much larger shifts in the spectra of carboxylates than would the corresponding EDTA chelates. This is demonstrated with the spectrum of *n*-valerate shown in Figure 8. It is seen that while it is possible to resolve the spectrum with a fourfold molar excess of Pr(EDTA)$^-$, a smaller amount of Pr^{3+} affords a much higher resolution. Thus, if a shift reagent is sought for spectral resolution of a carboxylate in an aqueous medium and below the neutral pH, the aquolanthanides would be the ones of choice.

Conclusions

The EDTA chelates of the lanthanides form effectively 1:1 complexes with acetate inducing chemical shifts in the proton resonance of the latter. The induced shifts are of pseudocontact origin and the complexes of Pr(EDTA)$^-$ and Yb(EDTA)$^-$ are isostructural. Therefore Ln(EDTA)$^-$ chelates would be useful as shift reagents for structural studies of carboxylate substrates in aqueous solution. The practical pH range is between 6 and 10. At higher pH values there is effective competition due to the formation of hydroxo complexes. The usefulness of the aquolanthanides as shift reagents is not only confined to the acidic side of neutral pH but may also be complicated by the formation of higher than 1:1 complexes. They may however by preferred as reagents for spectral resolution.

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Synthesis and Structural Characterization of 9-Ethylguaninium Tetrachloroplatinate(II) Dihydrate. A Crystallographic and ^{1}H Nuclear Magnetic Resonance Study

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Abstract: The purine salt 9-ethylguaninium tetrachloroplatinate(II) dihydrate, (9-EGH)$_2$[PtCl$_4$]·2H$_2$O, C$_{14}$H$_{24}$Cl$_4$N$_{10}$O$_4$Pt, has been synthesized and its molecular structure has been determined by single crystal x-ray diffraction and 100 MHz ^{1}H NMR techniques. The material crystallizes in the triclinic space group $P\bar{1}$ with one formula unit in a cell of dimensions a = 7.916 (8), b = 16.30 (2), c = 9.13 (1) Å, α = 138.25 (5), β = 118.3 (1), and γ = 86.6 (1)°. The observed and calculated densities are 2.02 (3) and 2.037 g cm^{-3}, respectively. The structure has been refined by full-matrix least-squares techniques to a final value of the conventional R factor (on F) of 0.025 based on 2853 independent intensities. The complex consists of 9-EGH$^+$ cations which are hydrogen bonded to [PtCl$_4$]$^{2-}$ anions and to water molecules. The purine cation is protonated at N(7), and its geometry is similar to that of other 9-substituted guanine derivatives. The [PtCl$_4$]$^{2-}$ anion is planar, with Pt-Cl distances of 2.298 and 2.299 (3) Å and Cl-Pt-Cl angles of 90.0 (2)°. There is extensive intermolecular hydrogen bonding in the crystals. The ^{1}H NMR spectrum in DMSO-d_6 is consistent with the observed solid state structure, but the spectrum suggests that in solution there may be tautomerism in which the acidic proton resides on both N(7) and N(3).

The importance of metal-nucleic acid and peptide-metal-nucleic acid interactions in living systems has stimulated considerable research in the area of metal interactions with nucleic acid constituents.[1-19] This research increased in importance with the discovery that some platinum compounds exhibit carcinostatic properties.[20] Rosenberg's studies with *cis*- and *trans*-dichlorodiammineplatinum(II) indicate that although both forms bind to the purine and pyrimidine bases, only the cis form is effective as an antitumor agent.[21] Roberts and Pascoe have also noted that cross links are formed between strands of DNA with the cis compound.[22] Disruption of the hydrogen bonding scheme within the nucleic acid has also been suggested as a possible result of the interaction with the platinum compounds.[23]

Recently, three crystallographic studies have been reported dealing with the question of platinum binding as found in the solid state. Inosine-5′-monophosphate[18] binds to platinum at the N(7) position of the purine ring forming $[Pt(NH_3)_2(5'\text{-}IMP)_2]^{2-}$. Using Pd^{2+} as a substitute for Pt^{2+} in their study, Kindberg and Amma[17] find that $PdCl_4{}^{2-}$ ions form a network of hydrogen bonds with cytosine cations, but no direct interaction occurs. The presence of the anion prohibits the formation of the hydrogen bonds found in the base stacking interactions present in cytosine structures. Terzis, however, has shown[14] that Pt binds to N(7) of 9-methyladeninium ion in $[Pt(9MeAH)Cl_3]$.

Theophanides and co-workers[19] have also studied the interaction of platinum with nucleosides and nucleoside derivatives through the use of NMR spectroscopy. By observing the chemical shifts which occur upon complexation of the nucleoside with the platinum salt, they suggest that adenosine binds to Pt at N(1) forming $Pt(adenosine)_2Cl_2 \cdot 3H_2O$.

In the majority of these studies involving metal interactions with nucleic acid constituents, little attempt has been made to correlate the results of solid state studies and solution studies; this may result in a significant loss and/or misevaluation of experimental information. Therefore, we present here the result of both the crystallographic and spectroscopic investigations of the interaction of platinum(II) with 9-ethylguanine.

Experimental Section

Preparation. The complex was prepared using a method similar to that used by Hadjiliadis, Kourounakis, and Theophanides[19] for the synthesis of $Pt(adenosine)_2Cl_2 \cdot 3H_2O$. The orange crystals were analyzed and found to be 9-ethylguaninium tetrachloroplatinate dihydrate (hereafter referred to as $(9EGH)_2[PtCl_4]$). Anal. Calcd for $PtCl_4C_{14}N_{10}O_4H_{24}$: C, 22.9; N, 19.2; H, 3.3. Found:[24] C, 23.0; N, 19.2; H, 3.3.

Spectra. ^1H NMR spectra were measured on a Varian XL-100 spectrometer with Varian S-124 FT system, VDM 620-L computer system, and Varian disk system accessory. The software system was 994 120-B DISKFT system (16K)—2/14/75. Data were collected on the sample dissolved in DMSO-d_6, using an internal ^2H lock, a sweep width of 2048 Hz, a Fourier number of 16 384, and a pulse angle of 62°. All shifts were measured using DMSO-d_5 as a reference.

Collection and Reduction of the X-Ray Data. On the basis of Weissenberg and precession photographs, the crystals were assigned to the triclinic system with a space group of either P1 or $P\bar{1}$. Subsequent successful refinement of the structure revealed that the space group was $P\bar{1}$. Using the least-squares method of Busing and Levy,[25] the lattice constants were refined to be $a = 7.916\,(8)$, $b = 16.30\,(2)$, $c = 9.13\,(1)$ Å, $\alpha = 138.25\,(5)$, $\beta = 118.3\,(1)$, $\gamma = 86.6\,(1)°$. The observed density, obtained by flotation in diiodomethane and methylene chloride, is 2.02 (3) g cm^{-3}. The density calculated for one formula unit per unit cell is 2.037 g cm^{-3}. Hence, the Pt atom is constrained to lie on an inversion center.

A parallelepiped crystal with faces of (101), ($\bar{1}0\bar{1}$), ($11\bar{1}$), ($\bar{1}\bar{1}1$), ($03\bar{1}$), and ($0\bar{3}1$) was mounted on a glass fiber and oriented normal to the (101) face. The distances between the pairs of opposite faces were 0.520, 0.160, and 0.139 mm, respectively. Using the narrow-source, open-counter ω-scan technique to test the mosaicity of the crystal, it was found that several peaks were split. Examination of the ω scans of several other crystals, however, showed that they were more severely split; hence, data collection was continued using the original crystal. Twelve unsplit reflections were centered as a take-off angle of 1.0° through a narrow vertical slit and used as a basis for the least-squares refinement. The cell parameters and orientation matrix were refined using the logic of Busing and Levy[25] in the PDP-8/L computer.

Table I. Positional Parameters ($\times 10^4$)[a] for $(9EGH)_2[PtCl_4] \cdot 2H_2O$

Atom	*X*	*Y*	*Z*
Pt	0	0	0
Cl(1)	2406 (2)	−323 (1)	−895 (3)
Cl(2)	2907 (2)	1546 (1)	4710 (2)
N(1)	2355 (6)	−5771 (3)	−3130 (7)
C(2)	1573 (6)	−5375 (4)	−1738 (8)
N(2)	1099 (8)	−6176 (4)	−1800 (9)
N(3)	1337 (6)	−4235 (3)	−307 (7)
C(4)	1936 (6)	−3534 (4)	−406 (8)
C(5)	2644 (6)	−3884 (4)	−1833 (7)
C(6)	2956 (7)	−5083 (4)	−3323 (8)
O(6)	3625 (8)	−5504 (4)	−4606 (9)
N(7)	3067 (6)	−2854 (4)	−1333 (8)
C(8)	2654 (8)	−1906 (5)	374 (11)
N(9)	1980 (6)	−2269 (4)	1018 (9)
C(9)	1591 (9)	−1402 (5)	3132 (11)
C(10)	−835 (10)	−1883 (8)	1593 (13)
OW	4144 (7)	−2964 (4)	−3799 (9)
HN(1)	252 (9)	−652 (6)	−398 (12)
HN(2)	106 (10)	−699 (7)	−302 (13)
HN(2)′	45 (9)	−598 (6)	−105 (13)
HOW	489 (13)	−215 (9)	−290 (17)
HOW′	496 (16)	−336 (10)	−423 (20)
HC(9)	202 (11)	−129 (7)	441 (14)
HC(9)′	235 (9)	−43 (6)	466 (12)
HN(7)	345 (11)	−291 (7)	−226 (15)
HC(8)	253 (10)	−122 (6)	64 (13)
HC(10)	−167 (14)	−309 (9)	−17 (19)
HC(10)′	−118	−164	88
HC(10)″	−108	−141	289

[a] Hydrogen parameters are $\times 10^3$.

Data were collected on an automatic four-circle Picker diffractometer using Mo Kα radiation and a graphite monochromator. The take-off angle for collecting intensity data was 1.5°, which was the angle at which the peak intensity of a strong reflection was approximately 85% of the maximum value as a function of take-off angle. The counter aperture, positioned 32 cm from the crystal, was 5.0 mm high and 5.0 mm wide. The data were collected using the θ–2θ scan technique at a scan rate of 1.0°/min. To allow for the presence of both Kα_1 and Kα_2 radiations and for the splitting of the peaks, the scan range was from 1.0° below the calculated Kα_1 peak to 1.0° above the calculated Kα_2 position. Stationary-counter, stationary-crystal background counts of 20 s were taken at both ends of the scan.

A unique data set having $2\theta(\text{Mo}) \leq 55°$ was obtained, yielding 2854 intensities. After every 100 reflections, the intensities of three standard reflections were measured; these standards showed no deviations other than those predicted from counting statistics.

Data processing was carried out as described by Ibers and coworkers.[26] The intensities were assigned standard deviations according to the formula

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{1/2}$$

after the data were corrected for background. A value of 0.045 was given p, the term in the expression used to prevent extremely high weight being given to a very intense reflection.[27] The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects and for absorption. The absorption coefficient was calculated to be 66.58 cm^{-1} for Mo Kα radiation, and the transmission coefficients evaluated for the chosen crystal ranged from 0.32 to 0.51.

Solution and Refinement of the Structure. All least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$; the weights, w, were taken as $4F_o{}^2/\sigma^2(F_o)^2$. In all calculations of F_c, the atomic scattering factors for Pt were taken from ref 28, those for N were from Cromer and Waber,[29] those for C and O were from tabulations of Ibers,[30] those for Cl from Hanson et al.,[31] and those for H from Stewart, Davidson, and Simpson.[32] The effects of the anomalous dispersion of platinum and chlorine were included in calculations of F_c,[33] the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulations of Cromer and Liberman.[34]

The platinum atom was placed at the origin in $P\bar{1}$. The locations of the Cl, O, N, and C atoms were obtained from and refined in sub-

Table II. Thermal Parameters (U_{ij} in Å^2) for $(9EGH)_2[PtCl_4]\cdot 2H_2O$[a]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	287 (1)	242 (1)	328 (1)	162 (1)	210 (1)	229 (1)
Cl(1)	525 (5)	528 (5)	699 (6)	336 (4)	497 (5)	478 (5)
Cl(2)	495 (5)	405 (4)	362 (4)	267 (4)	214 (4)	275 (4)
N(1)	590 (18)	375 (15)	480 (17)	315 (14)	413 (16)	350 (14)
C(2)	438 (17)	314 (15)	396 (17)	214 (14)	300 (15)	280 (15)
N(2)	822 (26)	436 (17)	694 (23)	428 (19)	627 (23)	472 (19)
N(3)	484 (16)	331 (14)	481 (16)	242 (13)	371 (14)	314 (14)
C(4)	357 (15)	308 (15)	405 (17)	189 (13)	264 (14)	277 (15)
C(5)	359 (15)	326 (15)	343 (15)	179 (13)	225 (13)	269 (14)
C(6)	497 (19)	366 (17)	375 (17)	250 (15)	313 (16)	299 (15)
O(6)	1059 (29)	623 (20)	735 (22)	585 (21)	770 (23)	576 (19)
N(7)	474 (16)	459 (17)	537 (18)	258 (14)	334 (15)	430 (16)
C(8)	535 (22)	442 (20)	672 (26)	307 (18)	423 (21)	474 (21)
N(9)	555 (19)	413 (16)	677 (22)	324 (15)	470 (18)	447 (17)
C(9)	625 (26)	428 (22)	587 (26)	306 (20)	426 (23)	395 (29)
C(10)	706 (30)	692 (31)	746 (32)	470 (27)	565 (28)	598 (29)
OW	694 (21)	616 (20)	744 (22)	407 (18)	550 (19)	588 (20)
HN(1)	6 (1)					
HN(2)	6 (2)					
HN(2)′	6 (1)					
HOW	9 (2)					
HOW′	9 (3)					
HC(9)	7 (2)					
HC(9)′	6 (1)					
HN(7)	8 (2)					
HC(8)	7 (2)					
HC(10)	10 (3)					
HC(10)′	6					
HC(10)″	6					

[a] Anisotropic thermal parameters are $\times 10^4$. Isotropic thermal parameters are $\times 10^2$. The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

sequent difference Fourier maps and least-squares calculations.[35] Anisotropic refinement of all nonhydrogen atoms gave values of the conventional agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ of 0.027 and 0.035, respectively. The hydrogen atoms were located in a difference Fourier map. The positions of two of the hydrogen atoms on C(10) were later assigned values that were calculated on the basis of tetrahedral geometry[36] and not varied in the subsequent least-squares calculations. Anisotropic refinement of the nonhydrogen atoms and isotropic refinement of the hydrogen atoms gave a final R_1 of 0.025 and R_2 of 0.031.

The final values of F_o and F_c suggested to us that no correction for secondary extinction was necessary. In the final cycle of least-squares refinement, no atomic parameter experienced a shift of more than 0.9 times its estimated standard deviation, which is taken as evidence for convergence. A final difference Fourier showed peaks in the vicinity of the Pt atom of approximately 1.0 and 2.4 e Å^{-3}. There were also peaks in the vicinity of the hydrogen atoms on C(10) of 1.2–1.7 e Å^{-3}, which may be due to some disorder in the terminal methyl group but could not be interpreted on the basis of any reasonable model. No other peaks larger than 0.6 e Å^{-3} were observed.

Tables I and II contain the positional and thermal parameters from the last cycle of least-squares refinement, respectively, along with their standard deviations as estimated from the inverse matrix. A tabulation of observed and calculated structure amplitudes is available.

Description of the Structure

The structure consists of 9-ethylguaninium cations hydrogen bonded to tetrachloroplatinate(II) anions and water molecules. Figure 1 shows a view of the unit cell. Tables III and IV contain the intramolecular distances and bond angles, respectively. The coordination around the platinum atom is strictly planar, since platinum is on the inversion center. The Pt–Cl bond lengths of 2.299 (3) and 2.298 (10) are in the normal range of Pt–Cl distances in structures with trans chlorine atoms.[37,38] The Cl(2)–Pt–Cl(1) angle of 90.0 (2)° suggests that the hydrogen-bonding interactions with the 9-ethylguaninium cations cause little distortion of the $[PtCl_4]^{2-}$ anion.

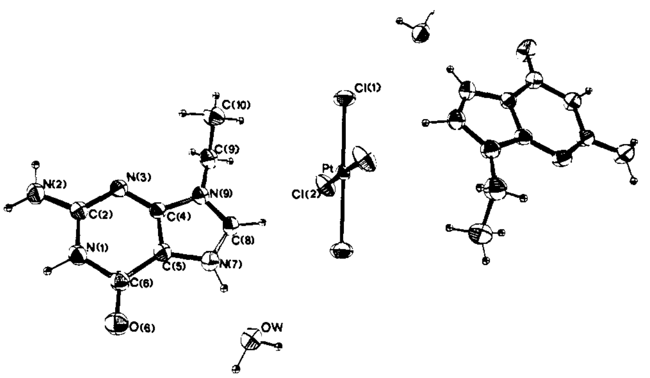


Figure 1. View of the unit cell of $(9\text{-}EGH)_2[PtCl_4]\cdot 2H_2O$.

The site of protonation is N(7); this is also the site of protonation in 9-methylguanine hydrobromide[39] and in guanine hydrochloride.[40] The bond angles of the 9-ethylguaninium cation are consistent with those in other 9-substituted guanine compounds.[41] Protonation at N(7) leads to a slight lengthening of the C(8)–N(7) bond (to 1.324 (6) Å), and a slight shortening of the C(8)–N(9) bond (to 1.354 (6) Å), relative to the values found in neutral 9-substituted guanine compounds.[41] The resulting bond angles within the purine are also in excellent agreement with the range of bond angles found in 9-substituted guanines. Notably, the angles within the imidazole portion of the ring correlate well with the dependence on extra-annular substitution postulated by Ringertz.[41]

The purine can be best viewed as being composed of two approximately planar rings. The imidazole ring is planar, with no atom deviating from the best five-atom least-squares plane by more than 0.008 Å. The C(9) atom is 0.16 Å below the plane, and the HN(7) atom is 0.08 Å above the plane; HC(8) is 0.20 Å above the plane. The pyrimidine portion of the ring

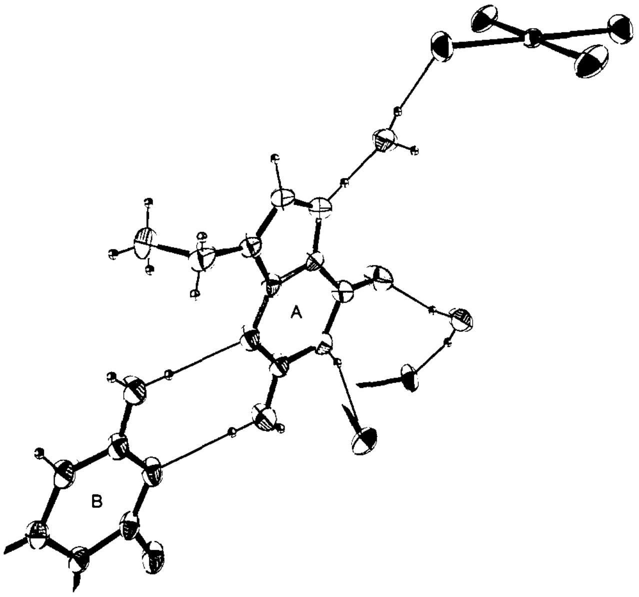


Figure 2. The hydrogen bonding in (9-EGH)$_2$[PtCl$_4$]·H$_2$O. Chlorine atoms are marked by shaded ellipsoids. Purine B is a symmetry-related purine translated by one unit cell in the *b* direction. The lower water molecule is also symmetry related to the reference molecule.

is also approximately planar, with no atom deviating from the best six-atom least-squares plane by more than 0.017 Å. Here, N(2) is in the plane, O(6) is 0.02 Å below the plane, and HN(1) is 0.03 Å below the plane. The dihedral angle between the imidazole and pyrimidine portions of the ring is 3.18°.

The hydrogen bonding in this structure is extensive. The [PtCl$_4$]$^{2-}$ anion contains four potential acceptors, two of which are used. The water molecule is hydrogen bonded through both of its hydrogen atoms and its oxygen atom. The 9-ethylguaninium cation has four donor and two acceptor sites. All but one of these sites are used. The distances and angles associated with these possible hydrogen bonds are listed in Table V. The criterion used for inclusion of an interaction in Table V is that of Hamilton and Ibers,[42] who note that an A–H···B hydrogen bond probably exists if both the A–H and H···B separations are less than the sum of the van der Waals radii of the two atoms (i.e., H and A or H and B) even if the A···B separation exceeds the sum of the van der Waals' radii of A and B; the values for the atomic van der Waals radii used are from the tabulations of Pauling.[43]

All of the hydrogen bonds are intermolecular, as is shown in Figure 2. The 9-ethylguaninium rings are linked together by two hydrogen bonds between the N(2) and N(3) atoms with N(2)···N(3) separations of 3.050 Å and N(2)–HN(2)′···N(3) angles of 174°. The water molecule interacts with the ring at N(7) and at O(6), and with Cl(1). The N(7)···OW distance is 2.650 Å, with an associated N(7)–HN(7)···OW angle of 179°; the OW···O(6) distance is 2.821 Å, with an OW–HOW′···O(6) angle of 168°; and the OW–Cl(1) distance is 3.308 Å, with an OW–HOW···Cl(1) angle of 162°. The ring also interacts with the [PtCl$_4$]$^{2-}$ anion through an N(1)···Cl(2) hydrogen bond of distance 3.308 Å, with an N(1)–HN(1)···Cl(2) angle of 162°. The other proton on N(2) does not appear to be involved in hydrogen bonding.

With reference to the biological significance of the interaction of PtCl$_4$$^{2-}$ ions with 9-ethylguanine, we can only note that the hydrogen bonding of the 9EGH$^+$ with the chlorides of [PtCl$_4$]$^{2-}$ would disturb the interchain hydrogen bonding found in DNA if the interaction were to occur in nature.

Description of Spectra

The ^{1}H NMR spectrum of the (9EGH)$_2$[PtCl$_4$]$_2$ compound dissolved in DMSO-d_6 is consistent with the crystal structure; in particular, the absence of any ^{195}Pt coupling suggests that the metal is not coordinated in solution. It is apparent that the chemical shifts seen in Figure 3 and Table VI are the result of protonation and not of platinum coordination. Since the pK_a for the proton at N(7) in 9-methylguanine is 2.9,[44] the proton

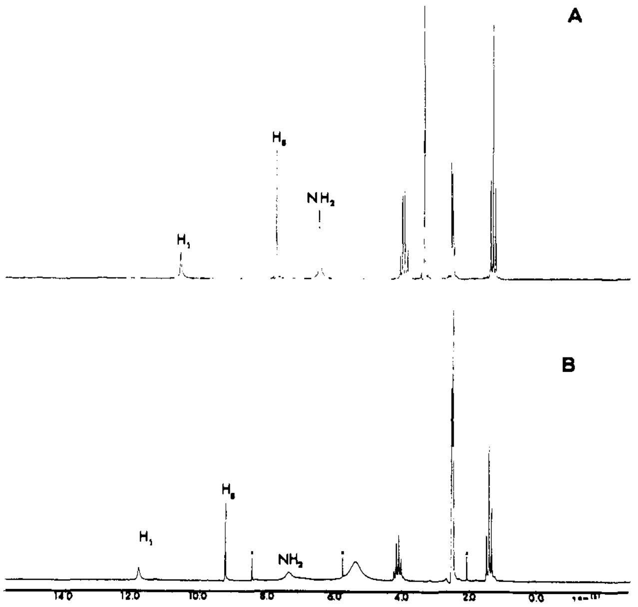


Figure 3. ^{1}H NMR on 9EG(A) and (9EGH)$_2$[PtCl$_4$]·2H$_2$O(B) in DMSO-d_6. Signals marked by x are from an impurity in solution.

Table III. Interatomic Distances for (9EGH)$_2$[PtCl$_4$]·2H$_2$O

Atoms	Distance, Å	Atoms	Distance, Å
Pt–Cl(1)	2.299 (3)	N(9)–C(9)	1.502 (7)
Pt–Cl(2)	2.298 (10)	C(9)–C(10)	1.502 (9)
N(1)–C(2)	1.373 (5)	N(1)–HN(1)	0.88 (6)
C(2)–N(3)	1.328 (5)	N(2)–HN(2)	0.87 (6)
C(2)–N(2)	1.334 (6)	N(2)–HN(2)′	0.91 (6)
N(3)–C(4)	1.341 (5)	OW–HOW	0.89 (9)
C(4)–C(5)	1.372 (5)	OW–HOW′	0.89 (9)
C(5)–C(6)	1.423 (5)	C(9)–HC(9)	0.92 (7)
C(6)–N(1)	1.399 (5)	C(9)–HC(9)′	0.91 (6)
C(6)–O(6)	1.212 (5)	N(7)–HN(7)	0.97 (6)
C(5)–N(7)	1.385 (5)	C(8)–HC(8)	0.96 (6)
N(7)–C(8)	1.324 (6)	C(10)–HC(10)	1.15 (9)
C(8)–N(9)	1.354 (6)	C(10)–HC(10)′	0.93
N(9)–C(4)	1.382 (5)	C(10)–HC(10)″	0.93

Table IV. Bond Angles in (9EGH)$_2$[PtCl$_4$]·2H$_2$O

Atoms	Angle, deg	Atoms	Angle, deg
Cl(2)–Pt–Cl(1)	90.0 (2)	N(1)–C(6)–C(5)	109.6 (3)
C(2)–N(1)–C(6)	126.2 (3)	C(8)–N(7)–C(5)	107.2 (4)
N(3)–C(2)–N(2)	119.8 (4)	N(7)–C(8)–N(9)	110.6 (4)
N(3)–C(2)–N(1)	123.4 (4)	C(8)–N(9)–C(4)	107.2 (4)
N(2)–C(2)–N(1)	116.8 (3)	C(8)–N(9)–C(9)	127.3 (4)
C(2)–N(3)–C(4)	112.0 (3)	C(4)–N(9)–C(9)	125.2 (4)
N(3)–C(4)–C(5)	128.4 (3)	C(10)–C(9)–N(9)	110.4 (5)
N(3)–C(4)–N(9)	124.8 (4)	HN(2)–N(2)–HN(2)′	124 (5)
C(5)–C(4)–N(9)	106.8 (3)	HC(9)′–C(9)–HC(9)	88 (5)
C(4)–C(5)–N(7)	108.1 (3)	HC(10)′–C(10)–HC(10)″	113
C(4)–C(5)–C(6)	120.3 (3)	HC(10)′–C(10)–HC(10)	114
N(7)–C(5)–C(6)	131.4 (4)	HC(10)″–C(10)–HC(10)	113
O(6)–C(6)–N(1)	122.1 (4)	HOW–OW–HOW′	99 (7)
O(6)–C(6)–C(5)	128.3 (4)		

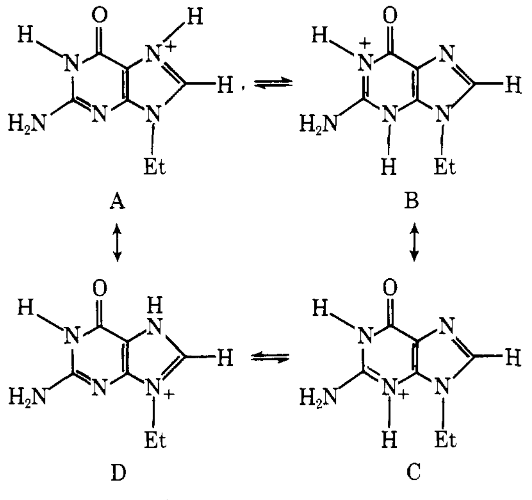
Table V. Possible A-H···B Hydrogen bonds in $(9EGH)_2[PtCl_4]\cdot 2H_2O$

A	B	A···B, Å	H···B, Å	A-H···B angle, deg
OW	Cl(1)	3.308	2.455	162
N(1)	Cl(2)	3.307	2.467	160
N(2)	N(3)	3.050	2.142	174
OW	O(6)	2.821	1.941	168
N(7)	OW	2.650	1.682	179

Table VI. Chemical Shifts (ppm) for 9-EG and $(9EGH)_2[PtCl_4]\cdot 2H_2O$

	δ		
Proton	9EG	$(9EG)_2[PtCl_4]\cdot 2H_2O$	Δδ
H_1	10.60	11.84	1.24
H_8	7.76	9.24	1.48
NH_2	6.48	7.34	0.86
CH_2	4.0	4.12	0.12
CH_3	1.36	1.50	0.14
H_2O	3.40	5.36	

exchanges rapidly with the water and does not appear as a separate signal in the spectrum. The proton H(8) experiences the largest chemical shift owing to the protonation at N(7) which is seen in the solid state (see A, below). However, H(1) also experiences a large chemical shift; this can be explained by postulating the tautomerism of 9-ethylguaninium in solution (see B) which places the proton on N(3) and the positive charge on N(1). The shift of the NH_2 protons could also be due to this tautomer and to its resonance equivalent form C (see below) which places the positive charge on N(3). The small shifts associated with the ethyl protons may be due to the resonance form of the solid state configuration D. Chemical shifts due to protonation of nucleosides have been seen by Broom and Milne.[45]



The results of the ^1H NMR investigation clearly demonstrate the importance of viewing the information found in the solid state and in solution simultaneously, if possible. Without the results of the crystallographic study, our interpretation of the ^1H NMR spectra might have been made in terms of platinum coordination and not in terms of protonation. This leads us to suggest that researchers must be extremely careful in evaluating chemical shifts which may result from metal coordination since chemical shifts due to protonation may be of the same order of magnitude.

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Supplementary Material Available: A listing of structure factor amplitudes for $(9EGH)_2[PtCl_4]\cdot 2H_2O$ (16 pages). Ordering information is given on any current masthead page.

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