

1979), but the Cl—Fe—Cl angles varied from 106.6 (1) to 110.7 (2)°, similar to those found for the present structure. A possible explanation of the differences in Fe—Cl distances lies in the different interactions of the FeCl₄ anion with the cation and the solvate water molecules.

The methyltriphenylphosphonium cation was found to have a nearly regular tetrahedral arrangement about the P atom (Table 2). The phenyl C atom planes show only minimal deviations from the P—C bond directions; the P atom lies practically in the C(11)—C(16) plane (1) [0.032 (1) Å] and is displaced by 0.119 (2) and 0.154 (2) Å from the C(21)—C(26) (2) and the C(31)—C(36) (3) planes, respectively. The C—C distances for the phenyl groups range from 1.36 (1) to 1.40 (1) Å. The phenyl-group planes form dihedral angles of 113.7 (1) (1,2), 75.2 (1) (1,3) and 104.9 (2)° (2,3), respectively.

The structure determination of the title compound contributed to the explanation of the course of the reaction in one system of Fe^{III} + PPh₃ + O₂ + solvent: when methanol was used as solvent, PPh₃ was not oxidized to OPPh₃, but was quaternized by the CH₃ group of methanol to a CH₃PPh₃⁺ cation. On the other

hand, with acetonitrile as solvent, PPh₃ was oxidized to OPPh₃ and FeCl₃(OPPh₃)₂ was formed [*i.e.* [FeCl₂(OPPh₃)₄][FeCl₄]]. While the title compound did not show any catalytic properties, the FeCl₃(OPPh₃)₂ catalysed the oxidation in the above system. Structural investigation of the last complex as well as of other FeX₃(OPPh₃)₂ compounds (X = Cl, Br or NCS) should contribute to the explanation of the relationship between the structures and their different catalytic activity (the next object of our structural study).

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Structure of Bis(4-hydroxy-L-prolinato-N,O)palladium(II) Trihydrate

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Abstract. [Pd(C₅H₈NO₃)₂].3H₂O, *M_r* = 420.4, m.p. = 483 K (dec.), monoclinic, *P*2₁, *a* = 9.780 (8), *b* = 7.682 (5), *c* = 11.044 (9) Å, β = 114.36 (3)°, *V* = 755.9 (15) Å³, *Z* = 2, *D_m* = 1.83 (solvents CCl₄ and 1,2-dibromoethane), *D_x* = 1.86 g cm⁻³, Mo *K*α, Zr filter, λ = 0.7107 Å, μ = 12.27 cm⁻¹, *F*(000) = 428, *R* = 0.044 and *wR* = 0.063 for 2036 unique reflections. Palladium has a near-planar coordination with the imino nitrogens and carboxyl oxygens in the *cis* configuration. The Pd—N and Pd—O distances are normal [Pd—N(1),N(2) = 2.016 (5), 2.022 (5) and Pd—O(1),O(4) = 2.000 (5), 2.008 (5) Å]. The proline rings are in envelope conformations with the hydroxy-substituted C(4) and C(9) atoms lying 0.65 (2) and

0.58 (2) Å out of the least-squares planes of the other four atoms of pyrrolidine rings *A* and *B*, respectively. An elaborate network of hydrogen bonds interlinks the molecules.

Introduction. In continuation of our studies on the structure of palladium(II) complexes (Padmanabhan, Patel & Ranganathan, 1985), the crystal-structure determination of the present complex was undertaken. Preliminary findings on the structure have been reported (Sinh, Padmanathan, Patel, Ranganathan & Rao, 1982). As optically active proline and related amino acids are stereospecific (coordinating in the *cis* configuration) (Haines & Reimer, 1973), it was

presumed that the coordination of the hydroxyprolinato ions to palladium(II) in the present complex would be *cis* square planar. The crystals when dried over P₂O₅ crumbled to powder. Elemental analysis showed the presence of three water molecules. Microthermogravimetric analysis confirmed this and also indicated the water was uncoordinated.

Experimental. Yellow needle-shaped crystals obtained from reaction of PdCl₂ and 4-hydroxy-L-proline in 1:2 molar ratio in water. Intensity data for 2365 reflections (crystal size 0.15 × 0.42 × 0.62 mm) collected on an indigenously fabricated computer-controlled four-circle diffractometer (Padmanabhan *et al.*, 1979) with Zr-filtered Mo K α radiation, $6 < 2\theta < 55^\circ$, ω - 2θ step-scan width 1.8°, 33 steps deg⁻¹ and 2.0 s step⁻¹. Data corrected for Lorentz, polarization and absorption (max. and min. absorption coefficients 0.735 and 0.697 respectively). Unit-cell parameters from least-squares fit of 2 θ values of 25 reflections measured on diffractometer. Two standard reflections measured every 100 reflections showed no significant change during data-collection process. Palladium atom position found from Patterson map. Positions for other non-hydrogen atoms located from successive Fourier maps. H positions of water molecules and hydroxyl groups located in difference Fourier synthesis. Remaining H atoms fixed at calculated positions with isotropic temperature factors (0.05 Å²). Other atoms refined on *F* with isotropic and anisotropic temperature factors. Scattering factor for palladium with corrections for dispersion effects from *International Tables for X-ray Crystallography* (1974). *SHELX76* (Sheldrick, 1976) used for all calculations. For 2036 unique reflections with $I \geq 2.5\sigma(I)$, final *R* was 0.044 and *wR* was 0.063 with $w = k/[\sigma^2(F_o) + g(F_o)^2]$, *k* and *g* refined to 0.79 and 0.0026 respectively. * (Δ/σ)_{max} = 2.1; large Δ/σ because no correction for secondary extinction; $\Delta\rho$ in final difference map -2.0 to 0.9 e Å⁻³.

Discussion. The final parameters for all atoms are given in Table 1. A perspective view of the molecule is shown in Fig. 1 (Johnson, 1970). Bond distances and their e.s.d.'s are given in Table 2. The palladium atom is four coordinated, having a near-planar geometry with the two nitrogen atoms and the two oxygen atoms of the ligand in the *cis* configuration. The infrared spectrum (examined as mull in Nujol and hexachlorobutadiene) shows bands at 1610 ($\nu_{as}^{COO^-}$) and 1387 ($\nu_s^{COO^-}$) cm⁻¹ and a decrease of 20 cm⁻¹ in the N-H stretching frequency. This confirms the coordination of the

carboxyl oxygen and the imino nitrogen to palladium to form a five-membered chelate ring. The absorption spectrum in aqueous solution shows one broad band centered at 320 nm ($\epsilon = 276$ cm² mol⁻¹). The circular dichroism (CD) spectrum recorded in aqueous solution, however, reveals two bands with opposite signs. The band at 360 nm ($\Delta\epsilon = +0.58$ cm² mol⁻¹) has been assigned to the transition of *A* symmetry and the other at 314 nm ($\Delta\epsilon = -0.92$ cm² mol⁻¹) has been assigned to the transition of *E* symmetry. These assignments are in agreement with those reported for related complexes using a similar technique (Sullivan, 1979). The two Pd-N bond distances, 2.016 (5), 2.022 (5), and Pd-O

Table 1. Final atomic coordinates and equivalent isotropic temperature factors (Å² × 10³; Å² × 10⁴ for Pd) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} *
Pd	0.04676 (4)	0.0350	0.12052 (4)	279 (4)
N(1)	0.1337 (5)	0.0345 (12)	0.3208 (5)	30 (1)
O(1)	0.2612 (5)	0.0154 (10)	0.1473 (4)	43 (2)
O(2)	0.4911 (5)	-0.0139 (8)	0.2984 (5)	46 (1)
O(3)	0.2320 (7)	0.0710 (9)	0.6083 (5)	54 (1)
C(1)	0.2990 (6)	-0.0006 (8)	0.3766 (6)	32 (1)
C(2)	0.3552 (7)	0.0003 (8)	0.2672 (6)	32 (1)
C(3)	0.3693 (8)	0.1437 (12)	0.4798 (8)	52 (1)
C(4)	0.2421 (8)	0.1940 (11)	0.5188 (7)	43 (1)
C(5)	0.1096 (8)	0.1913 (10)	0.3856 (8)	44 (1)
N(2)	-0.1725 (5)	0.0582 (7)	0.0850 (4)	24 (1)
O(4)	-0.0295 (5)	0.0541 (9)	-0.0779 (5)	38 (1)
O(5)	-0.2316 (6)	0.0701 (10)	-0.2617 (5)	56 (1)
O(6)	-0.4861 (5)	-0.0040 (7)	0.0517 (5)	40 (1)
C(6)	-0.2661 (6)	0.0710 (8)	-0.0622 (6)	31 (1)
C(7)	-0.1729 (7)	0.0614 (9)	-0.1415 (6)	36 (1)
C(8)	-0.3792 (9)	-0.0774 (11)	-0.0965 (8)	55 (1)
C(9)	-0.3889 (7)	-0.1226 (9)	0.0331 (8)	39 (1)
C(10)	-0.2295 (8)	-0.0978 (10)	0.1308 (8)	46 (1)
O(W1)	-0.2102 (6)	0.4148 (8)	0.1434 (6)	42 (1)
O(W2)	0.7448 (7)	0.1936 (10)	0.3642 (8)	74 (1)
O(W3)	-0.0455 (6)	0.1825 (8)	-0.3799 (6)	46 (1)

$$* U_{eq} = (U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)/3(1 - \cos^2\beta).$$

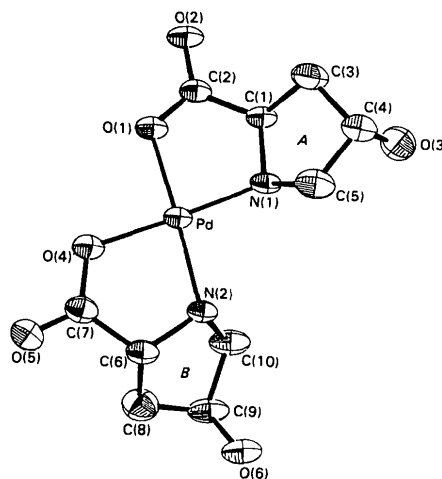


Fig. 1. View of the molecule showing the atomic numbering (H atoms omitted).

* Lists of structure factors, anisotropic temperature factors, H-atom parameters and details of least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42843 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distances, 2.000 (5), 2.008 (5) Å, are normal (Ito, Marumo & Saito, 1971). The O—Pd—O and O—Pd—N bond angles deviate from 90° due to chelation strains. The chelating rings consisting of atoms Pd, N(1), C(1), C(2), O(1) and Pd, N(2), C(6), C(7), O(4) are planar, making angles of 1.00 (9) and 1.52 (9)° respectively with the coordination plane containing atoms Pd, N(1), N(2), O(1), O(4) and are inclined at 1.95 (10)° to each other. The bond distances and bond angles of the two hydroxyproline moieties are in reasonable agreement with the values reported in the literature (DeTar & Luthra, 1977; Ito *et al.*, 1971). As can be seen from Table 3, the torsion angles N(1)—C(1)—C(2)—O(1) and N(2)—C(6)—C(7)—O(4) show that the C—O(Pd) bond is eclipsed with the C—N bond in both the rings. It may also be noted that the hydroxyl and carboxyl groups are

trans to the plane of the pyrrolidine ring as observed in 4-hydroxy-L-proline (Donohue & Trueblood, 1952). The two pyrrolidine rings are in envelope conformations with C(4) and C(9) atoms out of the least-squares planes of the other four atoms of the respective rings. The conformation of these rings may also be described using the conformational equations of DeTar & Luthra (1977). According to these authors, the *i*th torsional angle in the five-membered ring is given by the equation $\chi_i = a_0 \cos[t + 4\pi(i - 2)/5]$, where a_0 is the puckering amplitude and t is the phase angle. Envelope conformations occur when $t = 18, 54, 90^\circ$ *etc.* (odd multiples of 18°), while half-chair conformations occur when $t = 0, 36, 72^\circ$ *etc.* In the present case, ring *A* has parameters $a_0 = 43.4$, $t = 198.9$ and $d_1 [(\chi_3 - \chi_1/2)] = 8.3^\circ$ and ring *B* $a_0 = 38.9$, $t = 199.6$ and $d_1 = 7.7^\circ$. The agreement between observed and calculated torsion angles is within $\pm 2^\circ$. The molecular packing is illustrated in Fig. 2. The crystals are stabilized by a three-dimensional network of hydrogen bonds (listed in Table 4).

Table 2. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

Pd—N(1)	2.016 (5)	C(2)—O(2)	1.232 (8)
Pd—N(2)	2.022 (5)	C(2)—O(1)	1.268 (7)
Pd—O(1)	2.000 (5)	N(2)—C(10)	1.496 (10)
Pd—O(4)	2.008 (5)	N(2)—C(6)	1.505 (7)
N(1)—C(5)	1.469 (12)	C(10)—C(9)	1.498 (8)
N(1)—C(1)	1.498 (7)	C(9)—O(6)	1.392 (10)
C(5)—C(4)	1.507 (9)	C(9)—C(8)	1.514 (13)
C(4)—O(3)	1.400 (11)	C(8)—C(6)	1.523 (10)
C(4)—C(3)	1.524 (13)	C(6)—C(7)	1.503 (11)
C(3)—C(1)	1.534 (10)	C(7)—O(5)	1.211 (8)
C(1)—C(2)	1.521 (11)	C(7)—O(4)	1.285 (7)
N(2)—Pd—N(1)	98.4 (2)	C(1)—C(2)—O(2)	118.6 (5)
N(1)—Pd—O(1)	84.0 (2)	C(1)—C(2)—O(1)	119.1 (6)
O(1)—Pd—O(4)	93.5 (2)	O(2)—C(2)—O(1)	122.3 (7)
O(4)—Pd—N(1)	175.1 (3)	Pd—N(2)—C(6)	109.8 (4)
O(4)—Pd—N(2)	84.0 (2)	Pd—N(2)—C(10)	112.1 (4)
O(1)—Pd—N(2)	177.4 (2)	C(10)—N(2)—C(6)	105.8 (4)
Pd—N(1)—C(1)	110.3 (4)	C(9)—C(10)—N(2)	106.3 (6)
Pd—N(1)—C(5)	116.9 (5)	C(10)—C(9)—O(6)	112.5 (6)
C(5)—N(1)—C(1)	108.1 (5)	C(8)—C(9)—O(6)	107.6 (6)
C(4)—C(5)—N(1)	103.9 (6)	C(10)—C(9)—C(8)	101.5 (7)
C(5)—C(4)—O(3)	113.4 (6)	C(9)—C(8)—C(6)	105.0 (6)
C(3)—C(4)—O(3)	109.3 (7)	C(8)—C(6)—N(2)	106.0 (5)
C(5)—C(4)—C(3)	101.2 (7)	C(8)—C(6)—C(7)	111.8 (6)
C(4)—C(3)—C(1)	103.0 (6)	N(2)—C(6)—C(7)	112.4 (5)
C(3)—C(1)—N(1)	104.6 (6)	C(6)—C(7)—O(5)	120.5 (6)
C(3)—C(1)—C(2)	112.9 (6)	C(6)—C(7)—O(4)	118.1 (5)
N(1)—C(1)—C(2)	110.8 (5)	O(5)—C(7)—O(4)	121.2 (7)

Table 3. Torsion angles (°) (*e.s.d.*'s ~ 0.7–0.9°)

		Experimental	Calculated*
χ_1	N(1)—C(1)—C(3)—C(4)	25.0	25.0
	N(2)—C(6)—C(8)—C(9)	22.0	22.0
χ_2	C(1)—C(3)—C(4)—C(5)	-41.1	-41.1
	C(6)—C(8)—C(9)—C(10)	-36.7	-36.7
χ_3	C(3)—C(4)—C(5)—N(1)	42.1	41.5
	C(8)—C(9)—C(10)—N(2)	38.4	37.4
χ_4	C(4)—C(5)—N(1)—C(1)	-27.1	-26.1
	C(9)—C(10)—N(2)—C(6)	-25.3	-23.4
χ_5	C(5)—N(1)—C(1)—C(3)	1.0	0.7
	C(10)—N(2)—C(6)—C(8)	1.7	0.6
	N(1)—C(1)—C(2)—O(1)	-5.4	N(2)—C(6)—C(7)—O(4) -3.9
	N(1)—C(1)—C(2)—O(2)	174.7	N(2)—C(6)—C(7)—O(5) -179.8
	N(1)—C(5)—C(4)—O(3)	78.8	N(2)—C(10)—C(9)—O(6) -76.3

* Angles calculated using equation and conformational parameters given in text.

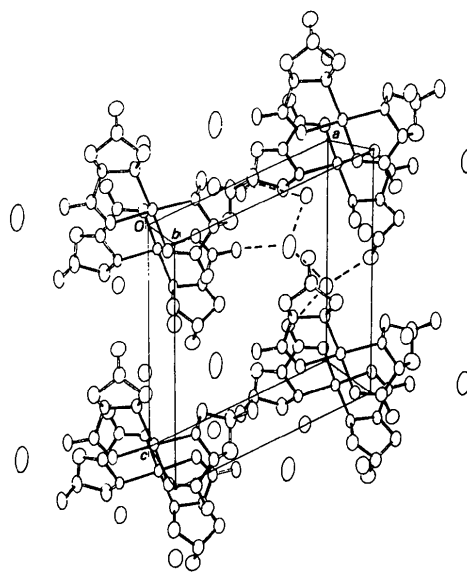


Fig. 2. Packing diagram, viewed approximately down *b*. Dashed lines indicate possible hydrogen bonds.

Table 4. Hydrogen-bond distances (Å) (*e.s.d.*'s ~ 0.01 Å)

Bond	Distance	Symmetry code
N(1)...O(W3)	2.99	$-x, -\frac{1}{2} + y, -z$
O(3)...O(W2)	2.91	$1 - x, -\frac{1}{2} + y, 1 - z$
N(2)...O(W1)	2.87	x, y, z
O(6)...O(2)	2.82	$-1 + x, y, z$
O(W1)...O(6)	2.93	$-x, \frac{1}{2} + y, -z$
O(W1)...O(W2)	3.15	$-1 + x, y, z$
O(W2)...O(2)	2.78	x, y, z
O(W2)...O(W3)	2.72	$1 + x, y, 1 + z$
O(W3)...O(5)	2.78	x, y, z
O(W3)...O(3)	2.90	$x, y, -1 + z$

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Three Crystalline Forms of 9-(2-Hydroxyethyl)adenine Resulting from the Different Stacking of Hydrogen-Bonded Layers

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Abstract. Three crystalline forms of the title compound [$C_7H_9N_5O$, $M_r = 179.2$, $\lambda(\text{Cu } K\alpha) = 1.54184 \text{ \AA}$, room temperature] were examined by X-ray diffraction. Form (I): orthorhombic, $P2_12_12_1$, $a = 13.566 (2)$, $b = 8.271 (1)$, $c = 7.340 (1) \text{ \AA}$, $V = 823.6 (2) \text{ \AA}^3$, $Z = 4$, $D_x = 1.445 \text{ g cm}^{-3}$, $F(000) = 376$, $\mu = 8.88 \text{ cm}^{-1}$, $R = 0.070$, 701 observed reflexions. Form (II): orthorhombic, $P2_12_12_1$, $a = 13.572 (3)$, $b = 8.248 (2)$, $c = 14.508 (3) \text{ \AA}$, $V = 1624.1 (6) \text{ \AA}^3$, $Z = 8$, $D_m = 1.466$, $D_x = 1.466 \text{ g cm}^{-3}$, $F(000) = 752$, $\mu = 9.01 \text{ cm}^{-1}$, $R = 0.047$, 1478 observed reflexions. Form (III): monoclinic, $P2_1/c$, $a = 13.543 (1)$, $b = 8.290 (1)$, $c = 22.591 (2) \text{ \AA}$, $\beta = 104.97 (1)^\circ$, $V = 2450.2 (4) \text{ \AA}^3$, $Z = 12$, $D_x = 1.457 \text{ g cm}^{-3}$, $F(000) = 1128$, $\mu = 8.96 \text{ cm}^{-1}$, $R = 0.105$, 2339 observed reflexions. In the three forms, the values of a and b remain nearly the same, but those of c are in the ratio of 1:2:3. In all three structures, adenine moieties are connected by N(6)H...N(1) and N(6)H...N(7) hydrogen bonds to form infinite ribbons along b , and the ribbons are linked side by side *via* O(12)H...N(3) to construct hydrogen-bonded pleated sheets. The sheet in form (I) consists of one crystallographic kind of molecule, A , while that in form (II) contains two kinds of molecules, B and C . Form (III) has two kinds of sheet: one consists of D and the other of E and F molecules. There are no significant differences in molecular dimensions among the molecules A – F , and the four kinds of sheets are almost the same. However, three different stacking modes exist between successive layers. Different combinations of the stacking modes result in poly-

morphism. Disorder along c^* observed in forms (I) and (III) and twinning in form (III) are interpreted in terms of the stacking modes.

Introduction. Polymorphism, twinning and disorder owing to layer stacking can give much information for intermolecular interactions of complicated molecules. However, detailed reports on these crystallographic aspects for organic substances are not common, one example being that of *o*-chlorobenzamide (Kato, Takaki & Sakurai, 1974).

The present compound, which was synthesized as a model of protein–nucleic acid interactions, gives rise to three crystalline forms; the values of one of the lattice parameters are in the approximate ratio 1:2:3, while the other two do not change significantly. Forms (I) and (III) reveal features of disorder about this multiplicable lattice vector, dependent on the crystallization conditions, and form (III) is also constituted of finely polysynthetic twins. The present paper describes the varieties of stacking of the typical hydrogen-bonded molecular layers, found in the structures of the three forms.

Experimental. The title compound was kindly supplied by Dr Minoru Ohki, Research Institute, Wakamoto Pharmaceutical Co. Ltd. By cooling a saturated aqueous solution of the compound, plate crystals were deposited. Observation under a microscope indicated that the crystals were composites of fine lamellae, whose end-on photograph (Fig. 1) suggests poly-