distant from N, is involved in two hydrogen bonds, whereas the other two oxygen atoms only accept one. O(3) takes part in a stronger hydrogen bond than O(1). Similar effects as discussed above have also been correlated in other hydrogen-bonded structures with NO_3^- ions (*cf.* Narasinga Rao & Parthasarathy, 1973).

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Platinum Compound Binding by Purine and Pyrimidine Bases. I. The Structure of [Cytosine.H$^+$]$_2$[PdCl$_4^{2-}$]

BY B. L. KINDBERG AND E. L. AMMA

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208, *U.S.A.*

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Abstract. $[C_4H_6N_3O]_2[PdCl_4]$, monoclinic, $P2_1/c$, $a=8\cdot437$ (2), $b=13\cdot776$ (4), $c=7\cdot191$ (2) Å, $\beta=111\cdot07$ (1)°, $\varrho_o=2\cdot01$, $\varrho_c=2\cdot00$ g cm^{-3}. The dominant structural features are ionic moieties, hydrogen bonding and base stacking. Base–base hydrogen bonding is replaced by Cl–H interactions, but base stacking persists.

Introduction. Since the discoveries by Rosenberg (1971), compounds containing certain platinum metals have been shown to be effective in the treatment of various types of animal and human carcinomas. Several metal-binding modes have been proposed for this interaction, including specific metal-base binding (Howle, Gayle & Smith, 1972), disruption of hydrogen bonding and base stacking in the double helix (Drobnik & Horacek, 1973), and cross strand linkages (Roberts & Pascoe, 1972; Zakharenko & Moshkovskii, 1972). Investigation of the interactions between Pt^{2+} and Pd^{2+} compounds and nucleotides, nucleosides, and nucleotide bases is, therefore, of considerable interest. The simplest model for this system employs the use of bases in which the site of ribose attachment has been blocked with an alkyl group. As the first of this series a proton is placed on cytosine. Since the difference in Pt and Pd chemistry is frequently one of rates and Pd is more suitable for X-ray studies, parallel experiments with Pd^{2+} and Pt^{2+} compounds were carried out, and the Pd^{2+} analog was used in the structural studies where possible.

Brick-red crystals of $[C_4H_6N_3O]_2[PdCl_4]$ were prepared by slow evaporation of a solution made by mixing 3 ml of $0\cdot02M$ cytosine acidified to a *p*H of 1·0 by HCl with 3 ml of $0\cdot02M$ K_2PdCl_4.

Source: Mo $K\alpha$, $\lambda=0\cdot710683$ Å, $2\theta_{\max}=90°$; θ–2θ scan on a Picker automated diffractometer, $\Delta 2\theta=1\cdot5°$. Number of reflections: 3781 taken, 2498 non-zero, confidence level $=2\sigma$. $\mu=17\cdot58$ cm^{-1}, transmission factor min and max: 0·393, 0·613; crystal size: $0\cdot66\times0\cdot53\times0\cdot33$ mm; $R=0\cdot049$, weighted $R=0\cdot059$.

Structure solution was by standard heavy-atom techniques and refinement was by full-matrix least-squares calculations. The function minimized was $\sum w(F_o-F_c)^2$ with weights determined from counting statistics. Scattering factors for Pd^{2+}, Cl$^-$, and neutral nitrogen, oxygen and carbon were from Cromer & Waber (1965), those for hydrogen were from Stewart, Davidson & Simpson (1965). The effects of anomalous dispersion were included in the structure-factor calculations by addition to F_c (Ibers & Hamilton, 1964). Values for $\Delta f'$ and $\Delta f''$ for palladium and chlorine were those given by Cromer (1965). Hydrogen atom peaks were seen in the difference Fourier map and idealized hydrogen-atom coordinates were calculated for use in further refinement but only isotropic hydrogen temperature factors were varied. All other thermal parameters were varied anisotropically. A final difference electron-density map was qualitatively featureless.

Table 1. *Final positional and thermal parameters*

(*a*) Non-hydrogen atoms. The anisotropic temperature factors are of the form

$$\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)];\ \text{values are } \times 10^4.$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	(0)*	(0)*	(0)*	67 (1)	23 (0)	118 (1)	−5 (0)	12 (1)	−1 (0)
Cl(1)	0·0691 (2)	0·1117 (1)	0·2540 (2)	136 (2)	50 (1)	221 (4)	−31 (1)	69 (2)	−56 (1)
Cl(2)	−0·1138 (2)	−0·0980 (1)	0·1779 (2)	125 (2)	52 (1)	151 (3)	−33 (1)	20 (2)	20 (1)
N(3)	−0·5423 (5)	0·1183 (3)	0·2127 (7)	75 (6)	19 (2)	213 (11)	1 (2)	16 (6)	2 (3)
C(2)	−0·4254 (7)	0·0511 (4)	0·3188 (9)	89 (7)	28 (2)	224 (14)	5 (3)	40 (8)	5 (4)
N(1)	−0·2739 (6)	0·0862 (4)	0·4326 (8)	87 (6)	34 (2)	237 (13)	12 (3)	24 (8)	19 (4)
C(6)	−0·2390 (6)	0·1832 (4)	0·4476 (8)	80 (7)	40 (3)	179 (12)	−4 (4)	26 (8)	−5 (5)
C(5)	−0·3567 (7)	0·2499 (4)	0·3476 (8)	99 (8)	25 (2)	158 (12)	−9 (3)	31 (8)	−1 (4)
C(4)	−0·5178 (6)	0·2160 (3)	0·2243 (7)	85 (7)	18 (2)	135 (10)	1 (3)	39 (7)	−1 (3)
N(4)	−0·6436 (6)	0·2720 (3)	0·1193 (8)	106 (7)	19 (2)	220 (12)	5 (3)	14 (7)	7 (4)
O(2)	−0·4657 (6)	−0·0364 (3)	0·3010 (8)	135 (8)	17 (2)	415 (17)	15 (4)	57 (9)	20 (4)

(*b*) Final hydrogen atom positions and thermal parameters

	x	y	z	B
H(1)	−0·188	0·042	0·505	6 (5)
H(3)	−0·650	0·095	0·009	7 (5)
H(4)	−0·751	0·246	0·038	1 (1)
H(4′)	−0·633	0·341	0·119	1 (1)
H(5)	−0·331	0·317	0·360	5 (3)
H(6)	−0·130	0·205	0·531	3 (2)

* Fixed by symmetry.

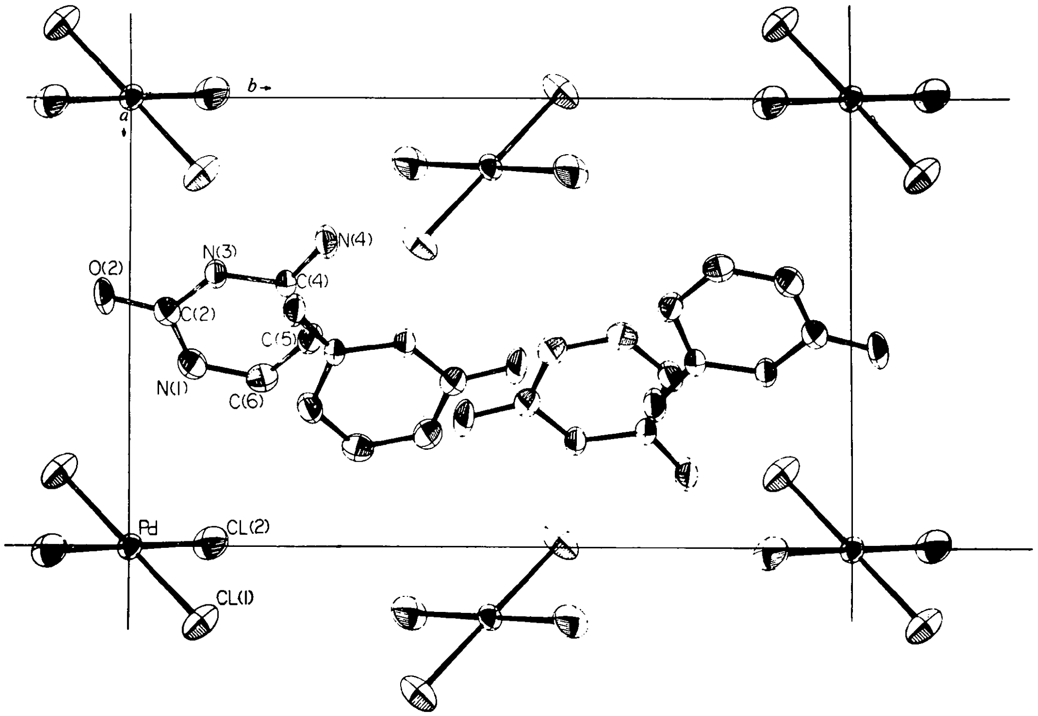

Fig. 1. An *ORTEP* (Johnson, 1965) drawing showing the unit-cell packing down [001]. The cytosine rings are all tipped 21° in the same direction relative to the *ab* plane, *i.e.* lie in the *a***b** plane. The hydrogens have been omitted in this view.

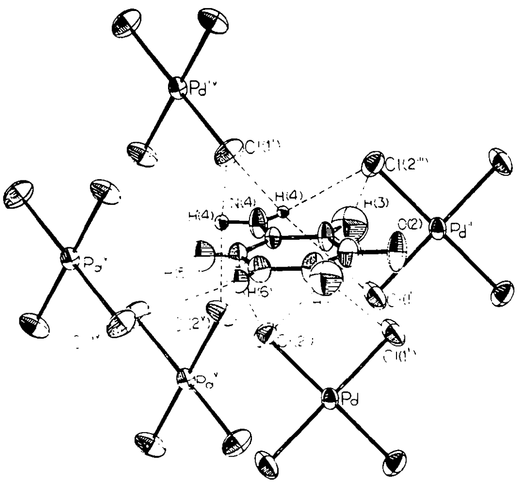

Fig. 2. An *ORTEP* (Johnson, 1965) drawing of a cytosine ring and surrounding $PdCl_4^{2-}$ units. The hydrogen bonding is shown by dotted lines. The notation is such that H(1) is bound to N(1), H(3) is bound to N(3), H(5) is bound to C(5), H(6) is bound to C(6), and H(4) and H(4′) are bound to N(4) which is in turn bound to C(4). Pd and Cl notations are: i $-x,-y,1-z$; ii $-1+x,y,z$; iii $-1-x,-y,-z$; iv $-1+x,\frac{1}{2}-y,-\frac{1}{2}+z$; v $-1-x,\frac{1}{2}+y,\frac{1}{2}-z$; vi $x,\frac{1}{2}-y,\frac{1}{2}+z$.

Final atomic positional and thermal parameters are in Table 1. Interatomic distances and angles and their errors were computed using parameters and variance–covariance matrix from the last cycle of least-squares and are listed in Table 2.*

Discussion. The structure consists of discrete $PdCl_4^{2-}$ ions and protonated cytosine rings in a complex network of hydrogen bonds. Some base stacking is retained but hydrogen bonding between cytosine rigns as found in cytosine, cytosine monohydrate, cytosine hydrochloride and cytidine hydrochloride is completely disrupted by the presence of the $PdCl_4^{2-}$ ion.

The protonated cytosine rings are planar, with the greatest deviation from the least-squares plane being 0·03 (8) Å for N(3). The amine hydrogens, H(4) and H′(4), also lie in this plane. The ring planes are parallel, overlapping at C(5) and N(4), with the closest atomic contact being 3·375 (7) Å (Fig. 1). Each ring is hydrogen-bonded to five different square planar $PdCl_4^{2-}$ ions (Table 2, Fig. 2) and lies along the bisector of the Cl–Pd–Cl angle of the closest $PdCl_4^{2-}$ group. The dihedral angle thus formed is 101·6°.

The pyrimidine ring distances (Table 2) are in general not significantly different from those found in cytosine (Barker & Marsh, 1964), cytosine monohydrate (Jeffrey & Kinoshita, 1963), 2′-deoxycytidine hydrochloride (Subramanian & Hunt, 1970), and 1-methylcytosine hydrochloride (Trus & Marsh, 1972) with the exception of the N(1)–C(2) bond, which is somewhat shortened. We have no explanation for this at this time, except that the shortening is possibly due to cumulative hydrogen bonding effects, which presumably also cause some differences in the ring angles.

Table 2. *Bond distances* (Å) *and angles* (°)

Pd—Cl(1)	2·298 (1)	Cl(2)–Pd—Cl(1)	89·34 (5)
Pd—Cl(2)	2·295 (1)	N(1)–C(2)–N(3)	115·9 (5)
N(3)–C(2)	1·368 (6)	C(2)–N(3)–C(4)	124·9 (4)
C(2)–N(1)	1·336 (7)	C(2)–N(1)–C(6)	122·3 (5)
N(1)–C(6)	1·364 (7)	N(1)–C(6)–C(5)	121·7 (5)
C(6)–C(5)	1·354 (8)	C(4)–C(5)–C(6)	117·8 (5)
C(5)–C(4)	1·409 (7)	C(5)–C(4)–N(3)	117·2 (4)
C(4)–N(3)	1·360 (6)	C(5)–C(4)–N(4)	124·5 (4)
C(4)–N(4)	1·310 (6)	N(3)–C(4)–N(4)	118·2 (4)
C(2)–O(2)	1·247 (7)	N(3)–C(2)–O(2)	118·8 (5)
		N(1)–C(2)–O(2)	125·3 (5)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30865 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.