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The Crystal Structure of L-Ornithine Hydrochloride

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The crystal structure of L-ornithine hydrochloride, $NH_3^+(CH_2)_3CH(NH_3^+)COO^-.Cl^-$, has been determined by using complete three-dimensional intensity data obtained with Mo $K\alpha$ radiation. The crystal data are: $a=10{\cdot}005$, $b=7{\cdot}992$, $c=5{\cdot}000$ Å and $\beta=96{\cdot}98°$, the space group $P2_1$. The structure including the hydrogen atoms has been refined by the block-diagonal matrix least-squares method. The final R is 0·04, and the e.s.d.'s of positional parameters for C, N and O atoms are about 0·004 Å.

All the bond lengths and angles are normal. The ornithine molecule exists as a zwitterion, each N atom having an extra proton and making three hydrogen bonds. The molecule is characterized by the two planar groups; the carboxyl group and the aliphatic side chain, the latter including two amino nitrogen atoms. A comparison of the molecular structures of ornithine, lysine and arginine in the crystals showed that some parts of the three molecules have a common characteristic but, as a whole, there are substantial differences due to the internal rotations of the C_α–C_β bonds.

Introduction

L-Ornithine, $NH_2(CH_2)(NH_3CH_2)COOH$, is one of the four important amino acids having basic side chains. Although this acid is not a constituent amino acid of proteins, it plays an important role in the Krebs cycle in the metabolism of mammals. In addition, it is found in many antibiotics of oligopeptides. The molecular structure of ornithine is interesting from these biological viewpoints. In the present paper the crystal structure of L-ornithine hydrochloride is dealt with, and the molecular structure of ornithine is discussed in connexion with other basic amino acids, *i.e.* lysine and arginine.

Experimental

The crystal of L-ornithine monohydrochloride, $NH_3^+(CH_2)_3CH(NH_3^+)COO^-.Cl^-$, was obtained as a colorless plate from its aqueous solution. The unit-cell dimensions and three-dimensional intensity data were obtained from X-ray photographs using Cu $K\alpha$ radiation. These intensity data were used in the initial stage of the structure determination.

Later, however, all the X-ray experiments were done on a General Electric XRD-5 goniostat, with Mo $K\alpha$ radiation, by use of a krypton-filled proportional counter. The dimensions of the crystal used were 0·31 $\times$ 0·17 $\times$ 0·11 mm. By the stationary-crystal stationary-counter technique, 929 independent reflections permitted in the sphere with $\sin\theta/\lambda$ less than 0·641 ($2\theta<54°$) were measured with a counting time of 20 sec for each. Of these, 28 were assigned to be of zero intensity. The measured intensities were corrected for Lorentz and polarization factors. Since the linear absorption coefficient for Mo $K\alpha$ radiation is small ($\mu=3{\cdot}1$ cm^{-1}), the absorption correction was neglected. The extinction effects were also found to be negligible at the final stage of the structure refinement. The programs written by one of the authors (T.U.) were used for the goniostat setting and the data processing.

In order to obtain a clue for solving the structure of the hydrochloride, the intensity data of $h0l$ reflections of the crystal of L-ornithine hydrobromide were also collected by the photographic method.

Crystal data

The crystal of L-ornithine hydrochloride belongs to the monoclinic system. The unit-cell dimensions determined on a General Electric XRD-5 goniostat based on $\lambda=0{\cdot}71069$ Å for Mo $K\alpha$ are:

$$\begin{aligned} a &= 10{\cdot}005 \pm 0{\cdot}010 \text{ Å} \\ b &= 7{\cdot}992 \pm 0{\cdot}006 \\ c &= 5{\cdot}000 \pm 0{\cdot}010 \\ \beta &= 96{\cdot}98 \pm 0{\cdot}05° . \end{aligned}$$

The systematic absence of reflections for $0k0$ with k odd suggested that the space group is either $P2_1$ or $P2_1/m$, and the former was adopted throughout the investigation. The density of the crystal determined by the flotation method is 1·413 g.cm^{-3}, while the calculated value assuming two formula units in a cell is 1·401 g.cm^{-3}.

The unit-cell dimensions of L-ornithine hydrobromide, which are not known very accurately, are:

$$a=10{\cdot}21,\ b=8{\cdot}04,\ c=4{\cdot}98 \text{ Å};\ \beta=97° .$$

The unit-cell dimensions of these two crystals show that they are isomorphous with each other.

Determination of the structure

The structure determination was initiated using the photographic data. The position of the chloride ion was deduced from the Patterson projection on the b plane. However, neither the b-axis electron-density

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projection nor the three-dimensional electron-density distribution, both based on the coordinates of the chloride ion, showed up the structure. The approximate structure became revealed when these two electron-density maps were compared with the electron-density projection on the *b* plane for the crystal structure of L-ornithine hydrobromide. A subsequent three-dimensional electron-density map showed up the structure more clearly. The structure refinement was then made by a series of least-squares calculations. After several cycles, the *R* value decreased to 0·12. However, an inspection of the results showed that any more refinement could hardly be fruitful with the photographic data.

Refinement of the structure

Further refinement of the structure was done by the use of a set of the complete three-dimensional intensity data obtained on a General Electric XRD-5 goniostat with Mo $K\alpha$ radiation. The coordinates and anisotropic temperature factors of all the non-hydrogen atoms were first refined by the least-squares method, and after two cycles the *R* index decreased from 0·16 to 0·06. A three-dimensional difference Fourier series synthesized at this stage showed all the hydrogen atoms at the sites expected. The coordinates of all the hydrogen atoms, together with their isotropic temperature factors, were then included in the subsequent least-squares refinement. After two more cycles *R* decreased to 0·040 (or 0·046 if 28 reflections with zero intensity are included). At the last cycle, the maximum parameter shift for the non-hydrogen atoms was less than one third of their standard deviations, and that for the hydrogen atoms was less than their standard deviations.

Table 1. *The final atomic coordinates and their standard deviations, σ (in* 10^{-3} Å)

	x	σ(*x*)	*y*	σ(*y*)	*z*	σ(*z*)
Cl	0·0809	1	0·2500	2	0·9032	1
O(1)	0·5028	3	0·5327	3	0·3258	3
O(2)	0·5945	3	0·5351	4	0·7561	3
N(1)	0·3897	3	0·3285	4	0·8886	3
N(2)	0·1438	4	0·9986	4	0·4211	3
C(1)	0·5007	4	0·5089	4	0·5737	3
C(2)	0·3656	4	0·4488	4	0·6583	4
C(3)	0·2865	4	0·5972	4	0·7510	4
C(4)	0·2406	4	0·7179	4	0·5209	4
C(5)	0·1783	4	0·8718	5	0·6358	4

The final parameters for the non-hydrogen atoms and their standard deviations are listed in Tables 1 and 2, those for hydrogen atoms in Table 3, and the observed and the calculated structure factors in Table 4. The three-dimensional electron-density distribution, and the difference function based on the calculated structure factors discarding the hydrogen atoms, are shown in Figs. 1 and 2, respectively. In the latter some of the coordinates of the peaks of the electron density due to the hydrogen atoms deviate significantly from those obtained by the least-squares refinement. Every hydrogen atom peak in the difference map is higher than 0·45 e.Å^{-3}, and the density does not exceed 0·3 e.Å^{-3} in other regions.

Table 3. *The final parameters of the hydrogen atoms*

	x	*y*	*z*	*B*	Bonded to
H(1)	0·302	0·293	0·947	2·1 Å^2	N(1)
H(2)	0·442	0·393	1·050	3·1	N(1)
H(3)	0·433	0·250	0·837	3·8	N(1)
H(4)	0·111	1·087	0·520	2·8	N(2)
H(5)	0·088	0·955	0·286	1·3	N(2)
H(6)	0·224	1·034	0·343	2·4	N(2)
H(21)	0·312	0·389	0·503	1·6	C(2)
H(31)	0·206	0·561	0·839	2·2	C(3)
H(32)	0·362	0·661	0·903	1·9	C(3)
H(41)	0·326	0·753	0·404	3·1	C(4)
H(42)	0·168	0·657	0·370	2·0	C(4)
H(51)	0·097	0·839	0·707	1·3	C(5)
H(52)	0·241	0·926	0·779	1·9	C(5)

$\langle\sigma(x)\rangle = 0{\cdot}05$ $\langle\sigma(y)\rangle = 0{\cdot}06$ $\langle\sigma(z)\rangle = 0{\cdot}05$ Å
$\langle\sigma(B)\rangle = 1{\cdot}2$ Å^2

The refinement was done on an IBM 7090 and a HITAC 5020 computer with the programs written by one of the authors (T.A.). The program performs a block-diagonal least-squares refinement, and Fourier synthesis after the least-squares refinement. The program forms a 9×9 matrix for an atom with anisotropic thermal parameters and a 4×4 for an isotropic atom. The scale factor and the overall isotropic temperature factor are refined in a 2×2 matrix, and the shift of the latter is modified by a 1×1 matrix (Cruickshank, 1961). The minimized function used was $\Sigma\, w(\Delta F)^2$. The standard deviations of the parameters were calculated from the sum of the weighted residuals and the diagonal terms of the inverse matrices of the normal

Table 2. *The thermal parameters and their standard deviations (in* 10^{-4})

The thermal parameters are of the form: $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$.

	β_{11}	σ	β_{22}	σ	β_{33}	σ	β_{12}	σ	β_{13}	σ	β_{23}	σ
Cl	57	1	104	1	369	4	14	3	59	3	25	1
O(1)	78	3	113	5	224	10	−28	7	74	9	4	14
O(2)	60	3	173	7	252	11	−43	8	27	9	−74	16
N(1)	59	3	79	5	222	13	10	8	65	10	50	15
N(2)	75	4	85	6	285	14	32	8	48	12	47	16
C(1)	56	3	71	6	229	15	18	8	62	13	−5	18
C(2)	48	3	78	6	188	13	−4	8	27	11	12	16
C(3)	56	4	80	6	262	15	28	9	51	13	39	17
C(4)	78	4	96	8	255	15	26	9	46	13	20	18
C(5)	72	4	91	7	273	16	27	9	89	14	54	18

Table 4. *Observed and calculated structure factors* ($\times 10$)

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
H,L= 0			0	77	75	6	121	126	5	102	106	2	56	58	H,L= 5		-5	4	27	28	2	101	104	7	82	87	2	18	16
2	117	105	1	339	349	7	27	27	4	76	79	3	60	57	0	35	16	5	16	11	3	97	95	H,L= 8		0	3	31	31
4	345	352	2	175	170	8	65	63	5	45	45	4	23	18	1	11	11	H,L= 6		-4	4	53	54	0	67	62	H,L= 10		-3
6	81	95	3	285	276	H,L= 2		-2	6	38	38	5	51	50	2	44	45	0	29	33	5	48	54	1	88	83	0	67	68
8	98	100	4	262	253	0	180	178	7	38	37	H,L= 4		-4	3	49	47	1	125	132	6	21	19	2	130	125	1	82	80
10	47	46	5	96	94	1	136	142	H,L= 3		-3	0	53	44	4	28	33	2	80	84	7	53	51	3	74	74	2	62	61
H,L= 0		1	6	46	48	2	84	78	0	277	280	1	97	100	5	34	31	3	103	107	H,L= 7		-2	4	27	34	3	44	46
0	144	137	7	119	122	3	121	117	1	52	57	2	33	36	H,L= 5		-4	4	38	40	0	27	30	5	76	68	4	50	53
1	284	294	8	79	81	4	261	261	2	58	64	3	21	25	0	57	56	5	28	32	1	95	89	6	79	79	5	0	9
2	414	427	9	43	45	5	119	118	3	128	135	4	42	38	1	117	119	6	34	30	2	100	98	7	76	74	H,L= 10		-2
3	224	215	10	24	22	6	68	62	4	128	133	5	49	52	2	45	47	H,L= 6		-3	3	139	136	H,L= 8		1	0	0	4
4	69	65	H,L= 1		0	7	58	58	5	34	34	6	27	26	3	68	68	0	15	6	4	10	19	0	171	166	1	58	58
5	110	106	0	185	184	8	34	34	6	76	69	7	58	59	4	99	102	1	151	155	5	43	41	1	48	51	2	120	118
6	122	124	1	37	40	9	43	46	7	43	43	H,L= 4		-3	5	70	75	2	32	30	6	38	37	2	32	36	3	0	7
7	21	20	2	455	457	H,L= 2		-1	8	46	46	0	8	14	6	25	22	3	142	145	7	74	77	3	0	6	4	50	50
8	13	10	3	206	202	0	106	105	H,L= 3		-2	1	103	106	7	58	55	4	34	37	8	0	7	4	191	191	5	12	15
9	35	37	4	137	141	1	346	353	0	298	300	2	132	131	H,L= 5		-3	5	49	49	H,L= 7		-1	5	35	41	H,L= 10		-1
10	51	53	5	100	102	2	193	184	1	84	87	3	88	93	0	93	90	6	43	41	0	49	48	6	45	43	0	146	151
H,L= 0		2	6	139	142	3	105	107	2	148	154	4	154	157	1	108	99	7	38	38	1	194	194	7	9	10	1	56	52
0	32	26	7	85	85	4	126	121	3	178	184	5	90	85	2	47	46	H,L= 6		-2	2	32	27	H,L= 8		2	2	69	71
1	267	272	8	92	95	5	174	169	4	130	131	6	81	79	3	128	130	0	15	0	3	61	63	0	15	26	3	14	20
2	239	228	9	41	40	6	68	70	5	39	37	7	8	8	4	118	120	1	189	182	4	47	41	1	49	50	4	40	46
3	273	265	10	44	48	7	115	116	6	43	43	8	40	39	5	57	56	2	178	175	5	123	125	2	67	67	5	15	21
4	117	113	H,L= 1		1	8	81	79	7	45	41	H,L= 4		-2	6	28	27	3	70	70	6	39	40	3	40	44	6	41	46
5	32	30	0	413	435	9	64	71	8	78	81	0	136	133	7	89	90	4	28	18	7	24	20	4	35	42	H,L= 10		0
6	17	8	1	292	301	H,L= 2		0	9	0	13	1	0	21	8	16	20	5	131	134	8	52	56	5	26	28	0	90	86
7	95	93	2	176	184	0	139	139	H,L= 3		-1	2	147	143	H,L= 5		-2	6	41	38	H,L= 7		0	6	64	67	1	80	82
8	45	47	3	73	73	1	241	257	0	251	245	3	124	125	0	126	123	7	36	35	0	160	152	H,L= 8		3	2	14	16
9	44	47	4	114	113	2	97	87	1	320	321	4	53	52	1	84	83	8	12	16	1	95	91	0	30	31	3	89	90
H,L= 0		3	5	48	47	3	296	299	2	370	366	5	57	54	2	76	77	H,L= 6		-1	2	100	94	1	50	54	4	46	48
0	23	22	6	157	157	4	229	228	3	180	173	6	101	99	3	128	133	0	273	269	3	79	77	2	67	71	5	62	69
1	178	179	7	62	62	5	95	93	4	108	103	7	8	9	4	101	99	1	135	136	4	135	135	3	46	50	6	0	15
2	144	143	8	62	64	6	36	36	5	26	31	8	83	79	5	103	101	2	141	133	5	20	20	4	21	20	H,L= 10		1
3	70	61	9	15	7	7	146	149	6	138	136	9	9	13	6	91	74	3	118	117	6	57	53	5	48	44	0	52	55
4	29	32	10	42	44	8	73	73	7	58	56	H,L= 4		-1	7	58	61	4	123	122	7	25	6	H,L= 8		4	1	66	70
5	132	131	H,L= 1		2	9	26	25	8	27	30	0	361	360	8	47	45	5	24	23	8	31	33	0	28	6	2	22	27
6	20	9	0	295	301	10	37	42	9	40	48	1	265	259	H,L= 5		-1	6=	0	4	H,L= 7		1	1	34	30	3	88	91
7	55	55	1	133	133	H,L= 2		1	H,L= 3		0	2	192	191	0	55	53	7	64	65	0	50	49	2	20	14	4	17	15
8	23	26	2	120	116	0	213	212	0	183	184	3	140	136	1	62	59	8	55	60	1	46	50	3	54	52	5	15	15
H,L= 0		4	3	100	98	1	202	198	1	450	509	4	200	193	2	229	230	H,L= 6		0	2	170	165	H,L= 9		-5	H,L= 10		2
0	90	87	4	207	206	2	328	333	2	205	203	5	128	123	3	104	101	0	117	106	3	79	78	0	21	16	0	64	64
1	114	116	5	189	188	3	197	194	3	148	149	6	84	83	4	119	115	1	63	63	4	60	62	1	74	73	1	63	66
2	105	109	6	34	32	4	97	99	4	115	110	7	34	34	5	26	24	2	256	247	5	50	53	H,L= 9		-4	2	60	64
3	70	69	7	20	16	5	58	58	5	182	177	8	45	44	6	137	134	3	51	46	6	77	73	3	52	53	3	18	22
4	42	41	8	36	39	6	162	162	6	134	129	9	53	53	7	30	32	4	89	84	7	12	14	1	37	37	4	53	53
5	96	95	9	57	59	7	35	35	7	63	63	H,L= 4		0	8	69	73	5	75	71	8	37	36	2	93	92	H,L= 10		3
6	24	12	H,L= 1		3	8	74	75	8	78	78	0	154	150	9	81	80	6	126	123	H,L= 7		2	3	75	77	0	41	40
7	32	35	0=	0	13	9	37	41	9	67	66	1	252	247	H,L= 5		0	7	26	21	0	110	114	4	26	21	1	20	16
H,L= 0		5	1	71	73	H,L= 2		2	H,L= 3		1	2	181	177	0	132	130	8	33	33	1	84	86	H,L= 9		-3	2	57	56
0	81	77	2	172	167	0	122	122	0	259	264	3	191	189	1	55	58	H,L= 6		1	2	86	85	0	76	71	H,L= 11		-3
1	76	75	3	112	111	1	110	107	1	164	163	4	35	27	2	126	118	0	188	183	3	79	79	1	16	20	0	45	43
2	85	85	4	16	22	2	56	49	2	175	176	5	74	74	3	81	76	1	128	120	4	49	49	2	55	56	1	43	45
3	48	47	5	36	36	3	142	138	3	90	90	6	68	67	4	159	152	2	36	41	5	51	49	3	14	5	2	27	27
4	40	37	6	20	22	4	158	155	4	126	124	7	94	91	5	36	27	3	141	140	6	37	34	4	80	77	3	40	38
5	53	50	7	76	76	5	71	76	5	122	121	8	26	17	6	88	85	4	119	117	7	48	46	5	61	59	H,L= 11		-2
6	43	45	8	12	8	6	129	124	6	47	43	9	57	59	7	58	56	5	44	43	H,L= 7		3	6	18	19	0	30	29
H,L= 0		6	H,L= 1		4	7	44	43	7	45	47	H,L= 4		1	8	84	84	6	36	35	0	84	88	H,L= 9		-2	1	50	54
0	51	49	0	9	13	8	75	73	8	58	60	0=	0	2	9	65	65	7	45	46	1	40	42	0	122	121	2	34	36
1	24	27	1	98	95	9	27	24	9	48	48	1	194	196	H,L= 5		1	8	72	72	2	33	30	1	103	102	3	27	26
2	20	18	2	63	65	H,L= 2		3	H,L= 3		2	3	144	137	C	5	14	H,L= 6		2	3	89	91	2	73	71	4	60	61
3	29	24	3	127	129	0	29	30	0	148	144	2	192	189	1	206	202	0	26	27	4	43	43	3	42	47	H,L= 11		-1
H,L= 1		-6	4=	0	11	1	125	125	1	125	120	4	28	27	2	120	119	1	107	104	5	25	26	4	60	64	C	66	66
0	15	11	5	55	56	2	128	132	2	251	241	5	131	124	3	115	111	2	45	42	6	9	3	5=	C	6	1	15	15
1	34	31	6	57	55	3	61	60	3	116	112	6	77	75	4	69	65	3	129	127	H,L= 7		4	6	86	84	2	53	54
2	12	12	7	69	68	4	57	57	4	91	88	7	86	85	5	208	206	4	73	74	0	59	56	H,L= 9		-1	3	19	21
3	45	42	H,L= 1		5	5	74	73	5	83	81	8	8	6	6	80	78	5	59	78	1	88	87	0	44	45	4	105	104
H,L= 1		-5	C	41	42	6	104	102	6	68	65	9	42	40	7	41	42	6	44	45	2	17	19	1	89	85	5=	C	4
0=	0	6	1	63	60	7	37	36	7	53	51	H,L= 4		2	8=	C	6	7	28	28	3	33	30	2=	0	12	H,L= 11		0
1	61	59	2	26	27	8	30	30	8	44	42	0	130	120	9	63	66	8	18	17	4	20	18	3	72	72	0	35	18
2	102	102	3	47	48	H,L= 2		4	9	37	35	1	204	198	H,L= 5		2	H,L= 6		3	H,L= 8		-5	4	27	32	1	25	25
3	50	51	4	50	54	0	32	30	H,L= 3		3	2	125	124	C=	C	1	C	178	179	0	24	17	5	60	61	2	86	87
4	40	40	5	36	37	1	122	124	0	138	137	3	118	118	1	48	48	1	102	104	1	18	13	6	15	19	3	30	29
5	43	43	6=	0	18	2	16	23	1	153	153	4	96	95	2	73	70	2=	0	7	2	16	11	7	24	24	4	27	28
6	66	63	H,L= 1		6	3	72	77	2	74	78	5	60	56	3	104	104	3	45	49	3	49	49	H,L= 9		0	5	35	35
H,L= 1		-4	0	35	35	4	13	10	3	105	99	6	77	76	4	49	55	4	38	39	H,L= 8		-4	0	139	139	H,L= 11		1
0	121	123	1	20	22	5	108	106	4	83	77	7	49	45	5	102	101	5	86	90	0	24	27	1	98	98	0	52	55
1	49	53	2	40	37	6	19	13	5	49	46	8	45	47	6	68	67	6	30	27	1	37	44	2	57	58	1	52	54
2	20	22	H,L= 2		-6	7	31	34	6	90	88	9	21	22	7	85	80	7	20	21	2	86	90	3	116	117	2	19	22
3	37	44	0	28	26	H,L= 2		5	7=	C	7	H,L= 4		3	8	30	31	H,L= 6		4	3	40	38	4	58	61	3	57	58
4	69	75	1	42	45	0	11	3	8	24	22	0	44	39	H,L= 5		3	C	14	8	4	44	40	5	76	73	4	37	39
5	25	27	2	34	35	1	37	38	H,L= 3		4	1	69	70	C	55	49	1	27	29	5	85	82	6	35	33	H,L= 11		2
6	47	47	3	37	37	2	22	24	0	125	125	2	73	71	1	80	81	2	74	75	H,L= 8		-3	7	51	51	C	22	20
7	43	41	H,L= 2		-5	3	75	78	1	162	162	3	59	61	2	49	50	3	35	37	0	73	73	H,L= 9		1	1	25	30
H,L= 1		-3	0	63	61	4	19	21	2=	0	8	4	106	109	3	88	85	4	23	11	1	73	73	0	15	20	2	9	7
0	166	163	1	36	34	5	37	41	3	82	76	5	19	23	4	82	83	5	16	18	2	45	43	1	59	63	H,L= 12		-2
1	50	53	2=	0	11	H,L= 2		6	4	54	51	6	27	23	5	20	20	H,L= 6		5	3	31	30	2	118	127	C	82	78
2	49	54	3	35	36	0	16	12	5	44	45	7	28	27	6	43	43	C	27	25	4	83	85	3	30	30	1	60	60
3	166	163	4	43	39	1	18	18	6	26	24	8	54	58	7	93	92	1	32	24	5	64	60	4=	0	5	2	26	31
4	104	105	5	56	54	2	29	29	7	30	29	H,L= 4		4	H,L= 5		4	2	57	55	6	82	79	5	37	44	H,L= 12		-1
5	117	119	6	18	24	H,L= 3		-6	H,L= 3		5	0	94	91	C=	0	5	H,L= 7		-5	H,L= 8		-2	6	35	39	C	9	2
6	63	64	H,L= 2		-4	0	31	20	C	83	79	1	76	76	1	41	38	C	68	71	C	43	37	H,L= 9		2	1	32	26
7	51	50	0	115	110	1	51	52	1	62	62	2	110	109	2	57	60	1	30	32	1	73	73	0	32	34	2	76	79
8	8	16	1	17	24	2	30	26	2	29	31	3	21	23	3	47	43	2	52	50	2	81	87	1	20	20	3	20	15
9	31	30	2	98	98	3	39	38	3	73	73	4	39	38	4	77	80	3	20	17	3	24	30	2	79	82	H,L= 13		0
H,L= 1		-2	3	90	91	H,L= 3		-5	4	18	16	5	40	41	5	21	24	4	42	38	4	34	33	3	57	61	C	77	76
C	78	73	4	89	88	0	35	34	5	46	42	6	60	59	6	46	45	H,L= 7		-4	5	100	98	4	58	65	1	36	36
1	183	190	5	30	31	1	123	127	H,L= 4		-6	H,L= 4		5	H,L= 5		5	0	115	117	6	46	51	5	32	37	2	38	41
2	155	151	6	59	54	2	48	48	0	47	48	0	56	53	C	63	61	1	62	60	7	24	26	H,L= 9		3	3	56	56
3	41	40	7	39	38	3	51	50	1	18	19	1	28	30	1	37	35	2	23	23	H,L= 8		-1	C	82	87	H,L= 12		1
4	10	10	H,L= 2		-3	4	8	14	2	32	30	2	21	21	2	15	14	3=	0	13	0	42	43	1	56	57	0	32	35
5	115	117	0	64	59	5	44	44	0	47	48	3	32	30	3	18	17	4	47	50	1	82	82	2	12	10	1	40	43
6	52	53	1	34	36	6	23	22	1	18	19	4	27	32	H,L= 6		-5	5	71	70	2	28	31	3	15	14	2	13	7
7	105	108	2	207	204	H,L= 5		-4	2	32	30	H,L= 5		-6	C	117	119	6	51	51	3	170	164	4	52	58			
8	20	20	3	112	117	0	63	66	H,L= 4		-5	C	56	53	1	14	10	H,L= 7		-3	4=	0	22	H,L= 10		-4			
9	49	53	4	48	49	1	61	62	0	35	36	1	33	35	2	53	53	0	64	65	5	85	84	0	36	37			
H,L= 1		-1	5	12	7	2	86	87	1	71	73	2	36	33	3	26	29	1	98	100	6	8	13	1	62	63			

equations. Unit weight was assigned for all the reflections, except for those of zero intensity to which a weight of 0·2 was given; the latter reflections are shown with asterisks in Table 4. The fudge factor of 0·8 was applied to the scale factor, the overall temperature factor and the parameters of non-hydrogen atoms, and 0·5 to those of hydrogen atoms. Atomic scattering factors used for Cl^-, O, N, C and H are those listed in *International Tables for X-ray Crystallography* (1962).

Description of the structure

The bond lengths and angles in the ornithine molecule are shown in Tables 5 and 6 and also in Fig. 3. The estimated standard deviations of the bond lengths and angles among C, N and O are about 0·006 Å and 0·4°, respectively.

The dimensions of the amino acid group are similar to those reported for many amino acids. The average value of the two C–NH_3^+ bond lengths, 1·491 Å, is as usual longer than the normal single-bond length between the carbon and nitrogen atoms. The value, 1·491 Å, is close to 1·493 Å, the average bond length* of many amino acids so far determined by three-dimensional analysis. The lengths of the three C–C bonds in the aliphatic side chain are equal to one another, while the bond C(1)–C(2) in the carboxyl group is a little longer than these three. The latter is close to the standard value commonly accepted. The average of the other three, 1·526 Å, is significantly smaller than the standard value. However, it is interesting that the present value, 1·526 Å, is very close to 1·524 Å, the average of all the C–C bonds in lysine (Wright & Marsh, 1962). The average value of the seven C–H bond lengths, 1·05 Å, and that of the six N–H's, 0·95 Å, are also very close to those found in lysine, 1·06 and 0·94 Å, respectively. It is concluded, therefore, that all the bond lengths and angles in the ornithine molecule are normal, and are as a whole quite similar to those found in lysine, although the molecular conformations of these two amino acids in the crystals of their hydrochlorides are considerably different from each other, as will be discussed later.

The ornithine molecule is characterized by two planar groups, one being the carboxyl group and the other the aliphatic side chain containing two amino

* Hahn (1957) deduced a value, 1·503 Å, as the average of C–NH_3^+ bonds in amino acids. However, this value is a little too high as was pointed out by Wright & Marsh (1962).

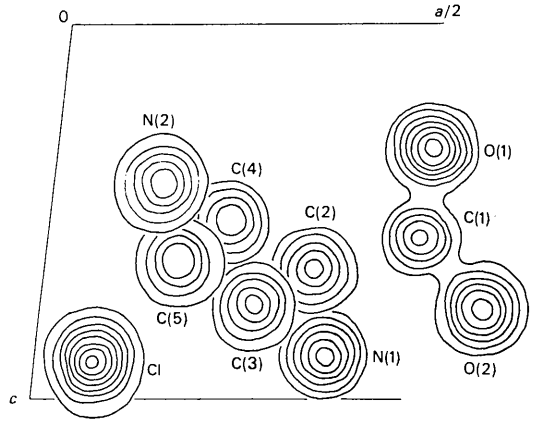

Fig. 1. A composite drawing of the final electron density map, viewed along the *b* axis. Contours are drawn at 2, 4, 6 e.Å^{-3} · · · for light atoms, and at 2, 6, 10 e.Å^{-3} · · · for the chlorine atom.

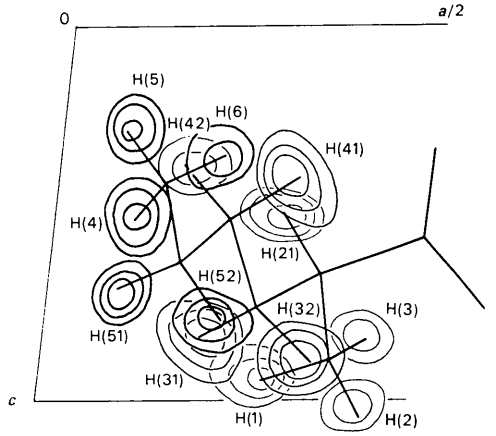

Fig. 2. A composite drawing of the final difference map, viewed along the *b* axis. Contours are at intervals of 0·1 e.Å^{-3}, beginning with the 0·3 e.Å^{-3} contour. The contributions of hydrogen atoms were omitted from the structure factor calculations.

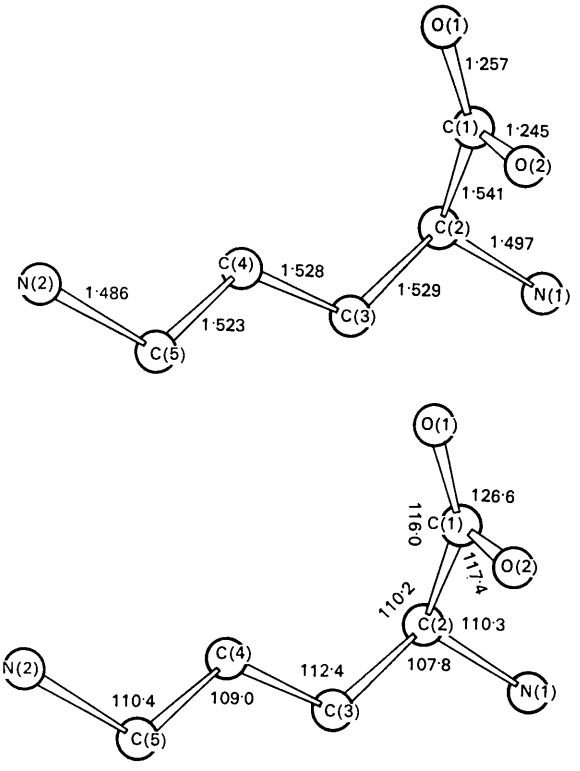

Fig. 3. Bond distances and angles.

nitrogen atoms. The equation of the least-squares plane of the carboxyl group and the C(2) atom is:

$$0{\cdot}3108X-0{\cdot}9465Y-0{\cdot}0873Z+2{\cdot}6638=0\,,$$

where the direction cosines are referred to the orthogonal axes a, b and c^*, and X, Y and Z are expressed in Å. The deviations of atoms from the plane are:

O(1) −0·006, O(2) −0·005, C(1)0·014, C(2) −0·004 Å.

The deviation, 0·838 Å, of the α-nitrogen atom N(1) from the plane is one of the biggest found in the amino acids so far investigated.† The aliphatic side chain with both the amino nitrogen atoms takes a fully extended planar configuration. The equation of the best plane is given by

$$-0{\cdot}8507X-0{\cdot}4631Y-0{\cdot}2486Z+5{\cdot}1839=0\,,$$

and the deviations of atoms from the plane are:

N(1)0·015, C(2) −0·061, C(3) −0·003,
C(4)0·106, C(5) −0·016, N(2) −0·038 Å.

The dihedral angle between the two planes is 78·7°.

† Hahn (1957) listed the values 1·18 Å in glutamine and 0·99 Å in β-glutamic acid. However, these values are in error and they were estimated as 0·35 and 0·82 Å respectively (Ashida, Sasada & Kakudo, 1967).

There are six independent hydrogen bonds in the crystal, and each nitrogen atom is the donor for three hydrogen bonds. Their dimensions are listed in Table 7. The angles of C–N–acceptor are significantly smaller than the regular tetrahedral angle, while those corresponding to C–H–N listed in Table 6 are all close to 109·5°. Thus each hydrogen atom participating in the hydrogen bond lies significantly out of the line joining the donor and the acceptor. Each nitrogen atom has another nearest neighbor at a distance corresponding to the hydrogen-bond distance, that is, N(1)–O(2) 2·943 Å and N(2)–Cl 3·278 Å. However, they cannot be hydrogen bonds in view of the positions of the hydrogen atoms and of the large angles of C(2)–N(1)–O(2) and C(5)–N(2)–Cl. These contacts may be due to electrostatic forces. The small angles of C–N–acceptor of all the hydrogen bonds may be due to the presence of such negatively charged atoms. The chloride ion accepts three hydrogen bonds and has one more close contact with N(2). The O(1) atom accepts two hydrogen bonds, while O(2) accepts only one and has another close contact with N(1). These six hydrogen bonds and two close electrostatic contacts make a three-dimensional network in the crystal; the packing in the crystal is shown in Figs. 4 and 5.

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

Bond		Angle	
C(1)–O(1)	1·257 ± 0·006 Å	O(1)–C(1)–O(2)	126·6 ± 0·4°
C(1)–O(2)	1·245 ± 0·006	O(1)–C(1)–C(2)	116·0 ± 0·4
		O(2)–C(1)–C(2)	117·4 ± 0·4
C(2)–N(1)	1·497 ± 0·006		
C(5)–N(2)	1·486 ± 0·006	C(1)–C(2)–N(1)	110·3 ± 0·3
		C(3)–C(2)–N(1)	107·8 ± 0·3
C(1)–C(2)	1·541 ± 0·006	C(4)–C(5)–N(2)	110·4 ± 0·4
C(2)–C(3)	1·529 ± 0·006		
C(3)–C(4)	1·528 ± 0·006	C(1)–C(2)–C(3)	110·2 ± 0·3
C(4)–C(5)	1·523 ± 0·006	C(2)–C(3)–C(4)	112·4 ± 0·4
		C(3)–C(4)–C(5)	109·0 ± 0·4

Table 6. *Bond lengths and angles involving the hydrogen atoms*

Bond	d(X–H)	Angle	$\binom{C}{N}$–X–H	Angle	(H–X–H)
N(1)–H(1)	1·00 Å	C(2)–N(1)–H(1)	110°	H(1)–N(1)–H(2)	107°
N(1)–H(2)	1·04	C(2)–N(1)–H(2)	107	H(2)–N(1)–H(3)	113
N(1)–H(3)	0·82	C(2)–N(1)–H(3)	107	H(3)–N(1)–H(1)	113
N(2)–H(4)	0·94	C(5)–N(2)–H(4)	101	H(4)–N(2)–H(5)	118
N(2)–H(5)	0·89	C(5)–N(2)–H(5)	110	H(5)–N(2)–H(6)	106
N(2)–H(6)	0·98	C(5)–N(2)–H(6)	111	H(6)–N(2)–H(4)	110
⟨N–H⟩	0·95				
C(2)–H(21)	1·01	N(1)–C(2)–H(21)	108	H(31)–C(3)–H(32)	110
C(3)–H(31)	1·01	C(1)–C(2)–H(21)	110	H(41)–C(4)–H(42)	103
C(3)–H(32)	1·13	C(3)–C(2)–H(21)	111	H(51)–C(5)–H(52)	110
C(4)–H(41)	1·13	C(2)–C(3)–H(31)	112		
C(4)–H(42)	1·10	C(2)–C(3)–H(32)	103	⟨e.s.d.⟩ = 5°	
C(5)–H(51)	0·96	C(4)–C(3)–H(31)	109		
C(5)–H(52)	0·99	C(4)–C(3)–H(32)	110		
		C(3)–C(4)–H(41)	112		
⟨C–H⟩	1·05	C(3)–C(4)–H(42)	110		
⟨e.s.d.⟩ = 0·07 Å		C(5)–C(4)–H(41)	112		
		C(5)–C(4)–H(42)	111		
		C(4)–C(5)–H(51)	109		
		C(4)–C(5)–H(52)	112		
		N(2)–C(5)–H(51)	109		
		N(2)–C(5)–H(52)	107		
		⟨e.s.d.⟩ = 3·5°			

Molecular configurations of three basic amino acids, ornithine, lysine and arginine

It is interesting to compare the molecular configurations of the three basic amino acids, ornithine, lysine and arginine, all having basic groups at the ends of the aliphatic side chains. Each aliphatic side chain in these amino acids so far reported has a fully extended planar configuration. The side chains of lysine residues in myoglobin have been reported also as having a similar configuration (Kendrew, 1962). Therefore, in these amino acids the planar-zigzag conformation of the aliphatic side chain seems to be generally the most stable form. The ornithine residues in ferrichrome-A (Zalkin, Forrester & Templeton, 1966) are not planar, but this case may be put aside in view of the large substituents on the terminal δ-N atoms.

The dihedral angles between the carboxyl groups and the side chains are 78·7, 71·4 and 74°, respectively, in ornithine hydrochloride, lysine hydrochloride dihydrate (Wright & Marsh, 1962) and arginine dihydrate (Karle & Karle, 1964). These dihedral angles are fairly close to each other. Moreover, the angles found in arginine hydrochloride monohydrate* and arginine hydrochloride* are about 70°. Thus some parts of these amino acids have several common features. Nevertheless, there is a substantial difference in their molecular conformations, as is shown in Fig. 6. The difference comes from the internal rotations of the C_α–C_β bonds‡.

* The data for these two crystals are taken from the review of Ramachandran, Mazumdar, Venkatesan & Lakshminarayanan (1966), because the original publications were not available.

Table 7. *Hydrogen-bond lengths and angles*

Donor	Acceptor	N···A	H···A	∠C–N···A	∠N–H···A	∠N–H···A	∠A···N···A	
C(2)–N(1)–H(1)···Cl*1		3·161 Å	2·22 Å	94·5°	156°	16°	Cl*1 —N–O(1)*2	113·2°
C(2)–N(1)–H(2)···O(1)*2		2·850	1·82	103·5	169	7	Cl*1 —N–O(1)*3	105·0
C(2)–N(1)–H(3)···O(1)*3		2·859	2·06	106·0	166	10	O(1)*2–N–O(1)*3	128·9
C(2)–N(1)·····O(2)*4		2·934		166·1				
C(5)–N(2)–H(4)···Cl*5		3·258	2·37	86·3	157	16	Cl*5 —N–Cl*6	123·9
C(5)–N(2)–H(5)···Cl*6		3·278	2·46	91·7	153	20	Cl*5 —N–O(2)*7	115·5
C(5)–N(2)–H(6)···O(2)*7		2·879	1·94	98·7	161	13	Cl*6 —N–O(2)*7	120·3
C(5)–N(2)·····Cl*8		3·278		173·8				

*1 x, y, z *2 $x, y, 1+z$ *3 $1-x, -\frac{1}{2}+y, 1-z$ *4 $1-x, -\frac{1}{2}+y, 2-z$
*5 $x, 1+y, z$ *6 $-x, \frac{1}{2}+y, 1-z$ *7 $1-x, \frac{1}{2}+y, 1-z$ *8 $x, 1+y, -1+z$

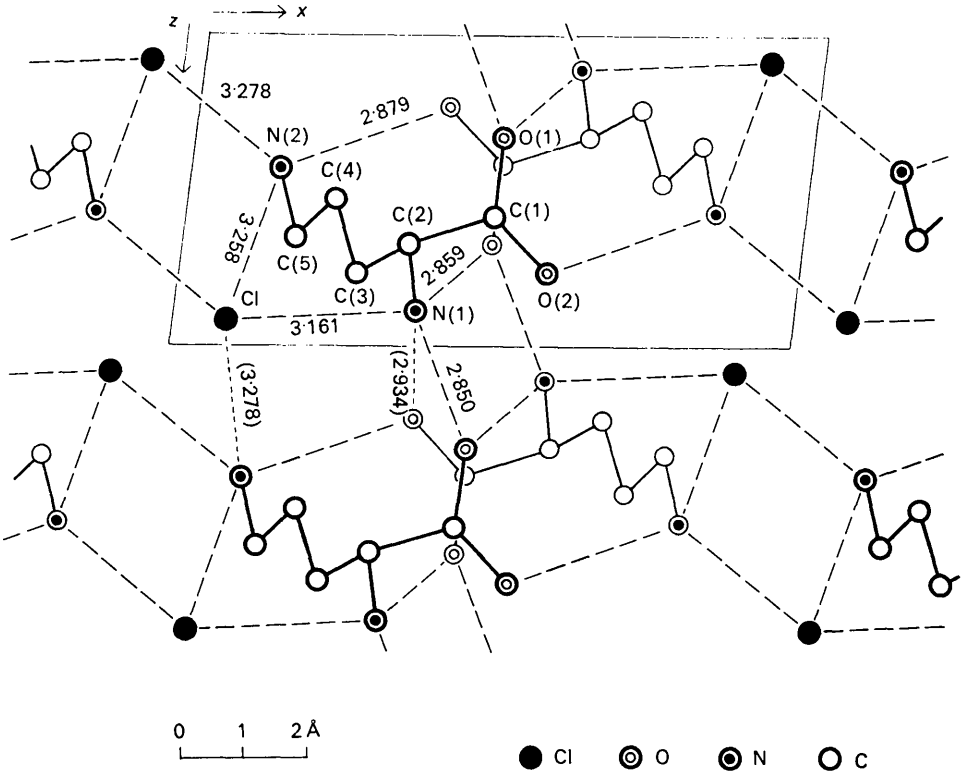

Fig. 4. The structure viewed along the *b* axis. Hydrogen bonds are shown by broken lines and other close contacts by dotted lines.

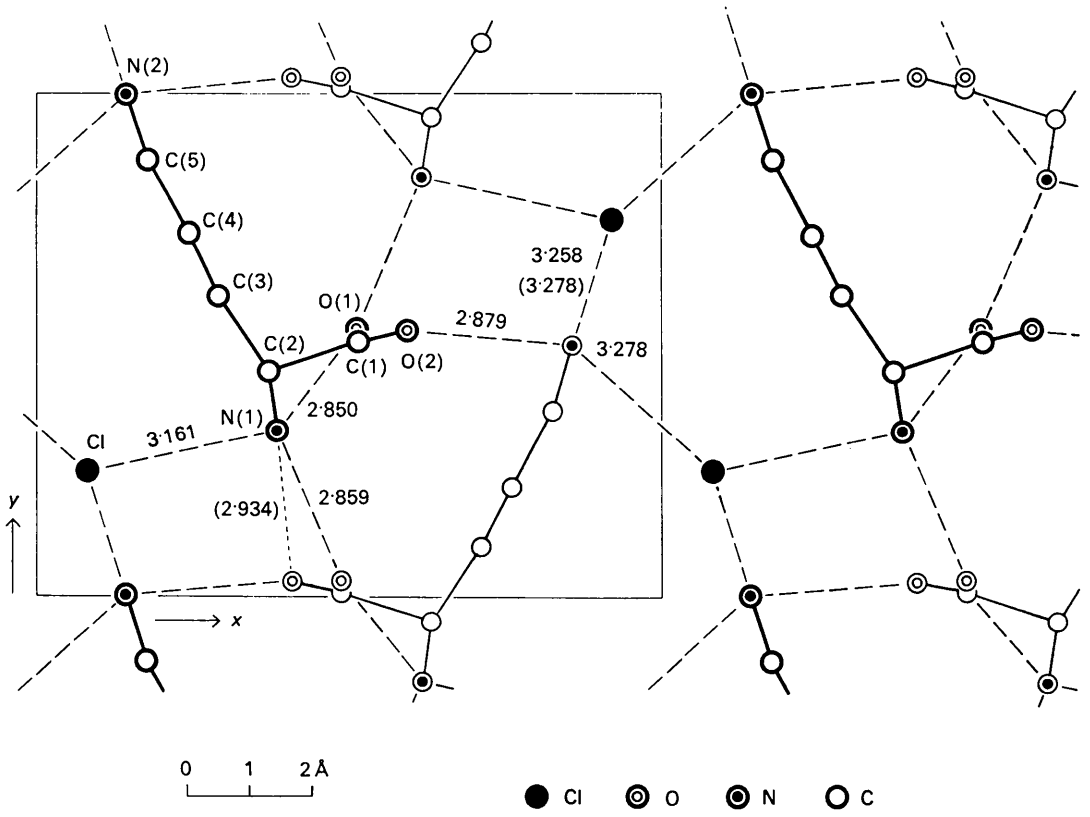

Fig. 5. The structure viweed along the *c* axis.

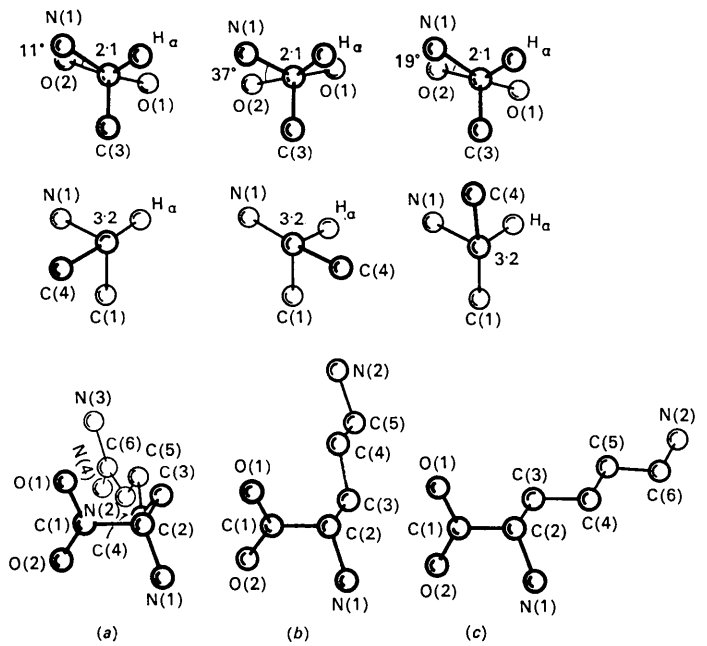

Fig. 6. A comparison of the molecular structure of (*a*) arginine in its dihydrate, (*b*) ornithine in the hydrochloride and (*c*) lysine in the hydrochloride dihydrate. Top to bottom; the nearest neighbors of C(2) and C(1) viewed down along the C(2)–C(1) bond; those of C(3) and C(2) viewed down along the C(3)–C(2) bond; and the molecules viewed down on the planes of C(1)–C(2)–N(1). (*a*) is after Ramachandran, Mazumdar, Venkatesan & Lakshminarayanan (1966), and the atomic coordinates for (*c*) are taken from Table 2 of Wright & Marsh (1962).

According to Ramachandran & Lakshminarayanan (1966), the γ atoms‡ in amino acids or peptides can occupy one of the three positions, (I), (II) and (III), as a result of the internal rotation of the C_α–C_β bond, where (I) is the *trans* position to the α-N atom, (II) is that to C′‡ and (III) is that to α-H. They found some systematic relations between the positions of the γ atoms and the properties of the relevant amino acids. In arginine the C_γ atoms occupy all three positions (Ramachandran, Mazumdar, Venkatesan & Lakshminarayanan, 1966). It may be of some significance to extend these considerations to ornithine and lysine. The C_γ atom of ornithine in the hydrochloride is on (I), while the C_γ atoms of the ornithine residues in ferrichrome-A occupy positions (II) and (III). Since lysine has a number of common characteristics with ornithine and arginine, it may be expected that all these amino acids in the crystals can take any of the three conformations according to the three positions of the C_γ atom. These conformations seem to depend on the intermolecular forces, especially on those due to hydrogen bonds. Although there are not enough examples, there seems to exist a simple relation between the molecular conformations and the other components in the crystals. In the hydrochlorides (ornithine.HCl and arginine.HCl), C_γ is on (I), and α-N is on the plane of the side chain; the deviation of the α-N atom from the plane of the carboxyl group is one of the biggest among the amino acids so far investigated. In the hydrate crystal (arginine.$2H_2O$) C_γ is on (III). In the crystals of hydrochloride hydrates (lysine.HCl.$2H_2O$ and arginine.HCl.(H_2O) C_γ is on II), and C′ is on the plane of the side chain.

‡ C′, C_α, C_β and C_γ are respectively C(1), C(2), C(3) and C(4) in the other paragraphs.

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Crystal and Molecular Structure of *N*-Salicylideneglycinatoaquocopper(II) Hemihydrate

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Crystals of *N*-salicylideneglycinatoaquocopper(II) hemihydrate, $[Cu(C_9H_7NO_3.H_2O)].\frac{1}{2}H_2O$, are monoclinic, space group $C2/c$, with eight formula units in the unit cell with dimensions $a=17{\cdot}16$, $b=6{\cdot}84$, $c=17{\cdot}57$ Å, $\beta=111{\cdot}29°$. A three-dimensional analysis has been performed, using a complete set of diffractometer data. The final R index for 1881 'observed' reflections is 0·069. The molecule is not planar. Rather, it consists of two planes, one formed by salicylaldiminatocopper groups and the other formed by glycinatocopper groups. The coordination of copper ion is square pyramidal and the distances of copper environment are: Cu–O 1·953, 1·928, Cu–N 1·949, Cu–OH_2 2·016 and Cu–O″ (the bond to the carboxyl oxygen of the adjacent molecule) 2·334 Å.

The molecules are bound together by hydrogen bonds, the coordination bond of copper ion to oxygen atoms in neighboring molecules, and unusually close intermolecular contacts.

Introduction

Some evidence suggested that the chelation of the Schiff bases to metal ions may play an important role in the nonenzymatic transamination reaction of the Schiff bases prepared from vitamin B_6 and amino acids. These bases are of much interest as model compounds for the transaminase enzymes (Metzler & Snell, 1952; Metzler, Ikawa & Snell, 1954; Longenecker & Snell, 1957; Metzler, Longenecker & Snell, 1954). It was recently proved that the coordination of copper ion with the Schiff base derived from salicylaldehyde and glycine results in stabilization of the double bond,

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