The Structure of L-Valine Hydrochloride

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The crystal structure of L-valine hydrochloride, $(CH_3)_2CHCH(NH_2)COOH \cdot HCl$, has been determined and refined by analysis of complete three-dimensional diffraction data from copper X-radiation. The crystals are monoclinic with space group $P2_1$; the unit-cell dimensions are $a = 10\cdot38$, $b = 7\cdot08$, $c = 5\cdot46$ Å, $\beta = 91\degree\ 30'$. Refinement of the positional parameters and the individual anisotropic temperature factors for the nine atoms was carried out by the method of least squares. The final R index for the observed reflexions of non-zero weight is $0\cdot13$.

The dimensions of the amino acid group are, in general, similar to those reported recently. There are some significant differences, however.

Introduction

Valine, $(CH_3)_2CHCH(NH_2)COOH$, is one of the amino acids essential for animal growth. The detailed crystal structure analysis of L-valine hydrochloride is one of a series of X-ray studies on the structure of amino acids undertaken at Madras. This paper reports the detailed investigation and the three-dimensional refinement of the positions of the atoms and the results obtained.

Experimental

Crystallization

L-Valine was dissolved in dilute hydrochloric acid and, by rapidly evaporating the solution in a desiccator, crystals of L-valine hydrochloride were obtained. Almost all the crystals were slightly elongated along [001]. The crystals were soft, unstable and highly hygroscopic. The freshly prepared crystals were immediately dried and sealed in Lindemann-glass capillaries. Crystals of L-valine hydrobromide also have similar properties, and, in fact, the two crystals are isomorphous (Table 1).

Table 1. *Crystallographic data for* L-*valine hydrohalides*
(λ Cu $K\alpha = 1\cdot5418$ Å)

L-Valine hydrochloride		L-Valine hydrobromide	
Space group $P2_1$		Space group $P2_1$	
Number of molecules per unit cell, $Z = 2$		Number of molecules per unit cell, $Z = 2$	
$a = 10\cdot38$ Å		$a = 10\cdot18$ Å	
$b = 7\cdot08$		$b = 7\cdot34$	
$c = 5\cdot46$		$c = 5\cdot55$	
$\beta = 91\degree 30'$		$\beta = 90\degree 15'$	
$V = 400\cdot8$ Å³		$V = 414\cdot4$ Å³	
ϱ obs $= 1\cdot28$ g.cm⁻³		ϱ obs $= 1\cdot56$ g.cm⁻³	
Molecular weight (calculated)	306	Molecular weight (calculated)	396
Molecular weight (observed)	308·8	Molecular weight (observed)	388·6

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Unit cell and space group

The unit-cell dimensions and other crystal data are given in Table 1. The values of a, b, c and β were obtained directly from measurements made on precession photographs. Standard deviations are less than $0\cdot01$ Å for cell edges and $0\cdot1\degree$ for β. A study of the Weissenberg and Buerger precession photographs of these crystals revealed that the compounds are isomorphous and the only observed absences were those for k odd in the $0k0$ reflexions. This information and the fact that the compounds are optically active indicated that they belong to the space group $P2_1$. The density was determined by the flotation method. It indicated that there are two molecules in the unit cell and that there is no water of hydration.

Intensity measurements

The intensity data were collected by the multiple-film equi-inclination Weissenberg technique and 690 reflexions out of a possible total of 950 in the Cu $K\alpha$ sphere were recorded (Table 2). To minimize any intensity measurement errors due to contraction and elongation of the higher level spots, the film cassette was shifted periodically. The intensities were estimated visually using a standard set of spots, and no absorption corrections were applied ($\mu r < 1$). The inter-layer scaling was carried out by collecting data by rotation of crystals about the c and b axes. The usual corrections were applied, and the data placed on an absolute scale by Wilson's method.

Determination of the structure

The positions of the Cl atoms were readily deduced from the Patterson projections along **b** and **c**. The structure of the isomorphous hydrobromide had been approximately solved earlier from the data for the two projections. Since the chlorine positions were close to the corresponding bromine positions in the hydrobromide, the coordinates of the other light atoms were taken to be the same as in the hydrobromide for a trial structure. A structure factor calculation gave $R_{h0l} =$

Table 2. *The observed and calculated structure factors*

FOBS = $10|F_o|$, FCAL = $10|F_c|$. Reflexions too weak to be recorded were given zero weight in the least-squares calculation and were omitted from the R index.

H	K	L	FOBS	FCAL
0	0	1	147	181
0	0	2	195	226
0	0	3	82	81
0	0	4	23	13
0	0	5	109	104
0	0	6	39	35
0	1	1	527	462
0	1	2	249	230
0	1	3	110	132
0	1	4	78	102
0	2	0	233	287
0	2	1	167	159
0	2	2	136	148
0	2	3	83	90
0	2	4	21	22
0	3	1	80	78
0	3	2	157	156
0	3	3	104	100
0	3	4	35	39
0	4	0	326	323
0	4	1	67	74
0	4	2	83	79
0	4	3	0	14
0	4	4	19	18
0	5	1	84	87
0	5	2	50	45
0	5	3	44	45
0	5	4	28	35
0	6	0	93	91
0	6	1	39	48
0	6	2	30	40
0	6	3	37	28
0	6	4	0	6
0	7	1	36	42
0	7	2	57	65
0	7	3	71	58
0	8	0	75	66
0	8	1	0	14
0	8	2	50	54
0	9	1	36	35
1	0	0	277	292
1	0	1	229	211
-1	0	1	0	21
1	0	2	132	128
-1	0	2	200	275
-1	0	3	81	104
1	0	3	91	117
-1	0	4	30	26
1	0	4	35	46
-1	0	5	54	59
1	0	5	17	27
-1	0	6	47	38
1	0	6	14	15
1	1	0	233	177
1	1	1	126	127
-1	1	1	157	218
-1	1	2	226	221
-1	1	2	174	185
-1	1	3	186	170
1	1	3	109	118
1	1	4	123	139
-1	1	4	15	18
1	2	0	179	195
-1	2	1	496	443
1	2	1	177	180
-1	2	2	70	72
1	2	2	148	151
-1	2	3	110	107
-1	2	3	72	60
1	2	4	66	44
-1	2	4	64	58
1	3	0	138	150
-1	3	1	130	125
-1	3	1	42	34
-1	3	2	76	99
1	3	2	186	187
-1	3	3	159	158
1	3	3	35	30
1	3	4	102	100
-1	3	4	0	14
1	4	0	160	157
-1	4	1	76	81
-1	4	1	139	143
-1	4	2	35	40
1	4	2	177	169
-1	4	3	124	96
-1	4	3	63	66
-1	4	4	28	31
-1	4	4	69	65
-1	5	0	64	60
-1	5	1	102	101
-1	5	1	58	67
-1	5	2	96	98
-1	5	2	147	149
-1	5	3	139	121
-1	5	3	0	3
-1	5	4	49	40
-1	5	4	74	84
1	6	0	38	28
1	6	1	125	122

H	K	L	FOBS	FCAL
-1	6	1	125	125
1	6	2	0	31
-1	6	2	0	11
1	6	3	52	54
1	6	3	63	50
1	6	4	26	36
-1	6	4	0	46
1	7	0	86	84
1	7	1	25	25
-1	7	1	0	16
1	7	2	41	49
-1	7	2	0	29
1	7	3	31	33
-1	7	3	63	54
1	8	0	40	34
-1	8	1	39	38
1	8	1	35	35
1	8	2	39	38
-1	8	2	31	34
1	9	0	19	20
1	9	1	28	7
-1	9	1	0	25
2	0	0	287	299
-2	0	1	134	179
2	0	1	343	352
-2	0	2	18	0
2	0	2	92	135
-2	0	3	57	43
2	0	3	65	69
2	0	4	56	59
-2	0	4	49	38
2	0	5	59	44
-2	0	5	91	37
2	0	6	56	46
-2	0	6	55	44
2	1	0	237	173
2	1	1	485	430
-2	1	1	111	101
2	1	2	281	255
-2	1	2	126	155
-2	1	2	90	68
2	1	3	147	142
2	1	4	48	41
-2	1	4	151	148
2	2	0	36	37
2	2	1	322	286
-2	2	1	370	369
-2	2	2	96	83
2	2	2	135	117
-2	2	3	156	133
2	2	3	83	71
2	2	4	56	52
-2	2	4	39	36
-2	3	0	36	70
2	3	1	180	183
-2	3	1	153	144
2	3	2	107	107
-2	3	2	116	122
-2	3	3	21	30
2	3	3	97	89
2	3	4	52	55
-2	3	4	90	101
2	4	0	67	63
-2	4	1	140	142
-2	4	1	85	83
-2	4	2	26	24
-2	4	2	0	9
-2	4	3	0	13
-2	4	3	0	18
-2	4	4	27	33
-2	4	4	41	36
2	5	0	88	92
2	5	1	97	97
-2	5	1	35	44
-2	5	2	116	129
-2	5	2	65	63
-2	5	3	58	50
2	5	3	53	45
2	5	4	39	36
-2	5	4	27	68
-2	6	1	54	48
-2	6	1	153	157
-2	6	1	129	130
-2	6	2	42	28
-2	6	2	0	38
-2	6	3	44	41
2	6	3	72	59
2	6	4	25	42
-2	6	4	0	24
2	7	0	84	84
2	7	1	29	27
2	7	1	27	36
-2	7	2	76	79
2	7	2	40	36
2	7	3	21	31
2	7	3	82	66
2	8	0	0	10
2	8	1	39	41
-2	8	1	64	58
-2	8	2	31	26

H	K	L	FOBS	FCAL
2	8	2	0	30
2	9	0	29	33
3	0	0	478	444
3	0	1	123	173
-3	0	1	70	34
3	0	2	70	73
-3	0	2	267	250
3	0	3	28	29
-3	0	3	15	27
3	0	4	87	84
-3	0	4	0	12
3	0	5	68	66
-3	0	5	44	46
3	0	6	49	42
-3	0	6	0	4
3	1	0	263	223
3	1	1	251	225
-3	1	1	279	245
3	1	2	26	40
-3	1	2	156	158
-3	1	3	56	49
3	1	3	153	155
3	1	4	40	34
-3	1	4	149	132
3	2	0	349	282
-3	2	1	144	125
3	2	1	148	172
3	2	2	68	77
-3	2	2	144	148
-3	2	3	165	143
3	2	3	44	33
3	2	4	66	58
-3	2	4	24	29
3	3	0	186	173
3	3	1	201	183
-3	3	1	147	130
3	3	2	33	20
-3	3	2	158	159
3	3	3	125	116
-3	3	3	19	31
3	3	4	113	113
3	4	0	228	208
-3	4	1	20	28
-3	4	1	80	90
3	4	2	66	71
-3	4	2	137	147
-3	4	3	58	56
-3	4	3	25	38
3	4	4	0	18
3	5	0	36	32
3	5	1	95	89
-3	5	1	65	70
3	5	2	78	76
3	5	2	72	67
3	5	3	75	69
3	5	3	27	35
-3	5	4	0	55
3	6	0	0	23
3	6	1	68	67
-3	6	1	43	52
-3	6	2	60	49
-3	6	2	0	50
-3	6	3	56	55
3	6	3	25	15
3	7	0	0	28
3	7	1	26	39
-3	7	1	0	12
-3	7	2	49	45
3	7	2	0	10
3	7	3	66	50
-3	7	3	0	31
3	8	0	29	34
3	8	1	0	5
-3	8	1	0	18
-3	8	2	41	40
3	8	2	0	34
3	9	0	0	5
-4	0	1	476	400
-4	0	1	20	26
4	0	1	27	36
4	0	2	28	21
-4	0	2	296	250
-4	0	3	105	101
4	0	3	155	145
4	0	4	33	38
4	0	4	0	10
4	0	5	24	31
-4	0	5	55	56
-4	0	5	28	28
4	0	6	0	3
4	1	0	95	78
-4	1	1	121	154
4	1	1	167	200
-4	1	2	68	72
4	1	2	191	221
4	1	3	50	46
-4	1	3	126	110

H	K	L	FOBS	FCAL
4	1	4	51	59
-4	1	4	54	41
4	2	0	205	204
4	2	1	65	67
4	2	1	0	24
-4	2	2	32	33
-4	2	2	0	22
4	2	3	57	57
4	2	3	62	55
-4	2	4	38	34
-4	2	4	19	15
-4	3	0	36	35
4	3	1	93	88
4	3	1	114	104
-4	3	2	121	109
-4	3	2	87	105
-4	3	3	56	53
-4	3	3	65	56
-4	3	4	40	38
-4	4	0	175	173
4	4	1	29	30
-4	4	1	64	77
-4	4	2	56	54
4	4	2	96	99
-4	4	3	98	83
-4	4	3	89	81
-4	4	4	28	40
4	4	4	39	16
4	5	0	53	48
4	5	1	40	57
-4	5	1	65	62
4	5	2	105	119
-4	5	3	0	11
-4	5	3	84	79
-4	5	3	0	27
-4	5	4	45	48
-4	5	4	0	18
-4	6	0	77	70
-4	6	1	54	57
-4	6	1	55	51
-4	6	2	0	18
-4	6	2	0	51
-4	6	3	24	26
-4	6	3	54	40
4	7	0	82	66
-4	7	1	40	54
-4	7	1	35	45
-4	7	2	43	49
-4	7	3	0	23
-4	7	3	18	19
-4	7	3	27	52
-4	8	0	66	59
4	8	1	29	36
-4	8	1	43	45
5	0	0	77	67
5	0	1	137	138
-5	0	1	83	112
5	0	2	66	71
-5	0	3	63	75
-5	0	3	65	53
5	0	3	0	20
-5	0	3	26	31
-5	0	4	17	22
5	0	5	16	19
-5	0	5	0	2
-5	0	6	40	34
5	0	6	22	19
-5	1	0	111	118
5	1	1	78	73
-5	1	1	149	154
5	1	2	65	65
5	1	2	120	140
5	1	3	27	26
5	1	3	115	103
5	1	4	38	38
5	1	4	65	62
5	2	0	29	18
5	2	1	58	62
-5	2	1	241	246
5	2	2	49	41
-5	2	2	87	90
-5	2	3	124	116
5	2	3	54	49
5	2	4	19	22
5	2	4	74	56
5	3	0	82	97
5	3	1	114	118
-5	3	1	109	105
-5	3	2	94	95
-5	3	3	126	132
-5	3	3	105	105
5	3	3	72	61
5	3	4	28	33
5	4	0	49	56
-5	4	1	114	109
5	4	1	145	141
5	4	2	41	27
-5	4	2	88	86

H	K	L	FOBS	FCAL
-5	4	3	58	64
5	4	3	32	38
-5	4	4	58	60
5	4	4	37	39
5	5	0	105	104
5	5	1	27	37
-5	5	1	0	20
-5	5	2	0	50
5	5	3	36	29
5	5	4	25	35
-5	5	4	0	27
5	6	0	38	24
-5	6	1	93	97
5	6	2	0	30
5	6	2	0	16
5	6	3	39	35
-5	6	3	0	34
5	7	0	48	36
-5	7	1	32	34
5	7	1	0	2
-5	7	2	37	38
5	7	2	0	23
5	7	3	33	31
-5	7	3	55	21
5	8	0	29	29
5	8	1	26	20
6	0	0	97	74
-6	0	1	70	87
-6	0	1	156	166
-6	0	2	141	148
6	0	2	37	58
-6	0	3	84	90
-6	0	3	58	57
6	0	4	70	71
-6	0	4	0	8
6	0	5	27	25
-6	0	5	45	49
-6	0	6	28	16
6	1	0	0	18
6	1	0	15	34
6	1	1	70	84
-6	1	1	79	81
6	1	1	164	161
-6	1	2	85	77
6	1	2	37	65
6	1	3	94	88
-6	1	3	20	21
6	1	4	28	26
-6	2	0	132	121
6	2	0	153	146
6	2	1	167	156
-6	2	2	96	87
-6	2	2	60	68
-6	2	3	0	12
6	2	3	63	75
6	2	4	50	43
6	2	4	0	18
-6	3	0	49	51
6	3	1	50	41
-6	3	1	118	123
-6	3	2	65	68
-6	3	2	64	76
-6	3	3	64	61
-6	3	4	80	87
6	3	4	0	2
6	4	0	0	9
-6	4	1	69	72
-6	4	1	43	50
-6	4	2	42	46
6	4	3	0	33
-6	4	3	26	25
6	4	3	0	18
6	5	0	39	36
6	5	1	34	34
-6	5	1	27	33
-6	5	2	29	21
-6	5	2	60	39
-6	5	3	55	41
-6	5	3	0	31
-6	6	0	74	49
-6	6	1	31	33
-6	6	2	55	44
-6	6	2	0	42
6	6	3	41	42
6	6	3	0	10
6	7	0	30	18
-6	7	1	51	62
-6	7	2	35	31
-6	7	2	0	5
-6	7	3	32	33
-6	7	3	0	12
6	8	0	21	23

H	K	L	FOBS	FCAL
6	8	1	0	15
7	0	0	98	94
7	0	1	31	26
7	0	1	0	9
7	0	2	37	37
7	0	2	62	65
7	0	3	26	31
-7	0	3	0	5
7	0	4	26	35
-7	0	4	0	3
7	0	5	24	26
-7	0	5	0	0
7	1	0	34	31
7	1	1	59	66
7	1	1	0	9
-7	1	1	69	75
7	1	2	41	50
-7	1	2	63	55
7	1	3	55	53
-7	1	3	41	38
7	1	4	28	31
-7	1	4	0	13
7	2	0	141	129
-7	2	1	41	44
7	2	1	42	50
-7	2	2	120	132
7	2	2	0	24
7	2	3	62	54
-7	2	3	0	19
7	3	0	70	65
-7	3	1	135	124
7	3	1	45	53
7	3	2	74	72
-7	3	2	52	54
7	3	3	26	29
-7	3	3	32	43
7	3	4	27	34
7	3	4	0	26
-7	4	0	112	88
-7	4	1	28	44
7	4	1	70	73
-7	4	2	96	88
7	4	2	0	28
7	4	3	50	51
7	4	3	0	31
7	5	0	66	77
-7	5	1	40	43
7	5	1	27	52
7	5	2	40	46
-7	5	2	0	14
7	5	3	22	20
-7	5	3	43	43
7	6	0	75	58
-7	6	1	22	17
7	6	2	46	51
-7	6	2	0	14
7	7	0	0	14
7	7	1	32	41
-7	7	1	0	42
-7	8	1	0	19
7	8	1	0	8
8	0	0	52	31
8	0	1	56	65
-8	0	1	110	115
8	0	2	59	55
8	0	2	17	28
8	0	3	58	53
8	0	3	119	105
8	0	4	28	37
8	0	4	23	21
8	0	5	0	9
-8	1	1	68	67
8	1	1	37	39
-8	1	1	42	41
-8	1	2	89	77
8	1	2	0	93
-8	1	3	68	66
8	1	3	0	17
8	1	4	38	38
-8	1	4	0	12
8	2	0	38	20
8	2	1	31	37
8	2	1	34	42
-8	2	2	0	42
8	2	2	0	43
8	2	3	31	33
-8	2	3	53	64
8	3	0	55	46
8	3	1	42	42
-8	3	1	25	16
-8	3	3	51	56
-8	3	3	35	36
-8	3	4	19	27
8	3	4	0	19
-8	4	0	67	61
8	4	1	60	58
-8	4	1	51	49
8	4	2	51	49
-8	4	3	51	49
-8	4	3	60	49

H	K	L	FOBS	FCAL
8	5	0	60	43
8	5	1	49	23
-8	5	1	0	33
-8	5	3	31	34
8	5	3	0	4
8	6	0	30	23
8	6	1	19	20
-8	6	1	0	28
-8	7	1	20	16
8	7	1	0	6
9	0	0	0	9
-9	0	1	82	84
-9	0	2	23	26
-9	0	2	0	2
9	0	3	44	38
-9	0	3	0	1
-9	0	4	24	30
-9	0	4	0	7
-9	1	1	27	21
9	1	1	0	60
-9	1	3	25	23
-9	1	4	20	39
9	1	4	0	4
9	2	0	67	54
-9	2	1	42	47
-9	2	1	72	72
9	2	2	0	48
-9	2	2	0	13
-9	2	3	34	37
9	3	0	54	42
9	3	1	48	64
-9	3	1	32	31
-9	3	3	23	28
9	3	3	35	34
-9	3	4	37	41
9	4	0	0	13
9	4	1	36	26
-9	4	1	22	29
-9	4	2	37	13
-9	4	3	51	45
-9	5	0	0	17
-9	5	1	0	10
-9	5	3	0	16
-9	6	1	25	23
-9	6	1	0	8
9	7	1	0	17
-9	7	1	0	3
10	0	0	38	12
10	0	1	11	22
-10	0	1	0	8
10	0	3	29	32
-10	0	3	0	19
-10	1	0	0	10
10	1	0	38	50
10	1	1	0	31
10	2	0	51	48
10	3	0	28	27
-10	3	3	0	14
-10	4	1	28	31
10	5	1	28	33
10	5	1	25	30
10	0	0	35	33
-11	0	1	30	33
-11	0	1	0	20
-11	0	3	17	24
-11	0	3	0	25
-11	1	0	39	29
-11	1	1	23	24
-11	1	1	0	17
11	3	0	47	35
11	4	0	29	22
12	0	0	28	20
-12	0	1	13	21
-12	1	0	18	36
12	1	0	45	30
12	1	1	20	19
12	3	0	33	24
13	1	0	28	23

0·34 and $R_{hk0} = 0·21$, indicating that the structure proposed was reasonable, After nine cycles of least-squares refinement the R value, taking both the $hk0$ and $h0l$ reflexions together, dropped to 0·15 ($F_{obs} = 0$ not included).

The structure, now essentially determined, was refined by a series of least-squares analyses of the 3-D data. Six cycles of three-dimensional least-squares refinement with individual isotropic temperature factors were carried out on an IBM 7090. The final R values for all the observed reflexions fell to 0·16. Another five cycles of refinement, with individual anisotropic temperature factors and the block-diagonal matrix approximation, reduced R to 0·13 ($F_{obs} = 0$ not included). A $1/f$ weighting with f corresponding to the scattering factor of the nitrogen atom was adopted in the final stages of the least-squares analysis. This weighting is approximately equivalent to the differential synthesis weighting and was adopted for convenience. Atomic scattering factors were those reported in *International Tables for X-ray Crystallography* (1962). None of the shifts in the final cycle were greater than one-quarter of the standard deviation, and refinement was considered to be complete. A difference electron density map was calculated, but it was not possible to fix the positions of the hydrogen atoms with certainty. The final atomic and thermal parameters are those of the final least-squares cycle and are given in Table 3. The averages of the estimated accuracies of the bond distances and angles are 0·020 Å for C–C bonds, 0·018 Å for C–N bonds, 0·017 Å for C–O bonds, and 1°30′ for the bond angles. The maximum mean square amplitudes of thermal motion of the various atoms range from 0·149 Å² for C(3) to 0·067 Å² for Cl; the minimum amplitudes range from 0·038 Å² for C(2) to 0·013 Å² for C(4). Any detailed explanation of magnitudes and orientations of the thermal ellipsoids in terms of the structure is not obvious.

Discussion

Intramolecular features

The bond lengths and angles for the valine molecule are illustrated in Figs. 1 and 2. The C–C bonds are normal with lengths ranging between 1·501 Å and
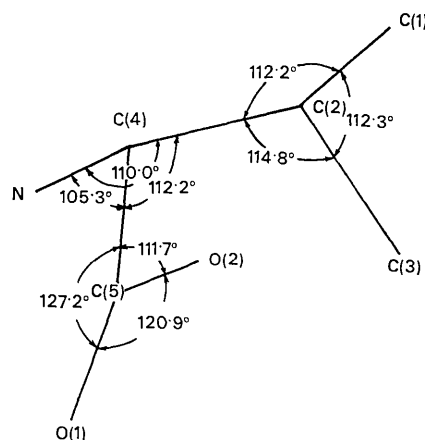
Fig. 2. The bond angles as observed in the valine molecule.
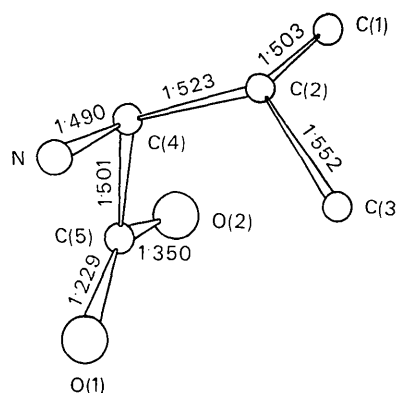
Fig. 1. The bond distances as observed in the valine molecule.

Table 3. *Final atomic and thermal parameters and the average estimated accuracy of the coordinates*

Temperature factor $= \exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$\sigma(x)$*
Cl	0·149	0·750	0·283	0·011	0·016	0·039	−0·002	0·005	0·012	0·003 Å
O(1)	0·118	0·234	1·120	0·016	0·015	0·033	−0·002	0·005	0·017	0·014
O(2)	0·229	0·028	0·895	0·015	0·015	0·065	0·003	0·017	0·001	0·011
N	0·109	0·495	0·764	0·014	0·011	0·052	0·007	0·003	0·027	0·014
C(1)	0·409	0·228	0·572	0·012	0·025	0·049	−0·012	0·016	0·019	0·012
C(2)	0·331	0·384	0·683	0·008	0·019	0·044	0·004	−0·003	−0·002	0·011
C(3)	0·398	0·470	0·914	0·006	0·047	0·056	−0·006	0·002	0·044	0·009
C(4)	0·191	0·327	0·715	0·012	0·017	0·041	−0·015	0·002	0·026	0·009
C(5)	0·175	0·199	0·930	0·010	0·013	0·021	−0·005	−0·001	0·011	0·011

* Averaged over the x, y, z coordinates.

Table 4. *Hydrogen bond distances and angles*

NH--Cl	3·222 Å	Cl----N--Cl′	111·5°	C(5)—O(2)--Cl′	129·0°
NH--Cl′	3·379	Cl----N--Cl″	111·3	C(4)—N--Cl	102·4
NH--Cl″	3·200	Cl′---N--Cl″	116·1	C(4)—N--Cl′	121·2
NH—O(1″)	2·990	O(1″)--N--Cl	88·5	C(4)—N--Cl″	91·9
O(2)H---Cl′	3·027	O(1″)--N--Cl′	66·4	C(4)—N--O(1)″	161·5
		O(1″)--N--Cl″	69·9	C(5)—O(1)--N″	117·3
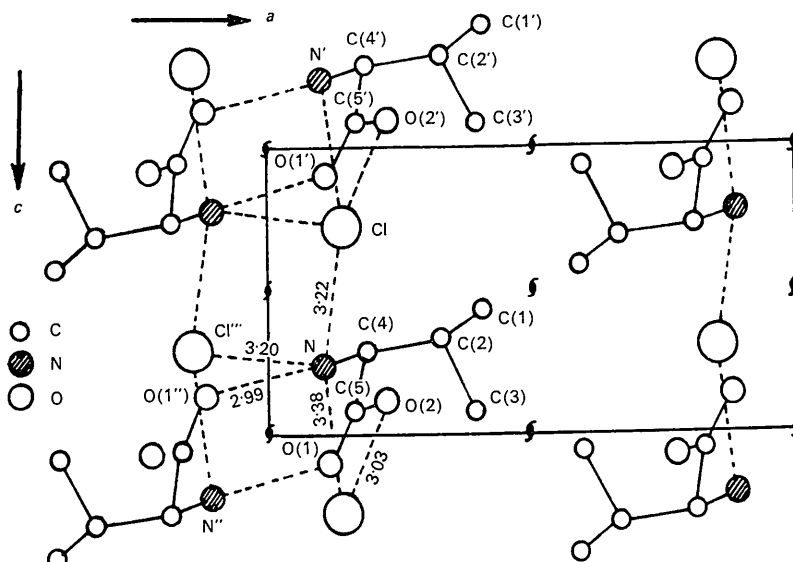
Fig. 3. The intermolecular packing arrangement. The hydrogen bonds are indicated by dashed lines.
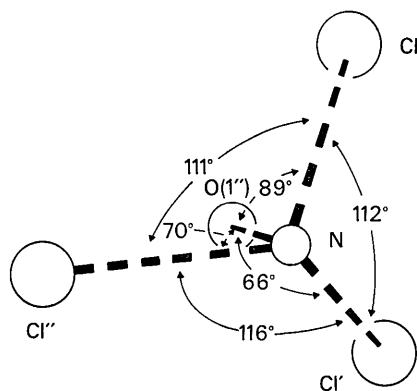
Fig. 4. The environment of the nitrogen atom viewed along the C(4)–N bond. The deviation of O(1″) from the plane passing through C(4), N and Cl″ is exaggerated in the Figure.

1·552 Å and averaging 1·520 Å. The C–Ĉ–C angles are also normal and range between 111° and 114°. The bond distance between C(4) and N is 1·490 Å.

The dimensions of the amino acid group are, in general, similar to those reported recently. The two C–O bond lengths are not equal [C(5)–O(1) = 1·229 Å, C(5)–O(2) = 1·350 Å], and the difference is quite significant. The carboxyl group in valine hydrochloride is closely similar to the un-ionized carboxyl group (–COOH) (Nardelli, Fava & Giraldi, 1962).

The atoms O(1), O(2), C(4), and C(5) are closely coplanar and all lie within 0·003 Å of the plane $0.8515X + 0.3412Y + 0.3982Z = 4.005$ Å where the coefficients are the direction cosines relative to a, b, and c*. The deviations of the individual atoms from the plane are −0·001 Å for O(1), O(2) and C(4) and 0·003 Å for C(5). The N atom lies 0·210 Å out of this plane; some values exceeding 0·20 Å in other cases are: 0·446 Å in

lysine (Wright & Marsh, 1962), 0·31 Å in α-glycine (Marsh, 1958), 0·280 Å in arginine (Karle & Karle, 1964).

Intermolecular features and hydrogen bonds

The structure projected on (010) is shown in Fig. 3. The hydrogen bonds are shown by dashed lines. The hydrogen bond distances and angles are listed in Table 4.

There are four hydrogen atoms in the molecule of L-valine hydrochloride which can be expected to take part in hydrogen bond formation. The nitrogen is at hydrogen bonding distances from four atoms – three chloride ions (Cl, Cl′ and Cl″) and one oxygen atom, O(1″). It forms two normal hydrogen bonds, one to Cl and another to Cl′, which would orient the third proton in a direction approximately half-way between the other two atoms Cl″ and O(1″). The distance NH···O(1″) (2·985 Å) is slightly longer than the normal distance of 2·9 Å for the NH···O bond. Such long bonds have been often found in various structures, however. Some examples from the recent literature (1963–64) are: 2·97 Å in cytosine monohydrate (Jeffrey & Kinoshita, 1963); 2·99 Å, 3·01 Å in urea (Caron & Donohue, 1964); 2·97 Å in glycylglycylglycine copper(II) chloride sesquihydrate (Freeman, Robinson & Schoone, 1964); 3·01, 3·03, 3·04, 3·08 Å in bisethylenediaminecopper(II) nitrate (Komiyama & Lingafelter, 1964). Thus, the third hydrogen bond from the nitrogen seems to be a 'bifurcated hydrogen bond'. A similar hydrogen bond has been proposed in the case of L-lysine monohydrochloride dihydrate by Wright & Marsh (1962). The environment of the nitrogen atom is shown in Fig. 4.

The Cl ion, in addition to being hydrogen bonded to the three nitrogen atoms (N, N′, N″), is also at a distance of 3·028 Å from O(2′) which is of the right

order for hydrogen bond formation. This Cl–O(2') distance is shorter than the normal value of 3·2 Å and indicates that the bond is comparatively strong. The non-bonding interatomic distances less than 4 Å are Cl–C(2), 3·867 Å; Cl–C(3)', 3·837 Å; Cl–C(4'), 3·572 Å; and Cl–C(5'), 3·563 Å. The observed distances are all larger than the sum of the radii of the corresponding atoms. It is seen from Fig.3 that the molecules are packed in such a way that the non-polar groups face each other across planes and similarly for the polar groups.

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The Crystal Structure of CeFe7, PrFe7, NdFe7, and SmFe7*

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The isostructural phases $CeFe_7$, $PrFe_7$, $NdFe_7$, and $SmFe_7$ are rhombohedral; the probable space group is $R\bar{3}m$. The lattice constants for the triply primitive hexagonal unit cells are:

	a	c	c/a
$CeFe_7$	$8\cdot488 \pm 0\cdot003$ Å	$12\cdot402 \pm 0\cdot007$ Å	$1\cdot461$
$PrFe_7$	$8\cdot582 \pm 0\cdot003$	$12\cdot462 \pm 0\cdot007$	$1\cdot452$
$NdFe_7$	$8\cdot578 \pm 0\cdot003$	$12\cdot462 \pm 0\cdot007$	$1\cdot453$
$SmFe_{17}$	$8\cdot554 \pm 0\cdot003$	$12\cdot441 \pm 0\cdot007$	$1\cdot454$

The hexagonal unit cells contain seven rare earth and forty-nine iron atoms. The atomic arrangements are intermediate between those of the $D2_d$-$CaCu_5$ and Th_2Zn_{17} structural types. A statistical occupancy of one set of positions has been proposed to account for the observed rhombohedral symmetry.

Introduction

Nassau, Cherry & Wallace (1960) have reported a phase corresponding to the formula $CeFe_5$ as having the $D2_d$-$CaCu_5$ structure. Jepson & Duwez (1955) also reported $CeFe_5$ but observed that only 32 of 39 lines on their powder pattern could be accounted for by the $CaCu_5$ structure and that the intensity match was poor. Zarechnyuk & Kripyakevich (1963) reported the phase Ce_2Fe_{17} ($a = 8\cdot47$, $c = 12\cdot41$ Å) to be isostructural with Th_2Zn_{17} (Markarov & Vinogradov, 1956). Kripyakevich, Terekhova, Zarechnyuk & Burov (1963) reported

a Nd–Fe phase, in equilibrium with α-Fe, to be isostructural with Th_2Zn_{17}. Savitskii, Terekhova, Burov, Naumkin & Markova (1965) have indicated that this Nd–Fe phase corresponds to the composition Nd_2Fe_{17} ($a = 8\cdot59$, $c = 12\cdot47$ Å). Kripyakevich & Frankevich (1966) have recently reported the phase Pr_2Fe_{17} ($a = 8\cdot58$, $c = 12\cdot47$ Å) to have the Th_2Zn_{17} structure.

Ray, Strnat & Feldmann (1964) have reported the preparation and magnetic properties of isostructural intermediate phases having the approximate compositions RFe_7 (R = Ce, Pr, Nd). They have shown these RFe_7 phases to form peritectically and that each represents the most iron-rich intermediate phase existing in its alloy system. The powder X-ray diffraction patterns of the RFe_7 phases have been indexed on the