble component occurs with no complex formation.

With respect to possible implications on base mispairing of platinated, deprotonated G, it has been found[15] that there is strong hydrogen bonding between a Pt(G-H) unit and a neutral

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G in Me_2SO solution. A corresponding compound has now been isolated in crystalline form and is currently being examined. More information concerning the possible biological relevance for a platinum-caused base-mispairing mechanism might be expected from this compound.

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Registry No. I, 79301-66-9; II, 81857-49-0; III, 81875-69-6.

Supplementary Material Available: Listings of temperature factors, hydrogen-bonding distances, least-squares planes and dihedral angles, and moduli of F_o and F_c (49 pages). Ordering information is given on any current masthead page.

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Ketoximato Complexes. Structural and Spectroscopic Study of Tris(5,5-dimethylcyclohexane-1,2,3-trione 2-oximato)cobalt(III) and -ruthenate(II)

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The complexes $Co(dmho)_3$ and $H[Ru(dmho)_3]$ have been isolated and characterized by UV-visible, infrared, and ^1H and ^{13}C NMR spectroscopy ($dmho^-$ is the monoanion of 5,5-dimethylcyclohexane-1,2,3-trione 2-oxime). The crystal and molecular structure of $Co(dmho)_3$ has been investigated by X-ray diffraction techniques. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell of dimensions $a = 11.96$ (1), $b = 18.85$ (2), and $c = 11.89$ (1) Å. The structure was solved by using 1207 symmetry-independent reflections. Refinement by full-matrix least-squares methods with anisotropic temperature factors for all nonhydrogen atoms gave a final R factor of 0.043. The neutral complex $Co(dmho)_3$ has spontaneously resolved upon crystallization to the *fac*-Λ isomer. The coordination polyhedron around cobalt is practically an octahedron with oxygen and nitrogen atoms disposed on opposite triangular faces in a facial configuration. The three five-membered chelate rings have been found to be strictly planar. The cyclohexane rings are puckered and adopt a δ' or λ' conformation. The crystal for which the structure was determined contains one *fac*-Λ(λ'λ'δ') isomer. ^1H and ^{13}C NMR measurements have been done on $Co(dmho)_3$ and $H[Ru(dmho)_3]$. The comparison of the spectra obtained by application of gated-decoupling techniques allows assignments of most resonances to individual carbons. It is found that ^1H and ^{13}C NMR results agree with a facial configuration of the tris chelates in solution. However, there is no conformational preference for the cyclohexane rings in solution.

The current interest in complexes of transition metals with ketoxime[2,3] and nitrosophenol[4] ligands as potential models for metal binding sites in ferroverdin[5,6] has prompted the investigation of the structures and the overall coordination geometry of the metal center in these complexes.[7,8] A further feature of interest is the role played by the (ketoximato)ruthenium complexes in the activation of nitrogen monoxide.[10,11] Oximes and nitroso derivatives[12,13] are interesting ligands since they have low-lying π^* systems which may be accessible for back-bonding and there is a possible ambiguity with regard to the site of binding at N or O atoms.[14-18] More particularly the ketoximes were found to chelate to transition metals through the N (oxime) and O (ketone) atoms.[7-9,19-21] However, monodentate coordination via only one O or N atom has been reported.[10,22] In view of the general interest in the factors determining the geometries and structures of ketoximato complexes, we have investigated the structure of $Co(dmho)_3$ ($dmho^-$ is the monoanion of 5,5-dimethylcyclohexane-1,2,3-trione 2-oxime) to establish the absolute configuration of one diastereoisomer in the solid state. The ^1H and ^{13}C NMR spectra are used as means of investigation of the stereochemistries of $Co(dmho)_3$ and $[Ru(dmho)_3]^-$ in solution.

Experimental Section

Reagent grade materials dimedone, $C_8O_2H_{11}$ (5,5-dimethyl-1,3-cyclohexanedione), and $Na_3[Co(NO_2)_6]$ were used as purchased; $Na_2[Ru(NO)(NO_2)_4OH]\cdot 2H_2O$ was prepared by a previous procedure.[23] The elemental analyses were performed by the Microanalytical Laboratory of CNRS, Villeurbanne, France.

1. $Co(O_3C_8H_{10}N)_3$. A 4.3-g quantity (1.07×10^{-2} mol) of $Na_3[Co(NO_2)_6]$is dissolved in 150 mL of water, and 4.48 g (3.2×10^{-2}

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