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The Crystal and Molecular Structure of Bis(L-serinato)palladium(II)

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Abstract

$Pd(C_3H_6NO_3)_2$, $C_6H_{12}N_2O_6Pd$, is orthorhombic, space group $P2_12_12_1$, with $a = 8.828$ (8), $b = 9.705$ (9), $c = 11.315$ (7) Å, $Z = 4$. The structure was refined to $R = 0.054$ for 1763 photographic intensities. The two amino acid molecules are bonded in an irregular *cis* square-planar arrangement about the Pd atom [average Pd—N 2·023 (7), average Pd—O 2·005 (7) Å]. One five-membered chelate ring is almost planar whereas the other is distorted. The two serine molecules have different conformations for the hydroxyl groups, one having a *gauche–gauche* and the other a *gauche–anti* conformation. The structure is stabilized by intermolecular hydrogen bonds in which all active protons are involved.

Introduction

The induction of filamentous growth in *Escherichia coli* has been reported (Charlson, Banner, Gale, McArdle, Trainor & Watton, 1977) as a preliminary test system for evaluating the potential antitumour activity of amino acid–metal systems involving L-asparagine, L-glutamine, glycine and L-serine. Recent studies on the effect of metal ions on the L-asparaginase-catalysed hydrolysis of L-asparagine (Charlson, Coman, Karossi, Stephens, Vagg & Watton, 1978) showed that the greatest degree of inhibition occurs in the presence of Pd^{II}. As part of an associated structural study on metal–amino acid complexes the structures of bis(L-asparaginato)copper(II) (Stephens, Vagg & Williams, 1975) and bis(L-asparaginato)zinc(II) (Stephens, Vagg & Williams, 1977*a*) have appeared. Here the structure of bis(L-serinato)palladium(II), Pd(L-ser)$_2$, is reported.

Experimental

The complex was isolated by Charlson (1978) as bright-yellow rectangular plates by a modified method of von Kollmann, Schroter & Hoyer (1975) for the preparation of Pd(DL-ser)$_2$.

Crystal data

$C_6H_{12}N_2O_6Pd$, $M_r = 314.6$, orthorhombic, $a = 8.828$ (8), $b = 9.705$ (9), $c = 11.315$ (7) Å, $U = 969.4$ Å^3, $D_m = 2.168$ (by flotation), $D_c = 2.155$ Mg m^{-3}, $Z = 4$, $F(000) = 624$, μ(Mo $K\alpha$) = 1·896 mm^{-1}. Systematic absences: $h00$ when $h = 2n + 1$, $0k0$ when $k = 2n + 1$, $00l$ when $l = 2n + 1$; space group $P2_12_12_1$.

Cell parameters were determined from oscillation photographs with Cu $K\alpha$ radiation. With Mo $K\alpha$ radiation, 2274 non-zero reflexions were recorded on layers 0–6kl and hk0–4 by the equi-inclination Weissenberg technique with packs of three films separated by Al sheets. Their intensities were read visually and corrected for Lorentz and polarization effects but not for absorption or extinction. Internal correlation yielded a final data set of 1763 unique non-zero reflexions.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations were carried out on a Univac 1106 computer with programs written by F. S. Stephens.

Structure determination

The structure was solved by the heavy-atom method. Refinement was by full-matrix least-squares calculations in which the function minimized was $\sum w\Delta^2$. Weights $w = (1.00 + 0.04|F_o| + 0.0005|F_o|^2)^{-1}$ were used. Reflexions for which $|F_o| < 0.25|F_c|$ were omitted from the refinement. After isotropic refinement the positions of the H atoms were determined from a difference synthesis. They were placed in these positions with $B = 3.5$ Å^2 and their positions varied during early anisotropic refinement. As H(131) and H(221) moved into chemically doubtful positions they were returned to and subsequently held in the positions indicated by the difference synthesis. Anisotropic refinement was continued with the other H atoms held in the positions to which they had refined.

Refinement was terminated when the maximum shift in any parameter was $<0.01\sigma$. A final difference synthesis showed no maximum positive electron densities >1 e Å^{-3}. R based on 1763 reflexions was 0·054 and R' $[= (\sum w\Delta^2/\sum |F_o|^2)^{1/2}]$ was 0·071. 1761 reflex-

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ions were included in the final cycle. Atomic coordinates are given in Table 1.*

Discussion

Bond lengths and angles are given in Table 2. A perspective drawing of the molecule is given in Fig. 1 with the atomic labelling. Fig. 2 shows the packing viewed down *a*.

The bidentate L-serine molecules bond to Pd in an irregular *cis* square-planar arrangement (Table 3, plane 1) which shows a small (3·3°) tetrahedral distortion. O(11)–Pd–O(21) [94·2 (3)°] is significantly less than N(1)–Pd–N(2) [100·2 (3)°], which is true for the corresponding Cu(L-ser)$_2$ (van der Helm & Franks, 1969) and Ni(L-ser)$_2$(H_2O)$_2$ (van der Helm & Hossain, 1969) complexes. Repulsion of the *cis* amino H atoms has been suggested as the cause (Delbaere, Kamenar & Prout, 1975).

The two amino acid molecules show several dissimilarities. One five-membered ring (Table 3, plane 2)

* Lists of structure factors and anisotropic thermal parameters, together with details relating to the hydrogen atoms, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34020 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates (fractional,* × 10^4) *for non-hydrogen atoms with e.s.d.'s in parentheses*

	x	*y*	*z*
Pd	1121·3 (7)	5827·7 (6)	4528·8 (5)
O(11)	2098 (8)	7587 (6)	3986 (6)
O(12)	2190 (9)	9827 (7)	4346 (7)
O(13)	−343 (9)	9193 (9)	7493 (6)
O(21)	1844 (9)	4735 (7)	3139 (7)
O(22)	1537 (12)	2762 (8)	2205 (8)
O(23)	−2003 (8)	2651 (8)	3535 (7)
N(1)	540 (9)	7026 (7)	5927 (6)
N(2)	104 (10)	4048 (7)	4989 (6)
C(11)	1675 (10)	8680 (8)	4583 (9)
C(12)	514 (10)	8490 (8)	5537 (8)
C(13)	747 (11)	9453 (8)	6572 (8)
C(21)	1331 (11)	3481 (8)	3083 (8)
C(22)	573 (11)	2918 (9)	4196 (9)
C(23)	−683 (12)	1922 (9)	3956 (9)

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

Pd–N(1)	2·030 (7)	Pd–N(2)	2·015 (7)
Pd–O(11)	2·008 (6)	Pd–O(21)	2·001 (7)
O(11)–C(11)	1·312 (10)	O(21)–C(21)	1·300 (11)
O(12)–C(11)	1·232 (10)	O(22)–C(21)	1·228 (11)
O(13)–C(13)	1·440 (12)	O(23)–C(23)	1·445 (13)
N(1)–C(12)	1·488 (10)	N(2)–C(22)	1·477 (11)
C(11)–C(12)	1·499 (12)	C(21)–C(22)	1·526 (13)
C(12)–C(13)	1·513 (12)	C(22)–C(23)	1·496 (13)
N(1)–Pd–N(2)	100·2 (3)	O(11)–Pd–O(21)	94·2 (3)
N(1)–Pd–O(11)	82·0 (3)	N(2)–Pd–O(21)	83·7 (3)
N(1)–Pd–O(21)	175·5 (3)	N(2)–Pd–O(11)	177·1 (3)
Pd–N(1)–C(12)	108·6 (5)	Pd–N(2)–C(22)	110·8 (5)
Pd–O(11)–C(11)	114·1 (5)	Pd–O(21)–C(21)	115·1 (6)
O(11)–C(11)–O(12)	120·8 (8)	O(21)–C(21)–O(22)	121·3 (10)
O(11)–C(11)–C(12)	117·8 (7)	O(21)–C(21)–C(22)	116·6 (8)
O(12)–C(11)–C(12)	121·4 (8)	O(22)–C(21)–C(22)	121·9 (8)
C(11)–C(12)–N(1)	108·7 (7)	C(21)–C(22)–N(2)	111·0 (6)
N(1)–C(12)–C(13)	111·0 (7)	N(2)–C(22)–C(23)	112·5 (8)
C(11)–C(12)–C(13)	112·9 (7)	C(21)–C(22)–C(23)	114·0 (7)
C(12)–C(13)–O(13)	111·2 (7)	C(22)–C(23)–O(23)	110·0 (7)

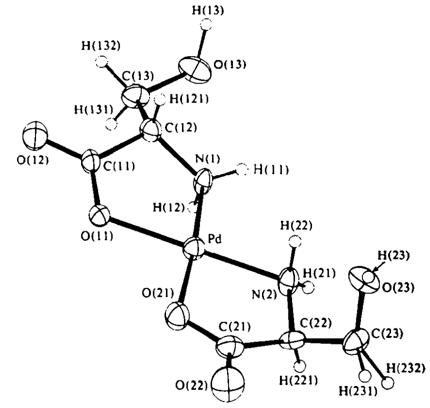

Fig. 1. Perspective drawing of the molecule (Johnson, 1965) showing the labelling of the atoms. For non-hydrogen atoms thermal ellipsoids are scaled to include 50% probability.

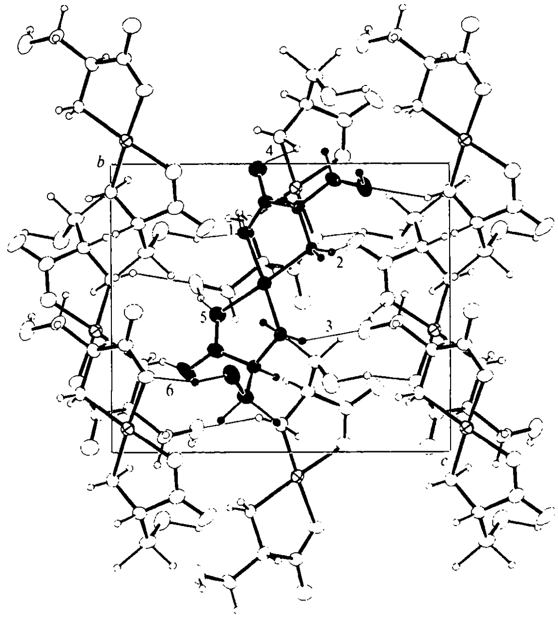

Fig. 2. Molecular packing in the crystal; the primary molecular unit is shown in emphasis. Details of numbered hydrogen-bond interactions are given in Table 5.

Table 3. *Least-squares planes and their equations given by* $lX + mY + nZ - p = 0$

Deviations (Å) of relevant atoms from the planes are given in square brackets.

	l	m	n	p
Plane (1): Pd, N(1), N(2), O(11), O(21)	0·8308	−0·2648	0·4895	1·8349
[Pd −0·002; N(1), O(21) 0·04; N(2), O(11) −0·04; C(11) −0·30; C(12) −0·57; C(21) −0·04; C(22) 0·16]				
Plane (2): Pd, N(1), O(11), C(11), C(12)	0·8282	−0·0954	0·5523	3·2430
[Pd −0·13; N(1) 0·20; O(11) 0·08; C(11) 0·04; C(12) −0·19; O(12) 0·16]				
Plane (3): Pd, N(2), O(21), C(21), C(22)	0·8386	−0·2376	0·4902	1·9790
[Pd 0·02; N(2) −0·07; O(21) 0·03; C(21) −0·09; C(22) 0·10; O(22) −0·25]				
Plane (4): O(11), O(12), C(11), C(12)	0·7347	−0·1514	0·6612	3·2310
[O(11), O(12), C(12) −0·003; C(11) 0·009]				
Plane (5): O(21), O(22), C(21), C(22)	0·8794	−0·3196	0·3528	1·2082
[O(21) 0·008; O(22) 0·009; C(21) −0·023; C(22) 0·007]				

shows considerable distortion from planarity, whereas the other (Table 3, plane 3) may be considered planar. The corresponding Pd—N and Pd—O distances are slightly shorter, and the N—Pd—O bite angle larger, in the planar ring. This feature was observed also in the *trans* amino acid complexes previously studied (Stephens, Vagg & Williams, 1975, 1977*a*,*b*) and comparative details are given in Table 4. The reason for this structural difference then is not related to a *cis* or *trans* bonding mode, as thought previously, but it implies that the steric requirements of the metal are enforced on one molecule to a greater extent than the other.

An additional structural variance is observable in Pd(L-ser)$_2$. The two side-chain hydroxyl groups have different conformations relative to the N and COO$^-$ groups (Fig. 1). The non-planar molecule (1) has a *gauche–anti* configuration relative to those two groups respectively, the rotation angle being −54·8° (van der Helm, Nicholas & Fisher, 1970); the more planar molecule (2) adopts a *gauche–gauche* configuration, the relevant rotation angle being +53·2°. The latter configuration is present in the structures of both DL-serine (Shoemaker, Barieau, Donohue & Lu, 1953), Cu(L-ser)$_2$ (van der Helm & Franks, 1969) and Cu(xyl-L-ser)$_2$ (Delbaere, Kaminar & Prout, 1975), whereas Ni(L-ser)$_2$(H$_2$O)$_2$ (van der Helm & Hossain, 1969) contains solely *gauche–anti* conformers. In Zn(L-ser)$_2$ (van der Helm, Nicholas & Fisher, 1970) both *gauche–gauche* and *gauche–anti* conformers were observed.

The bond dimensions in both acid molecules compare well with previously reported results. The two

Table 4. *Comparison of molecular dimensions in bis(α-amino acid) metal complexes*

Values in italics refer to the less-planar acid molecule.

Complex	Reference	*M*—N (Å)	*M*—O (Å)	N—*M*—O bite angle (°)	$\|\Delta C\|_\alpha$†
Pd(L-ser)$_2$	(1)	2·015 (7)	2·001 (7)	83·7 (3)	0·22
		2·030 (7)	*2·008* (6)	*82·0* (3)	*0·42*
Cu(L-asn)$_2$	(2)	2·004 (28)	1·947 (21)	86·9 (10)	0·19
		2·035 (26)	*1·954* (22)	*82·4* (9)	*0·63*
Zn(L-asn)$_2$*	(3)	2·092 (5)	2·086 (4)	81·1 (2)	0·12
		2·071 (5)	*2·102* (4)	*80·9* (2)	*0·52*
Cu(L-ornH)$_2$Cl$_2$.2H$_2$O	(4)	1·963 (5)	1·946 (4)	85·3 (11)	0·18
		1·989 (5)	*1·969* (4)	*84·6* (11)	*0·48*

References: (1) This work. (2) Stephens, Vagg & Williams (1975). (3) Stephens, Vagg & Williams (1977*a*). (4) Stephens, Vagg & Williams (1977*b*).

* Structure contains bridging carboxy groups.

† Deviation (Å) of the α-C atom from the least-squares plane defined by the other four atoms in the five-membered chelate ring.

Table 5. *Proposed hydrogen bonds; donor–acceptor distances* (Å) *are given with e.s.d.'s in parentheses*

Numbered H···O interactions are shown in Fig. 2.

Interaction		Acceptor at	
1	N(1)—H(11)···O(11)	$x-\frac{1}{2}, \frac{3}{2}-y, 1-z$	3·063 (9)
2	N(1)—H(12)···O(22)	$\frac{1}{2}-x, 1-y, \frac{1}{2}+z$	2·965 (10)
3	N(2)—H(21)···O(13)	$-x, y-\frac{1}{2}, \frac{3}{2}-z$	2·861 (11)
4	N(2)—H(22)···O(12)	$x-\frac{1}{2}, \frac{3}{2}-y, 1-z$	2·894 (10)
5	O(13)—H(13)···O(21)	$x-\frac{1}{2}, \frac{3}{2}-y, 1-z$	2·785 (10)
6	O(23)—H(23)···O(11)	$-x, y-\frac{1}{2}, \frac{1}{2}-z$	2·855 (10)

carboxylic acid groups show little deviation from planarity (Table 3, planes 4 and 5), the non-bonded C—O distances being the shorter. The angles subtended at the α-C atoms [average 111·8 (7)°] indicate slightly strained tetrahedra.

The six amino and hydroxyl protons are involved in hydrogen bonding (Fig. 2). Details are given in Table 5. The different hydrogen-bonding requirements of the two amino acid molecules may account for the different OH conformations observed.

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The Crystal Structures of Mixed-Ligand Copper(II) Complexes. II. Bis(2-aminoethyl)amine(2,2′-bipyridyl)copper(II) Nitrate Dihydrate and Bis(2-aminoethyl)amine(1,10-phenanthroline)copper(II) Nitrate

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Abstract

The crystal structures of bis(2-aminoethyl)amine(2,2′-bipyridyl)copper(II) nitrate dihydrate, $C_{14}H_{21}CuN_5^{2+}.2NO_3^-.2H_2O$, $[Cu(C_4H_{13}N_3)(C_{10}H_8N_2)](NO_3)_2.2H_2O$, (I), and bis(2-aminoethyl)amine(1,10-phenanthroline)copper(II) nitrate, $C_{16}H_{21}CuN_5^{2+}.2NO_3^-$, $[Cu(C_4H_{13}N_3)(C_{12}H_8N_2)](NO_3)_2$, (II), have been established by X-ray crystallographic analysis with photographic techniques. (I) crystallizes in the monoclinic space group $P2_1/c$ with a = 10·29 (5), b = 7·60 (5), c = 28·59 (5) Å, β = 106·9 (5)°, Z = 4, and (II) in the monoclinic space group $C2/c$, with a = 25·97 (5), b = 8·13 (5), c = 19·72 (5) Å, β = 100·0 (5)°, Z = 8. Both structures were solved by the heavy-atom method and refined to R = 0·0640 and 0·0933, respectively. Both structures are ionic, the cations involving a distorted five-coordinate square-pyramidal CuN_5 chromophore stereochemistry with closely comparable bond lengths and angles. The structure of (I) is atypical in that the 2,2′-bipyridyl ligand has an angle of twist of only 1·3°.

A wealth of crystallographic data (Muetterties & Schunn, 1966; Hathaway & Billing, 1970; Ray & Hathaway, 1978) has established the existence of the five-coordinate square-based pyramidal and trigonal-bipyramidal stereochemistries for the Cu^{II} ion, especially in mixed-ligand complexes. Due to the nature of the ligands, distorted geometries are involved, depending on the bite angles of the chelate ligands and the conformation of the polydentate chelate ligands (Gollogly & Hawkins, 1972). The present structures have been determined in order to establish how the stereochemistry about the Cu^{II} ion varies with pairs of closely related ligands and ultimately to relate these to the detailed electronic properties of the Cu^{II} ion present.

Preparation

The complexes Cu(bea*)(bpy*)$(NO_3)_2.2H_2O$, (I), and Cu(bea*)(phen*)$(NO_3)_2$, (II), were prepared by mixing a hot solution of $Cu(NO_3)_2.3H_2O$ in methanol (7 mmol in 5 ml) with an equimolar stoichiometric mixture of bis(2-aminoethyl)amine and 2,2′-bipyridyl (for I) and 1,10-phenanthroline (for II) in methanol (7 mmol in 25 ml). Blue-black crystals of (I) and (II) were formed on cooling. (I), found: C = 35·28, H = 5·20, N = 19·82, Cu = 13·06; $C_{14}H_{25}N_7O_8Cu$ requires: C = 34·82, H = 5·22, N = 20·30, Cu = 13·15%; and (II), found: C = 39·04, H = 4·44, N = 20·04, Cu = 12·79; $C_{16}H_{21}N_7O_6Cu$ requires: C = 39·30, H = 4·71, N = 20·0, Cu = 12·99%.

Experimental

The crystal and refinement data for (I) and (II) are summarized in Table 1. The unit-cell parameters were

* bea = bis(2-aminoethyl)amine; bpy = 2,2′-bipyridyl; phen = 1,10-phenanthroline.

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