The Crystal Structure of Bis-(L-prolinato)palladium(II)

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The crystal structure of bis-(L-prolinato)palladium(II) has been determined from three-dimensional X-ray data collected by a photographic method. The crystals are orthorhombic with $a = 10\cdot31$, $b = 12\cdot17$, $c = 9\cdot71$ Å; space group $B22_12$ with four molecules in the unit cell. The structure has been refined by block-diagonal least-squares methods to an R value of $0\cdot085$ for the 694 observed reflexions. This is a *cis* complex, and the palladium atom has square planar coordination (Pd–O $= 2\cdot02$ Å, Pd–N $= 2\cdot03$ Å). The complex molecule has a twofold axis of rotation. The five-membered chelate ring is bent at the two coordinating atoms. Bond lengths are substantially normal. All the imino hydrogen atoms are involved in hydrogen bonds which form layers of the molecules parallel to (010).

Introduction

L-Proline is one of the two naturally occurring amino acids in which the α-nitrogen forms part of a ring system. Because of this unique conformation, L-proline may exhibit stereospecificity on forming metal complexes. It can function as a bidentate ligand and the secondary nitrogen atom will add one asymmetric centre when coordinated to a metal atom. In the square-planar complex such as bis-(L-prolinato)palladium(II), there are two possible structures: *cis* and *trans* form.

The crystal structure of bis-(L-prolinato)palladium-(II) has been determined in order to establish the molecular structure and to contribute a better knowledge to the relation between the structure and the optical properties.

Experimental

Bis-(L-prolinato)palladium(II) was prepared according to the method described by Ito (1967). Single crystals of the complex for X-ray work were obtained as pale yellow plates by slow evaporation of an aqueous solution at room temperature. The cell dimensions were determined from high-angle reflexions on Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1\cdot5418$ Å).

The crystal data are: $[Pd(C_5H_8NO_2)_2]$,
M.W. $334\cdot65$, orthorhombic,
$a = 10\cdot312 \pm 0\cdot007$, $b = 12\cdot172 \pm 0\cdot009$,
$c = 9\cdot707 \pm 0\cdot005$ Å, $U = 1218$ Å^3,
$D_m = 1\cdot833$ g.cm^{-3}, $Z = 4$,
$D_x = 1\cdot838$ g.cm^{-3},
space group $B22_12$,
$F(000) = 672$, μ(Cu $K\alpha$) $= 128$ cm^{-1}.

For intensity measurements two approximately cubic crystals of dimension 0·34 mm were cut from a larger specimen. Nickel filtered copper radiation was used. The intensity data were recorded on multiple-film equi-inclination Weissenberg photographs taken around [010] up to the ninth layer and around [101] up to the second layer. The relative intensities of the reflexions were estimated visually by comparison with calibrated intensity scales prepared from the crystals used for the intensity data collection. The usual Lorentz and polarization and spot shape corrections were made: the absorption correction was also applied, assuming the crystal to be a sphere (*International Tables for X-ray Crystallography*, 1962). The sets of intensities around the two axes were scaled by correlating the common reflexions. In total 694 independent $|F|$ values were obtained.

Structure analysis

In the space group, $B22_12$, the general positions are eightfold. Since there are only four molecules in a unit cell, the palladium atoms must occupy a set of fourfold special positions, and each molecule is required to have a twofold axis of rotation. The positions of palladium atoms were easily determined from the prominent peaks in the Patterson function. A three-dimensional electron-density map was then calculated with all the terms, the phases of which were determined by palladium atoms. This Fourier synthesis showed, in addition to large palladium peaks, smaller peaks around the palladium atoms corresponding to other lighter atoms. Positions of these lighter atoms were then included in the calculation of the structure factors. Successive Fourier syntheses of electron density revealed the positions of all the lighter atoms except those of hydrogen atoms.

The positional parameters and isotropic temperature factors were refined by least-squares methods with a block-diagonal program *HBLS* written by Dr Ashida. The weighting scheme employed was a modification of the method of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) $1/w = c + |F_o| + a|F_o|^2$ if $|F_o| \geq 20\cdot0$, oth-

erwise $w=0.03$. The coefficients a and c were as follows: $a=2F_{min}$ and $c=2.0/F_{max}$. After six cycles of the refinements, the R value reduced from 0·18 to 0·13. Five further cycles of the least-squares refinements were performed in anisotropic mode, taking the anomalous scattering into consideration. The R value then reduced to 0·089. A difference Fourier synthesis gave no significant indications about the positions of hydrogen atoms. The coordinates of hydrogen atoms were, therefore evaluated by idealized positions with a tetrahedral disposition about both carbon and nitrogen atoms, with C–H = 1·08 Å and with N–H = 1·00 Å. After inclusion of the hydrogen atoms the final set of the least-squares calculations was carried out, but the parameters of the hydrogen atoms were not varied.
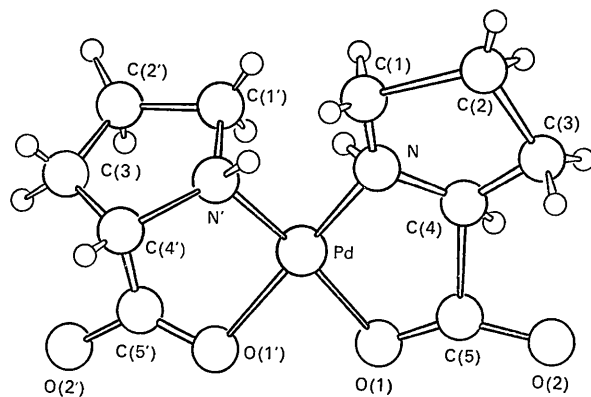
Table 1. *Observed and calculated structure factors*
$(\times 1.25)$

Fig. 1. A perspective drawing of bis-(L-prolinato)palladium(II) molecule and numbering scheme of atoms. The primed atoms are related to the unprimed ones by a twofold rotational axis through the palladium atom.

Temperature factors of the hydrogen atoms were assumed to be isotropic and were given the same values as those of the atoms to which the hydrogen atoms were attached (Hamilton, 1959). In the last cycle of the least-squares, all the parameter shifts were well within the corresponding standard deviations. The R value was 0·085 for all the 694 observed reflexions.

Table 1 gives the observed and calculated structure factors. The positional and thermal parameters together with their standard deviations are listed in Tables 2 and 3, respectively.

Table 2. *Fractional coordinates of the atoms and their standard deviation* $(\times 10^4)$

	x	y	z
Pd	692 (1)	2500 (0)	0 (0)
O(1)	−624 (11)	2972 (15)	1425 (12)
O(2)	−799 (11)	3387 (13)	3631 (15)
N	1977 (12)	3005 (13)	1446 (11)
C(1)	2437 (20)	4158 (15)	1282 (21)
C(2)	2896 (22)	4445 (17)	2722 (19)
C(3)	1971 (19)	3823 (18)	3693 (18)
C(4)	1314 (17)	2980 (15)	2840 (13)
C(5)	−137 (19)	3147 (17)	2670 (18)

The absolute configuration of L-proline was determined automatically, when the corrections of anoma-

Table 3. *Anisotropic temperature factors and their standard deviations* $(\times 10^4)$

The temperature factor term is of the form $\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+kl\beta_{23}+hl\beta_{13})\right]$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	48 (1)	69 (1)	55 (1)	0 (0)	0 (0)	−34 (3)
O(1)	71 (10)	147 (14)	57 (10)	58 (20)	30 (19)	−44 (22)
O(2)	80 (12)	106 (12)	112 (15)	−48 (21)	65 (24)	−102 (25)
N	61 (10)	86 (10)	37 (9)	−38 (20)	−28 (20)	−21 (18)
C(1)	103 (19)	67 (12)	113 (21)	−25 (28)	11 (35)	−26 (30)
C(2)	120 (19)	65 (12)	94 (18)	−44 (32)	39 (39)	−39 (27)
C(3)	93 (17)	98 (15)	75 (16)	−23 (31)	73 (32)	−48 (29)
C(4)	97 (16)	73 (11)	21 (9)	−32 (25)	−7 (23)	−52 (19)
C(5)	90 (16)	73 (14)	99 (18)	−7 (27)	91 (35)	4 (30)

lous dispersion were taken into account in the course of the refinements. Part of observed and calculated intensity relations between hkl and $hk\bar{l}$ are compared in Table 4.

Table 4. *Part of observed and calculated intensity relations between hkl and hk̄l*

Indices	$[|F_c(hkl)|/1\cdot25]^2$	Observed relations	$[|F_c(hk\bar{l})|/1\cdot25]^2$
1 1 5	1600	<	2401
1 1 9	576	>	361
4 1 8	2704	>	2209
8 1 6	529	>	441
3 2 7	169	<	361
5 2 1	5041	<	5929
11 2 3	64	<	100
1 3 9	1444	>	1024
5 3 7	1681	<	2116
8 3 2	729	>	576
3 4 5	2704	<	3364
4 4 2	1024	<	1296
4 4 10	324	>	225

The atomic scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962). The computations for the structure analysis were carried out on the HITAC 5020E at the Computer Centre of the University of Tokyo with the programs of the *UNICS* system, and also on the electronic computer FACOM 270-30 at this Institute.

Description of the molecular structure and discussion

The structure of bis-(L-prolinato)palladium(II) consists of discrete molecules in which the central palladium atom is four coordinated and has square planar environment. A perspective drawing of the complex is illustrated in Fig. 1, together with the atom numbering scheme. The two proline residues are equivalent; the primed atoms are related to the unprimed ones by a twofold rotational axis through the palladium atom.

Two L-prolinate ions are coordinated to a palladium atom in *cis*-positions with respect to each other through imino nitrogen atoms and the carboxyl oxygen atoms O(1) and O(1′). Fig. 1 represents correctly the

absolute configuration. The absolute configuration of the prolinate ion agrees with that determined by Freeman & Maxwell (1970).

The bond distances and the bond angles within the molecule are listed in Table 5. The Pd–N and Pd–O(1) distances are 2·03 and 2·02 Å, respectively. These values are in good agreement with those reported for other palladium complexes (for example, Frasson, Panattoni & Sacconi, 1964). The carbon–oxygen distances, C(5)–O(1) and C(5)–O(2) are 1·33 and 1·19 Å, respectively. Such asymmetric carboxyl groups are observed in various amino acid metal complexes [for example, bis(glycinato)aquocopper(II) monohydrate (Freeman, Snow, Nitta & Tomita, 1964)]. The C(1)–N distance of 1·49 Å may be compared with the corresponding distance of 1·516 Å reported for DL-proline hydrochloride (Mitsui, Tsuboi & Iitaka, 1969). However the C(4)–N distance of 1·52 Å is rather longer than that of 1·473 Å in DL-proline hydrochloride and may be compared to the values observed for L-proline, 1·53 Å (Kayushina & Vainshtein, 1965), for bis-(DL-prolinato)copper(II) dihydrate, 1·52 Å (Mathieson & Welsh, 1952) and for L$(-)_{589}$-β_2-(RRS)-(triethylene-tetramine-(S)-prolinato)cobalt(III) diiodide dihydrate, 1·54 Å (Freeman & Maxwell, 1970).

Table 5. *Bond lengths and angles with their standard deviations*

E.s.d.'s for least significant figures are in parentheses

Pd —O(1)	2·021 (12) Å	O(1)–Pd —O(1)′	95·6 (5)°
Pd —N	2·026 (12)	N——Pd —N′	98·3 (5)
O(1)–C(5)	1·327 (22)	N——Pd —O(1)′	178·4 (5)
O(2)–C(5)	1·192 (23)	O(1)–Pd —N	83·0 (5)
N——C(1)	1·490 (24)	Pd —O(1)–C(5)	114·5 (10)
N——C(4)	1·516 (18)	Pd —N——C(1)	114·8 (10)
C(1)–C(2)	1·516 (27)	Pd —N——C(4)	108·5 (9)
C(2)–C(3)	1·540 (28)	C(1)–N——C(4)	105·0 (12)
C(3)–C(4)	1·483 (26)	N——C(1)–C(2)	102·6 (15)
C(4)–C(5)	1·519 (26)	C(1)–C(2)–C(3)	104·9 (16)
		C(2)–C(3)–C(4)	106·3 (14)
		N——C(4)–C(3)	106·2 (14)
		N——C(4)–C(5)	110·2 (12)
		C(3)–C(4)–C(5)	114·7 (15)
		O(1)–C(5)–O(2)	122·3 (17)
		O(1)–C(5)–C(4)	116·8 (15)
		O(2)–C(5)–C(4)	120·8 (17)

Table 6. *Least-squares planes*

Equations are expressed in the form $Ax + By + Cz = D$, where D is expressed in Å, and x, y and z are the coordinates in Å referred to the crystal axes a, b and c.

Plane	Atoms in plane	A	B	C	D
1	PdO(1)NO(1)′N′	−0·0000	−0·9198	0·3924	−2·7990 Å
2	O(1)O(2)C(4)C(5)	−0·1443	−0·9656	0·2162	−3·1054
3	NC(2)C(3)C(4)	0·7120	−0·6398	0·2895	−0·5281

Atoms	Displacements from plane 1	Atoms	Displacements from plane 2	Atoms	Displacements from plane 3
Pd	0·00 Å	O(1)	0·00 Å	N	0·04 Å
O(1)	0·01	O(2)	0·00	C(1)	−0·56
N	−0·01	C(4)	0·00	C(2)	−0·04
C(4)	0·55	C(5)	−0·01	C(3)	0·04
C(5)	0·29			C(4)	−0·03

Some least-squares planes are given in Table 6. The largest deviation of the atoms from the mean plane through the palladium atom and the four coordinating atoms is 0·01 Å. The five-membered chelate ring is not planar. The carbon atoms C(4) and C(5) are displaced 0·55 and 0·29 Å, respectively, from the plane of the palladium and the four coordinating atoms. The three atoms of the carboxyl group C(5) O(1)O (2) and C(4) are highly planar within 0·01 Å, the sum of the three angles around C(5) being 360°.

In the proline residue, the conformation of the pyrrolidine ring is not identical with any of the five-membered rings hitherto reported for the related compounds, though the rings are in envelope form (Eliel, 1967). Four atoms, N, C(2), C(3) and C(4), are coplanar within 0·04 Å, whereas C(1) is 0·56 Å away from this plane in the present case. On the other hand, the atom C(2) (in the present numbering system) is about 0·5 Å away from the best plane formed by the remaining four atoms in most of the related compounds [L-proline, hydroxyproline (Donohue & Trueblood, 1952), bis-(DL-prolinato)copper(II) dihydrate, the prolyl and hydroxyprolyl residues in tosyl-prolylhydroxyproline (Fridrichsons & Mathieson, 1962), leucylprolyl-glycine (Leung & Marsh, 1958) and L(−)₅₈₉-β₂-(RRS)-(triethylenetetramine-(S)-prolinato)cobalt(III) ion]. And the atom C(4) is displaced by about 0·5 Å from the plane formed by the remaining four atoms in the case of DL-proline.

The crystal structure of [Pd(L-prol)₂] and [Cu(DL-prol)₂]2H₂O indicate that the proline molecules prefer to coordinate to the metal atom with two pyrrolidine rings disposed on opposite sides of the coordination plane, when they form a square-planar complex. Thus

DL-proline gives a trans-isomer, while the optically active proline forms a cis-isomer. In fact, the absorption spectra of [Pd(L-prol)₂] and [Pd(oxy-L-prol)₂] in aqueous solutions are very similar:

[Pd(L-prol)₂], $\nu_{max}=31\cdot1\times10^3$ cm⁻¹, $\varepsilon_{max}=337$,
[Pd(oxy-L-prol)₂] $\nu_{max}=31\cdot1\times10^3$ cm⁻¹, $\varepsilon_{max}=326$.

Consequently we can safely conclude that [Pd(oxy-L-prol)₂] is a cis-isomer. But the absorption spectra of [Pd(DL-prol)₂] ($\nu_{max}=31\cdot9\times10^3$ cm⁻¹, $\varepsilon_{max}=292$) is different from those of [Pd(L-prol)₂] and [Pd(DL-prol)₂] is considered to be a trans-isomer. It may be certain that the pyrrolidine rings are disposed on opposite sides of the coordination plane in these complexes.

Molecular packing

Projections of the structure along the b and the a axes are presented in Figs. 2 and 3, respectively. Intermolecular contacts less than 3·5 Å are listed in Table 7. The molecules of bis-(L-prolinato)palladium(II) are linked by NH···O(2) hydrogen bonds of 2·85 Å to form a layer parallel to the plane (010). All the O(2) and N atoms are involved in this hydrogen bond. The hydrogen atom seems to be on a line N···O(2), as suggested by the angles around N, which are listed in Table 8. Such a packing scheme by the hydrogen bond is indicated by the broken lines in Figs. 2 and 3. The molecules are oriented in such a way that the coordination planes make an angle of 23·1° with respect to the plane (010). The layers of the molecules held by the hydrogen bonds are packed by van der Waals forces (Fig. 3).
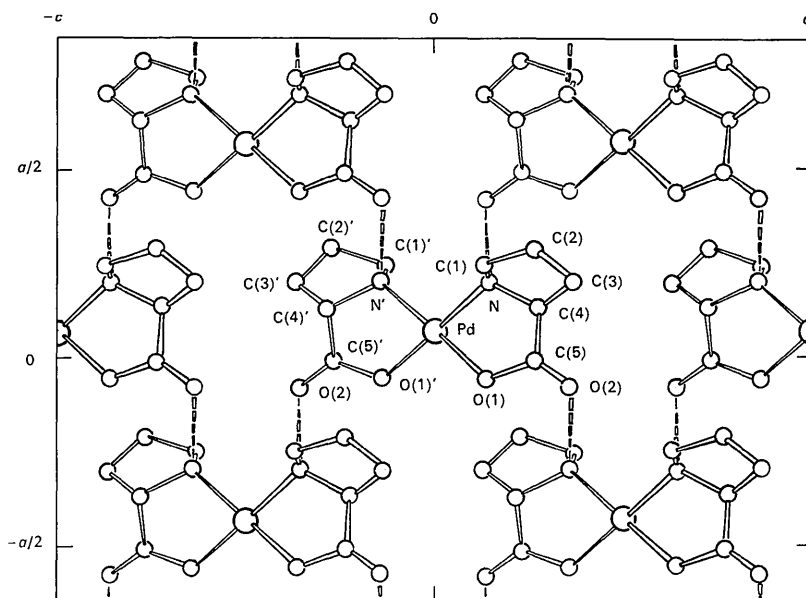

Fig. 2. A projection of the crystal structure along the b axis (from y=0 to y=0·5).

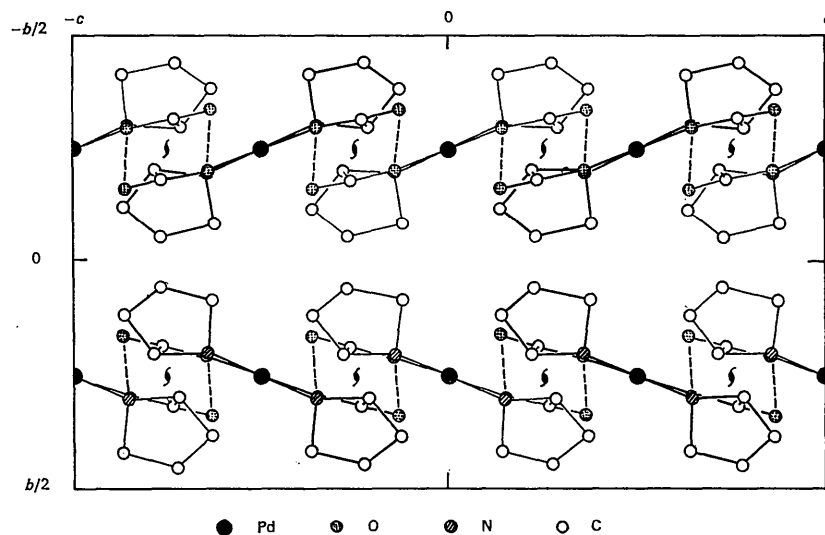Fig. 3. A projection of the crystal structure along the a axis.

Table 7. *Intermolecular contacts less than* 3·5 Å

Molecule I	x	y	z
II	x	$\frac{1}{2}-y$	$1-z$
III	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}-z$
IV	$\frac{1}{2}+x$	y	$-\frac{1}{2}+z$

From molecule I	To atom	Of molecule	Distance
O(2)	O(2)	II	3·43 Å
N	O(1)	III	3·44
N	O(2)	III	2·85
N	C(5)	III	3·40
C(1)	O(2)	IV	3·29
C(2)	O(1)	III	3·42
C(3)	O(1)	III	3·31
C(4)	O(1)	III	3·44

Table 8. *Hydrogen bond distance and angles*

Distance

N——H···O(2)	2·85 Å

Angle

Pd——N···O(2)	109·1°
C(4)–N···O(2)	111·9
C(1)–N···O(2)	107·5

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