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Crystal and Molecular Structure of Trichloro(9-methyladeninium)platinum(II)

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The crystal and molecular structure of the title compound has been determined from three-dimensional x-ray data. The structure was solved by the Patterson method and has been refined by least-squares procedures to a conventional R of 0.017 for 2492 nonzero reflections. The yellow compound crystallized in space group $P\bar{1}$ of the triclinic system in a cell of dimensions $a = 9.495$ (5) Å, $b = 9.924$ (5) Å, $c = 6.961$ (4) Å, $\alpha = 104.56$ (3)°, $\beta = 93.48$ (3)°, $\gamma = 114.94$ (3)°, and $V = 565.2$ Å^3. Graphite-monochromated Mo radiation was used. There are two molecules per unit cell ($\rho_{\text{exptl}} = 2.63$ g cm^{-3}; $\rho_{\text{calcd}} = 2.652$ g cm^{-3}). Comparison of the bond distances and angles with those of other structures indicates that metal coordination at N(7) has only small and short-range electronic effects.

Introduction

The importance of metal ions in nucleic acid processes has now been recognized, their involvement in these processes has received much attention, and their interactions with the bases of nucleotides have been the subject of numerous articles.[1] The purine bases incorporated in the nucleic acids have several potential coordination sites. The nitrogen atoms N(1), N(3), and N(7) are more or less exposed, and so is the substituent in the C(6) position. Many crystallographic studies have been undertaken in order to elucidate the coordination site of the metal. Unfortunately, in most of these studies[2] the purine bases have the N(9) position exposed and therefore are not directly related to biological systems of nucleic acids where N(9) carries a ribosyl residue. Consequently, in some of these studies[2d,e,g,h] it was found that only N(9) coordinates to the metal, while in others[2a,b,c,f] the purine acts as a bridging bidentate ligand via both N(3) and N(9). We know of only few recent studies[3] of metal coordination to purines in which the N(9) position is blocked by a methyl group, and in all of these the purine base coordinates through N(7).

Since the discovery by Rosenberg and his collaborators of the activity of certain platinum compounds[4] and subsequent demonstration[5] of the formation of cross-links in the double-helix structure of DNA by *cis*-$\text{Pt(NH}_3)_2\text{Cl}_2$ there has been a great interest in the chemistry and structure of platinum complexes with nucleotides and nucleotide bases.[6] We report here the structure of a platinum–9-methyladenine complex. A preliminary account of this work has been published.[7]

Experimental Section

Crystal Data. A sample of the compound was kindly supplied by N. Hadjiliades and T. Theophanides. The yellow crystals are stable to air and to x rays. The reciprocal lattice symmetry observed from precession photographs showed that the crystals are triclinic, thus indicating that the space group is either $P1$ or $P\bar{1}$. The cell parameters were calculated by least-squares refinement of the setting angles of 12 automatically centered reflections (Mo K$\bar{\alpha}$ radiation, λ 0.7107 Å, $27° < 2\theta < 38°$): $a = 9.495$ (5) Å, $b = 9.924$ Å (5), $c = 6.961$ (4) Å, $\alpha = 104.56$ (3)°, $\beta = 93.48$ (3)°, $\gamma = 114.94$ (3)°, $V = 565.2$ Å^3, and a calculated density of 2.652 g cm^{-3} for $\text{C}_6\text{N}_5\text{H}_8\text{Cl}_3\text{Pt}$ with $Z = 2$. The density measured by flotation in a mixture of dibromoethane and bromoform at 23 °C is 2.63 ± 0.02 g cm^{-3}. The esd's of the cell parameters are assigned twice the values computed in the least-squares refinement, which reflects our experience with reproducibility of results.

Collection and Reduction of Intensity Data. The intensity data were collected from a well-formed crystal of approximate dimensions 0.16 × 0.18 × 0.32 mm. The crystal was mounted on a Picker FACS-1 four-circle automatic diffractometer with its long dimension aligned approximately along the ϕ axis of the instrument. Graphite-monochromated Mo Kα radiation was used and the takeoff angle was 3.5°. The source-to-crystal distance was 16 cm and the crystal-to-counter distance was 35 cm. The data were collected with the θ–2θ scan technique, at a scan rate of 1° (2θ)/min. The scan range was $(1.90 + \tan\theta)°$, starting 0.95° below the Mo Kα_1 peak. Stationary-counter, stationary-crystal background counts of 40 s were taken at each limit of the scan range. During the course of the data collection, three standard reflections were measured at a period of 30 reflections. Their variations were less than 2.5% from their respective means.

A total of 2869 intensity measurements were made in the form $\pm h$, k, $\pm l$ in the region of $2\theta < 55°$ and reduced to a set of 2590 independent reflections, after averaging the equivalent ones, whose intensities were within $2\sigma(I)$ of each other. The integrated intensity was calculated as $I(\text{net}) = I(\text{scan}) - 0.5t_\text{T}/t_\text{B}(B_1 + B_2)$ where I(scan) is the number of counts over the scan range, t_T is the scan time, and t_B is the time for each background count B_1 and B_2. The standard deviations $\sigma(I)$ were calculated according to the expression $\sigma(I) = [N_\text{T} + 0.25(t_\text{T}/t_\text{B})^2(B_1 + B_2) + (cI)^2 + 0.02^2(I - I_\text{c})^2]^{1/2}$, where N_T is the total integrated scan count obtained in time t_T, c is a factor to account, among other things, for instrumental instability[8] during data collection (for this structure determination c was 0.025), I is the net intensity, and I_c is I corrected for absorption. The last term in the brackets is a factor accounting for the errors in the absorption correction.

Only data for which $I > 2.0\sigma(I)$ were used, which left 2492 reflections to be entered into the least-squares refinement.

Absorption correction was applied[9] and the calculated transmission coefficients, based on a linear absorption coefficient of 135.0 cm^{-1} for Mo Kα radiation, ranged from 0.151 to 0.217. Finally, the Lorentz and polarization corrections were applied.

Solution and Refinement of the Structure. We presumed the space group to be $P\bar{1}$ and this assumption was corroborated by the final structural results. The structure was solved by the standard heavy-atom method and refined by full-matrix least squares initially and by block-diagonal least squares in the later stages. The platinum position was evident from the three-dimensional Patterson map. A Fourier synthesis phased on this position revealed the positions of all the nonhydrogen atoms. Refinement proceeded normally using unit weights and the block-diagonal least-squares approximation (in block of 9 × 9) and converged initially at an R_1 $(=\sum\lVert F_\text{o}| - |F_\text{c}\rVert/\sum|F_\text{o}|)$ of 0.064, after varying the positional and individual isotropic temperature factors for all nonhydrogen atoms. At this stage, a secondary extinction correction was entered.[10] Inclusion of anisotropic temperature factors reduced R_1 to 0.019. A difference map easily revealed the positions of the hydrogen atoms. Inclusion of these positions in the refinement, as well as the weights $w = 1/\sigma^2(F_\text{o})$, leads after three cycles to a final R_1 of 0.017 (observed data, 2492 reflections) and $R_2 = (\sum w(|F_\text{o}| - |F_\text{c}|)^2/\sum w|F_\text{o}|^2)^{1/2}$ of 0.024 (observed and unobserved data, 2590 reflections). The function $w(|F_\text{o}| - |F_\text{c}|)^2/N$, where N is the number of reflections in the particular range, showed no significant variation with $|F_\text{o}|$, h (the slowest varying index during data collection), or $(\sin\theta)/\lambda$. Average and maximum shifts in the final least-squares refinement were 0.1σ and 0.3σ, respectively. The scattering factors for all atoms were taken from Cromer and Mann,[11] and the anomalous dispersion components for Pt, Cl, and N were taken from Cromer and Lieberman.[12]

The calculated and observed structure factors are available[13] and the final atomic positional and thermal parameters are found in Table I.

Discussion

Platinum Coordination. The compound exists in the crystal as discrete trichloro(9-methyladeninium)platinum(II) molecules in which the platinum has a slightly distorted

Table I. Final Atomic Positional[a] and Thermal[b] Parameters of Trichloro(9-methyl-adeninium)platinum(II)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	2608.3 (1)	2011.0 (1)	1337.8 (2)	271.1 (3)	221.7 (4)	283.7 (3)	96.5 (2)	38.7 (2)	117.3 (2)
Cl(1)	2639 (1)	555 (1)	−1792 (1)	482 (4)	260 (3)	375 (3)	167 (1)	5 (1)	15 (1)
Cl(2)	2466 (1)	3455 (1)	4399 (1)	497 (5)	662 (6)	296 (3)	332 (3)	118 (2)	137 (2)
Cl(3)	3884 (1)	943 (1)	2913 (1)	502 (5)	383 (4)	503 (4)	227 (2)	1 (2)	223 (1)
N(1)	3713 (4)	7169 (3)	431 (5)	387 (9)	234 (9)	409 (9)	91 (6)	34 (6)	95 (5)
N(3)	1336 (4)	5932 (4)	−1962 (4)	443 (13)	324 (12)	367 (9)	215 (6)	52 (6)	159 (6)
N(7)	1585 (3)	2988 (3)	−106 (4)	309 (9)	226 (9)	298 (9)	118 (5)	25 (5)	94 (5)
N(9)	−33 (3)	3178 (3)	−2346 (4)	284 (9)	262 (9)	250 (9)	113 (5)	15 (4)	72 (5)
N(10)	4670 (4)	6031 (4)	2350 (5)	408 (12)	323 (12)	415 (11)	77 (6)	−93 (6)	91 (6)
C(2)	2637 (5)	7159 (4)	−961 (6)	493 (20)	282 (15)	428 (17)	202 (8)	79 (7)	148 (7)
C(4)	1173 (4)	4644 (4)	−1490 (4)	330 (12)	355 (12)	259 (9)	161 (6)	62 (5)	80 (5)
C(5)	2171 (4)	4522 (4)	−71 (4)	303 (9)	250 (9)	242 (8)	129 (6)	66 (5)	92 (5)
C(6)	3560 (4)	5891 (4)	982 (5)	331 (12)	258 (11)	297 (9)	127 (6)	73 (6)	74 (6)
C(8)	270 (4)	2217 (4)	−1510 (5)	313 (12)	237 (11)	318 (9)	94 (6)	29 (6)	79 (6)
C(11)	−1293 (4)	2717 (5)	−4064 (5)	332 (14)	426 (18)	304 (11)	137 (7)	−24 (6)	104 (7)

Atom	x	y	z	B_{iso}, Å^2	Atom	x	y	z	B_{iso}, Å^2
H(1)	453 (5)	810 (6)	100 (7)	4.4 (9)	H(10B)	540 (6)	692 (7)	298 (8)	6 (1)
H(2)	295 (6)	830 (5)	−113 (6)	3.9 (9)	H(11A)	−162 (5)	340 (6)	−395 (7)	4 (1)
H(8)	−40 (5)	121 (5)	−192 (6)	2.9 (8)	H(11B)	−81 (4)	268 (5)	−513 (5)	2.5 (8)
H(10A)	443 (5)	532 (5)	280 (6)	2.7 (8)	H(11C)	−236 (6)	171 (7)	−399 (9)	8 (2)

[a] $\times 10^4$ for the nonhydrogens; $\times 10^3$ for the hydrogen atoms. [b] $\times 10^4$ for the nonhydrogens.

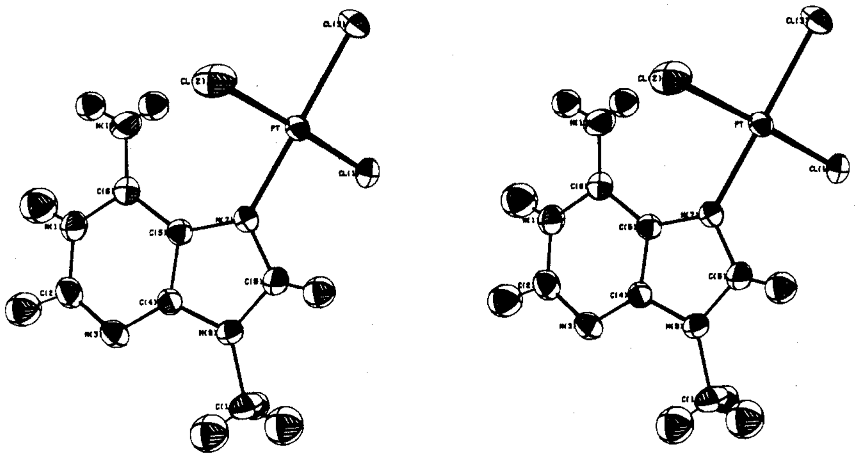


Figure 1. Stereodrawing of the molecule with 50% probability ellipsods.

square-planar coordination. While the platinum atom is essentially in the "plane" of its four ligands, the best plane calculation indicates that there is a substantial tetrahedral distortion of the square-planar geometry; Cl(1) and Cl(2) are 0.038 Å above the "plane" while Cl(3) is 0.034 Å and N(9) is 0.041 Å below the "plane". Cl(1) and Cl(2) are both bent toward the hydrogen bonds that they form (Figure 1). The Pt-Cl3 best plane makes an angle of 62.6° with the adenine (N(1)-N(9)) best plane. All Pt-Cl distances are equal within experimental error (two standard deviations). Interatomic distances and angles are given in Figure 2. Standard deviations, estimated from the inverted full matrix are as follows: Pt-Cl, 0.002 Å; Pt-N, 0.004 Å; C-C(or N), 0.006 Å; H-C(or N), 0.06 Å; 0.3° in angles other than hydrogen.

Interatomic Distances in the Adeninium Ligand. One of the reasons for undertaking this work is to provide information on the structural changes induced on the ligand by the metal. The suggestion has been made,[2e] and subsequently challenged,[14] that metal ions binding at one site distort the electronic configuration of the whole molecule. This point is particularly relevant to the interpretation of NMR line-broadening experiments. From a careful comparison of many structures we come to the conclusion that metal coordination to the N(7) position has very small and short-range effects. It turns out that protonation of N(1) has more pronounced electronic effects on the pyrimidine ring than coordination to the (N7) position has on the imidazole ring while coordination has no effect whatsoever on the pyrimidine ring. These data are presented in Tables II and III. Table II demonstrates the kind of changes that occur in the pyrimidine ring upon

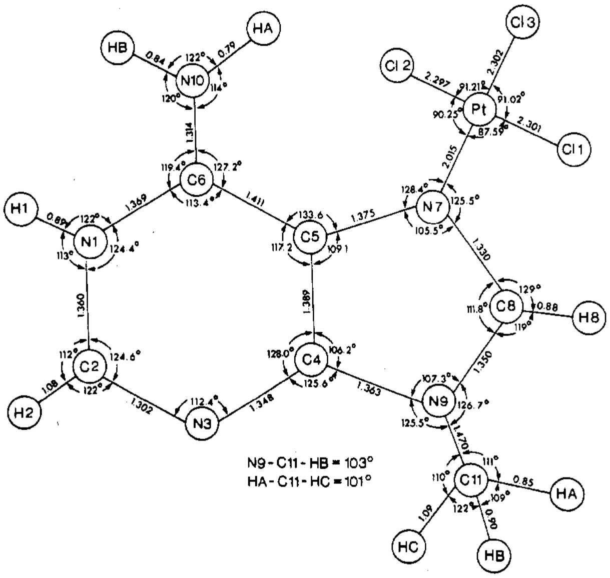


Figure 2. Interatomic bond distances and angles. (See text for standard deviations.)

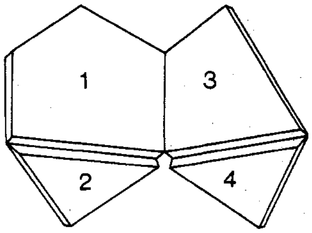
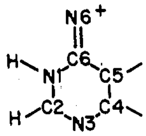


Figure 3. A schematic representation of the relationship between planar segments of the molecule. (See text for angles between planes.)

protonation of N(1), both for the free and for the coordinated ligand. Only the most significant changes are indicated. All other differences in bond distances and angles are ≤0.01 Å and ≤1.2°, respectively, for the free ligand and ≤0.006 Å and ≤1.6°, respectively, for the coordinated ligand. The changes in bond distances upon protonation of N(1) indicate a major contribution from the structure[17]



while the increase in the C(2)–N(1)–C(6) angle and the concomitant decrease in the angles N(1)–C(6)–C(5) and N(1)–C(2)–N(3) are consistent with the empirical rule for six-membered nitrogen heterocycles put forth by Singh.[20] The rule states that the angle around nitrogen will fall in the range 125 ± 3° if there is a proton on the nitrogen atom and in the range 116 ± 3° if there is no proton. We can take this as a confirmation of the existence of the proton on N(1) in the present structure. Similar behavior has been observed also with the N(7)-substituted purines.[21-23]

Table III shows the kind of changes that occur in the *whole purine* molecule upon coordination to the N(7) position, both for the protonated and for the neutral ligand. Only the most significant changes appear. All other differences in bond distances and angles are ≤0.006 Å and ≤1.2°, respectively, for the protonated ligand and ≤0.009 Å and ≤1.0°, respectively, for the neutral ligand. We see from Table III that the effects of coordination are similar for the protonated and for the neutral ligand. The changes in bond distances upon coordination indicate a contribution from the structure

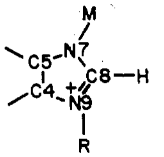


Table II. Comparison of Averaged Data between Protonated and Neutral 9-Substituted Adenine as a Free Ligand and as a Coordinated Ligand (See Text)

	Free ligands		Coordinated ligand	
	Protonated[a]	Neutral[b]	Protonated[c]	Neutral[d]
N(1)–C(6), Å	1.363	1.351	1.369	1.356
C(6)–N(10), Å	1.319	1.338	1.314	1.322
N(1)–C(2), Å	1.360	1.336	1.360	1.340
C(2)–C(3), Å	1.307	1.323	1.302	1.327
N(1)–C(6)–N(3), deg	113.9	117.1	113.4	116.7
C(6)–N(1)–C(2), deg	123.0	118.5	124.4	119.6
N(1)–C(2)–N(3), deg	125.5	129.3	124.6	128.9

[a] Averaged data from ref 15–17 (five structures). [b] Averaged data from ref 17–19 (six structures). [c] Present work. [d] Averaged data from ref 3a, b (two structures).

Table III. Comparison of Averaged Data between the Free and Coordinated Ligand for the Protonated and for the Neutral 9-Substituted Adenine (See Text)

	Protonated		Neutral	
	Free ligand[a]	Coordinated ligand[b]	Free ligand[c]	Coordinated ligand[d]
N(7)–C(8), Å	1.316	1.330	1.311	1.323
C(8)–N(9), Å	1.388	1.350	1.366	1.347
C(4)–C(5), Å			1.373	1.385
C(4)–C(5)–N(7), deg	111.2	109.1	110.5	108.8
C(6)–C(5)–N(7), deg	131.0	133.6	132.4	134.0
C(5)–N(7)–C(8), deg	104.2	105.5		

[a] Averaged data from ref 15–17 (five structures). [b] Present work. [c] Averaged data from ref 17–19 (six structures). [d] Averaged data from ref 3a, b (two structures).

That is the metal, much like the proton on N(1), acts as an electron sink. The changes in bond angles upon coordination are probably due to steric hindrance; C(6)–C(5)–N(7) increases to accommodate the coordination sphere of the metal and C(4)–C(5)–N(7) decreases as a result of this.

Planarity of the Adeninium Ligand. The results of least-squares planes calculations are shown in Figure 3. The purine is not planar. There are three folds in the molecule, along the C(4)–C(5), C(2)–C(4), and C(4)–C(8) lines. The angle between plane 1 and plane 2 is 1.4°, between plane 3 and plane 4 is 1.9°, and between plane 1 and plane 3 is 3.2°. The fold along C(4)–C(5) and distortions from planarity in the six-membered ring have been noted before.[2f,24,25]

Hydrogen Bonding. The molecules are linked in pairs (Figure 4) by a hydrogen bond between Cl(1) and H(1) across the center of symmetry and there is another hydrogen bond between Cl(2) and H(10A). Another intermolecular interaction of interest, which may be described as a weak hydrogen

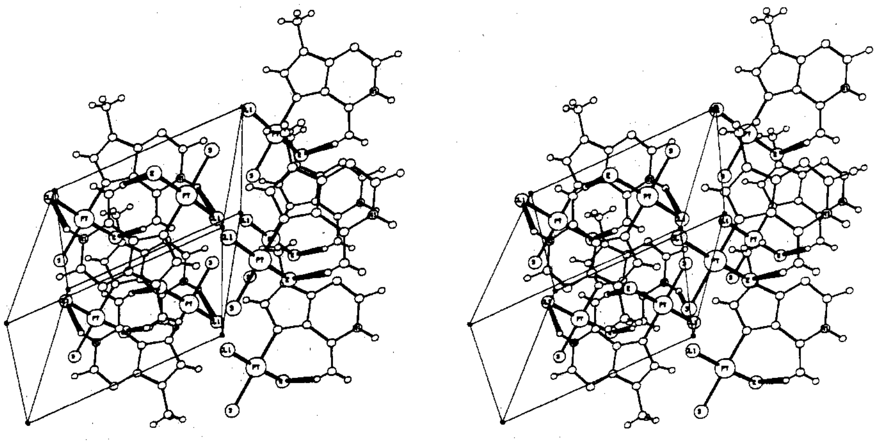


Figure 4. Stereodrawing of the crystal packing. Heavy lines represent hydrogen bonds.

Table IV. Hydrogen-Bond Distances and Angles

A	B	A–B, Å	H–B, Å	A–H–B, deg
N(1)–H······	Cl(1)[a]	3.150 (3)	2.39 (6)	143 (5)
C(2)–H······	Cl(1)[b]	3.559	2.52	160
N(10)–H(A)··	Cl(2)	3.257	2.55	144

[a] Symmetry positions $1-x$, $1-y$, $-z$. [b] Symmetry positions x, $1+y$, z.

bond, is between Cl(1) and H(2) (Table IV). Carbon is usually too electropositive to donate a proton to a hydrogen bond but this can occur when the carbon is activated by adjacent nitrogens. The acidity of H(8) has been noted before,[26] as well as weak interactions between H(2) and a chlorine atom[25] and between H(2) and oxygen.[19]

Conclusion

In addition to the structure described here the structures of several other metal complexes of 9-substituted adenine[3a,b,25,27,28] and 9-substituted guanine[27,29] are now known. In the vast majority of these, N(7) is the sole site of attachment of the metal to the base.[3a,b,25,27,29] In two of these[27,28] the metal is coordinated to N(1) of one ligand and N(7) of an adjacent ligand, and in one structure[28] the metal (Zn) coordinates only through N(1). In four structures the ligand is protonated and in the other four it is neutral, indicating that N(7) is the primary site of metal–base interaction under a variety of conditions. Furthermore, none are chelate complexes involving the C(6) substituent, a possibility that has been suggested previously[6,30,31] but discounted later[29] on steric grounds. As a matter of fact, a common feature of these structures is an intramolecular hydrogen bond forming between a metal ligand and the C(6) substituent. Chelation *is* observed when the C(6) substituent is sulfur and a "soft" metal like Pt(II) is involved,[3c] presumably because the donor properties of sulfur exceed those of oxygen or nitrogen.[29]

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Registry No. Trichloro(9-methyladeninium)platinum(II), 55272-66-7.

Supplementary Material Available: Listing of structure factor amplitudes (45 pages). Ordering information is given on any current masthead page.

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(9) The computer programs used were locally modified versions of the following: F. R. Ahmed and C. P. Huber, NRC-2 (data reduction); F. R. Ahmed and P. Singh, NRC-3 (absorption correction); C. T. Prewitt, SFLS5 (least-squares refinement); A. Zalkin, FORDAP (Fourier, Patterson maps); R. J. Doedens and J. A. Ibers, NUCLS (least-squares refinement), with block-diagonal option introduced by J. Sygusch; and C. K. Johnson, ORTEP (drawings).

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