$$\langle S_1S_2(S^I)\ S_{2'}(S^{II})\ S_{1'}SM|S_i\cdot S_j|S_1S_2(S^{III})\ S_2(S^{IV})\ S_{1'}SM\rangle$$

These matrix elements can be expressed as products of phase factors and 6-j coefficients according to standard procedures.[29]

The energies of the total spin state $S = 2$ were calculated through the expression

$$E(S = 2) = {}^1/_2J_{12} + {}^1/_4J_{22'}$$

The energies of the $S = 1$ and $S = 0$ states were obtained by diagonalization of the Hamiltonian matrices

$$E(S=1) = \begin{matrix} -{}^1/_6J_{12} + {}^1/_4J_{22'} & {}^2/_3J_{12} & 0 \\ {}^2/_3J_{12} & {}^1/_6J_{12} - {}^1/_2J_{22'} & {}^3/_4J_{22'} \\ 0 & {}^3/_4J_{22'} & -{}^1/_2J_{12} \end{matrix}$$

$$E(S=0) = \begin{matrix} {}^1/_2J_{12} - {}^1/_2J_{22'} & {}^3/_4J_{22'} \\ {}^3/_4J_{22'} & -{}^3/_2J_{12} \end{matrix}$$

Registry No. $[Cu(SALMedpt)Cu(hfa)_2]_2\cdot 6CHCl_3$, 82598-70-7; Cu(SALMedpt), 15378-53-7; $Cu(hfa)_2$, 14781-45-4.

Supplementary Material Available: A listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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Preparation and Structure of *cis*-Chlorodiammine(N^2,N^2-dimethyl-9-methylguanine)platinum(II) Hexafluorophosphate. A Model for the Intermediate in the Proposed Cross-Linking Mode of Action of Platinum(II) Antitumor Agents

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The synthesis and molecular and crystal structure of *cis*-chlorodiammine(N^2,N^2-dimethyl-9-methylguanine)platinum(II) hexafluorophosphate, *cis*-$[Pt(NH_3)_2(Dmmg)Cl](PF_6)$, are reported. The compound crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 5.467$ (2) Å, $b = 9.784$ (5) Å, $c = 32.309$ (17) Å, $\beta = 92.20$ (4)°, $V = 1726.9$ Å^3, $Z = 4$ [based on a formula weight of 602.78 for $[Pt(NH_3)_2(C_8N_5H_{11}O)Cl](PF_6)$], $D_{measd} = 2.34$ (1) g cm^{-3}, and $D_{calcd} = 2.32$ g cm^{-3}. A structural model was obtained by conventional Patterson and Fourier methods and refined by full-matrix least-squares techniques to an R value of 0.054 based on 4554 counter-collected F_o's. The *cis*-$[Pt(NH_3)_2(Dmmg)Cl]^+$ complex cation is four-coordinate with the Dmmg base bound through the N(7) position of the five-membered imidazole ring. Principal geometrical parameters for the primary coordination sphere are as follows: Pt–N(ammine trans to the chloro ligand) = 2.059 (6) Å; Pt–N(ammine trans to the Dmmg base) = 2.027 (7) Å; Pt–N(7)(Dmmg) = 2.035 (6) Å; Pt–Cl = 2.300 (2) Å; base/PtN_3Cl coordination plane dihedral angle = 81.3°. The significant difference in the two Pt–NH_3 bond lengths is attributable to a greater structural trans effect for the chloro ligand over that of the N(7)-bound purine base. The molecular dimensions of the coordinated Dmmg ligand are in excellent agreement with those reported for the free base. The crystal structure is stabilized by hydrogen bonding between the exocyclic oxygen atom O(6) of the Dmmg ligand as an acceptor and the coordinated ammine ligands as donors and by general electrostatic interactions. The complex cation affords a model for a species of the type *cis*-$[Pt(NH_3)_2(N(7)\text{-bound guanine})Cl]^+$, where the guanine residue is part of a polynucleotide chain. Such species have been postulated as possible intermediates in the reaction sequence leading to the cross-linking of DNA by the antitumor agent *cis*-$[Pt(NH_3)_2Cl_2]$.

Introduction

The class of coordination compounds typified by *cis*-$[Pt(NH_3)_2Cl_2]$ (cisplatin) are clinically successful antineoplastic agents.[2] Diverse experimental evidence implicates that the primary targets for these drugs are regions of DNA rich in guanine–cytosine residues.[3] These findings have stimulated considerable research into the chemistry of platinum compounds containing nucleic acid components as ligands. These investigations have led to numerous proposals for ways in which platinum compounds may bind to the nucleobases of DNA so as to cause mutagenesis (by inducing base mispairing) or cell death (by introducing one or more different kinds of "defects" that cancer cells may find difficult or impossible to repair). Both the cis and trans isomers of these platinum compounds are mutagenic, and to some extent carcinogenic, but only the cis isomers have significant antitumor activity.[2,4] This suggests a structural basis for the antineoplastic properties of the cis compounds. Consequently, many structural studies have been performed on model systems containing two nucleic acid constituents bound to a *cis*-A_2Pt^{II} moiety, where A = NH_3 or A_2 = a bidentate chelate such as ethylenediamine (en) or trimethylenediamine (tn).[5,6] All of these systems model potential products of bifunctional attack of *cis*-A_2PtCl_2 on a DNA polymer, with the replacement of the two chloro ligands by donor atoms from two nucleic acid bases. The ultimate product is envisioned as a DNA polymer containing a metal-mediated intrastrand or interstrand cross-link.

To a much lesser extent, attention has been directed toward the structural characterization of possible intermediate species. For example, one postulated mechanism for the antineoplastic

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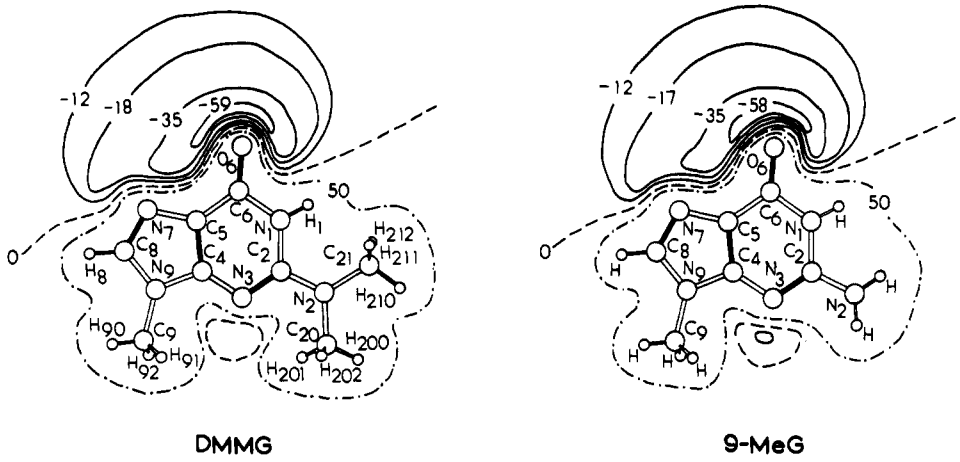

Figure 1. Molecular topology, atom numbering, and in-plane molecular electrostatic potentials for the purine bases N^2,N^2-dimethyl-9-methylguanine (Dmmg) and 9-methylguanine (9-MeG). Contours are given in kcal/mol.

action of cisplatin is via an intermediate of the type *cis*-[Pt(NH$_3$)$_2$(nucleic acid base)Cl]$^+$, a so-called "monoadduct".[4b] Recently, structures of two crystalline modifications of the complex *cis*-[Pt(NH$_3$)$_2$(1-MeC)Cl](NO$_3$), where 1-MeC is 1-methylcytosine, have been reported by Lippert and coworkers.[7] In a subsequent publication,[8] these same authors report that *cis*-[Pt(NH$_3$)$_2$(1-MeC)Cl]Cl interconverts to *trans*-[Pt(NH$_3$)(1-MeC)Cl$_2$], with the loss of ammonia, under quite mild reaction conditions (aqueous solution, room temperature).

In this present report, we extend the structural investigation of such monoadducts with a study of the preparation and molecular and crystal structure of *cis*-[Pt(NH$_3$)$_2$(Dmmg)Cl](PF$_6$), where Dmmg is the modified purine N^2,N^2-dimethyl-9-methylguanine (Figure 1). Although a monoadduct of guanine would probably be of greater relevance to the potential mode of attack of Pt antitumor agents, no such compound is known, possibly because of polymer formation. The Dmmg base was chosen because the N(1) position (see Figure 1), even when deprotonated, is quite inaccessible to metal attack due to the presence of the bulky dimethylamino substituent at C(2). Deprotonation of a guanine base at N(1) is known to be stimulated[6b] through platinum coordination at N(7), and the isolation of 1:1 monomeric complexes for A$_2$PtCl$_2$ reagents is often complicated by the formation of N(7),N(1) coordination polymers. A distinct advantage of the modified purine Dmmg is that polymer formation is prevented by a chemical modification (methylation of the exocyclic amino group) that does not substantively alter the electronic structure compared to that for 9-methylguanine (9-MeG) itself; vide infra.[9] Moreover, Dmmg is a naturally occurring base in a number of tRNA's,[10] and a knowledge of its electronic properties and its metal binding affinity is of some interest in its own right.

Experimental Section

(a) Preparations. A warm aqueous solution (80 mL, 70 °C) of 0.2630 g of *cis*-[Pt(NH$_3$)$_2$Cl$_2$] (0.87 mmol)[11] was added to an aqueous solution (100 mL, 70 °C) of 0.1693 g of N^2,N^2-dimethyl-9-methylguanine (0.87 mmol).[12] The pale yellow solution was allowed to slowly evaporate at 60 °C. The pH of the final solution was ca. 5. After several days of slow evaporation at 60 °C, 0.1745 g of white powder was collected by filtration. A bulk chemical analysis of the collected powder was consistent with the formulation [Pt(NH$_3$)$_2$(Dmmg)Cl]Cl·HCl. Anal. Calcd: C, 18.14, H, 3.42; N, 18.51; Cl, 20.08. Found: C, 18.23; H, 3.35; N, 18.61; Cl, 19.97.

This material was water soluble, and sizable crystals were readily isolated after the addition of excess NH$_4$PF$_6$. A density measurement (neutral buoyancy in CCl$_4$/CHBr$_3$) and preliminary X-ray data were in accord with the composition [Pt(NH$_3$)$_2$(Dmmg)Cl](PF$_6$). This was confirmed by an elemental analysis. Anal. Calcd: C, 15.97; H, 2.66; N, 16.30. Found: C, 16.30; H, 2.74; N, 16.18.

(b) Collection and Reduction of the X-ray Intensity Data. Preliminary oscillation and Weissenberg photography showed the crystal system to be monoclinic, with systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) consistent with the space group $P2_1/c$. A well-formed single crystal was cleaved parallel to the (010) plane to give a prismatic fragment with the following face assignments and dimensions: (100)–($\bar{1}$00), 0.28 mm; (010)–(0$\bar{1}$0), 0.28 mm; (001)–(00$\bar{1}$), 0.12 mm. Precise cell dimensions were derived from a least-squares fit to the setting angles for 15 carefully selected reflections on a Syntex P$\bar{1}$ automated diffractometer. The crystallographic b axis was approximately aligned along the ϕ axis of the spectrometer. Pertinent crystallographic data are collected in Table I.

Table I. Crystal Data for *cis*-[Pt(NH$_3$)$_2$(Dmmg)Cl](PF$_6$)

a = 5.467 (2) Å	[Pt(NH$_3$)$_2$(C$_8$N$_5$H$_{11}$O)Cl](PF$_6$)
b = 9.784 (5) Å	space group $P2_1/c$
c = 32.309 (17) Å	mol wt = 602.78
β = 92.20 (4)°	D_{measd} = 2.34 (1) g cm^{-3}
V = 1726.9 Å^3	D_{calcd} (Z = 4) = 2.32 g cm^{-3}

Employing graphite-monochromatized Mo Kα radiation ($\bar{\lambda}$ = 0.71069 Å) and using the θ–2θ scan mode with a variable scan rate of 2.0–8.0° min^{-1} in 2θ, we surveyed the intensities of 5735 reflections in the $h,k,\pm l$ quadrant to 2θ = 60°. Three standards were monitored after every 100 reflections collected and showed no systematic variations other than those expected from counting statistics. Out of a symmetry-unique set of 4993 reflections, 4554 had net intensities above zero; these were assigned observational variances based on counting statistics plus a correction term of the form $(pI)^2$, where p was taken to be 0.03.[13]

The nonzero intensities and their estimated standard deviations were corrected for Lorentz and polarization effects and for the effect of absorption. On the basis of the above face assignments and crystal dimensions and a calculated linear absorption coefficient of 88.7 cm^{-1}, the maximum and minimum transmission factors were 0.36 and 0.11, respectively. An approximation to the absolute scale factor was obtained by the method of Wilson.[14]

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Table II. Final Non-Hydrogen Atom Coordinates for *cis*-$[Pt(NH_3)_2(Dmmg)Cl](PF_6)$[a]

atom	x	y	z	atom	x	y	z
Pt[b]	25097 (4)	655 (2)	23138 (1)	C(6)	−400 (13)	1773 (6)	1427 (2)
Cl	−536 (4)	−1538 (2)	2218 (1)	C(8)	4779 (13)	−487 (7)	1502 (2)
O(6)	−1513 (9)	2128 (5)	1734 (2)	C(20)	170 (15)	2290 (13)	−70 (3)
N(10)	5235 (12)	1498 (7)	2407 (2)	C(21)	−2903 (16)	3578 (9)	320 (3)
N(11)	1899 (15)	−18 (6)	2928 (2)	C(9)	6073 (14)	−782 (8)	770 (3)
N(1)	−1133 (10)	2270 (5)	1032 (2)	P	6986 (4)	631 (2)	3824 (1)
N(2)	−904 (12)	2582 (6)	320 (2)	F(1)	8267 (10)	2074 (5)	3905 (2)
N(3)	1895 (11)	1165 (6)	644 (2)	F(2)	6807 (16)	903 (10)	3336 (2)
N(7)	3087 (12)	150 (5)	1696 (2)	F(3)	7238 (20)	316 (11)	4297 (2)
N(9)	4591 (11)	−224 (5)	1087 (2)	F(4)	5644 (12)	−794 (6)	3757 (2)
C(2)	47 (13)	1994 (7)	665 (2)	F(5)	9625 (16)	−1 (5)	3799 (3)
C(4)	2630 (12)	648 (6)	1011 (2)	F(6)	4424 (11)	1297 (8)	3816 (4)
C(5)	1671 (12)	874 (6)	1399 (2)				

[a] Estimated standard deviations in the least significant figure are enclosed in parentheses in this and all the following tables. [b] Parameters × 10^5; for all other atoms, parameters × 10^4.

(c) Solution and Refinement of the Structure. The positional coordinates of the Pt atom were deduced from a Patterson synthesis. A subsequent structure factor–Fourier calculation allowed the location of the 24 other non-hydrogen atoms of the asymmetric unit. Several cycles of isotropic and anisotropic least-squares refinement, minimizing the quantity $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, gave an R value $[\sum||F_o| - |F_c||/\sum|F_o|]$ of 0.065. At this stage, a difference-Fourier synthesis yielded coordinates for all 17 hydrogen atoms; the isotropic thermal parameters for the H atoms were fixed at values ca. 1.0 Å^2 larger than for the atom to which they were bonded. Two subsequent cycles of refinement, holding the H atom parameters fixed, led to convergence (maximum shift/error of 0.8) and to a final R value of 0.054. The final weighted R value $[(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}]$ and goodness of fit $[(\sum w(|F_o| - |F_c|)^2/(NO - NV))^{1/2}$, where NO = 4554 nonzero observations and NV = 226 variables] were 0.062 and 2.0, respectively. A final difference-Fourier map was essentially featureless, showing a maximum peak of 1.8 e/Å^3 near the Pt atom and peaks on the order of ±1.0 e/Å^3 in the region of the PF_6^- anion.

Neutral-atom scattering curves for the non-hydrogen[15] and the hydrogen[16] atoms were taken from common sources. Anomalous dispersion corrections[17] were applied to the scattering factors for all non-hydrogen atoms. Final atomic coordinates for the non-hydrogen atoms are collected in Table II. Tables of anisotropic thermal parameters, parameters for the hydrogen atoms, and final calculated and observed structure factor amplitudes are available as supplementary material. The crystallographic computations were performed with a standard set of computer programs.[18]

Results and Discussion

Below we describe the crystal and molecular structure of the *cis*-$[Pt(NH_3)_2(Dmmg)Cl](PF_6)$ coordination compound. As noted above, the Dmmg ligand was chosen because the bulky dimethylamino group at C(2) prevents metal attack at the potential N(1) binding site and, thus, the formation of polymeric species. To assess the magnitude of the perturbation of the electronic structure of the 9-MeG base due to the methyl substituents of the amino group, we have undertaken a study of the electronic structures of the Dmmg and 9-MeG bases under the INDO approximation.[19]

Generally, we find the electronic structures of these two 6-oxopurine bases to be virtually identical. For example, the derived molecular dipole moments for 9-MeG and Dmmg of 7.30 and 7.25 D are essentially indistinguishable. Secondly, and important to the coordination properties of each base, we find that the in-plane molecular electrostatic potentials for the 9-MeG and the Dmmg bases are very similar, both showing rather deep minima near the O(6),N(7) cleft (−69.6 and −70.2 kcal/mol, respectively; see Figure 1). Thus, the desired discrimination against polymer formation has been achieved without a discernible perturbation in the electronic structure

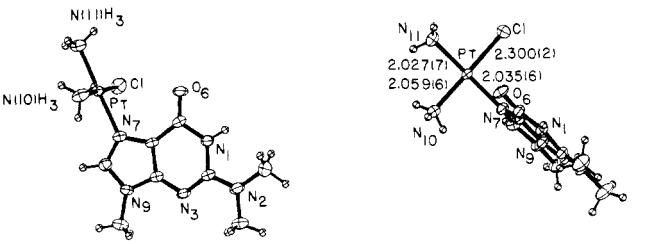

Figure 2. Two perspective views of the *cis*-$[Pt(NH_3)_2(Dmmg)Cl]^+$ cation: left, approximately normal to the plane of the purine base; right, along the perpendicular to the PtN_3Cl coordination plane.

Table III. Molecular Geometry for *cis*-$[Pt(NH_3)_2(Dmmg)Cl](PF_6)$

(a) Primary Coordination Sphere about the Pt Atom

Bond Lengths (Å)

Pt-N(10)	2.059 (6)	Pt-N(7)	2.035 (6)
Pt-N(11)	2.027 (7)	Pt-Cl	2.300 (2)

Bond Angles (Deg)

N(10)-Pt-N(11)	91.7 (3)	N(11)-Pt-N(7)	179.5 (3)
N(10)-Pt-N(7)	88.7 (2)	N(11)-Pt-Cl	87.6 (2)
N(10)-Pt-Cl	179.3 (2)	N(7)-Pt-Cl	92.0 (2)

(b) N^2,N^2-Dimethyl-9-methylguanine Base

Bond Lengths (Å)

O(6)-C(6)	1.233 (8)	N(7)-C(8)	1.297 (9)
N(1)-C(6)	1.410 (9)	N(9)-C(4)	1.384 (9)
N(1)-C(2)	1.398 (9)	N(9)-C(8)	1.366 (9)
N(2)-C(20)	1.439 (12)	N(9)-C(9)	1.438 (10)
N(2)-C(21)	1.464 (11)	C(2)-N(2)	1.341 (9)
N(3)-C(2)	1.299 (9)	C(4)-C(5)	1.394 (9)
N(3)-C(4)	1.338 (9)	C(5)-C(6)	1.440 (9)
N(7)-C(5)	1.402 (9)		

Bond Angles (Deg)

Pt-N(7)-C(8)	126.5 (5)	N(1)-C(2)-N(2)	116.4 (6)
Pt-N(7)-C(5)	126.2 (4)	N(2)-C(2)-N(3)	120.1 (6)
C(5)-N(7)-C(8)	107.3 (6)	N(3)-C(4)-N(9)	126.4 (6)
C(2)-N(1)-C(6)	125.2 (6)	N(3)-C(4)-C(5)	128.8 (6)
C(2)-N(2)-C(20)	118.9 (7)	C(5)-C(4)-N(9)	104.8 (6)
C(2)-N(2)-C(21)	123.5 (7)	C(6)-C(5)-N(7)	132.9 (6)
C(20)-N(2)-C(21)	117.5 (7)	C(4)-C(5)-N(7)	108.6 (6)
C(2)-N(3)-C(4)	113.4 (6)	C(6)-C(5)-C(4)	118.6 (6)
C(4)-N(9)-C(8)	108.5 (6)	C(5)-C(6)-O(6)	129.5 (6)
C(4)-N(9)-C(9)	124.2 (6)	N(1)-C(6)-O(6)	120.0 (6)
C(9)-N(9)-C(8)	127.2 (6)	N(1)-C(6)-C(5)	110.5 (6)
N(1)-C(2)-N(3)	123.4 (6)	N(7)-C(8)-N(9)	110.9 (6)

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or the coordination propensity of the 6-oxopurine ligand.[9]

Molecular Geometry of the *cis*-[Pt(NH$_3$)$_2$(Dmmg)Cl]$^+$ Cation. Two projection views of the *cis*-[Pt(NH$_3$)$_2$(Dmmg)Cl]$^+$ cation are presented in Figure 2; one view is approximately along the normal to the plane of the purine base and the other perpendicular to the PtN$_3$Cl coordination plane. Bond lengths in the primary coordination sphere and for the coordinated Dmmg ligand are given in Table III. The coordination geometry about the Pt(II) center is essentially planar, with the four-coordination sites occupied by the N(7) atom of the five-membered imidazole ring of the Dmmg base, the N atoms of the cis-coordinate ammines [N(10)H$_3$ and N(11)H$_3$], and the chloro ligand.

The Pt–N(7) bond length to the Dmmg base at 2.035 (6) Å is in excellent agreement with other N(7)-bound 6-oxopurine bases: 2.035 (13) Å for the [Pt(diethylenetriamine)(guanosine)]$^{2+}$ cation;[20] 2.029 (9) Å for the [Pt(diethylenetriamine)(inosine)]$^{2+}$ cation;[21] 2.021 (7) Å for [Pt(tn)(Me-5′-GMP)$_2$]^0 (where Me-5′-GMP is the phosphate methyl ester of guanosine 5′-monophosphate).[22] Similarly, the Pt–Cl distance at 2.300 (2) Å is typical of mono- and bis(purine or pyrimidine)platinum(II) chloro complexes.[7-8,23]

The most interesting aspect of the geometry of the primary coordination sphere in the present complex cation lies in the comparison of the two cis-Pt–N(ammine) bond lengths. For the ammine, N(11)H$_3$, trans to the N(7)-bound purine base, we find a Pt–N distance of 2.027 (7) Å. This value is very close to those we have previously reported for the *cis*-[Pt(NH$_3$)$_2$(3-methyladenine)$_2$]$^{2+}$ cation (2.031 (6) and 2.039 (6) Å)[9] and the *cis*-[Pt(NH$_3$)$_2$(1-MeC)$_2$]$^{2+}$ cation (2.031 (7) and 2.033 (7) Å)[24] and that (2.04 (1) Å) reported by Lippert and co-workers[8] for *trans*-[Pt(NH$_3$)(1-MeC)Cl$_2$]. In contrast, for the ammine (N(10)H$_3$) trans to the chloro ligand, a Pt–N distance of 2.059 (6) Å is observed. The 0.032-Å difference between the two Pt-N(ammine) bond lengths is significant ($\sim 5\sigma$) and, we presume, reflects a measurable difference in the relative structural trans effects[25] for the chloro and the N(7)-bound Dmmg ligands. The magnitude of the difference in the Pt–N(ammine) bond lengths observed here is on the order expected for two ligands of nearly equal strength in the structural trans-effect series for Pt(II).[25]

Finally, it is of interest to consider the conformation of the complex. In another study[26] we have analyzed the conformations of several *trans*-bis(nucleic acid base)platinum(II) and mono(nucleic acid base)platinum(II) complexes. It was found[26] possible in some cases to rationalize a large (near 90°) or a small (near 50°) base/coordination plane dihedral angle in terms of intramolecular effects. For example, interligand hydrogen bonding tends to favor a small dihedral angle, while weak Pt···O(exocyclic oxygen atom) and repulsive interligand steric factors tend to favor a large dihedral angle. For most systems, these intramolecular forces are weak, and intermolecular interactions (the ubiquitous "crystal-packing forces") are nonnegligible and can sometimes be determinative of the observed molecular conformation in the solid.

In the title complex, the base/PtN$_3$Cl coordination plane dihedral angle is large at 81.3°. It is unlikely that this conformation is strongly influenced by the Pt···O(6) interaction,

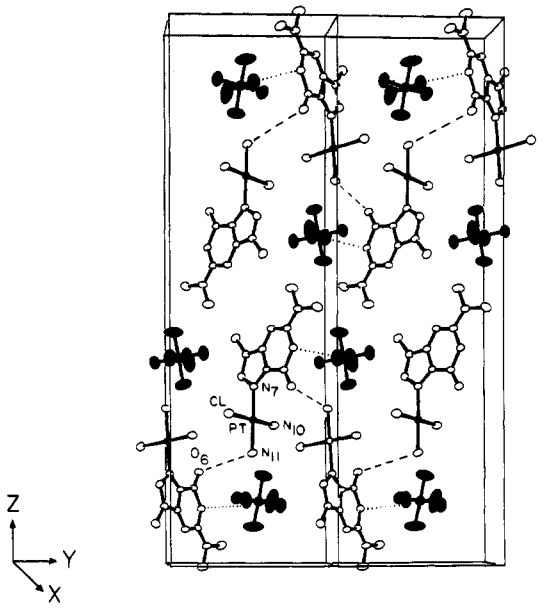

Figure 3. Perspective view of the crystal packing. Dashed lines indicate hydrogen bonds; dotted lines suggest electrostatic interactions.

since the Pt···O(6) distance at 3.479 (7) Å is typically large for an N(7)-bound 6-oxopurine base.[5] The large dihedral angle is, moreover, inconsistent with the presence of interligand hydrogen bonding of the type N–H···O(6) as found, for example, in [Pt(diethylenetriamine)(7,9-dimethylhypoxanthine)]$^{2+}$ (where the base/PtN$_4$ dihedral angle is 48°).[27] In fact, the plane of the Dmmg base is oriented so that the exocyclic O(6) atom is tilted toward the chloro rather than the N(10)H$_3$ ammine ligand (see Figure 2). Thus, crystal-packing forces, notably two intermolecular hydrogen bonds involving O(6) and base···PF$_6^-$ electrostatic interactions (see Figure 3), surely contribute significantly to the observed molecular conformation. The likely absence of such specific intermolecular interactions in a polar solvent may well lead to a molecular conformation in solution that is quite different from the one observed in the solid. We do note, however, that the molecular conformation observed here for *cis*-[Pt(NH$_3$)$_2$(Dmmg)Cl]$^+$ is similar to that found for *cis*-[Pt(NH$_3$)$_2$(1-MeC)Cl]$^+$,[7] where large base/PtN$_3$Cl dihedral angles of 84 and 88° have been reported for two crystalline modifications of its nitrate salt. In the 1-MeC complex cation, the presence of a stronger Pt···O atom (O(2)) interaction at $\sim$3.08 Å may play a larger role in determining the large dihedral angles.

Molecular Dimensions for the N^2,N^2-Dimethyl-9-methylguanine Ligand and the Hexafluorophosphate Anion. The bond lengths in the N(7)-coordinated Dmmg ligand, Table III, are in excellent agreement with those reported earlier for the free base,[10] with minor differences in some of the bond angles of the imidazole ring apparently related to the metal binding at N(7).

The nine-atom framework of the coordinated Dmmg ligand shows a degree of nonplanarity (Table IV) that is somewhat larger than in the free base.[10] The dihedral angle between the pyrimidine and the imidazole rings for coordinated Dmmg is 1.4°, while that for the free base is 0.6°.[10] In the present complex, the exocyclic O(6) and N(2) atoms show normal displacement magnitudes from the plane of the purine; however, the pyramidal character reported for N(2) in free Dmmg [N(2) being displaced by 0.08 Å from the plane through C(2), C(20), and C(21)] is not as pronounced for the coordinated

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Table IV. Least-Squares Planes and the Deviation of Individual Atoms (Å) from These Planes for *cis*-$[Pt(NH_3)_2(Dmmg)Cl](PF_6)$[a]

(a) Primary Coordination Sphere ($-0.6734X + 0.7317Y - 0.1056Z = -1.4697$ Å)

Pt*	−0.003	Cl	−0.004
N(7)	0.004	N(10)	−0.005
		N(11)	0.004

(b) Imidazole Ring ($-0.5998X - 0.7897Y - 0.1291Z = -1.7061$ Å)

N(9)	0.002	C(5)	0.004
N(7)	−0.003	C(8)	0.001
C(4)	−0.003		

(c) Pyrimidine Ring ($-0.6106X - 0.7779Y - 0.1485Z = -1.7845$ Å)

O(6)*	−0.030	C(20)*	0.013
N(1)	0.018	C(21)*	−0.099
N(2)*	−0.008	C(4)	0.005
N(3)	0.005	C(5)	−0.003
C(2)	−0.017	C(6)	−0.008

(d) Dmmg Ligand ($-0.6055X - 0.7833Y - 0.1410Z = -1.7683$ Å)

O(6)*	−0.021	C(20)*	−0.016
N(1)	0.012	C(21)*	−0.134
N(2)*	−0.033	C(4)	0.017
N(3)	0.004	C(5)	0.014
N(7)	−0.013	C(6)	0.000
N(9)	0.007	C(8)	−0.011
C(2)	−0.028	C(9)*	0.065

[a] In each of the equations of the planes, X, Y, and Z are coordinates referred to the orthogonal axes a, b, and c^*. Atoms designated by an asterisk were given zero weight in calculating the planes; the atoms used to define the planes were given equal weight.

Table V. Distances (Å) and Angles (Deg) in Interactions of the Type D–H···A

D	H	D–H	A[a]	H···A	D···A	∠D–H···A
N(10)	H(101)	0.92	$O(6)^{i}$	2.06	2.927 (8)	154
N(11)	H(112)	0.86	$O(6)^{ii}$	2.17	3.009 (8)	164
N(1)	H(1)	0.87	$F(5)^{iii}$	2.70	2.841 (8)	90

[a] All superscripts in this column refer to symmetry transforms (space group $P2_1/c$): (i) $1 + x, y, z$; (ii) $\bar{x}, -1/2 + y, 1/2 - z$; (iii) $1 - x, 1/2 + y, 1/2 - z$.

base [the corresponding displacement of N(2) here being only 0.026 Å]. Furthermore, the dimethylamino group is twisted at an angle of ca. 3° with respect to the base plane in the coordinated ligand compared to nearly 6° for the free base.

The hexafluorophosphate anion exhibits evidence of librational disorder, with the fluorine atoms showing varying degrees of exaggerated thermal motion. The average P–F bond length is 1.58 (2) Å, with individual contributors ranging from 1.54 to 1.60 Å. The average F–P–F angle is 90 (4)° (range 84–94°).

Crystal Structure. The contents of two unit cells are shown in Figure 3. Possible hydrogen-bonding interactions are collected in Table V. The extended crystal structure is stabilized by these hydrogen bonds, which are of the type N(ammine)H···O(6)(Dmmg), and by general electrostatic interactions between platinated-purine bases that "sandwich" PF_6^- anions (note the columnar arrays parallel to b in Figure 3). These purine/PF_6^- electrostatic interactions saturate both sides of the delocalized purine π system to the preclusion of base/base stacking, which has been shown to be favorable for the free base in solution.[28]

Summary. The preparation and molecular structure of the complex cation *cis*-chlorodiammine(N^2,N^2-dimethyl-9-methylguanine)platinum(II) have been reported and discussed above. In this first example of a model complex containing a 6-oxopurine base for the intermediate in the proposed cross-linking mode of action of platinum(II) antitumor agents, two ground-state structural features are of interest: there is a measurable, albeit slight, difference in the Pt(II)–NH_3 bond lengths trans to the chloro and the N(7)-bound purine ligands; and the coordinated purine base is orientated nearly normal to the coordination plane of the complex. Neither of these structural features would seem to play a primary role in the further reaction of such an intermediate through the loss of the chloro ligand.

Types of ground-state structural features that could have a role in promoting further reaction of such an intermediate and lead to the formation of a metal-mediated cross-link or the controversial Pt–N(7),O(6) chelation mode are the following: a significant interaction of O(6) and the Pt(II) center; a cis effect of the N(7)-bound purine base augmenting the trans effect of Cl^- or acting on the chloro ligand; a distortion such that the Pt atom is out of the plane of the purine base; and a hydrogen bond between O(6) and one of the ammine ligands. None of these features are observed (or their effect is too small to be observed). If there is any special reactivity of a 6-oxopurine base monoadduct, it may well be manifest in the transition-state species or in a strained environment imposed by the nucleic acid.

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Registry No. $[Pt(NH_3)_2(Dmmg)Cl]Cl·HCl$, 82752-91-8; $[Pt(NH_3)_2(Dmmg)Cl](PF_6)$, 82752-93-0; *cis*-$[Pt(NH_3)_2Cl_2]$, 15663-27-1.

Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms, parameters for the hydrogen atoms, and calculated and observed structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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