Acta Cryst. (1969). B**25**, 2317

The Crystal Structure of $CaCl_2$.glycylglycylglycine.$3H_2O$*

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(*Received* 12 *December* 1968)

The crystal structure of $CaCl_2$(glycylglycylglycine).$3H_2O$ has been determined and refined by three-dimensional least-squares techniques based on 2327 intensities measured on a diffractometer. The crystals are triclinic, space group $P\bar{1}$, with $a=6{\cdot}961$, $b=8{\cdot}558$, $c=12{\cdot}115$ Å, $\alpha=85{\cdot}82°$, $\beta=91{\cdot}49°$ and $\gamma=94{\cdot}28°$. The final R value for 2327 reflections is 0·114; the standard deviations are about 0·01 Å for the positions of the C, N and O atoms. The tripeptide molecule is in the form of the zwitterion. The Ca^{2+} ion is bonded to seven oxygen atoms from four different peptide molecules and two water molecules which form an approximate pentagonal bipyramid. Each Cl^- ion accepts hydrogen bonds from two water molecules, from an amide NH group of one peptide molecule and from the terminal NH_3^+ group of another peptide molecule. The peptide molecules are held together by means of this complex hydrogen-bond network which makes use of all the available hydrogen atoms for hydrogen bonding, and by means of the bonding of the Ca^{2+} ion to the oxygen atoms of different peptide molecules. There is no hydrogen bonding between the peptide molecules themselves.

Introduction

The determination of the structure of $CaCl_2$(glycylglycylglycine).$3H_2O$ was undertaken as a part of an overall program for studying the influence of metal ions on the conformation of peptides. This study is being carried out primarily on compounds which have been crystallized from neutral solutions. The Ca complex was of particular interest for it afforded an opportunity to study interactions between a non-transition metal and a peptide.

Experimental

Crystals of $CaCl_2$(glycylglycylglycine).$3H_2O$ were obtained by evaporation of an aqueous solution containing equimolar amounts of glycylglycylglycine (ggg) and $CaCl_2$. This compound was first prepared by Pfeiffer (1927). The crystals grown in this manner were almost invariably twinned; however, it was found that crystals with only a small percentage of twinning could be obtained by adding a large excess of $CaCl_2$ to the solution before evaporation. Colorless rectangular crystalline plates belonging to the triclinic system were obtained in this manner. The plate face was chosen as the (001) plane. Cell dimensions determined at 22° C by least-squares analysis were calculated to be $a=6{\cdot}961\pm0{\cdot}002$, $b=8{\cdot}558\pm0{\cdot}002$, $c=12{\cdot}115\pm0{\cdot}003$ Å, $\alpha=85{\cdot}82\pm0{\cdot}03°$ $\beta=91{\cdot}49\pm0{\cdot}02°$ and $\gamma=94{\cdot}28\pm0{\cdot}04°$ (λ(Cu $K\alpha$) = 1·5418 Å). The F.W. for $CaCl_2$(ggg).$3H_2O$ is 354·22, yielding $\varrho_c=1{\cdot}64$ g.cm^{-3}; the observed density measured by flotation is $\varrho_o=1{\cdot}63$ g.cm^{-3}. There are two formula units in the unit cell. The space group was assumed to be the centric $P\bar{1}$ and, indeed, this was demonstrated by $N(z)$ test (Howells, Phillips & Rogers, 1950) from all of the data (Willoughby, 1968). The Delaunay reduced cell has dimensions $a'=10{\cdot}622$, $b'=14{\cdot}315$, $c'=12{\cdot}115$ Å, $\alpha'=143{\cdot}40°$, $\beta'=92{\cdot}39°$ and $\gamma'=114{\cdot}66°$ and can be obtained by the transformation matrix $S=\begin{pmatrix}1 & 1 & 0\\ 0 & -1 & 1\\ 0 & 0 & -1\end{pmatrix}$. The angle α' especially is awkward and it was therefore decided to use the former cell.

Four different crystals were used in obtaining the intensity data. The crystals were thin rectangular plates with largest dimensions ranging from 0·1 mm to 0·4 mm. The integrated intensites were taken on a General Electric XRD–5 diffractometer unit equipped with a single-crystal orienter, a scintillation counter and a pulse-height analyzer, using the θ–2θ scan method and Ni-filtered Cu $K\alpha$ radiation. A total of 2327 reflections were measured below a 2θ-value of 145°. This represents all of the reflections within a 2θ-limit of 110° and approximately one-third of the reflections between 110° and 145°. Of the 2327 reflections, 346 did not show a peak on the recorder while scanning through their diffraction position. The intensities recorded for these unobserved reflections was a fraction of the background intensity measured at the location of the reflection. Lorentz, polarization and absorption corrections ($\mu=73{\cdot}8$ cm^{-1}) were applied to the data.

Structure determination

The sharpened Patterson synthesis could be interpreted for three different sets of positions for the Ca and two Cl ions. For one set of positions the Patterson map was further interpreted yielding the positions of 6 oxygen atoms surrounding the Ca ion at distances ranging from 2·2 to 2·6 Å (Willoughby, 1968). Structure-factor calculations were made and the first Fourier synthesis using the signs of the structure factors determined by the Ca, two Cl and six oxygen atoms yielded the locations of all other atoms present in the structure.

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* Research supported by Grant G.M. 10514 from the National Institutes of Health.

The first structure-factor calculation with all atoms given isotropic temperature factors resulted in an $R\left(=\frac{\Sigma\,||KF_o|-|F_c||}{\Sigma\,|KF_o|}\right)$ of 0·24. Structure-factor least-squares cycles with isotropic temperature factors for all atoms reduced the R value to 0·18. At this point the Ca, 2 Cl and 7 O atoms were given anisotropic temperature factors and the structure was further refined by block-diagonal least-squares computations to an R value of 0·13. Refining the structure further with all atoms given anisotropic temperature factors did not significantly lower the R value.

At this point the observed structure factor amplitudes were corrected for anomalous dispersion (Patterson, 1963). The positions of the hydrogen atoms were calculated. This calculation was possible for all hydrogen atoms either from the geometry of the molecule or from the predicted hydrogen-bonding scheme (See *Discussion of the structure*). A difference Fourier synthesis was then calculated showing peaks at 11 of the 17 positions calculated for the hydrogen atoms. The 11 hydrogen atoms were included in the subsequent structure-factor calculations but their parameters were not refined. The positional and anisotropic thermal parameters of the calcium, chlorine, carbon, oxygen and nitrogen atoms were further refined by block-diagonal least-squares methods until the parameter shifts for the coordinates were less than 1/15 σ, and for the temperature factors less than 1/5 σ, in which σ is the calculated standard deviation. A second difference map was then calculated based on a structure-factor calculation which did not include the hydrogen atom contributions. The 11 hydrogen atoms which had been found in the first difference map were relocated but the remaining 6 hydrogen atoms still could not be located. Peak heights and parameters of the 11 hydrogen atoms still could not be located. Peak heights and parameters of the 11 hydrogen atoms are given in Table 4. The maximum spurious peaks in the difference map were +0·7 and −1·2 e.Å^{-3}. The map did not indicate any significant coordinate shifts for the non-hydrogen atoms. The quantity minimized in the least-squares calculations was $\Sigma w(|KF_o|-|F_c|)^2$. The final weighting scheme used was $\sqrt{w}=|KF_o|/P$ if $|KF_o|\le P$ and $\sqrt{w}=P/|KF_o|$ if $|KF_o|>P$ (P=15·0 electrons). The final positional and thermal parameters and their estimated standard deviations, as calculated from the inverse of the least-squares matrix, for all atoms except hydrogens are given in Tables 1 and 2. The final R value for all data is 0·114. The principal axes of the thermal ellipsoids were determined and the magnitudes together with their direction cosines with respect to the cell edges are listed in Table 5. A list of calculated and observed structure factors is given in Table 3. The SFLS program used was written by Ahmed (1966). A

Table 1. *Final atomic positions*

Standard deviations are given in parentheses.

	x	y	z
Ca	0·4161 (3)	0·1418 (2)	0·8719 (2)
Cl(1)	0·2934 (6)	0·2057 (4)	0·4999 (3)
Cl(2)	0·1767 (4)	0·6669 (3)	0·6824 (2)
N(1)	0·2571 (17)	0·7706 (11)	0·4327 (8)
$C^{\alpha}(1)$	0·2246 (17)	0·6079 (12)	0·4045 (8)
$C'(1)$	0·3008 (14)	0·5888 (12)	0·2894 (8)
O(1)	0·3333 (11)	0·7001 (8)	0·2241 (6)
N(2)	0·3234 (12)	0·4398 (9)	0·2684 (6)
$C^{\alpha}(2)$	0·3950 (14)	0·4003 (11)	0·1667 (9)
$C'(2)$	0·2577 (13)	0·3450 (10)	0·0771 (8)
O(2)	0·3178 (10)	0·3192 (8)	−0·0119 (5)
N(3)	0·0675 (12)	0·3267 (8)	0·0986 (6)
$C^{\alpha}(3)$	−0·0785 (15)	0·2821 (12)	0·0214 (8)
$C'(3)$	−0·1744 (15)	0·1192 (11)	0·0458 (7)
O(3)	−0·3273 (10)	0·0854 (8)	−0·0074 (6)
O(4)	−0·1130 (10)	0·0258 (8)	0·1196 (5)
O*w*(1)	0·1382 (11)	0·0315 (9)	0·2930 (7)
O*w*(2)	0·2315 (13)	0·2939 (9)	0·7392 (6)
O*w*(3)	0·5307 (13)	0·0367 (9)	0·2592 (7)

Table 2. *Final anisotropic thermal parameters**

Standard deviations in parentheses.

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Ca	0·0143 (4)	0·0046 (2)	0·0030 (1)	0·0006 (3)	−0·0007 (4)	−0·0005 (5)
Cl(1)	0·0417 (12)	0·0141 (5)	0·0049 (2)	−0·0009 (5)	−0·0048 (8)	0·0011 (12)
Cl(2)	0·0183 (6)	0·0108 (4)	0·0046 (2)	−0·0021 (4)	0·0023 (5)	−0·0009 (8)
N(1)	0·0398 (35)	0·0086 (14)	0·0047 (7)	−0·0009 (16)	0·0026 (25)	0·0020 (35)
$C^{\alpha}(1)$	0·0210 (28)	0·0080 (15)	0·0044 (7)	0·0015 (17)	0·0017 (23)	−0·0046 (32)
$C'(1)$	0·0123 (22)	0·0092 (15)	0·0041 (7)	−0·0027 (16)	−0·0067 (20)	−0·0042 (29)
O(1)	0·0189 (18)	0·0068 (10)	0·0048 (5)	0·0040 (11)	0·0029 (15)	−0·0040 (21)
N(2)	0·0166 (21)	0·0080 (13)	0·0024 (5)	−0·0018 (13)	0·0002 (16)	−0·0037 (25)
$C^{\alpha}(2)$	0·0129 (23)	0·0066 (14)	0·0060 (8)	0·0018 (17)	−0·0033 (22)	0·0038 (28)
$C'(2)$	0·0117 (21)	0·0039 (12)	0·0042 (7)	−0·0003 (14)	−0·0033 (19)	0·0007 (24)
O(2)	0·0142 (16)	0·0101 (11)	0·0041 (5)	−0·0064 (12)	0·0060 (14)	−0·0016 (21)
N(3)	0·0215 (22)	0·0028 (10)	0·0029 (5)	0·0028 (11)	−0·0069 (17)	−0·0050 (23)
$C^{\alpha}(3)$	0·0141 (24)	0·0083 (15)	0·0048 (7)	0·0018 (17)	−0·0041 (21)	−0·0093 (29)
$C'(3)$	0·0187 (26)	0·0073 (14)	0·0030 (6)	0·0002 (15)	0·0045 (21)	−0·0035 (30)
O(3)	0·0127 (16)	0·0101 (11)	0·0069 (6)	0·0056 (13)	−0·0059 (16)	−0·0127 (21)
O(4)	0·0168 (17)	0·0064 (9)	0·0046 (5)	0·0035 (11)	−0·0038 (14)	−0·0021 (20)
O*w*(1)	0·0184 (19)	0·0140 (13)	0·0071 (6)	−0·0051 (15)	−0·0081 (18)	0·0154 (25)
O*w*(2)	0·0295 (24)	0·0108 (13)	0·0052 (6)	−0·0009 (13)	−0·0040 (19)	0·0103 (27)
O*w*(3)	0·0254 (22)	0·0089 (12)	0·0080 (7)	−0·0047 (14)	0·0052 (20)	−0·0023 (25)

* Temperature factor = $\exp\,[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})]$.

logical routine has been added to this program such that reflections which are clearly observational errors, as for instance 010, are excluded from the least-squares refinement. This logical routine also excludes most of the reflections affected by extinction from the least-squares sums. The atomic scattering factors used for

Table 3. *Observed and calculated structure factors*

The listing shows for each reflection h, $|10KF_o|$ and $10F_c$. The reflections for which the intensity could not be distinguished from the background are indicated by a star.

H	FO	FC
K=	0, L=	0
-1	306	-248
-2	488	-768
-3	83	76
-4	164	-128
-5	46	-48
-6	32*	7
-7	84	77
-8	134	-101
K=	1, L=	0
0	162	31
1	250	-230
-1	13	-14
-2	140	-176
2	805	851
-3	87	-114
3	494	-483
-4	92	-94
4	237	-205
-5	157	161
5	246	-103
6	41*	-9
-6	115	-103
7	168	177
-7	124	-41
K=	2, L=	0
0	505	-457
-1	60	68
1	158	-174
-2	348	306
2	368	361
-3	54	-59
3	314	-249
-4	371	-407
4	185	149
-5	79	-56
5	83	-75
-6	144	44
6	85	26
-7	33*	22
7	40*	22
-8	132	119
8	31*	-28
K=	3, L=	0
0	530	537
-1	281	283
1	603	607
-2	227	-242
2	46	-57
3	421	-421
-3	58	35
-4	108	-97
4	87	73
-5	175	-103
5	133	-117
-6	196	167
6	73	68
-7	149	-125
7	197	-13
K=	4, L=	0
0	433	-213
-1	50	-57
1	467	459
-2	151	191
2	401	-163
-3	158	-161
3	148	145
4	32*	8
-4	137	139
-5	136	-126
5	362	-309
6	31*	27
-6	82	50
-7	122	-101
-8	30*	39
K=	5, L=	0
0	65	-90
-1	106	-104
1	52	33
-2	433	244
2	301	-274
-3	190	-204
3	286	211
-4	28*	-5
4	145	111
-5	207	-244
5	192	117
-6	33*	-5
6	127	-101
-7	108	124
7	53	-47
K=	6, L=	0
0	256	238
-1	40*	23
1	54	62
2	51*	-30
-2	109	126
3	45*	-25
-3	210	-224
-4	71	69
4	224	-175
-5	40*	-41
5	177	151
-6	47	-25
6	89	-45
K=	7, L=	0
0	96	126
-1	29*	-21
1	202	-195
-2	92	114
2	181	172
-3	63	-85
3	127	105
-4	29*	7
4	267	-244
-5	118	102
K=	8, L=	0
0	68	-67
-1	27*	-19
1	55	-66
-2	47	63
2	152	138
-3	20*	4
K=	9, L=	0
0	40	99
-1	77	81
1	25*	32
-2	150	-168
2	38	23
-3	25*	-15
K=	10, L=	0
-2	127	-146
K=	0, L=	1
0	380	385
1	140	-83
2	617	600
3	277	273
4	625	-660
5	84	92
6	57	-48
7	35*	11
8	29*	3
-1	45	-33
-2	189	196
-3	20	-28
-4	210	155
-5	54	-73
-6	100	-115
-7	34*	5
-8	65	-68
K=	1, L=	1
0	308	304
1	240	-214
2	565	-496
3	239	235
4	205	186
5	67	97
6	202	-162
7	64	49
-1	472	-507
-2	234	245
-3	72	29
-4	333	-301
-5	53	49
-6	32*	-27
-7	42	47
K=	-1, L=	1
0	165	204
1	639	626
2	453	-438
3	23*	-14
4	302	-264
5	179	211
6	143	109
7	63	-60
-1	81	-28
-2	565	556
-3	573	-571
-4	24	-31
-5	105	-54
-6	101	110
-7	52	49
K=	2, L=	1
0	426	472
1	117	119
2	66	-123
3	205	-210
4	147	182
5	134	105
6	56	-51
7	139	121
8	77	-66
-1	436	-466
-2	161	-177
-3	102	113
-4	332	-352
-5	156	166
-6	31*	18
-7	31*	5
-8	31*	33
K=	-2, L=	1
0	96	-120
1	636	-722
2	566	-587
3	348	350
4	83	88
5	60	-60
6	72	87
7	111	-101
8	31*	35
-1	748	774
-2	152	-152
-3	301	-293
-4	220	218
-5	330	-328
-6	101	100
-7	83	70
-8	59	65
K=	3, L=	1
0	67	-41
1	174	178
2	230	265
3	27	33
4	68	78
5	319	-349
6	75	-69
7	77	115
-1	145	160
-2	454	-460
-3	530	519
-4	169	141
-5	40*	-46
-6	79	-45
-7	109	-133
K=	-3, L=	1
0	494	505
1	212	223
2	71	-82
3	72	81
4	39*	-22
5	171	-205
6	52	72
7	42*	-32
-1	40	27
-2	399	-405
-3	315	350
-4	154	152
-5	244	-311
-6	38*	36
-7	87	-82
K=	4, L=	1
0	547	-596
1	28*	-29
2	43*	12
3	215	202
4	57	52
5	57	-54
6	36	48
-1	276	273
-2	62	-61
-3	126	119
-4	45	-1
-5	243	-141
-6	102	36
-7	51	-44
-8	65	76
K=	-4, L=	1
0	67	-55
1	332	372
2	252	159
3	526	-601
4	175	178
5	38*	26
6	48	31
8	30*	-46
-1	339	327
-2	122	100
-3	93	-105
-4	177	-183
-5	66	-50
-6	21	48
K=	5, L=	1
0	565	-527
1	303	342
2	114	-98
3	71	-9
4	128	126
5	86	120
6	56	33
7	52	-46
-1	235	228
-2	83	66
-3	300	-363
-4	62	-35
-5	63	62
-6	102	94
-7	41*	-44
K=	-5, L=	1
0	266	-270
1	574	-562
2	374	365
3	205	-230
4	41*	-7
5	59	35
6	81	-72
7	38*	74
-1	297	240
-2	307	281
-3	27*	-39
-4	248	-214
-5	85	103
-6	74	-66
-7	29*	32
K=	6, L=	1
0	128	-136
1	341	348
2	201	-231
3	172	165
4	62	-15
5	81	-73
6	67	-91
-1	183	-185
-2	123	125
-3	35*	-11
-4	240	184
-5	45*	-30
-6	56	9
K=	-6, L=	1
0	403	382
1	32	-52
2	155	133
3	47	-50
4	165	-149
5	41*	-1
6	52	-68
-1	252	-249
-2	30*	5
-3	45*	35
-4	82	81
-5	71	68
-6	137	-173
K=	7, L=	1
0	36	14
1	135	-139
2	32*	-22
3	164	154
4	148	-153
5	184	176
-1	118	-122
-2	85	88
-3	42*	48
-4	40*	47
-5	67	-45
K=	-7, L=	1
0	361	392
1	36	36
2	21	-10
3	57	-48
4	117	-121
5	102	97
-1	21*	-25
-2	30*	8
-3	209	-205
-4	41	21
K=	8, L=	1
1	38	-53
2	63	2
3	33*	24
4	47	51
-1	74	-81
-2	119	-131
-3	73	-79
-4	79	-78
K=	-8, L=	1
0	62	-63
1	40*	18
2	165	-166
3	42	58
4	45	-58
-1	64	-74
-2	346	327
-3	135	-139
K=	9, L=	1
0	47	-30
1	73	-74
2	213	213
3	33*	-27
-1	57*	2
-2	83	-83
-3	35	37
-5	132	153
K=	-9, L=	1
2	120	-136
-1	23*	-11
K=	10, L=	1
0	109	-133
2	117	123
-2	56	-67
K=	0, L=	2
0	44	-5
1	356	326
2	299	-321
3	520	541
4	30*	-4
5	65	-74
6	122	-149
7	100	-93
8	32*	16
-1	119	-75
-2	25	-13
-3	136	119
-4	191	141
-5	205	-185
-6	38*	1
-7	107	87
-8	33*	-26
K=	1, L=	2
0	269	293
1	237	-244
2	116	83
3	532	534
4	456	-460
5	195	191
6	180	167
7	30*	-48
-1	427	-426
-2	581	-552
-3	250	-240
-4	83	81
-5	101	83
-6	50	45
-7	140	179
K=	-1, L=	2
0	210	264
1	716	777
2	570	-546
3	465	486
4	95	73
5	205	-205
6	31	-24
7	41	-55
-1	340	-393
-2	335	-325
-3	125	85
-4	170	170
-5	49	-43
-6	81	102
-7	71	-93
K=	2, L=	2
0	70	-75
1	208	218
2	478	532
3	73	49
4	19*	-5
5	40	37
6	190	-206
7	123	120
8	29*	14
-1	668	-683
-2	172	-153
-3	42	36
-4	91	-86
-5	454	432
-6	145	-153
-7	91	-73
-8	28*	1
K=	-2, L=	2
0	819	-779
1	330	365
2	37	3
3	105	-179
4	82	24
5	130	119
6	187	213
7	141	-150
8	27*	-32
-1	369	410
-2	445	-428
-3	255	-252
-4	69	-47
-5	39*	-1
-6	228	242
-7	28*	-13
-8	33*	23
K=	3, L=	2
0	469	-429
1	106	-83
2	222	227
3	26*	39
4	265	257
5	193	-220
6	210	-178
7	35*	38
-1	28*	-16
-2	255	253
-3	287	306
-4	334	-299
-5	158	178
-6	55	-33
-7	43*	-16
K=	-3, L=	2
0	424	-432
1	457	-443
2	450	459
3	56	60
4	68	82
5	80	1
6	88	-84
7	118	-97
-1	754	718
-2	243	-247
-3	240	223
-4	84	-83
-5	130	-149
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7	88	-67
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6	50	33
7	34*	-23
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K=	3, L=	4
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K=	-5, L=	4
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K=	7, L=	4
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7	32*	-15
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K=	-6, L=	5
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K=	7, L=	5
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K=	8, L=	5
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K=	-8, L=	5
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K=	10, L=	5
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K=	0, L=	6
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3	74	-75
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K=	1, L=	6
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K=	2, L=	6
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2	254	-255
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7	30	-42
-1	123	129
-2	241	230
-3	164	-183
-4	205	-183
-5	36*	-26
-6	183	161
-7	32*	-11
K=	-3, L=	6
0	93	-90
1	250	-221
2	26*	7
3	247	253
4	282	-278
5	188	245
6	140	114
-1	147	134
-2	42	43
-3	333	-320
-4	47	53
-5	57	-36
-6	49	47
-7	110	142
K=	4, L=	6
0	187	190
1	390	363
2	58	-39
3	47	59
4	145	-155
5	56	48
6	36*	23
-1	306	-277
-2	44	-47
-3	26*	-10
-4	115	141
-5	124	-112
-6	55	-68
K=	-4, L=	6
0	377	-339
1	45	-60
2	212	-200
3	217	220
4	52	28
5	39	-53
6	33*	-55
-1	241	242
-2	223	206
-3	138	-115
-4	183	193
-5	74	-76
-6	36*	-47
K=	5, L=	6
0	168	159
1	156	-156
2	153	-134
3	58	45
4	24*	-10
5	35*	-7
-1	175	-161
-2	302	276
-3	64	47
-4	137	-128
-5	86	80
-6	122	-105
-7	26*	63
K=	-5, L=	6
0	145	-140
1	270	256
2	136	-125
3	34*	22
4	50	53
5	70	-44
-1	45	-14
-2	97	-80
-3	123	107
-4	174	155
-5	39	-50
K=	6, L=	6
0	218	230
1	246	-267
2	34	45
3	167	-174
4	50	-32
6	26*	6
-1	242	243
-2	62	-65
-3	169	-158
-4	165	-138
-5	149	133
-6	42	-2
K=	-6, L=	6
0	146	-134
1	36	37
2	100	-92
3	48	-52
4	188	172
5	28	-2
6	95	127
-1	25	33
-2	188	-182
-3	85	94
-4	41	-29
K=	7, L=	6
0	87	90
1	86	87
2	245	256
3	189	-175
5	39	-36
-1	31*	18
-2	143	-149
-3	55	62
-4	38	-44
K=	-7, L=	6
1	108	-128
2	157	148
3	85	-100
4	188	183
-1	78	77
-2	79	74
-3	98	89
K=	8, L=	6
0	102	-119
1	28*	-14
2	99	107
4	72	56
-1	96	111
-2	28*	-17
-3	105	102
K=	-8, L=	6
0	53	55
1	59	-33
2	166	157
-1	106	-112
K=	9, L=	6
1	131	128
3	90	-101
-1	43	45
K=	10, L=	6
0	38	47

Table 3 (*cont.*)

H	FO	FC
K=	0, L=	7
0	385	364
1	60	-11
2	250	242
3	198	-190
4	67	-73
5	30*	-13
6	34*	27
-1	280	-237
-2	171	-168
-3	144	104
-4	132	-151
-5	177	150
-6	63	-85
K=	1, L=	7
0	204	-185
1	127	-119
2	277	284
3	192	-201
4	145	128
5	73	-68
6	63	-46
7	30*	6
-1	103	102
-2	114	88
-3	321	366
-4	170	-137
-5	131	-165
-6	64	-64
-7	30*	42
K=	-1, L=	7
0	390	371
1	331	-345
2	107	-103
3	54	-124
4	280	-256
5	127	131
6	29	9
7	30*	22
-1	182	232
-2	166	181
-3	259	-282
-4	47	-54
-5	156	219
-6	89	-93
-7	60	54
K=	2, L=	7
0	254	241
1	22	-18
2	351	-372
3	253	-260
4	149	151
5	138	-141
6	85	122
-1	155	157
-2	37	7
-3	145	138
-4	134	-169
-5	25	-16
-6	71	100
K=	-2, L=	7
0	183	165
1	238	-220
2	31	-27
3	197	201
4	220	-246
5	24*	1
6	35*	12
-1	12*	0
-2	59	75
-3	139	146
-4	134	141
-5	268	-209
-6	62	-59
K=	3, L=	7
0	63	55
1	226	216
2	131	-129
3	34*	2
4	32	29
5	181	-204
6	203	146
-1	55	74
-2	130	-128

H	FO	FC
-3	49	-6
-4	88	64
-5	310	-129
-6	81	75
-7	81	-98
K=	-3, L=	7
0	25*	11
1	336	295
2	133	-131
3	44	41
4	117	-119
5	45*	44
6	111	91
7	25*	6
-1	56	-80
-2	64	-73
-3	153	-177
-4	126	124
-5	36*	-18
-7	24*	-1
K=	4, L=	7
0	117	-131
1	110	-101
2	54	-33
3	206	207
4	37*	-27
5	35	-18
6	33	-14
-1	307	284
-2	274	287
-3	278	-246
-4	110	116
-5	181	-169
-6	55	-78
K=	-4, L=	7
0	99	-100
1	246	241
2	410	-365
3	183	-184
4	139	133
5	23*	-37
6	33*	62
-1	232	238
-2	85	77
-3	135	-112
-4	38*	-52
-5	40	-38
-6	88	115
K=	5, L=	7
0	204	177
1	58	-49
2	182	-189
3	137	-120
4	99	-113
5	127	146
-1	32*	-13
-2	222	218
-3	201	-187
-4	32*	-21
-5	51	-4
-7	22*	64
K=	-5, L=	7
0	257	-233
1	19	2
2	55	97
3	156	-147
4	39	47
5	61	-55
-1	276	258
-2	25*	4
-3	226	210
-4	25*	7
-5	60	-79
K=	6, L=	7
0	109	111
1	201	211
2	51	44
3	200	-188
4	73	-64
-1	321	-339
-2	177	194
-3	38	-44
-4	79	-57

H	FC	FC
-5	75	77
-6	38	-35
K=	-6, L=	7
0	167	-161
1	123	-134
2	261	251
3	49	-44
4	50	-28
-1	146	151
-2	166	-146
-3	16*	3
K=	7, L=	7
0	230	225
1	190	-196
2	84	95
3	38	64
5	28*	-24
-1	30*	-14
-2	29*	5
-3	70	93
-4	50	-50
K=	-7, L=	7
0	76	90
1	81	-105
2	61	-60
3	73	-81
-1	26	-41
K=	8, L=	7
0	28*	16
1	157	-155
2	105	104
-2	71	-77
-3	24	-10
K=	9, L=	7
1	60	68
-1	34*	-19
K=	0, L=	8
0	327	334
1	314	-281
2	60	56
3	282	261
4	42*	-6
5	36	6
6	68	-63
-1	298	-278
-2	95	105
-3	194	170
-4	74	-81
-5	151	-121
-6	104	-94
K=	1, L=	8
0	371	338
1	345	-417
2	55	-25
3	30*	-29
4	64	60
5	32*	29
6	47	-45
7	131	43
-1	275	238
-2	36	-26
-3	67	-82
-4	11	-24
-5	28*	52
-6	98	-78
-7	55	74
K=	-1, L=	8
0	186	172
1	223	218
2	49	-78
3	42*	-54
4	256	-239
5	177	55
7	54	71
-1	449	-497
-2	201	231
-3	12	11
-4	57	66
-5	49	33

H	FO	FC
-7	25*	-28
K=	2, L=	8
0	130	-134
1	69	-197
2	360	327
3	169	-186
4	55	-101
5	79	-71
6	187	50
-1	85	86
-2	69	-69
-3	123	99
-4	38*	-25
-5	117	106
-6	34*	8
K=	-2, L=	8
0	61	51
1	25	3
2	209	-214
3	89	-107
4	86	-105
5	118	116
6	82	58
-1	261	307
-2	89	120
-3	232	-276
-4	204	213
-5	115	-109
-6	32*	35
K=	3, L=	8
0	222	-220
1	259	253
2	20*	-6
3	42	-40
4	244	242
5	135	-110
-1	31*	-51
-2	92	87
-3	193	206
-4	118	-101
-5	162	-180
-6	58	39
-7	62	-77
K=	-3, L=	8
0	238	-220
1	14*	31
2	26*	-1
3	43	64
4	53	57
5	33*	-10
-1	179	164
-2	139	123
-3	38	-79
-4	27	-27
-5	107	-125
K=	4, L=	8
0	48	57
1	239	232
2	325	-315
3	30	-15
4	228	161
6	26*	4
-1	86	71
-2	72	51
-3	90	-67
-4	51	-35
-5	125	-116
-6	92	121
K=	-4, L=	8
0	35	-23
1	30	24
2	52	21
3	113	-121
4	49	-37
5	114	-105
6	88	159
-1	182	181
-2	212	-189
-3	29*	-15
-4	63	92
-6	26*	4
K=	5, L=	8

H	FC	FC
0	135	-119
1	21	24
2	43	-34
3	107	94
4	139	-158
5	33*	-25
-1	65	83
-2	44	-40
-3	259	-228
-4	222	211
-5	47	25
K=	-5, L=	8
0	145	118
1	203	-185
2	30	-25
3	270	-243
5	41	-27
-1	340	310
-2	61	-53
-3	122	106
-4	93	-76
-5	30*	-18
K=	6, L=	8
0	53	53
1	57	60
2	73	-80
3	212	198
4	79	-50
-1	210	-215
-2	117	131
-3	24*	0
-4	59	39
-6	41	-39
K=	-6, L=	8
0	34	-13
1	66	-62
2	64	77
3	104	-107
-1	129	-126
-2	194	168
-3	144	132
K=	7, L=	8
0	147	151
1	75	-64
2	67	79
3	39*	-6
-1	30*	28
-2	30	12
-3	87	-91
K=	-7, L=	8
1	17*	-33
-1	155	-161
K=	8, L=	8
0	58	-56
2	147	143
-1	76	-82
-2	44	-39
K=	9, L=	8
1	31*	-10
-1	61	-71
K=	0, L=	9
0	63	63
1	210	193
2	43	58
3	77	78
4	98	-126
5	185	170
6	177	-48
-1	184	-153
-2	161	166
-3	129	-115
-4	91	-90
-5	106	-83
-6	31*	29
K=	1, L=	9
0	290	255

H	FO	FC
1	80	97
2	25	-10
3	36*	27
4	118	-117
5	41*	3
-1	336	-371
-2	29	-20
-3	33	51
-4	24*	5
-5	122	143
-7	22*	20
K=	-1, L=	9
0	141	-135
1	126	-137
2	73	41
3	273	357
4	201	-176
5	56	-63
-1	87	88
-2	33	48
-3	86	-124
-4	155	170
-5	90	-94
K=	2, L=	9
0	77	-85
1	173	-179
2	144	155
3	24	15
4	119	103
5	81	-58
6	113	-150
-1	36	-38
-2	50	-3
-3	184	154
-4	93	-111
-5	36	38
-6	56	-75
K=	-2, L=	9
0	93	-80
1	141	156
2	99	-85
3	49	49
4	88	-125
5	132	-130
6	77	62
-1	140	156
-2	129	-149
-3	156	-166
-4	250	290
-6	32*	23
K=	3, L=	9
0	153	129
1	6*	-12
2	24*	15
3	40*	43
4	99	109
5	78	-87
-1	183	186
-2	170	-139
-3	52	60
-4	250	-238
-5	35	-21
K=	-3, L=	9
0	129	124
1	237	203
2	119	-111
3	96	-97
4	137	154
5	34*	-29
-1	37	55
-2	185	-194
-3	134	113
-4	108	-111
-5	136	-156
K=	4, L=	9
0	65	66
1	126	118
2	22*	25
3	19*	-10
4	34*	-11
-1	137	147
-2	362	-399
-3	25	13

H	FO	FC
-4	129	105
-5	61	25
-6	27*	45
K=	-4, L=	9
0	199	-161
1	27	-41
2	222	174
3	93	-87
-1	74	66
-2	62	33
-3	60	57
-4	88	-124
K=	5, L=	9
0	408	-448
1	266	248
2	48	29
3	48	-60
4	41	49
5	28*	-11
-1	16	54
-2	100	100
-3	110	-107
-4	26	34
-5	43	-1
K=	-5, L=	9
0	23*	20
1	72	-63
2	165	160
3	247	-232
5	35	12
-1	97	90
-2	23*	-2
-5	79	101
K=	6, L=	9
0	39	47
1	166	176
2	137	-135
3	102	93
4	53	-40
-1	25*	-10
-2	64	69
-3	113	-97
-4	76	-70
K=	-6, L=	9
0	237	224
2	42	-23
-2	95	102
K=	7, L=	9
0	157	143
1	132	131
-2	86	-86
-3	27*	-40
K=	8, L=	9
0	23*	-15
2	77	80
-2	24*	19
K=	9, L=	9
1	73	-82
K=	0, L=	10
0	153	175
1	276	277
2	138	-125
3	245	228
4	90	-99
5	134	-103
6	25*	15
-1	148	-132
-2	28	-109
-3	88	-75
-4	80	95
-5	64	-47
-6	30*	34
K=	1, L=	10
0	91	78
1	196	-258

H	FC	FC
2	32	35
3	245	285
4	211	-214
5	29*	1
-1	122	-116
-2	6	-3
-3	53	73
-4	58	96
K=	-1, L=	10
0	142	-141
1	217	157
2	91	-68
3	39*	11
4	21	16
5	35*	-12
-1	167	185
-2	21*	-9
-3	142	-151
-4	48	-40
-5	68	-69
K=	2, L=	10
0	68	56
1	101	-106
2	93	13
3	65	-76
4	32*	18
6	54	-45
-1	96	88
-2	202	131
-3	190	-187
-4	147	-173
-5	142	130
-6	29*	-41
K=	-2, L=	10
0	249	-207
1	209	223
2	50	-9
3	85	-93
4	25*	29
6	23*	-7
-1	40	-44
-2	49	-66
-3	149	166
-4	39*	32
-6	23*	19
K=	3, L=	10
0	181	173
1	179	171
2	146	151
3	161	-178
5	29*	16
-1	124	-141
-2	65	-55
-3	130	84
-4	190	-175
-5	56	112
K=	-3, L=	10
0	25*	6
1	66	62
2	252	274
3	114	-111
4	83	-63
5	32*	-74
-1	219	186
-2	307	-312
-3	32*	6
K=	4, L=	10
0	101	-101
1	105	-108
2	125	127
3	42	-37
4	80	96
-1	57	58
-2	51	-95
-3	213	186
-4	80	-82
-6	23*	4
K=	-4, L=	10
0	122	106
1	140	-154
2	171	163

H	FC	FC
3	42	-34
4	41	12
-1	188	176
-2	87	-79
-3	117	-99
-4	161	-187
K=	5, L=	10
0	29	15
1	42	52
2	203	-195
3	51	-61
-1	131	127
-2	114	-108
-3	82	-55
-4	79	-64
-5	37	3
K=	-5, L=	10
0	125	116
1	64	-68
2	33	-49
-1	85	-83
-2	60	66
K=	6, L=	10
0	21*	-1
2	25*	25
4	69	-55
-1	62	64
-2	94	-113
-3	100	-79
K=	7, L=	10
1	35*	-15
-1	24*	-22
-3	23*	-21
K=	8, L=	10
0	19*	-17
-2	135	134
K=	0, L=	11
0	200	-194
1	75	93
2	35*	-3
3	169	160
4	25*	13
-1	28	-25
-2	77	111
-3	40	48
K=	1, L=	11
0	36	-51
1	73	-96
2	185	-177
3	68	50
4	53	22
5	82	102
-1	51	12
-2	157	139
-3	93	-111
-4	26	5
-5	60	-71
K=	-1, L=	11
0	144	-133
1	211	216
2	147	136
3	78	-112
5	36	-39
-1	77	94
-2	130	-170
-3	58	-64
-4	72	83
-5	31*	37
K=	2, L=	11
0	154	142
1	99	94
2	72	-67
3	52	54
4	55	-74
-1	298	-278
-2	77	96
-3	65	-57

H	FO	FC
-4	33*	13
-6	21*	-24
K=	-2, L=	11
0	158	114
1	281	-302
2	48	-23
3	40	25
4	35*	36
-1	195	214
-2	195	-257
-3	65	89
-4	35*	-34
K=	3, L=	11
0	237	221
1	233	-215
2	18*	15
3	89	130
5	24*	-17
-1	96	-103
-2	58	40
-3	114	87
-5	27*	8
K=	-3, L=	11
0	41	-10
1	54	-29
2	146	152
3	82	-68
5	24*	-33
-1	59	-63
-2	23*	-24
-3	108	133
-5	31	25
K=	4, L=	11
0	24*	38
1	248	-250
2	63	52
3	110	-101
4	85	93
-1	123	119
-2	49	-44
-3	30	-36
-4	77	-77
K=	-4, L=	11
0	155	143
1	131	127
2	155	137
4	35	-6
-1	140	-142
-2	45	-35
-4	82	-91
K=	5, L=	11
0	114	-105
2	191	178
3	151	-132
-1	40	-31
-2	74	-72
-3	56	29
-5	40	64
K=	-5, L=	11
0	124	73
K=	6, L=	11
0	135	-134
2	21*	-17
-1	40	-45
K=	7, L=	11
1	41	-43
-1	76	78
-3	73	-50
K=	0, L=	12
0	48	30
1	30	-18
2	120	-155
3	66	43
4	113	140
-1	88	80

H	FO	FC
-2	69	-91
-3	36	56
K=	1, L=	12
0	86	-86
1	34*	-46
2	78	-92
3	102	136
5	91	-60
-1	69	63
-2	173	-136
-3	104	-119
K=	-1, L=	12
0	167	-143
1	59	59
2	132	118
3	33*	27
-1	67	-86
-2	14*	26
-3	172	195
-5	51	-46
K=	2, L=	12
0	140	-148
1	26*	6
3	175	170
4	86	-86
-1	111	-80
-3	52	-47
-4	76	77
K=	-2, L=	12
0	88	-73
1	101	-124
2	258	261
4	27*	-41
-1	19*	-15
-2	119	-142
-4	26*	40
K=	3, L=	12
1	26*	36
2	69	-69
-1	114	-116
-2	221	212
-3	80	-56
-5	22*	27
K=	-3, L=	12
0	147	128
1	144	-114
3	55	-55
-1	79	-69
-2	42	37
-3	27*	-35
K=	4, L=	12
0	136	150
2	46	-43
4	65	18
-1	182	-157
-2	83	-94
-4	35	6
K=	5, L=	12
1	111	-105
3	29*	-16
-1	38	-21
K=	6, L=	12
0	19*	20
2	27	-34
K=	7, L=	12
-1	49	58
K=	0, L=	13
0	88	-98
1	95	72
2	49	76
4	37	42
-2	80	-84
-4	52	-54

H	FO	FC
K=	1, L=	13
0	269	-214
1	79	76
2	46	-45
3	27*	28
-1	44	-7
-2	37	-30
-3	55	79
K=	-1, L=	13
0	43	38
1	174	-167
3	28*	16
-1	112	135
-3	64	66
K=	2, L=	13
0	25*	7
1	44	45
2	159	-181
-1	156	142
-2	70	57
-4	24*	9
K=	-2, L=	13
0	31	8
2	99	95
-2	40	-48
K=	3, L=	13
0	173	141
1	89	95
3	40	59
-1	51	-61
-3	70	-64
K=	-3, L=	13
3	39	50
K=	4, L=	13
0	22*	-18
2	64	57
K=	5, L=	13
1	43	-28
-1	45	32
K=	6, L=	13
0	63	79
K=	0, L=	14
0	45	34
2	26*	-4
-2	97	-86
K=	1, L=	14
1	94	-139
-1	193	180
-3	40	47
K=	-1, L=	14
1	35	-4
-3	20*	3
K=	2, L=	14
0	57	-61
2	25*	-6
-2	35	-26
K=	-2, L=	14
-2	141	150
K=	3, L=	14
1	72	69
-3	27	12
K=	4, L=	14
0	55	34

Table 4. *Parameters and peak heights of hydrogen atoms*

Bonded to	x	y	z	B	Peak heights
N(2)	0·31	0·37	0·34	5·0 Å^2	0·8 e.Å^{-3}
Ow(2)	0·25	0·27	0·66	5·0	0·7
Ow(2)	0·21	0·41	0·72	5·0	0·6
N(3)	−0·01	0·33	0·17	3·9	1·1
N(1)	0·21	0·86	0·38	5·0	0·6
C$^\alpha$(1)	0·08	0·57	0·40	4·5	0·8
C$^\alpha$(1)	0·29	0·54	0·46	4·5	0·8
C$^\alpha$(2)	0·49	0·32	0·18	3·8	0·7
C$^\alpha$(2)	0·48	0·49	0·14	3·8	0·8
C$^\alpha$(3)	−0·02	0·29	−0·05	4·2	0·6
C$^\alpha$(3)	−0·18	0·36	0·02	4·2	0·7

Ca^{2+}, Cl^-, O, N, and C as well as the dispersive corrections ($\Delta f'$ and $\Delta f''$) for Ca and Cl were from *International Tables for X-ray Crystallography* (1962). The scattering factors for hydrogen atoms used were those of Stewart, Davidson & Simpson, (1965).

Discussion of the structure

A projection of the structure is shown in Fig. 1. The notation used in the labeling of atoms in the peptide molecule is that proposed during the 1965 Gordon Conference on Proteins (Edsall, Flory, Kendrew, Liquori, Nemethy, Ramachandran & Scheraga, 1966). The term 'residue' is reserved for the group of atoms $-N-C^{\alpha}-\overset{\overset{\displaystyle O}{\|}}{C'}-$. Residues are numbered starting with the terminal N atom. The number of the residue to which an atom belongs is given in parentheses after the symbol for the atom. With this notation, for example, the atoms

Table 5. *Values of anisotropic temperature factors along the principal axes*

Values of the temperature factors (in Å^2) along the major, intermediate and minor axes of the thermal ellipsoids are given together with the direction cosines of these axes with respect to the axes of the crystallographic unit cell.

	B_i	l_1	l_2	l_3
Ca	2·86	0·970	−0·220	−0·227
	1·81	0·236	0·388	0·903
	1·23	0·052	0·895	−0·365
Cl(1)	8·27	0·986	−0·129	−0·188
	4·07	0·053	0·992	0·050
	2·70	0·159	0·000	0·981
Cl(2)	3·86	0·831	−0·504	0·281
	2·95	0·499	0·821	−0·052
	2·51	−0·244	0·268	0·958
N(1)	7·70	0·997	−0·059	0·050
	2·72	−0·075	0·026	0·997
	2·50	−0·014	0·998	0·050
C$^\alpha$(1)	4·40	0·945	−0·397	−0·030
	2·93	0·164	0·506	0·869
	1·78	0·284	0·766	−0·494
C′(1)	3·71	−0·757	0·382	0·607
	2·89	−0·046	0·839	−0·482
	0·93	0·652	0·388	0·631
O(1)	3·94	0·949	−0·384	−0·033
	3·50	0·163	0·518	0·862
	1·18	0·268	0·764	−0·506
N(2)	3·58	0·900	−0·496	0·012
	2·08	0·427	0·811	−0·271
	1·32	0·082	0·310	0·962
C$^\alpha$(2)	3·92	−0·377	0·262	0·920
	2·52	0·788	0·529	0·198
	1·51	−0·486	0·807	−0·339
C′(2)	2·99	−0·664	0·111	0·764
	1·76	0·748	0·007	0·644
	1·12	−0·006	0·994	−0·016
O(2)	4·30	−0·529	0·609	−0·572
	2·44	0·741	0·614	0·015
	1·13	−0·414	0·502	0·820
N(3)	5·05	0·896	−0·294	−0·420
	1·36	0·444	0·410	0·796
	0·49	0·007	0·863	−0·436
C$^\alpha$(3)	4·61	−0·681	0·606	0·531
	2·29	0·320	−0·381	0·841
	1·33	0·649	0·698	0·101
C′(3)	4·00	0·931	−0·307	0·235
	2·20	0·083	0·867	0·535
	1·36	−0·356	−0·392	0·812
O(3)	6·31	−0·513	0·620	0·682
	2·51	−0·460	0·465	−0·731
	1·09	0·724	0·632	−0·017
O(4)	4·22	0·716	−0·437	−0·627
	2·44	0·697	0·387	0·578
	1·34	−0·039	0·812	−0·523
Ow(1)	6·22	0·575	0·518	−0·567
	3·28	0·067	0·684	0·765
	1·94	−0·815	0·514	−0·305

Table 5 (*cont.*)

	B_i	l_1	l_2	l_3
Ow(2)	6·06	0·928	0·226	−0·228
	3·11	−0·037	0·676	0·783
	2·59	−0·370	0·701	−0·578
Ow(3)	5·78	0·724	−0·261	0·622
	4·00	−0·686	−0·072	0·724
	2·30	0·067	0·963	0·298

of the first residue in ggg are denoted N(1)C$^\alpha$(1)C′(1)-O(1). The oxygen atoms of the three water molecules are labeled Ow(1), Ow(2) and Ow(3).

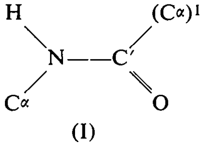
Geometry and conformation of the peptide molecule

Bond lengths and angles in the peptide molecule are shown in Figs. 2 and 3. Average values for free peptides have been tabulated by Marsh & Donohue (1967) (Table 6). The C$^\alpha$–C′ distances of 1·53, 1·51 and 1·51 Å are in close agreement with the average value of 1·51 Å. Except for the terminal C$^\alpha$–NH$_3^+$ distance, the N–C$^\alpha$ distances of 1·41 and 1·41 Å are shorter than the average value of 1·45 Å. The C′–N bond lengths of 1·34 and 1·35 Å are consistently longer than the average value of 1·32 Å and C′–O bond lengths of 1·21 and 1·21 Å are shorter than the average value of 1·24 Å. These differences are thought to be significant considering their consistency and the estimated standard deviations of the bond lengths.

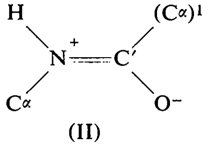
Table 6. *Reference bond lengths and angles in peptides*

	Peptides (Marsh & Donohue, 1967)	Metal-complexes of peptides (Freeman, 1967)
Bond	Length	Length
N—C$^\alpha$ (terminal)	1·49 Å	1·49 Å
C$^\alpha$–C′	1·51	1·53
C′–O	1·24	1·26
C′–N	1·325	1·30
N—C$^\alpha$	1·455	1·46
Angle	θ	θ
NC$^\alpha$C′	111°	111°
C$^\alpha$C′N	116	115
C$^\alpha$C′O	120·5	119
OC′N	123·5	126
C′NC$^\alpha$	122	123

The shortness of the C′-N bond in peptide linkages, 1·32 Å, can be attributed to partial double bond character as can be shown from the two resonance forms



(I)



(II)

To explain the longer than normal C′–N distances and the shorter than normal C′–O distances in the Ca complex, it is assumed that resonance form (I) contributes more to the actual structure than is normally the case when the peptide is not complexed. This is the exact opposite of the trend in the Cu–peptide complexes, where the average C′–N distance of 1·30 Å and the average C′–O distance of 1·26 Å indicate a greater than normal contribution of resonance form (II) (Freeman, 1966) (Table 6). It should be pointed out that these averages are weighted to structures where the peptide nitrogen atom has been deprotonated and is chelated to the Cu atom. Other transition metal complexes of peptides also show this trend (Freeman, 1967). In the Ca–peptide complex both peptide oxygens are bonded to Ca ions, Fig. 1. It may be that the standard deviations in the present structure are underestimated but it will be interesting to see if the deviations in the C′–O and C′–N bond lengths found in the Ca complex are characteristic of changes that occur in Ca–peptide complexes and in general non-transition metal complexes.

There seems to be no adequate explanation for the shorter than normal N–C$^{\alpha}$ bond lengths of the second and third residues. Although the N–C$^{\alpha}$ distance of 1·46 Å involving the terminal NH_3^+ group is appreciably longer than the other N–C$^{\alpha}$ distances, it is also shorter than the average value of 1·49 Å found in other structures.

Bond angles in the peptide molecule are in fairly close agreement with the average values tabulated by Marsh & Donohue. The only significant differences are

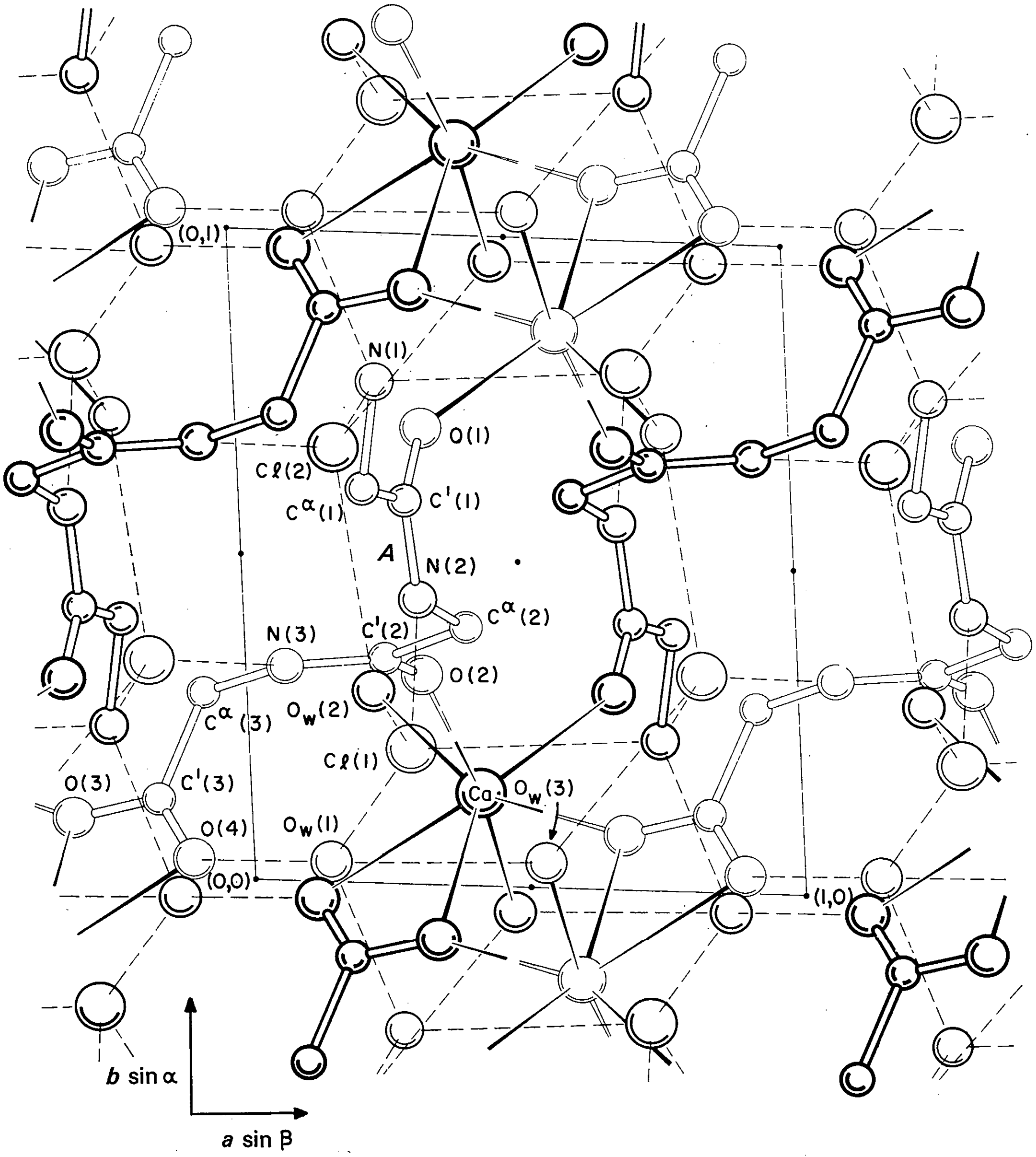


Fig. 1. View of the structure down the *c* axis.

in the N–Cα–C′ angles of the second and third residues. These are 120° and 115°, respectively, and are significantly larger than the average value of 111°. The N–Cα–C′ angle involving the terminal NH_3^+ group has the normal value of 111°.

The conformational angles φ, ψ and ω (Edsall *et al.*, 1966) for each residue are given in Table 7. The values of φ and ψ for each residue lie in the allowed regions of the conformation map calculated for glycyl residues (Ramakrishnan & Ramachandran, 1965) with the angle

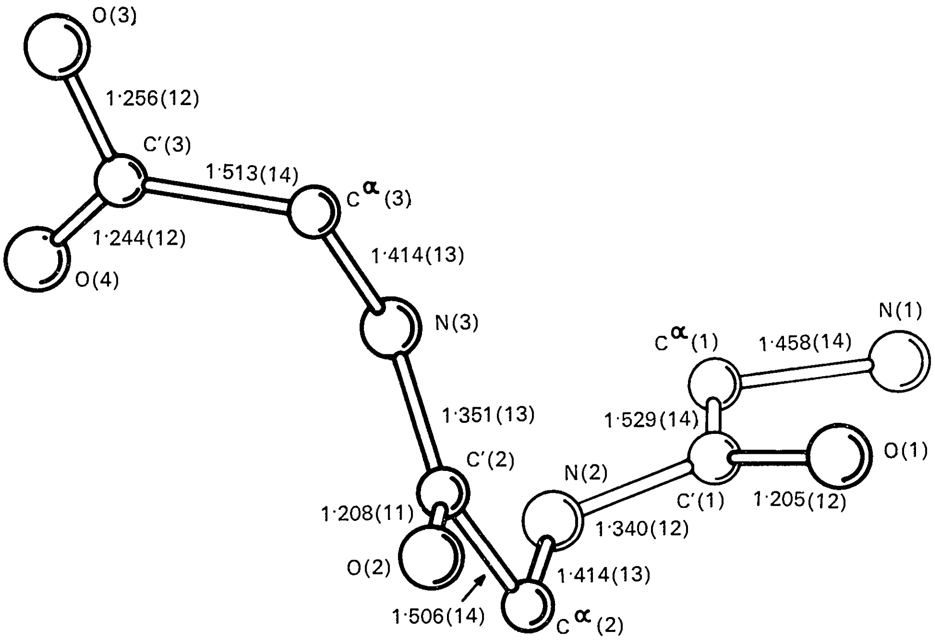


Fig. 2. Bond distances in the peptide molecule. Standard deviations in parentheses.

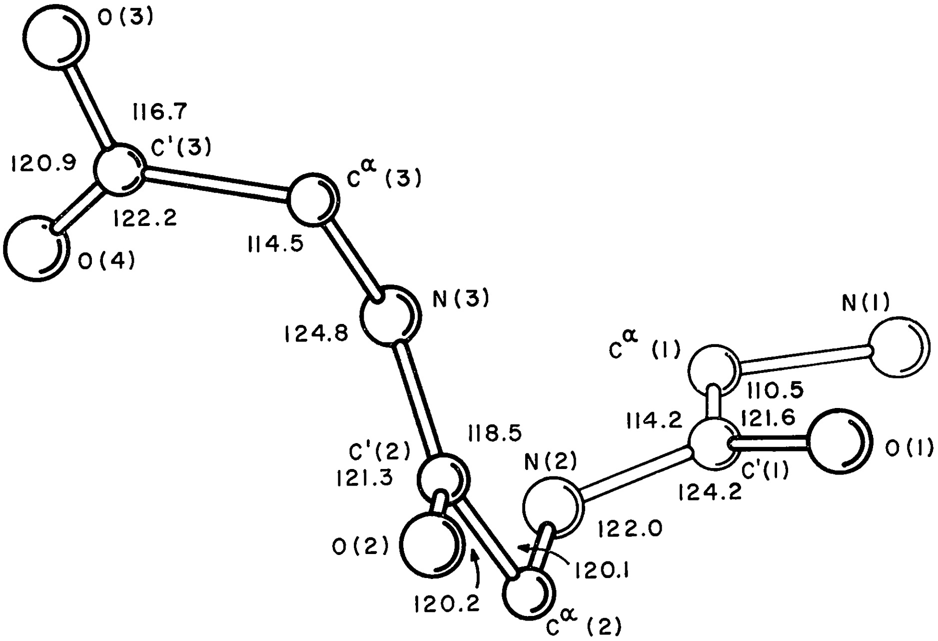


Fig. 3. Bond angles in the peptide molecule. Standard deviations between 0·8 and 0·9°.

N–C$^{\alpha}$–C′ equal to 115°. It should be pointed out, however, that the second residue is the only non-terminal residue in glycylglycylglycine and that the value of φ and ψ for this residue lie in the allowed region only when the 'outer limit' contact distances are used.

Table 7. *Conformational angles*

Residue	φ	ψ	ω	N–C$^{\alpha}$–C′
1	—	342·2°	2·1°	110·5°
2	81·7°	176·1	357·8	120·1
3	290·5	351·5	—	114·5

The large N–C$^{\alpha}$–C′ angles for the second and third residues give the peptide groups increased rotational freedom. The second residue has a somewhat unusual conformation in that the nitrogen atom [N(2)] is lying *trans* to the carbonyl oxygen atom [O(2)] and is therefore *cis* to the nitrogen atom of the third residue (ψ_2 is 176°, Table 7). This is opposite to the strong tendency in small peptides for the amino or peptide nitrogens to be as close as possible to the carbonyl oxygen atom of the same residue (Leung & Marsh, 1958). Although the present conformation is unusual, it is thought to have occurred in order to utilize more fully the hydrogen-bonding capabilities of both peptide nitrogen atoms while leaving the carbonyl oxygen atom [O(2)] more available for bonding to the Ca ion; these facts may be correlated with the large N(2) C$^{\alpha}$(2) C′(2) angle. The *cis* arrangement for the peptide nitrogen atoms of adjacent residues is also found in the transition metal complexes of tri– and higher peptides prepared from alkaline solutions (Freeman, 1967). Here the *cis* conformation is more of a necessity in that the peptide nitrogen atoms of adjacent residues have been deprotonated and are both coordinated to the same metal atom. In these structures, however, there seem to be no significant deviations of the N–C$^{\alpha}$–C′ angles from their normal value of 111°.

In addition to the constancy of the bond lengths and angles of the peptide, the most important characteristic which is common to the peptides whose structures have been determined is the approximate planarity of the group of atoms C^{α}_i C'_i O_i N_{i+1} C^{α}_{i+1}. If this group of atoms is not planar it is most often caused by a displacement of C^{α}_{i+1}, which in turn is qualitatively reflected in a non-zero value of ω_i. It was therefore decided to calculate least-squares planes (Schomaker, Waser, Marsh & Bergman, 1959) through the C^{α}_i C'_i O_i N_{i+1} and C^{α}_i C'_i O_i N_{i+1} C^{α}_{i+1} groups and through the acid group (Table 8). The largest deviation is observed for C$^{\alpha}$(3) which is 0·054 Å out of plane III.

Coordination of the Ca ion

The Ca ion is bonded to oxygen atoms from four different peptide molecules and is therefore very important in determining the packing of the peptides. In all it is bonded to seven oxygen atoms (Fig. 1 and 4) forming an approximate pentagonal bipyramid. Two of the oxygen atoms are centrosymmetrically related and are therefore shared by a second Ca ion. Seven-coordinated Ca ions have been reported elsewhere in the literature, for example, in dicalcium phosphate dihydrate (MacLennon & Beevers, 1955), where both seven and eight coordinated Ca ions are present, and

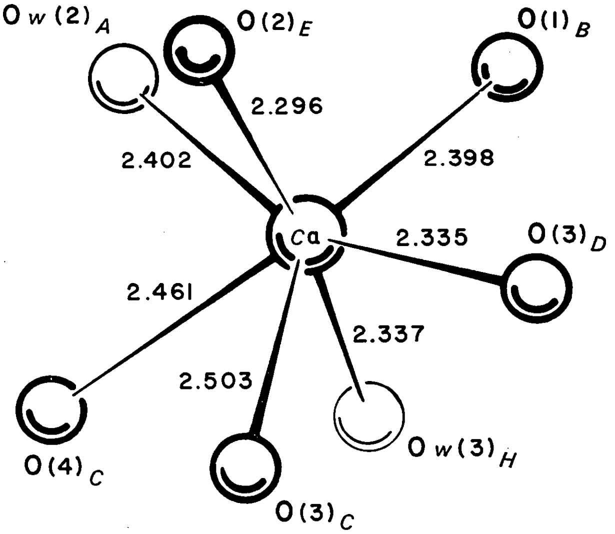


Fig. 4. Bond distances in the Ca-surrounding. Standard deviations are 0.008 Å.

Table 8. *Least-squares planes*

Equations are expressed in the form $Ax+By+Cz=D$, where D is expressed in Å, and x, y and z are fractional coordinates.

Plane	Atoms	A	B	C	D
I	C$^{\alpha}$(1) C′(1) O(1) N(2)	6·4475	0·4557	4·1208	3·3941
II	C$^{\alpha}$(1) C′(1) O(1) N(2) C$^{\alpha}$(2)	6·4347	0·4924	4·1651	3·4265
III	C$^{\alpha}$(2) C′(2) O(2) N(3)	−1·1504	8·0329	−3·1517	2·2346
IV	C$^{\alpha}$(2) C′(2) O(2) N(3) C$^{\alpha}$(3)	−1·0611	8·0529	−3·1153	2·2718
V	C$^{\alpha}$(3) C′(3) O(3) O(4)	−4·1449	3·9429	8·8406	1·6199

Atoms	Δ(I)	Δ(II)	Atoms	Δ(III)	Δ(IV)	Atoms	Δ(V)
C$^{\alpha}$(1)	−0·002 Å	0·003 Å	C$^{\alpha}$(2)	−0·001 Å	−0·013 Å	C$^{\alpha}$(3)	−0·006 Å
C′(1)	0·006	0·004	C′(2)	0·003	0·007	C′(3)	0·022
O(1)	−0·002	−0·004	O(2)	−0·001	0·002	O(3)	−0·008
N(2)	−0·002	−0·011	N(3)	−0·001	0·020	O(4)	−0·008
C$^{\alpha}$(2)	0·022	0·007	C$^{\alpha}$(3)	−0·054	−0·016		

in calcium thymidylate (Trueblood, Horn & Luzzatti, 1961). Ca ions exhibiting coordination numbers of anywhere from six to nine have been reported in the structures of phosphates and silicates.

The five oxygen atoms which form the pentagonal arrangement consist of a carbonyl oxygen atom $O(1)_B$ of one peptide molecule at a distance of 2·40 Å, an oxygen atom of a water molecule $Ow(2)_A$ at 2·40 Å, both oxygen atoms $O(3)_C$ and $O(4)_C$ of a carboxylate group of a second peptide molecule at distances of 2·50 and 2·46 Å, and one oxygen atom $O(3)_D$ of a carboxylate group of a third peptide molecule at a distance of 2·34 Å (subscript notation is explained in Table 9). Bonded on one side of this plane is a carbonyl oxygen atom $O(2)_E$ of a fourth peptide molecule at a distance of 2·30 Å and on the other side of the plane an oxygen atom $Ow(3)_H$ of a water molecule at a distance 2·43 Å. These bond lengths are in the normal range of 2·2 to 2·6 Å for Ca–O bonds. Bond angles in the Ca-surrounding are given by Willoughby (1968). The two Ca ions which share in the bonding of two centrosymmetrically related oxygen atoms are 4·00 Å apart. It is interesting to note that this is very close to the Ca–Ca distance of 3·95 Å found in the α-form of Ca.

Table 9. *Symmetry operations used in Table* 10, *Fig.*4 *and in the text*

Subscript	Coordinates		
A	x	y	z
B	$1-x$	$1-y$	$1-z$
C	$-x$	$-y$	$1-z$
D	$1+x$	y	$1+z$
E	x	y	$1+z$
F	$-x$	$1-y$	$1-z$
G	x	$1+y$	z
H	$1-x$	$-y$	$1-z$
K	x	$-1+y$	z

There is no bonding of the Ca ions to the Cl ions. In this respect the structure is similar to that of the cyclic amine complex $CaBr_2.10H_2O.2(CH_2)_6N_4$ (Mazarella, Kovacs, DeSantis & Liquori, 1967) where $Ca(H_2O)_6^{2+}$ octahedra are formed but no Ca–Br bonds. With the Ca ion being surrounded only by oxygen atoms, the Cl ions are used to fill in the many hydrogen bonding sites found at the peptide and amino nitrogen atoms and at the water molecules.

Details of the hydrogen bonding

The terminal NH_3^+ group forms three hydrogen bonds. Two bonds are formed with Cl^- ions and one to an oxygen atom of a water molecule. The N...Cl distances are 3·14 Å (to $Cl(2)_A$] and 3·21 Å [to $Cl(1)_B$]. These distances fall within the range of distances observed for NH_3^+...Cl hydrogen bonds observed in hydrochloride structures of amino acids and peptides. The third hydrogen bond formed by the NH_3^+ group is to $Ow(1)_G$, the distance being 2·86 Å, which is a normal value for a N–H...O hydrogen bond. The terminal N atom (NH_3^+) is approximately tetrahedrally surrounded by $C^\alpha(1)$, two chloride ions, and the oxygen atom of a water molecule. It is therefore expected that the H atoms are directed towards the Cl ions and the oxygen atom; however, only one of these positions corresponded to a peak in the difference electron density map. These H-bond distances and angles are given in Table 10.

The hydrogen atoms attached to the peptide nitrogen atoms N(2) and N(3), form hydrogen bonds with respectively $Cl(1)_A$ and $Cl(2)_F$. The surrounding of both peptide nitrogen atoms is plane trigonal (Table 10).

Both Cl^- ions accept four hydrogen bonds, including one bond each from a terminal amino group and a peptide nitrogen atom. In addition they both accept 2 hydrogen bonds from water molecules, at distances ranging between 3·10 and 3·26 Å (Table 10). These fall in the range of normal (Parthasarathy, 1960) or average (Clark, 1963) values for O–H...Cl bonds. The arrangements of the hydrogen bonds around the Cl^- ions are approximately tetrahedral (Fig. 1).

The water molecule which is not bonded to the Ca ion [$Ow(1)_A$] forms four hydrogen bonds, donating two bonds to $O(4)_A$ and $Cl(1)_A$ while accepting bonds from $N(1)_K$ and $Ow(3)_A$. The water molecules which are bonded to the Ca ion, $Ow(2)$ and $Ow(3)$, are each the donors in the formation of two hydrogen bonds. The hydrogen bonds around $Ow(1)$ are approximately tetrahedral with

Table 10. *Hydrogen bond lengths and angles*

Standard deviations are given in parentheses.

Bond		Angle	
$N(1)_A—H\cdots Cl(1)_B$	3·209 (13) Å	$Cl(2)_A–N(1)_A—Cl(1)_B$	87·1°
$N(1)_A—H\cdots Cl(2)_A$	3·142 (10)	$Cl(2)_A–N(1)_A—Ow(1)_G$	131·5
$N(1)_A—H\cdots Ow(1)_G$	2·861 (13)	$C^\alpha(1)_A–N(1)_A—Cl(2)_A$	90·2
$Ow(1)_A–H\cdots Cl(1)_A$	3·136 (9)	$C^\alpha(1)_A–N(1)_A—Cl(1)_B$	102·3
$Ow(1)_A–H\cdots O(4)_A$	2·699 (10)	$C^\alpha(1)_A–N(1)_A—Ow(1)_G$	123·4
$Ow(2)_A–H\cdots Cl(1)_A$	3·097 (8)	$Cl(1)_B–N(1)_A—Ow(1)_G$	114·2
$Ow(2)_A–H\cdots Cl(2)_A$	3·264 (8)	$C'(1)_A–N(2)_A—Cl(1)_A$	110·7
$Ow(3)_A–H\cdots Cl(2)_B$	3·240 (9)	$C^\alpha(2)_A–N(2)_A—Cl(1)_A$	125·7
$Ow(3)_A–H\cdots Ow(1)_A$	2·770 (12)	$C'(2)_A–N(3)_A—Cl(2)_F$	133·9
$N(2)_A—H\cdots Cl(1)_A$	3·327 (8)	$C^\alpha(3)_A–N(3)_A—Cl(2)_F$	101·1
$N(3)_A—H\cdots Cl(2)_F$	3·194 (8)	$Cl(1)_A–Ow(1)_A–O(4)_A$	146·9
		$Cl(1)_A–Ow(2)_A–Cl(2)_A$	97·7
		$Cl(2)_B–Ow(3)_A–Ow(1)_A$	122·0

angles ranging between 76° ($Ow(3)_A$–$Ow(1)_A$–$N(1)_K$] and 147° [$Cl(1)_A$–$Ow(1)_A$–$O(4)_A$], while the arrangements around $Ow(2)$ and $Ow(3)$ are close to trigonal with the sum of the three angles for $Ow(2)$ and $Ow(3)$ being 345 and 355° respectively.

This hydrogen bond network makes use of all the hydrogen atoms available for this type of bonding. There is no intramolecular or intermolecular hydrogen bonding between peptide molecules. However, by means of a single intermediary, either a water molecule, a Cl ion or a Ca ion, one peptide is bonded to ten other peptide molecules.

The authors wish to thank Dr F.R.Ahmed for the use of his IBM 360 programs, while they are also indebted to the Computing Center of the University of Oklahoma for putting computer time at their disposal.

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Etude Cristallographique du Manganite Spinelle Cubique $NiMn_2O_4$ par Diffraction de Neutrons

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(*Reçu le* 4 *février* 1969)

It is shown that the inversion parameter, ν, in the cubic spinel $(Mn_\nu Ni_{1-\nu})$ $[Mn_{2-\nu}Ni_\nu]O_4$ changes from 0·74 when the sample is quenched from a high temperature to 0·93 when slowly cooled. The cell parameter is a linear function of ν and is a minimum when ν is a maximum; the oxygen positional parameter is independent of thermal treatment. The short range order between nickel and manganese atoms in the B sites was examined and the correlation coefficients were determined. The variation of internal energy as a function of the degree of inversion was also calculated and discussed.

Introduction

Le manganite de nickel, $NiMn_2O_4$, est un spinelle cubique (Sinha, Sanjana & Biswas, 1957) (groupe d'espace $Fd3m$, O_h^7). Villers & Buhl (1965) ont décrit en détail la méthode de fabrication de ce corps et ont montré que certaines propriétés cristallines ou magnétiques variaient avec la température de trempe. Nous étudions ces échantillons par des mesures de diffraction de neutrons et determinons la valeur des paramètres caractérisant la structure cristalline.

Echantillons étudies; controle de pureté

Les échantillons ont été préparés suivant la méthode décrite dans Villers & Buhl (1965). Le corps, formé à

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* Partie de la Thèse de doctorat d'Etat, Paris, 2 Décembre 1968.

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