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The Crystal Structure of Bis-(L-phenylalaninato)copper(II)*

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The crystal structure of bis-(L-phenylalaninato)copper(II), $CuC_{18}H_{20}O_4N_2$, has been determined, and refined by three-dimensional least-squares techniques. The crystals are monoclinic, space group $P2_1$, with $a=16\cdot710$, $b=5\cdot317$, $c=9\cdot509$ Å and $\beta=98\cdot40°$. The final R value for 1745 reflections is 0·041. The standard deviations are between 0·004 and 0·010 Å for the C, N and O atom positions. The structure closely resembles that of bis-(L-alaninato)Cu(II). The copper coordination is best described as a tetragonally distorted octahedron. The conformations of both phenylalanine molecules are similar, although there are distinct differences in detail, and such that the aromatic rings are pointed away from the metal coordination.

Introduction

The structure of the Cu chelate of L-phenylalanine was determined as one of a series of chelates of amino acids and peptides with transition metal ions. This project is designed to elucidate the factors which determine the bonding geometry of metal ions in biological systems. In particular we were interested to see if in the present structure an interaction occurred between the aromatic ring and the Cu^{2+} ion. This kind of interaction was previously observed between the Cu^{2+} ion and the aromatic ring of a tyrosine residue in the copper chelates of L-tyrosine (Tatsch & van der Helm, 1969) and glycyl-L-leucyl-L-tyrosine (Franks & van der Helm, 1971).

Experimental

The bis-(L-phenylalaninato)copper(II) complex was prepared by slow diffusion of aqueous solutions of L-phenylalanine and copper(II) acetate (pH 5 to 6). The light-blue crystals grew as thin plates with the plate face being the (100) plane and all crystals examined showed a rather high mosaic spread ($\geq 1°$). This preparation yields the trans form of the complex which has also been prepared in a different way by Laurie (1967). The cis form has recently been prepared by Herlinger, Wenhold & Long (1970).

X-ray investigation of the crystals showed them to be monoclinic and the space group to be $P2_1$ (systematic absences: $0k0$, $k=2n+1$. Because L-phenylalanine was the ligand, the space group $P2_1/m$ could be excluded.). The cell dimensions, determined by a least-squares fit to the 2θ values of 43 reflections measured at 22°C, are: $a=16\cdot710\pm0\cdot014$, $b=5\cdot217\pm0\cdot009$, $c=9\cdot509\pm0\cdot007$ Å, and $\beta=98\cdot40\pm0\cdot06°$ $[\lambda(Cu\ K\alpha)=1\cdot5418$ Å]. The F.W. for $Cu(L-phenylalanine)_2$ is 391·91, yielding a ϱ_c of 1·587 g.cm^{-3} with $Z=2$. A density of 1·575 g.cm^{-3} was measured by the flotation method, using a mixture of carbon tetrachloride and hexane.

The integrated intensities were taken on a General Electric XRD-5 diffraction unit using the θ–2θ scan technique and nickel-filtered Cu $K\alpha$ radiation. The diffraction unit was equipped with a SPG single-crystal orienter, a scintillation counter, and pulse-height analyzer.

The data crystal had the dimensions of 0·36 ×0·10× 0·02 mm and a mosaic spread of 1°. All unique reflec-

tions with 2θ below 140° were measured. Of the 1745 reflections within this limit, 43 did not show a peak on the recorder while scanning through their diffraction position. The intensities recorded for these 43 unobserved reflections were taken as $\frac{1}{2}$ of the background intensity measured at the location of the reflection. Lorentz, polarization and absorption corrections ($\mu = 21.5$ cm^{-1}) were applied to the data. The absorption program used was made available to us by Coppens (1966).

Structure determination

A sharpened Patterson synthesis was calculated. The Harker section $(u,\frac{1}{2},w)$ yielded the x and z coordinates of the copper atom while its y coordinate was fixed at $\frac{1}{4}$. Further interpretation was made difficult by the pseudo special position of the copper atom (near $\frac{1}{2}$, $\frac{1}{4},\frac{1}{4}$). It was possible, however, to obtain a complete trial structure in which the L configuration was chosen for both phenylalanine molecules.

The initial structure factor calculation had an $R = (\sum||kF_o| - |F_c||/\sum|kF_o|)$ of 0.35. The structure was refined using a modification of the full-matrix least-squares program written by Busing, Martin & Levy (1962). The program was dimensioned to refine 386 parameters such that all nonhydrogen atoms could be refined anisotropically. The anisotropic refinement using unit weights decreased the R value to 0.074. A difference Fourier synthesis calculated at this stage revealed all the hydrogen atoms, but their electron densities were small in many instances (average elec-

tron density was 0.33 e.Å^{-3}). It was therefore decided to use the calculated hydrogen positions in the further refinement, with their positions recalculated after each cycle. They were given an isotropic temperature factor 1.0 Å^2 larger than the atom to which they

Table 1. *Atomic positions*

Fractional coordinates. Standard deviations for last digit given in parentheses

|	x	y	z
Cu	0.49075 (3)	0.2500	0.25036 (6)
O(1A)	0.4704 (2)	0.4555 (8)	0.0780 (3)
O(2A)	0.4028 (2)	0.4482 (9)	−0.1423 (3)
C(1A)	0.4164 (3)	0.3657 (12)	−0.0197 (5)
C(2A)	0.3630 (3)	0.1520 (11)	0.0248 (4)
N(A)	0.4065 (2)	0.0154 (10)	0.1498 (4)
C(3A)	0.2868 (3)	0.2856 (13)	0.0602 (5)
C(4A)	0.2151 (3)	0.1160 (12)	0.0772 (5)
C(5A)	0.1919 (3)	−0.0885 (14)	−0.0111 (7)
C(6A)	0.1213 (3)	−0.2265 (19)	−0.0023 (7)
C(7A)	0.0721 (4)	−0.1538 (17)	0.0944 (8)
C(8A)	0.0939 (4)	0.0501 (19)	0.1817 (7)
C(9A)	0.1654 (3)	0.1841 (15)	0.1750 (6)
O(1B)	0.5173 (2)	0.0395 (8)	0.4214 (3)
O(2B)	0.6057 (2)	0.0190 (9)	0.6206 (3)
C(1B)	0.5831 (3)	0.1069 (11)	0.5015 (4)
C(2B)	0.6363 (2)	0.2972 (10)	0.4321 (4)
N(B)	0.5804 (2)	0.4711 (9)	0.3428 (4)
C(3B)	0.7019 (3)	0.4274 (12)	0.5363 (5)
C(4B)	0.7744 (3)	0.4989 (12)	0.4669 (5)
C(5B)	0.7728 (4)	0.7120 (15)	0.3809 (7)
C(6B)	0.8398 (5)	0.7780 (22)	0.3166 (8)
C(7B)	0.9076 (4)	0.6251 (24)	0.3384 (8)
C(8B)	0.9099 (4)	0.4136 (24)	0.4219 (8)
C(9B)	0.8431 (3)	0.3483 (16)	0.4861 (7)
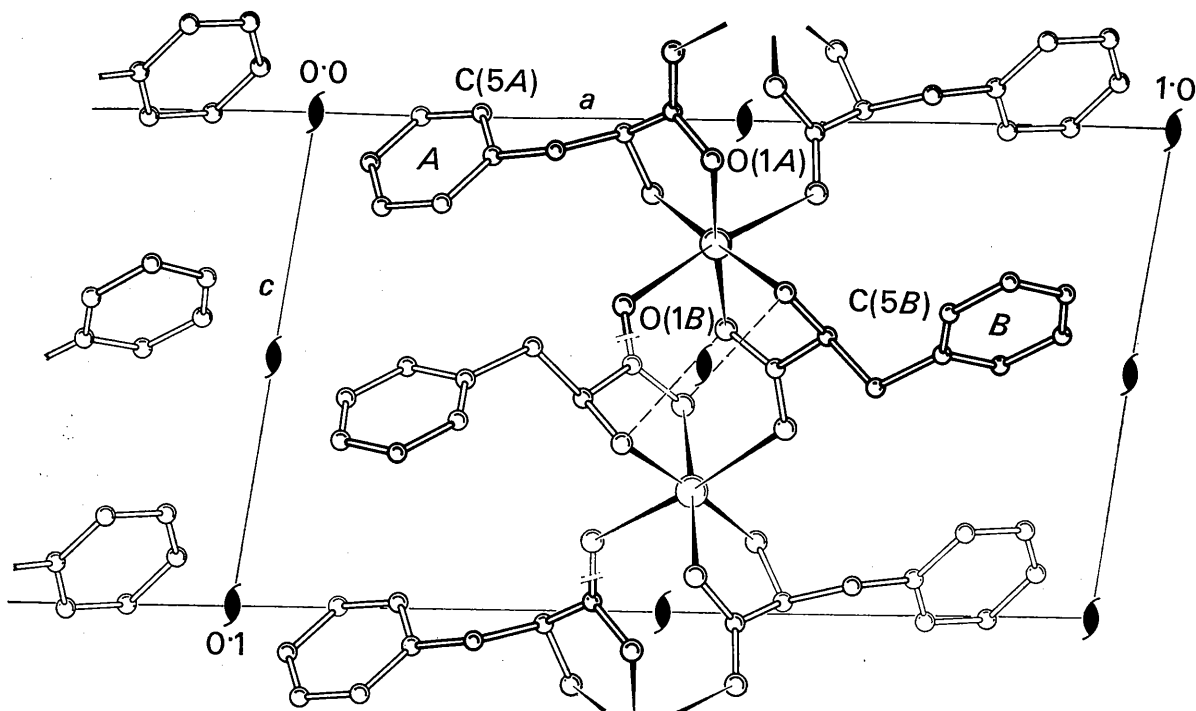
Fig. 1. Projection of the structure down the b axis.

Table 2. *Anisotropic temperature parameters*

All values are multiplied by 10^4. Standard deviation for last digit given in parentheses. The temperature factor is expressed in the form:

$$\exp\left[-(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + 2hk b_{12} + 2hl b_{13} + 2kl b_{23})\right]$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu	23 (0)	218 (2)	48 (1)	−19 (1)	0 (0)	21 (1)
O(1A)	23 (1)	206 (14)	50 (3)	−14 (4)	6 (2)	32 (6)
O(2A)	30 (1)	335 (18)	54 (4)	−10 (4)	4 (2)	44 (7)
C(1A)	22 (2)	258 (21)	50 (5)	10 (5)	9 (2)	2 (9)
C(2A)	17 (1)	259 (20)	52 (4)	0 (5)	8 (2)	−2 (8)
N(A)	21 (1)	208 (17)	55 (4)	−6 (4)	11 (2)	3 (8)
C(3A)	19 (1)	273 (25)	101 (6)	13 (6)	11 (2)	12 (11)
C(4A)	20 (2)	344 (24)	78 (5)	21 (6)	6 (2)	33 (10)
C(5A)	28 (2)	349 (28)	157 (9)	−21 (7)	27 (4)	−19 (14)
C(6A)	31 (2)	417 (31)	191 (9)	−32 (9)	25 (3)	−7 (19)
C(7A)	27 (2)	594 (42)	166 (9)	−19 (8)	16 (4)	76 (17)
C(8A)	26 (2)	776 (50)	145 (9)	7 (9)	31 (4)	40 (19)
C(9A)	27 (2)	636 (46)	95 (6)	7 (7)	20 (3)	0 (14)
O(1B)	22 (1)	212 (15)	47 (3)	−12 (3)	2 (2)	3 (6)
O(2B)	28 (1)	361 (19)	57 (4)	−8 (4)	−1 (2)	51 (7)
C(1B)	24 (2)	183 (19)	47 (5)	12 (5)	11 (2)	−3 (8)
C(2B)	17 (1)	176 (22)	56 (4)	1 (4)	5 (2)	3 (8)
N(B)	22 (1)	191 (17)	48 (4)	−6 (4)	9 (2)	3 (8)
C(3B)	20 (2)	341 (24)	64 (5)	−16 (5)	6 (2)	−10 (10)
C(4B)	23 (2)	293 (23)	65 (5)	−19 (5)	2 (2)	−29 (10)
C(5B)	41 (2)	333 (33)	165 (9)	−24 (8)	29 (4)	32 (15)
C(6B)	68 (4)	601 (47)	167 (10)	−69 (14)	45 (4)	44 (22)
C(7B)	37 (3)	995 (67)	145 (10)	−85 (12)	35 (4)	−68 (22)
C(8B)	26 (2)	1080 (69)	165 (10)	6 (11)	22 (4)	−65 (25)
C(9B)	28 (2)	535 (36)	129 (8)	11 (7)	10 (3)	10 (14)

are bonded. A virial weighting scheme was introduced: $1/w = A + B|F_o| + C|F_o|^2 + D|F_o|^3$. The coefficients were determined so that ΔF^2 was independent of $|F_o|$, yielding $A = 4.671$, $B = −0.1596$, $C = 0.004902$ and $D = −0.00002675$. The calculated structure factors were corrected for the anomalous dispersion of copper ($\Delta f' = −2.1$, $\Delta f'' = 0.7$) during the further refinement, and a logical routine was incorporated (van der Helm & Nicholas, 1970). The least-squares refinement was terminated when all parameter shifts were less than 0.28 of the calculated standard deviations. The final R value is 0.041. A final difference Fourier synthesis was calculated. It showed a remarkable set of four

positive peaks (between 0.30 and 0.46 e.Å^{-3}) and two negative peaks (0.80 and 0.42 e.Å^{-3}) around the copper, which will be discussed below, while all other peaks in the difference Fourier were below 0.3 e.Å^{-3}.

The final parameters are given in Tables 1, 2 and 3. The observed and calculated structure factors are given in Table 4.

Fig. 2. Copper coordination.

Table 3. *Assumed parameters of the hydrogen atoms*

|	x	y	z	B
H[C(2A)]	0.346	0.012	−0.059	3.17
H(1)[N(A)]	0.362	−0.034	0.206	3.14
H(2)[N(A)]	0.428	−0.143	0.107	3.14
H(1)[C(3A)]	0.303	0.388	0.160	3.86
H(2)[C(3A)]	0.267	0.421	−0.025	3.86
H[C(5A)]	0.230	−0.142	−0.089	5.04
H[C(6A)]	0.105	−0.390	−0.071	5.80
H[C(7A)]	0.016	−0.256	0.102	6.04
H[C(8A)]	0.054	0.106	0.257	6.34
H[C(9A)]	0.183	0.343	0.247	5.32
H[C(2B)]	0.666	0.193	0.355	2.90
H(1)[N(B)]	0.564	0.603	0.411	3.03
H(2)[N(B)]	0.615	0.553	0.276	3.03
H(1)[C(3B)]	0.677	0.602	0.577	3.72
H(2)[C(3B)]	0.722	0.296	0.624	3.72
H[C(5B)]	0.718	0.828	0.364	5.55
H[C(6B)]	0.839	0.947	0.250	7.45
H[C(7B)]	0.960	0.672	0.289	7.50
H[C(8B)]	0.964	0.298	0.437	7.74
H[C(9B)]	0.845	0.178	0.552	5.47
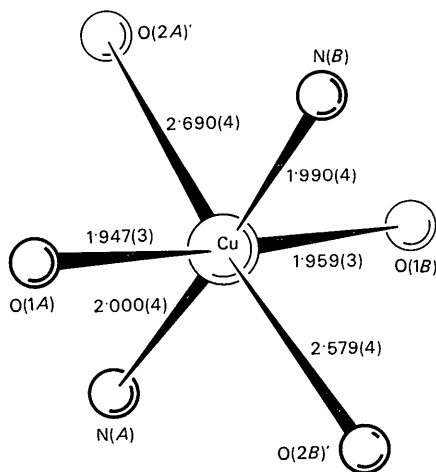
The quantity minimized in the least-squares calculations was $\sum w(|F_o| − |F_c|/k)^2$. The initial Fourier syntheses were calculated using a program written by Ahmed (1966), while the final difference Fourier was

calculated using a program written by Zalkin (1965). The atomic scattering factors for Cu^{2+}, N and C were taken directly from *International Tables for X-ray Crystallography* (1962). The scattering factors for oxygen were derived by taking the average of the curves for O^- and O given in the tables. The scattering factors for hydrogen atoms used were those of Stewart, Davidson & Simpson (1965).

Table 4. *Observed and calculated structure factors*

The listing shows $|10kF_o|$, $|10F_c|$ and the calculated phase angles (in centicycles). Unobserved reflections are indicated by †, while those unobserved reflections which were included in the last cycle of least-squares refinement are indicated by ††.

Description and discussion of the structure

A projection of the structure down the b axis is shown in Fig. 1. As mentioned earlier, one of the primary reasons for determining the structure was to ascertain the position of the aromatic rings with respect to the copper(II) ion. Contrary to what has been observed in the bis-(L-tyrosinato)-copper(II) complex and the copper complex of glycyl-L-leucyl-L-tyrosine, the rings in the L-phenylalanine complex are extended out and away from the coordination sphere.

The copper coordination, shown in Fig. 2, is octahedral with tetragonal distortion. The four short distances are to the O(1) and N atoms of phenylalanine molecules A and B, which form two five-membered

chelate rings with the copper. The two phenylalanine residues are *trans* with respect to each other. The distances (Table 5) compare well with the average values obtained from previously determined structures (Freeman, 1967) *i.e.* $1 \cdot 99 \pm 0 \cdot 01$ Å for Cu–N and $1 \cdot 96 \pm 0 \cdot 02$ Å for Cu–O distances. The two longer coordination bonds are formed by O(2) atoms of symmetry related related molecules A and B.

The present structure is quite similar to the one determined for bis-(L-alaninato)copper(II) (Dijkstra, 1966). The space groups are the same and the fractional coordinates for copper are similar; the a dimension of the unit cell of the present structure is considerably longer so as to accommodate the phenyl rings. A significant difference, however, is observed for the

Table 5. *Distances in copper coordination*

The standard deviations are between 0·003 and 0·004 Å for Cu–ligand distances, and between 0·006 and 0·007 Å for ligand–ligand distances.

Cu–O(1A)	1·947 Å	O(2A)′–O(1A)	3·391 Å	O(2B)′–O(1B)	3·225 Å
Cu–N(A)	2·000	O(2A)′–N(A)	3·218	O(2B)′–N(B)	3·189
Cu–O(2A)′	2·690	O(2A)′–O(1B)	3·177	O(1A) –N(A)	2·663
Cu–O(1B)	1·959	O(2A)′–N(B)	3·364	O(1B) –N(B)	2·640
Cu–N(B)	1·990	O(2B)′–O(1A)	3·318	O(1A) –N(B)	2·894
Cu–O(2B)′	2·579	O(2B)′–N(A)	3·442	O(1B) –N(A)	2·952

Table 6. *Least-squares planes*

The equations of the planes are expressed in the form:

$$Ax + By + Cz = D$$

where x, y and z are fractional coordinates and D is the distance from the origin in Å. The method of Schomaker, Waser, Marsh & Bergman (1959) was used to calculate the least-squares planes.

Plane		A	B	C	D
1	O(1A), O(1B), N(A), N(B)	12·534	−2·681	−4·959	4·299
2	O(1A), O(2A),′ O(1B), O(2B)′	11·766	3·227	2·302	7·186
3	O(2A)′, O(2B)′, N(A), N(B)	0·091	3·151	−7·504	−1·107
4	O(1A), O(2A), C(1A), C(2A)	11·583	−3·501	−3·436	3·592
5	O(1B), O(2B), C(1B), C(2B)	8·902	−3·934	−4·352	2·608
6	C(4A), C(5A), C(6A), C(7A,) C(8A), C(9A)	6·781	−3·223	5·771	1·531
7	C(4B), C(5B), C(6B), C(7B), C(8B), C(9B)	4·145	2·869	7·158	7·977

	$\varDelta(1)$		$\varDelta(2)$		$\varDelta(3)$
O(1A)	−0·012 Å	O(1A)	−0·002 Å	O(2A)′	−0·070 Å
O(1B)	−0·012	O(2A)′	0·002	O(2B)′	−0·069
N(A)	0·012	O(1B)	−0·002	N(A)	0·068
N(B)	0·012	O(2B)′	0·002	N(B)	0·071
Cu	−0·060	Cu	−0·028	Cu	0·060
O(2A)′	2·620				
O(2B)′	−2·631				

	$\varDelta(4)$		$\varDelta(5)$		$\varDelta(6)$
O(1A)	−0·006	O(1B)	0·007	C(4A)	0·000
O(2A)	−0·007	O(2B)	0·008	C(5A)	−0·008
C(1A)	0·018	C(1B)	−0·021	C(6A)	0·009
C(2A)	−0·005	C(2B)	0·006	C(7A)	−0·002
N(A)	0·548	N(B)	−0·787	C(8A)	−0·007
Cu	0·357	Cu	−0·313	C(9A)	0·008

	$\varDelta(7)$
C(4B)	0·006
C(5B)	−0·005
C(6B)	0·002
C(7B)	0·000
C(8B)	0·001
C(9B)	−0·004

longer coordination distances, which are 2·70 and 2·90 Å in bis-(L-alaninato)Cu(II) compared with 2·690 and 2·579 Å in this structure.

The least-squares planes for the coordination sphere are shown in Table 6 (planes 1, 2 and 3). Plane 1, through the four nearest neighbours of the metal ion, indicates a small displacement of the copper ion out of the plane in the direction of the nearest apical oxygen atom, O(2B)'. Plane 3 has a small tetrahedral distortion. Even so, except for the tetragonal distortion of the octahedron, the environment of the metal ion is quite regular as is indicated by the angles between the normals of planes 1, 2 and 3, which are 93·7° for planes 1 and 2, 91·5° for planes 1 and 3, and 95·7° for planes 2 and 3. The four positive peaks found in the final difference Fourier are located in plane 1 on the bisectrices of the lines formed by the coordinate bonds. The two negative peaks are located on the centres of the triangles formed by O(1A), N(B), O(2A)' and O(1B), N(A), O(2B)'. Fig. 3 shows a stereoscopic diagram (Johnson, 1965) of the coordination.

The two five-membered chelate rings are in the envelope conformation, i.e. the Cu and N atoms are displaced toward the same side of the least-squares planes through the carboxylic acid groups (planes 4 and 5, Table 6). The bond angles and bond distances in the rings are given in Table 7 and Fig. 2, 4 and 5. The chelate rings are non-planar and buckled primarily as a result of a rotation around the C^α–C' bond, by −25·3° for the C(2A)–C(1A) bond and 36·2° for the C(2B)–C(1B) bond (Table 8). The larger rotation around C(2B)–C(1B) is reflected in the observation that all bond angles in the chelate ring formed by molecule B are smaller than those in the one formed by molecule A (Table 7).

Table 7. Bond angles

Standard deviation for the last digit is given in parentheses

			Molecule A	Molecule B
Cu	O(1)	C(1)	115·2 (3)°	114·0 (3)°
Cu	N	C(2)	108·5 (3)	105·6 (3)
O(1)	Cu	N	84·8 (2)	83·9 (2)
C(1)	C(2)	N	109·6 (4)	106·6 (3)
O(1)	C(1)	C(2)	116·3 (4)	114·6 (4)
O(1)	C(1)	O(2)	124·7 (5)	124·2 (5)
O(1)	C(1)	C(2)	116·3 (4)	114·6 (4)
O(2)	C(1)	C(2)	118·8 (4)	121·0 (4)
C(1)	C(2)	C(3)	105·5 (4)	114·4 (4)
C(3)	C(2)	N	111·6 (4)	115·7 (4)
C(2)	C(3)	C(4)	116·9 (5)	111·9 (4)
C(3)	C(4)	C(5)	122·9 (5)	120·8 (5)
C(3)	C(4)	C(9)	119·0 (6)	120·5 (5)
C(5)	C(4)	C(9)	117·8 (5)	118·7 (5)
C(4)	C(5)	C(6)	121·9 (6)	120·8 (7)
C(5)	C(6)	C(7)	119·5 (8)	119·1 (8)
C(6)	C(7)	C(8)	119·3 (6)	120·8 (6)
C(7)	C(8)	C(9)	121·1 (6)	120·0 (8)
C(8)	C(9)	C(4)	120·4 (7)	120·5 (7)

The bond lengths for the two phenylalanine molecules are shown in Fig. 4 and 5. The bond angles are given in Table 7. In general the dimensions of the two molecules are very similar with the exception of the bond angles around C(2) and C(3). The angle C(1), C(2), C(3) is significantly different in the two molecules and from the average value (110°) given by Freeman (1967) for chelates of amino acids, and from the average value (111·5°) given by Marsh & Donohue (1967) for a free amino acid. The latter authors observed in their review a considerable variation for this angle, which was attributed to the exigencies of nonbonded contacts involving sidechain atoms. The enlargements of the O(2)–C(1)–C(2) and C(1)–C(2)–C(3)
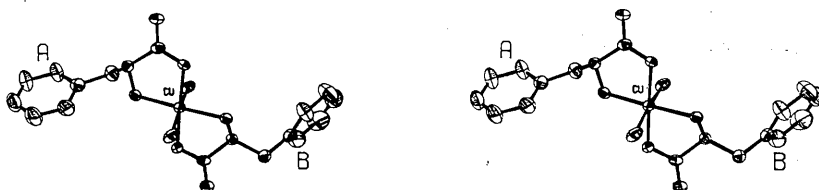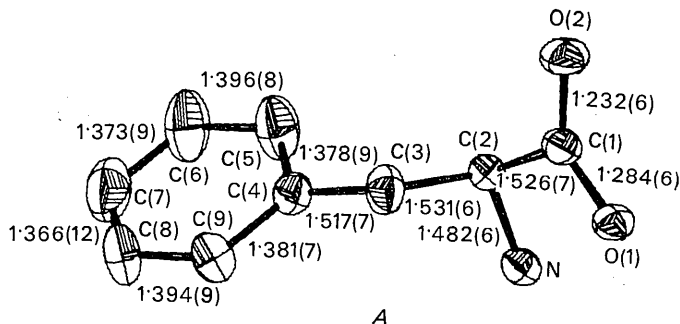

Fig. 3. A stereoscopic view of the molecule.

Fig. 4. Bond distances in molecule A.

angles and of the C(1)–C(2) bond distance in molecule B may be caused by the close approach of C(3) and O(2), which is a result of the unusual conformation around C(2)–C(1) (Table 8) in that molecule. Other effects, such as the intermolecular interactions of the phenyl rings or the chelation, may have influence on the bond angles around C(2). The side-chain of molecule A is definitely stretched [C(2) C(3) C(4): 116·9°]. The observation that variation of the bond angles of C^α and C^β does occur is important to those building proteins from Fourier syntheses. Whereas the usual procedure is to adjust the conformation angles ψ and φ so as to match the side chains to the observed electron density, it may be better to allow a certain variability in the valence angles of C^α and the side-chain carbons.

The differences between the C(1)–O(1) and C(2)–O(2) distances in the two molecules reflect the differences in strength of the coordinate bonds in which O(1) and O(2) are involved (Gramaccioli, 1966). The shortening of the C(3)–C(4) bonds is as expected for distances between sp^2 and sp^3 hybridized carbons. The phenyl rings are planar (planes 6 and 7, Table 6). The average of the twelve phenyl C–C distances is $1·380 \pm 0·012$Å, the standard deviation of which indicates that the e.s.d.'s calculated from the inverse of the least-squares matrix may be underestimated by about 20%.

The conformational angles are given in Table 8. There are two significant differences in the conformations of molecules A and B.

The ψ angles are opposite to each other in the two molecules and they yield the differences observed for the other conformational angles involving C(1)–C(2).

Another difference is observed in the X^2 angles. It has been noted (Ramachandran & Sasisekharan, 1968) that for planar side-groups of amino acids the plane is found to be either coplanar with, or perpendicular to, the plane defined by C(1), C(2) and C(3). It is seen from Table 8, that this is approximately true for L-phenylalanine.HCl and for molecule B. For molecule A, however, this generalization is not true: the X^2 angles are −41·2 and 146° in this case. The reason for the deviation can probably be attributed to packing forces. The X^1 angles, which are close to −60°, make that the phenyl rings point away from the amino and acid group in molecules A and B.

The coordination spheres are linked together by the carboxylic acid groups of both molecules and thus form an infinite sheet parallel to the (100) plane. Hydrogen bonding is not important in the structure. One hydrogen bond is drawn in Fig. 1, between N(B) and O(1B) ($1 − x$, $\frac{1}{2} + y$, $1 − z$) with a distance of 2·981 Å. The X–H … Y angle (126·4°), however, is not favourable for interaction and another possible hydrogen bond for the same hydrogen is given in Table 9. The Table also lists two other weak hydrogen bonds. All other interactions are of the van der Waals type. All intermolecular distances below 3·5 Å are listed in Table 9. There are two unusually close contacts: O(1A)–C(1A) ($1 − x$, $\frac{1}{2} + y$, $−z$) (2·962 Å) and C(1B)–O(1B) ($1 − x$, $\frac{1}{2} + y$, $1 − z$) (2·967 Å). The only interactions in the a direction are contacts between phenyl groups. This type of interaction is the probable cause for the high mosaic spread of the crystals and the unusual conformational angles, X^2, of molecule A.

Table 8. *Conformational angles*

Conformations of the two phenylalanine molecules in this structure and of L-phenylalanine.HCl (Vainshtein & Gurskaya, 1964). The notation and conventions of Ramachandran & Sasisekharan (1968) are used. The standard conformation for all angles is cis (I, IV), and rotations are positive for clockwise (right-handed) rotations of IV, around the II–III bond.

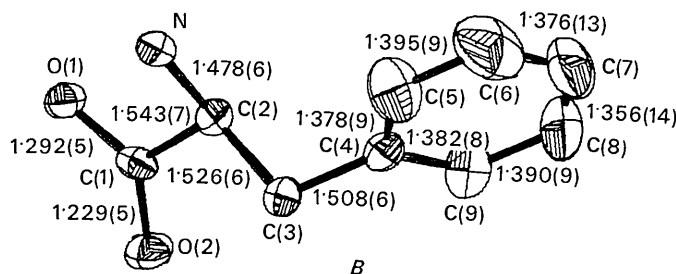| Angle	Atoms				Molecule A	Molecule B	L-Phenylalanine.HCl
	I	II	III	IV			
Ψ	N	C(2)	C(1)	O(1)	−25·3°	36·2°	−2·°
	C(3)	C(2)	C(1)	O(1)	95·0	165·4	
	N	C(2)	C(1)	O(2)	158·2	−147·8	
	C(3)	C(2)	C(1)	O(2)	−81·5	−18·6	
	C(1)	C(2)	C(3)	C(4)	167·2	151·3	
X^1	N	C(2)	C(3)	C(4)	−73·9	−84·2	62
X_1^2	C(2)	C(3)	C(4)	C(5)	−41·2	77·9	84
X_2^2	C(2)	C(3)	C(4)	C(9)	146·0	−100·7	−98

Fig. 5. Bond distances in molecule B.

Table 9. *Intermolecular distances*

Hydrogen bonding

Donor (X)	Acceptor (Y)	Hydrogen (H)	X–$H\cdots Y$	$H\cdots Y$	$X\cdots Y$
N(B)	O(1B) (a)	H(1) [N(B)] ⎱	126°	2·26 Å	2·981 Å
N(B)	O(1B) (b)	H(1) [N(B)] ⎰	141	2·42	3·270
N(B)	O(2A) (c)	H(2) [N(B)]	131	2·42	3·173
N(A)	O(1A) (d)	H(2) [N(A)]	162	2·24	3·217

Van der Waals contacts less than 3·5 Å

O(1A)	O(1A) (c)	3·227 Å	O(2A)	N(A) (c)	3·218 Å
O(1A)	O(2A) (c)	3·331	O(2B)	N(A) (a)	3·413
O(1A)	N(A) (c)	3·213	C(1A)	N(A) (c)	3·459
O(1A)	C(1A) (c)	2·962	O(2A)	C(2B) (c)	3·288
O(1A)	C(2A) (c)	3·249	N(B)	O(2B) (a)	3·189
O(1B)	O(1B) (a)	3·102	N(B)	C(1B) (a)	3·367
O(2B)	O(1B) (a)	3·393	C(6B)	C(5A) (c)	3·453
C(2B)	O(1B) (a)	3·341	C(7B)	C(5A) (c)	3·490
C(1B)	O(1B) (a)	2·967	C(9B)	C(8A) (a)	3·350

The small letter in parentheses indicates that one of the following operations has to be applied to the coordinates given in Table 1.

$$
\begin{array}{llll}
a & 1-x, & \tfrac{1}{2}+y, & 1-z \\
b & x, & 1+y, & z \\
c & 1-x, & \tfrac{1}{2}+y, & -z \\
d & x, & -1+y, & z
\end{array}
$$

The thermal ellipsoids have been calculated from the anisotropic temperature factors (Lawson, 1970) and are shown in Figs. 3, 4 and 5. Only in the phenyl rings does considerable anisotropy occur, and more so in molecule B than in molecule A. The major and minor (in parentheses) axes of the ellipsoids for atoms C(6), C(7), C(8) and C(9) are 6·90 (2·45), 7·76 (2·51), 8·65 (1·96) 6·93 (2·19) Å^2 for molecule A, and 9·51 (2·87), 12·19 (2·24) 12·02 (2·52) and 5·90 (2·96) Å^2 for molecule B.

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