(6) R. Mason, Proceedings of the 23rd IUPAC Conference, Boston, Mass., 1971, Vol. 6, p 31.
(7) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973).
(8) (a) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968); (b) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(9) This method of determining the positions of light atoms was described initially by S. J. LaPlaca and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965). Its use in locating bridging hydride ligands has been well illustrated by S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Am. Chem. Soc.*, **95**, 4532 (1973).
(10) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
(11) W. C. Hamilton, in "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, pp 287–292.
(12) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963); **23**, 558 (1967); A. C. Larson in "Crystallographic Computing", F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 251 ff.
(13) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, Table 7-4, p 226.
(14) D. W. Hart, R. Bau, and T. F. Koetzle, submitted for publication.
(15) Error estimates on average values are shown in brackets and are derived from the formula [esd] = $[\sum(\bar{d} - d_i)^2/(n^2 - n)]^{1/2}$, where the sum is over n "equivalent" measurements, d_i is the ith such measurement, and $\bar{d}$ is the mean value.
(16) M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, in press.
(17) A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Crystallogr. Sect. B*, **31**, 1630 (1975).

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Crystal and Molecular Structure of Dichlorobis(1-methylcytosine)palladium(II)

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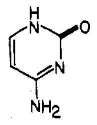
The title complex was synthesized and its structure determined by three-dimensional x-ray crystallography using counter methods. Crystal data for dichlorobis(1-methylcytosine)palladium(II), $Pd(cyt)_2Cl_2$, includes the following: space group $P\bar{1}$; $Z = 1$; $a = 6.831$ (2), $b = 7.377$ (2), $c = 8.824$ (1) Å; $\alpha = 117.94$ (1), $\beta = 105.34$ (2), $\gamma = 90.95$ (2)°; $V = 374$ Å^3; $R = 2.0\%$; 1141 reflections. The palladium atom is located at the inversion center of the cell. The 1-methylcytosine ligands are coordinated via the unsubstituted ring nitrogen atom which has been deprotonated. The ligand environment about the palladium atom is strictly planar, with Cl–Pd–Cl and N–Pd–N linear, due to the crystallographically imposed inversion center. There is a weak intramolecular hydrogen contact, between the palladium and one hydrogen atom of each cytosine group, to complete a very distorted octahedron about the metal. The other amino hydrogen atom of each group is linked to the carbonyl oxygen of an adjacent molecule via a weak hydrogen bond. Thus the crystal structure consists of parallel infinite chains of hydrogen bonded molecules.

Introduction

Most nucleic acid bases including cytosine, **1**, posses more than one basic site where interaction with a proton or a metal ion may take place. Either a proton or a substituent usually occupies the N(1) position so that N(3) and the carbonyl oxygen (O) are the most likely binding sites. The amino group attached to C(4) is not a basic site. Results of single-crystal x-ray diffraction investigations have shown that N(3), O, and chelation between them are possible binding modes for first-row divalent transition metal ions. Three different kinds of Cu(II) complexes have been shown to bind to N(3) of cytosine and also interact with O.[1–4] A similar chelation occurs in a Cu(II) complex to cytidine, **3**, where the N(1) position is substituted with ribose sugar.[5] With cytidine 5′-monophosphate the only base binding is at N(3) for Co(II), Cd(II),[6] and Zn(II).[7] In contrast, base coordination has been found at O(2) and not at N(3) for Mn(II).[8]



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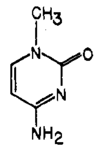

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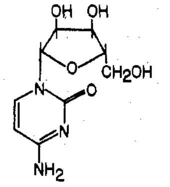

3

As part of a program to investigate the modes of interaction of antitumor Pt(II) complexes with nucleic acids we have undertaken studies of Pt(II) and Pd(II) complexes with nucleic acid bases and nucleosides. Both metal ions form similar diamagnetic tetragonal complexes with an advantage to Pd(II) because it reacts several powers of ten times more rapidly than Pt(II). A comparison has been made of identical complexes of the two metal ions and their interaction with some nucleosides.[9] In this paper we report the crystal structure of a complex of Pd(II) and 1-methylcytosine, **2**. In this ligand the pyrimidine base is substituted at the 1 position as is cytosine upon forming a nucleoside.

Experimental Section

The complex crystallized as small pale yellow prisms from an aqueous solution originally containing 1-methylcytosine and K_2PdCl_4. Every crystal of the sample was examined and the best was chosen for the x-ray study. Crystal data for dichlorobis(1-methylcytosine)palladium(II), $PdCl_2O_2N_6C_{10}H_{14}$, are the following: mol wt 428; pale yellow crystal; space group $P\bar{1}$; $Z = 1$; $a = 6.831$ (2), $b = 7.377$ (2), $c = 8.824$ (1) Å; $\alpha = 117.94$ (1), $\beta = 105.34$ (2), $\gamma = 90.95$ (2)°; $V = 374$ Å^3; $R = 2.0\%$; 1141 reflections; $\rho_{calcd} = 1.90$, $\rho_{obsd} = 1.88$ g cm^{-3}; μ(Mo Kα) = 15.9 cm^{-1}; crystal dimensions (distances in mm of faces from centroid) (100) 0.03; ($\bar{1}$00) 0.03; (010) 0.075; (0$\bar{1}$0) 0.075; (01$\bar{1}$) 0.05; (0$\bar{1}$1) 0.05.

The Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and judged to be satisfactory.

Collection and Reduction of the Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 48°$. Scan widths (SW) were calculated from the formula SW = $A + B \tan\theta$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width of the peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.60 and 0.30° respectively. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as NC = TOT − 2(BG1 + BG2) where TOT is the integrated peak intensity. Reflection data were considered insignificant if intensities registered less than 10 counts above background on a rapid prescan, such reflections being auto-

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a] for $Pdcyt_2Cl_2$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0.0000 (0)	0.0000 (0)	0.0000 (0)	0.01103 (5)	0.01290 (5)	0.00559 (3)	0.00443 (9)	0.00787 (6)	0.00543 (6)
Cl	0.1679 (1)	0.3050 (1)	0.05048 (8)	0.0260 (2)	0.0158 (1)	0.01155 (9)	−0.0008 (3)	0.0170 (2)	0.0090 (2)
O	0.3434 (3)	0.1210 (3)	0.3426 (2)	0.0131 (4)	0.0311 (5)	0.0113 (2)	0.0163 (7)	0.0129 (5)	0.0191 (5)
N(1)	0.1902 (3)	0.2473 (3)	0.5631 (2)	0.0138 (5)	0.0167 (4)	0.0073 (3)	0.0044 (7)	0.0077 (6)	0.0093 (5)
N(3)	0.0028 (3)	0.1406 (3)	0.2612 (2)	0.0106 (4)	0.0140 (4)	0.0068 (3)	0.0044 (7)	0.0077 (5)	0.0063 (5)
N(4)	−0.3353 (3)	0.1843 (4)	0.1859 (3)	0.0117 (5)	0.0271 (6)	0.0110 (3)	0.0109 (9)	0.0092 (6)	0.0098 (7)
C(1)	0.3860 (5)	0.2731 (5)	0.6971 (3)	0.0170 (6)	0.0295 (7)	0.0091 (4)	0.0074 (11)	0.0058 (8)	0.0167 (7)
C(2)	0.1867 (4)	0.1671 (4)	0.3856 (3)	0.0137 (5)	0.0144 (5)	0.0081 (3)	0.0035 (8)	0.0095 (6)	0.0087 (6)
C(4)	−0.1655 (4)	0.2012 (4)	0.3110 (3)	0.0119 (5)	0.0125 (5)	0.0097 (3)	0.0030 (8)	0.0093 (7)	0.0059 (6)
C(5)	−0.1591 (4)	0.2839 (4)	0.4925 (3)	0.0144 (5)	0.0191 (6)	0.0101 (3)	0.0072 (10)	0.0155 (7)	0.0069 (7)
C(6)	0.0190 (4)	0.3033 (4)	0.6129 (3)	0.0186 (6)	0.0176 (5)	0.0078 (3)	0.0034 (10)	0.0133 (7)	0.0071 (6)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å
H(11)	0.444 (5)	0.154 (5)	0.654 (4)	4.2 (8)	H(42)	−0.429 (5)	0.199 (4)	0.208 (4)	3.9 (7)
H(12)	0.486 (5)	0.393 (5)	0.713 (4)	4.5 (8)	H(5)	−0.273 (5)	0.324 (4)	0.525 (4)	3.3 (7)
H(13)	0.360 (5)	0.316 (4)	0.799 (4)	3.8 (7)	H(6)	0.034 (4)	0.358 (3)	0.724 (3)	2.1 (5)
H(41)	−0.338 (4)	0.130 (4)	0.080 (3)	2.5 (6)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

matically rejected by the computer.

The intensities of four standard reflections, monitored at 100 reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics (the greatest deviation from the mean was 1.9%). The raw intensity data were corrected for Lorentz–polarization effects (including the polarization effect of the crystal monochromator) and then for absorption. Of the 1170 independent intensities recorded, 1132 had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics, using an "ignorance factor" P of 0.03.[10] These data were used in the final refinement of the structural parameters.

Determination and Refinement of the Structure. The small volume of the unit cell requires that the molecule have space group $P\bar{1}$ with palladium in a special position at the origin or that it be in space group $P1$, in which case the palladium may also be placed at the origin for convenience. The three-dimensional Patterson function calculated from all intensity data confirmed this postulate. Using the space group $P1$, the positions of the palladium atom and four ligand donor atoms derived from the Patterson function phased the intensity data sufficiently well to permit location of the other nonhydrogen atoms from a three-dimensional Fourier synthesis. The molecule clearly showed inversion symmetry at the central palladium atom, and therefore space group $P\bar{1}$ was chosen for the remaining calculations. The data was transformed to space group $P\bar{1}$ with a multiplicity of 0.5 for palladium, for the remaining calculations. The choice of space group $P\bar{1}$ was confirmed by the solution of the structure; vide infra. A further Fourier synthesis permitted location of all the hydrogen atoms in the molecule, which were then included in the calculations.

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were then taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber,[11] and those for hydrogen from Stewart et al.[12] The effects of anomalous dispersion for all nonhydrogen atoms were included in F_c using values of Cromer and Ibers[13] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. The principal programs used have been described.[14]

Anisotropic temperature factors were introduced for all nonhydrogen atoms, and the position and thermal parameters of all atoms including methyl hydrogens were refined to convergence (except that the palladium positions were fixed at the origin). The model converged with $R = 2.0$, $R_w = 2.4\%$. A structure factor calculation with all observed and unobserved reflections included (no refinement) gave $R = 2.0\%$, indicating that no significant intensities had been rejected. A final Fourier difference map was featureless. Tables of the observed and calculated structure factor amplitudes are available.[15]

Results and Discussion

Final positional and thermal parameters are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figure 1 is a stereoscopic pair view of $Pd(cyt)_2Cl_2$, while Figure 2 shows the molecular packing in the unit cell.

Table II. Bond and Selected Intramolecular Distances (Å) for $Pd(cyt)_2Cl_2$

Pd–Cl	2.298 (1)	C(4)–C(5)	1.409 (3)
Pd–N(3)	2.031 (2)	C(5)–C(6)	1.341 (4)
O–C(2)	1.230 (2)	C(1)–H(11)	0.93 (3)
N(1)–C(1)	1.471 (3)	C(1)–H(12)	1.04 (3)
N(1)–C(2)	1.384 (3)	C(1)–H(13)	0.87 (3)
N(1)–C(6)	1.360 (3)	C(5)–H(5)	0.91 (3)
N(3)–C(2)	1.372 (3)	C(6)–H(6)	0.85 (3)
N(3)–C(4)	1.348 (3)	N(4)–H(41)	0.82 (3)
N(4)–C(4)	1.330 (3)	N(4)–H(42)	0.71 (3)
O · · · N(4′)	4.104 (3)	Pd · · · H(41)	2.66 (2)
O · · · H(41′)	3.29 (2)	H(11) · · · O	2.54 (2)
Pd · · · O	3.015 (2)	Pd · · · N(4)	3.128 (2)

Table III. Bond Angles (deg) for $Pd(cyt)_2Cl_2$

Cl–Pd–ClX	180.00	N(1)–C(2)–O	120.6 (2)
Cl–Pd–N(3)	89.82 (5)	N(1)–C(2)–N(3)	117.5 (2)
Cl–Pd–N(3)X	90.18 (5)	O–C(2)–N(3)	121.9 (2)
ClX–Pd–N(3)	90.18 (5)	N(3)–C(4)–N(4)	118.5 (2)
ClX–Pd–N(3)X	89.82 (5)	N(3)–C(4)–C(5)	120.3 (2)
N(3)–Pd–N(3)X	180.00	N(4)–C(4)–C(5)	121.2 (2)
Pd–N(3)–C(2)	116.0 (1)	C(4)–C(5)–C(6)	118.1 (2)
Pd–N(3)–C(4)	122.7 (1)	C(4)–C(5)–H(5)	120 (2)
C(2)–N(3)–C(4)	121.4 (2)	C(6)–C(5)–H(5)	122 (2)
C(1)–N(1)–C(2)	117.9 (2)	N(1)–C(6)–C(5)	121.4 (2)
C(1)–N(1)–C(6)	121.0 (2)	N(1)–C(6)–H(6)	116 (2)
C(2)–N(1)–C(6)	121.1 (2)	C(5)–C(6)–H(6)	122 (2)
C(4)–N(4)–H(41)	120 (2)	N(4)–H(41)–Pd	118 (2)
C(4)–N(4)–H(42)	119 (2)	N(4)–H(42)–O	147 (2)
H(41)–N(4)–H(42)	119 (3)	H(11)–C(1)–H(12)	107 (3)
N(1)–C(1)–H(11)	110 (2)	H(11)–C(1)–H(13)	118 (3)
N(1)–C(1)–H(12)	107 (2)	H(12)–C(1)–H(13)	107 (3)
N(1)–C(1)–H(13)	106 (2)		

Table IV. Closest Intermolecular Distances (Å)

Mol 1	Mol 2	Distance	Symmetry
	(a) "Nonhydrogen" Approaches		
O	N(4)	3.021 (3)	$1 + x, y, z$
	C(1)	3.400 (4)	$1 - x, -y, 1 - z$
	C(5)	3.277 (3)	$1 + x, y, z$
N(4)	N(4)	3.280 (5)	$-1 - x, y, -z$
C(4)	C(6)	3.469 (3)	$-x, 1 - y, 1 - z$
	(b) "Hydrogen" Contacts		
O	H(42)	2.40 (3)	$1 + x, y, z$
	H(11)	2.52 (2)	$1 - x, -y, 1 - z$

The complex consists of monomeric molecules which exhibit relatively close intermolecular approaches (Table IV, Figure

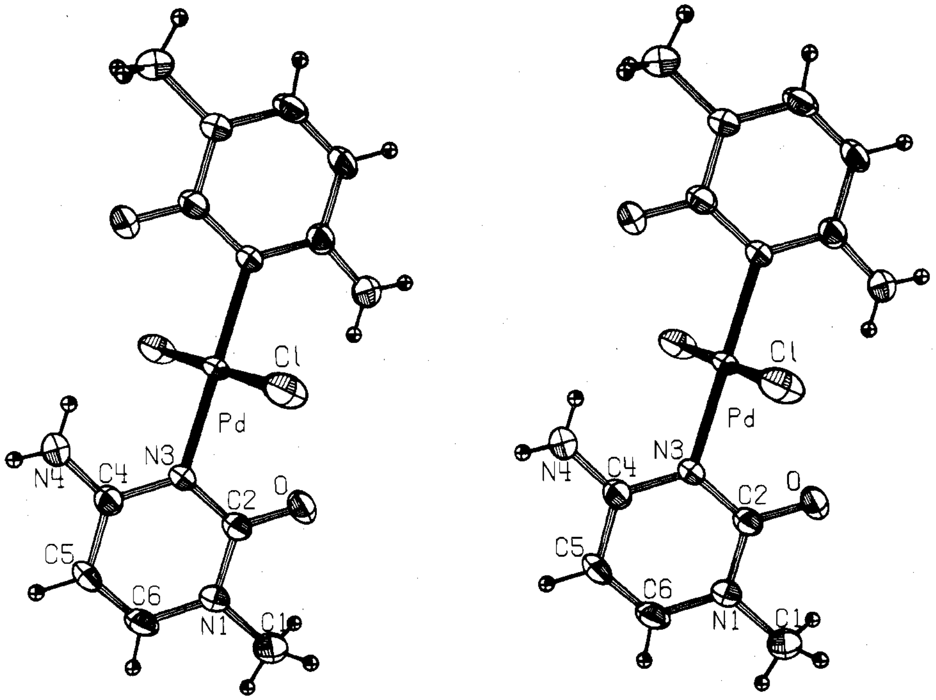

Figure 1.

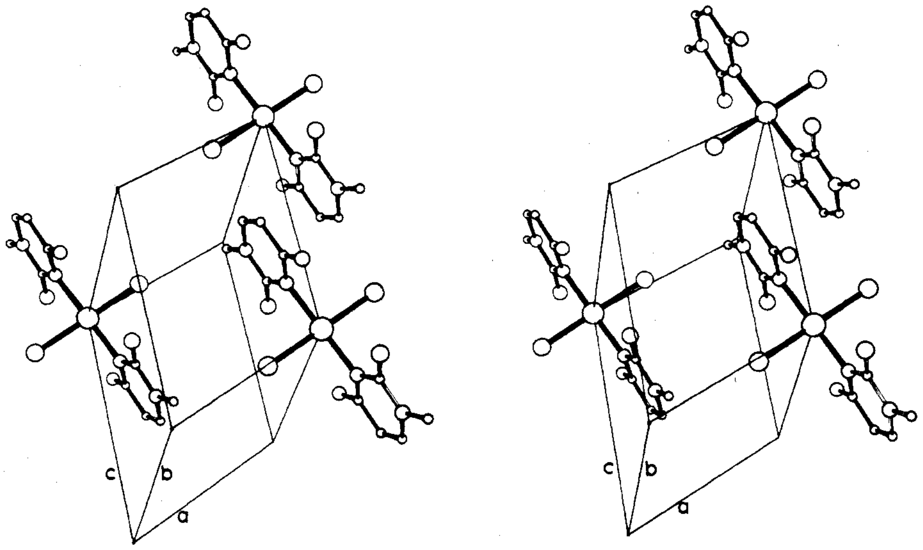

Figure 2.

Table V. Coefficients of Least-Squares Planes for $AX + BY + CZ = D$

Plane	Atoms	A	B	C	D	Distance from plane (Å)
I	Pd, Cl, ClX, N(1), N(1)X	−0.364	0.337	−0.868	0	Pd, 0; Cl, 0; ClX, 0; N(1), 0; N(1)X, 0
II	N(1), N(2), C(3)–C(6)	−0.210	−0.964	−0.166	−0.180	N(1), −0.03; N(2), 0.04; C(3), −0.01; C(4), −0.02; C(5), 0.01; C(6), 0.01
III	N(1)X, N(2)X, C(3)X–C(6)X	−0.210	−0.964	−0.166	0.180	N(1)X, 0.03; N(2)X, −0.04; C(3)X, 0.01; C(4)X, 0.02; C(5)X, −0.01; C(6)X, −0.01

Interplanar Angles, Deg

I,II	I,III	II,III
95.9	95.9	0

2). The closest nonhydrogen intermolecular contact (3.021 Å) is between atoms O and N(4) of adjacent molecules along the *x* axis. The closest intermolecular approach to a hydrogen atom is between O and H(42) (attached to atom N(4)) at a distance of 2.40 (3) Å, which could be considered a weak hydrogen bond. Thus infinite chains of molecules are formed along the *a* axis via the hydrogen bonding interaction between atoms O and N(4), but the relative weakness of this "hydrogen bond" must be stressed. The contacts between these chains (Table IV) are much weaker still. The nitrogen atom N(4) participates in the ring conjugation (confirmed by the short C(4)–N(4) distance (1.330 (3) Å), thereby forcing both the amine hydrogens H(41) and H(42) also to be coplanar with the palladium–ligand–ring.

There is a weak intramolecular hydrogen contact (2.66 (3) Å), between Pd and each of the H(41) atoms (attached to

N(4)), such as to complete a very distorted octahedron. Ignoring this hydrogen atom, the ligand environment about the metal atom is constrained to be precisely planar by the crystallographically imposed center of symmetry. The two 1-methylcytosine rings are parallel to each other and at 84.1° to the $Pd_2Cl_2N_2$ plane. The Pd–H(41) distance of 2.66 (2) Å is shorter than the sum of the van der Waals radii of Pd and H (3.1 Å). This corresponds to a metal–hydrogen interaction significantly weaker than observed by Roe et al.[16] (2.3 Å) but stronger than that observed by Dehand et al.[17] (2.86 (7) Å) for Pd–H interactions. The Pd–H interaction may therefore have a slight effect on the structure. The metal–hydrogen interaction may be forced upon the molecule by the position of the trigonal nitrogen atom N(4) on the ring carbon adjacent to the ligand donor atom. Since the angle Pd–N(3)–C(4) (122.7 (1)°) is significantly greater than Pd–N(3)–C(2) (116.0 (1)°), it appears that H(41) is pushed away from Pd. At the same time, chelation is avoided, the Pd–O distance (3.015 (2) Å) being almost as great as Pd–N(4) (3.128 (2) Å). Thus, the metal atom assumes a position of minimal interaction with both the carbonyl oxygen atom and the NH_2 group.

The amine hydrogen H(41) is well separated from the carbonyl oxygen of the other cytidine ring (3.29 (2) Å). Thus, the possibility of a hydrogen bonding interaction, observed in other systems, is sacrificed, possibly to avoid a closer Pd–H(41) approach.

The methyl hydrogens are unusually well resolved and two of them stagger the oxygen atom of the same ring. One of these hydrogen atoms H(11) is "clamped" between the carbonyl oxygen of the same ring and that of an adjacent molecule, with which it is in relatively close contact (2.52 (2), 2.54 (2) Å).

Only modest changes occur in bond lengths and bond angles within the cytosine ring compared to those found in neutral cytosine[18] and in three cytosine complexes where Cu(II) is bound at N(3).[1-4] The difference between the two exocyclic bond angles involving the metal ion, M–N(3)–C(4) and M–N(3)–C(2), is 7° in the Pd(II) complex and 18 and 22° in two Cu(II) complexes.[2,3] These larger values in the Cu(II) complexes are attributed in part to a weak intramolecular axial Cu–O(2) interaction near 2.8 Å. By comparison the Pd–O(2) distance is 3.015 (2) Å.

Protonation of cytosines produces changes in ring bond lengths and angles as demonstrated by comparing the crystal structures of neutral cytidine[19] with ring protonated 3′-cytidine monophosphate.[20] Complexation of 1-methylcytosine in the Pd(II) complex yields bond lengths and especially bond angles that are intermediate between neutral and protonated 1-substituted cytosines. In those cases where the changes are beyond experimental error, complexation of Pd(II) to the neutral ligand produces changes that are about 35% of those produced by protonation. This percentage is similar to that found for the C(2) and C(4) chemical shifts in carbon-13 magnetic resonance spectra of basic pyrimidine nucleosides produced upon complexation with Pd(II) as compared with protonation.[21]

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Registry No. $Pd(cyt)_2Cl_2$, 62973-71-1.

Supplementary Material Available: A listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) M. Sundaralingam and J. A. Carrabine, *J. Mol. Biol.*, **61**, 287 (1971).
(2) D. J. Szalda, L. G. Marzilli, and T. J. Kistenmacher, *Inorg. Chem.*, **14**, 2076 (1975).
(3) T. J. Kistenmacher, D. J. Szalda, and L. G. Marzilli, *Acta Crystallogr., Sect. B*, **31**, 2416 (1975).
(4) K. Saito, R. Terashima, T. Sakaki, and K. Tomita, *Biochem. Biophys. Res. Commun.*, **61**, 83 (1974).
(5) D. Szalda, L. G. Marzilli, and T. J. Kistenmacher, *Biochem. Biophys. Res. Commun.*, **63**, 601 (1975).
(6) G. R. Clark and J. D. Orbell, *J. Chem. Soc., Chem. Commun.*, 697 (1975).
(7) K. Aoki, *Biochem. Biophys. Acta*, **447**, 379 (1976).
(8) K. Aoki, *J. Chem, Soc., Commun.*, 748 (1976).
(9) M. C. Lim and R. B. Martin, *J. Inorg. Nucl. Chem.*, **38**, 1911 1915 (1976).
(10) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1976).
(11) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(12) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1975).
(13) D. T. Cromer and J. A. Ibers, ref 12.
(14) P. C. Healy, G. M. Mockler, D. P. Freyberg, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 691 (1975).
(15) Supplementary material.
(16) D. M. Roe, P. M. Bailey, K. Mosely, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1273 (1972).
(17) J. Dehand, J. Fisher, M. Pfeffer, A. Mitschler, and M. Zinsius, *Inorg. Chem.*, **15**, 2675 (1976).
(18) R. J. McClure and B. M. Craven, *Acta Crystallogr., Sect. B*, **29**, 1234 (1973).
(19) S. Furberg, C. S. Peterson, and C. Romming, *Acta Crystallogr.*, **18**, 313 (1965).
(20) M. Sundaralingam and L. H. Jensen, *J. Mol. Biol.*, **13**, 914 (1965); C. E. Bugg and R. E. Marsh, *ibid.*, **25**, 67 (1967).
(21) D. J. Nelson, P. L. Yeagle, T. L. Miller, and R. B. Martin, *Bioinorg. Chem.*, **5**, 353 (1976).