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The Crystal Structure of Dipotassium Bis(glycylglycinato)cuprate(II) Hexahydrate, $K_2\,[Cu\,(NH_2CH_2CONCH_2COO)_2]\,.\,6H_2O$

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The crystal structure of dipotassium bis(glycylglycinato)cuprate(II) hexahydrate has been determined from three-dimensional intensities obtained with Cu $K\alpha$ radiation. The plate-like, red-purple crystals are monoclinic, space group $P2_1/a$, with 2 formula units in a cell of dimensions $a=13{\cdot}73$, $b=6{\cdot}24$, $c=11{\cdot}67$ Å, $\beta=102°33'$. The final R index is 0·122 and the e.s.d.'s of the coordinates of the light atoms are about 0·007 Å. The complex ion consists of two molecules of glycylglycine coordinated to a copper atom through the amino and peptide nitrogen atoms. The primary coordination around the copper is approximately square, the Cu–N distances being 1·97 and 2·04 Å. Two water molecules approach the copper atom within 2·77 Å to form a secondary coordination grouping. Bond lengths and angles in the glycylglycine skeleton are all normal within acceptable limits. In the crystal, the water molecules play an important role to form a three-dimensional network of hydrogen bonds.

Introduction

The formation of the 2:1 glycylglycine–copper complex in solution has been reported and various structural formulae have been proposed by several authors using potentiometric and spectroscopic methods (Dobbie & Kermack, 1955; Datta & Rabin, 1956; Koltun, Roth & Gurd, 1963).

Nakahara, Sakurai, Suzuki & Nakao (1965) isolated the 2:1 glycylglycine–copper complex in crystalline form. The preparation and crystallization of the complex compound are carried out as follows. An aqueous solution of diketopiperazine and potassium hydroxide in the proportions of 1:2 is treated at room temperature with an excess of freshly precipitated copper(II) oxide to give an intense blue solution. Crystals of the complex are obtained as beautiful prisms by gentle evaporation of the solution. The color of the crystals is sensitive to moisture; in a humid atmosphere it is blue-purple, while in a comparatively dry atmosphere it is red-purple. Nakahara, Sakurai, Suzuki & Nakao (1965) deduced from spectroscopic observations that two molecules of diketopiperazine coordinate to one copper atom through nitrogen atoms. Subsequently the elementary analysis by Nakao, Sakurai & Nakahara (1966) and the present X-ray analysis revealed that diketopiperazine had undergone hydrolysis and that two glycylglycine molecules coordinate to one copper atom.

The present work was undertaken to study the steric relationships involved in metal–protein interaction. With a similar aim, Freeman and his collaborators made a series of crystallographic studies of metal–peptide complexes (Freeman, Robinson & Schoone, 1964; Freeman, Schoone & Sime, 1965; Freeman & Taylor, 1965; Blount, Fraser, Freeman, Szymanski & Wang, 1967; Freeman & Szymanski, 1967).

Experimental

The crystals are plate-like prisms and (001) is prominently developed. Since they are excessively hygroscopic, crystals were sealed in thin-walled capillaries. The lattice constants were determined by least-squares calculation, using twenty $hk0$ and $h0l$ reflections whose angles were measured on equatorial Weissenberg photographs taken with Cu $K\alpha$ radiation and calibrated with aluminum powder lines. The Weissenberg and precession photographs showed systematic absences in $h0l$ and $0k0$ reflections, and the space group was uniquely determined. The density was measured by flotation in an acetone–methyl iodide mixture.

The three-dimensional intensity data about the b axis ($k=0$–4) and the c axis ($l=0$–9) were collected by the multiple-film equi-inclination Weissenberg method with nickel-filtered Cu $K\alpha$ radiation. A total of 2122 reflections was obtained, of which 387 were too weak to be measured. Intensities were estimated visually for 1735 with a standard scale. The values of intensity ranged from 1 to 4800 for the b-axis data and from 1 to 6300 for the c-axis data. The crystals used in the experiment were about $0{\cdot}25\times0{\cdot}30\times0{\cdot}25$ mm. Two crystals were necessary for obtaining the c-axis data, because during the exposure of the fifth layer-line photograph the crystal in the capillary moved appreciably owing to the deliquescence of its surface.

The usual Lorentz and polarization corrections were applied, but no corrections were made for absorption and extinction. Corrections for variation in spot-size on the high layer-line photographs were made by the method presented by Phillips (1954). Most of the inten-

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sity data used in this analysis were based on the photographs taken around the c axis, which gave more reliable intensities.

Crystal data

$K_2[Cu(NH_2CH_2CONCH_2COO)_2].6H_2O$ F.W. 510·1
Monoclinic, $a = 13{\cdot}73 \pm 0{\cdot}014$ Å, $b = 6{\cdot}24 \pm 0{\cdot}010$ Å,
$c = 11{\cdot}67 \pm 0{\cdot}014$ Å, $\beta = 102°33' \pm 13'$,
$V = 975{\cdot}9$ Å^3.
$D_m = 1{\cdot}738$ g.cm^{-3}, $D_x = 1{\cdot}736$ g.cm^{-3}.
$Z = 2$. $\mu = 61{\cdot}2$ cm^{-1} (for Cu $K\alpha$).
$F(000) = 516$
Systematic absences $h0l$ with $h = 2n+1$
$0k0$ with $k = 2n+1$
Space group $P2_1/a$.

Structure determination

Since there are only two formula units in the cell, each complex anion is required to have a centre of symmetry, and the two copper atoms have to be placed in one of the sets of twofold centrosymmetric special positions. The pair chosen was (0,0,0) and ($\frac{1}{2}$,$\frac{1}{2}$,0).

The Patterson projection onto (001) showed the x and y coordinates of the potassium ion. The electron density projection along the b axis synthesized with positive signs for all the structure factors gave the third coordinate of the potassium ion. A three-dimensional Fourier synthesis was then made with signs based on the contributions from both the copper atoms and the potassium ions. All the non-hydrogen atoms were identified, though some spurious peaks appeared. The second electron density distribution showed the whole structure more clearly; the ligand molecules were recognized as two glycylglycine molecules.

The parameters thus obtained were refined by the block-diagonal matrix least-squares method. A 9 × 9 matrix is assigned for each atom with anisotropic temperature factors, and a 4 × 4 for each isotropic atom. Unit weight was given to the reflections which have structure factors equal to or larger than 1·0, and 0·5 to the rest of the reflexions. The damping factors for the shifts of all the parameters were 0·7. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The f curve for Cu^+ was used instead of that for Cu^{2+}, considering an effect of the electroneutrality principle (Pauling, 1960). To take account of the anomalous scattering by the copper atom, $\Delta f'$ ($-2{\cdot}1$) was included in the calculations (Dauben & Templeton, 1955).

Two cycles of least-squares refinement were carried out, assigning anisotropic temperature factors to the two heavy atoms. These two cycles decreased the R index to 0·146. Two more cycles of refinement were done, assigning anisotropic temperature factors to all non-hydrogen atoms, and the R value was reduced to 0·125. A three-dimensional difference synthesis was

Table 1. *The final atomic coordinates (fractional) and their standard deviations* (Å)

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Cu	0	—	0	—	0	—
K	0·1259	0·002	0·3702	0·002	0·4875	0·002
O(1)	−0·2018	0·006	0·1377	0·006	0·1951	0·005
O(2)	0·0623	0·006	0·0599	0·006	0·3223	0·005
O(3)	0·0335	0·006	−0·2447	0·006	0·4090	0·006
O(4)	0·0845	0·006	0·3366	0·007	0·1433	0·007
O(5)	0·2549	0·006	−0·0276	0·007	0·2914	0·007
O(6)	0·3062	0·006	0·4572	0·007	0·4321	0·006
N(1)	−0·1090	0·006	0·2145	0·007	−0·0698	0·006
N(2)	−0·0805	0·006	−0·0338	0·006	0·1196	0·005
C(1)	−0·1648	0·008	0·2743	0·008	0·0184	0·007
C(2)	−0·1477	0·007	0·1141	0·007	0·1215	0·007
C(3)	−0·0625	0·007	−0·1852	0·007	0·2173	0·007
C(4)	0·0162	0·007	−0·1184	0·008	0·3246	0·007

Table 2. *The thermal parameters and their standard deviations* (× 10^4)

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

	β_{11}	σ	β_{22}	σ	β_{33}	σ	β_{12}	σ	β_{13}	σ	β_{23}	σ
Cu	7	1	44	3	2	1	24	3	8	1	31	3
K	17	1	58	4	24	1	1	3	14	2	8	4
O(1)	18	3	125	16	18	4	32	12	28	6	7	14
O(2)	25	3	79	15	15	4	−50	11	4	6	30	12
O(3)	24	3	104	16	19	4	−1	12	1	6	75	14
O(4)	26	4	114	17	53	5	9	13	11	7	121	17
O(5)	30	4	97	17	42	5	−34	13	18	7	−17	15
O(6)	27	3	150	19	19	4	20	13	11	6	23	14
N(1)	12	3	57	16	14	4	49	12	6	6	55	14
N(2)	9	3	20	14	4	4	0	10	12	5	10	12
C(1)	17	4	70	19	14	5	53	14	17	7	26	16
C(2)	9	3	53	17	4	4	5	13	6	6	−2	15
C(3)	15	4	32	16	4	4	6	13	14	7	42	14
C(4)	7	3	88	20	6	4	8	14	4	6	29	16

Table 3. *Observed and calculated structure factors* (×2·5)

H	FO	FC
K,L= 0 0		
2	308	371
4	78	-47
6	45	47
8	222	195
10	141	145
12	46	41
14	132	123
16	151	175
K,L= 0 1		
-16	83	-83
-14	188	167
-12	375	397
-10	222	238
-8	95	71
-6•	0	18
-4	464	488
-2	197	172
2	252	232
4	260	-215
6	151	149
8	91	-67
10	130	119
12	248	262
14	67	86
16•	0	-27
K,L= 0 2		
-16	50	39
-14	62	40
-12	67	49
-10	152	148
-8	243	256
-6	296	259
-4	525	-461
-2	31	-9
0	324	411
2	381	403
4	127	-106
6	463	509
8	475	517
10	215	234
12	106	-93
14	37	43
16	139	172
K,L= 0 3		
-16	43	-49
-14	42	-34
-12	302	322
-10	197	176
-8	97	88
-6	271	250
-4	723	896
-2	397	421
0	114	-72
2	177	203
4	394	406
6	250	231
8	127	113
10	89	-77
12	200	205
14	55	55
K,L= 0 4		
-16	251	273
-14•	0	-7
-12	56	37
-10•	0	22
-8	305	277
-6	511	501
-4	44	27
-2	101	118
0	243	250
2	191	-154
4	129	116
6•	25	56
8	368	386
10	134	132
12	73	-64
K,L= 0 5		
-16•	0	-28
-14•	0	27
-12	127	120
-10	355	353
-8	215	-172
-6	169	159
-4	436	465
-2	144	153
0	85	-66
2	176	117
4	484	435
6	474	497
8	135	-128
10	55	40
12	106	98
14	77	75
K,L= 0 6		
-16	162	165
-14	291	269
-12	93	85
-10	100	25
-8	294	281
-6	193	157
-4•	26	-12
-2	107	118
0	421	391
2	336	259
4	58	44
6	166	149
8	237	208
10	111	91
12	74	54
K,L= 0 7		
-16•	0	24
-14	63	63
-12	252	252
-10	122	107
-8•	0	0
-6•	27	16
-4	510	562
-2	273	279
0	186	182
2	84	-44
4	215	183
6	252	239
8•	0	0
10	58	35
K,L= 0 8		
-16	103	113
-14	186	189
-12	90	111
-10	79	-69
-8	305	268
-6	317	303
-4	37	-4
-2	154	146
0	162	151
2	245	243
4	190	-180
6•	0	0
8	216	214
10	90	82
12	97	91
K,L= 0 9		
-16	69	80
-14	70	58
-12	274	243
-10	180	159
-8	245	-236
-6	153	142
-4	108	116
-2	269	268
0	204	183
2	160	148
4	283	285
6	169	176
8•	0	14
10•	0	31
K,L= 0 10		
-14	183	170
-12	48	42
-10	71	54
-8	232	213
-6	286	314
-4	189	190
-2	99	-92
0	300	334
2	270	295
4•	0	24
6	38	-32
8	99	111
10•	25	28
K,L= 0 11		
-14	72	-79
-12	172	157
-10	294	274
-8	106	98
-6	69	71
-4	147	134
-2	100	-92
0	115	-101
2•	0	15
4	212	208
6	162	170
8	55	46
K,L= 0 12		
-12	81	-70
-10	77	66
-8	203	197
-6	224	208
-4	126	104
-2	72	-52
0	163	147
2	349	372
4	61	60
6	108	103
K,L= 0 13		
-10	171	166
-8	146	127
-6	83	76
-4	201	214
-2	272	288
0•	0	-2
2	55	10
4	63	66
K,L= 0 14		
-10•	0	5
-8	55	55
-6	93	105
-4	42	7
-2	47	-26
0	131	148
2	72	88
K,L= 1 0		
1	417	504
2	65	-45
3	287	292
4	324	-277
5	422	431
6	218	211
7	66	-49
8	127	125
9•	0	19
10•	24	19
11	223	227
12	115	114
13	151	149
14	106	94
15	127	119
16•	0	-19
K,L= 1 1		
-17	78	93
-16	59	48
-15	84	87
-14	48	49
-13	136	138
-12•	24	32
-11•	0	-13
-10	149	-141
-9	403	410
-8	106	78
-7	285	278
-6	337	321
-5	159	140
-4	343	327
-3	45	-38
-2	114	-115
-1	259	291
0•	0	-13
1	396	444
2	496	528
3	215	169
4	102	-77
5	232	-180
6	307	-319
7	324	356
8	65	53
9	101	102
10	66	53
11	74	64
12	36	-25
13	44	41
14	123	-124
15	146	163
16•	0	-30
K,L= 1 2		
-17•	0	0
-16	126	129
-15	85	-74
-14	123	-100
-13	157	136
-12•	0	0
-11	327	329
-10	206	161
-9	165	141
-8•	0	-12
-7	145	125
-6	296	-254
-5	105	113
-4	331	-276
-3	76	61
-2	130	-64
-1	197	-197
0	186	-200
1	168	169
2•	15	-59
3	437	461
4•	20	-4
5	482	500
6	60	56
7	66	62
8	61	45
9	101	91
10	134	-133
11	109	102
12	60	-43
13	146	144
14	73	60
15	82	79
16•	0	1
K,L= 1 3		
-17	78	92
-16	34	-30
-15	130	126
-14	72	-63
-13	46	41
-12	70	-70
-11	117	107
-10•	0	-11
-9	224	217
-8	29	-14
-7	340	346
-6	191	194
-5	60	-28
-4	70	-67
-3	281	287
-2	217	-230
-1	159	187
0•	20	8
1	539	679
2	380	382
3	275	286
4	229	201
5	73	44
6	191	-178
7	207	224
8•	0	24
9	177	179
10	120	112
11•	0	26
12	46	-30
13	43	57
14	69	-69
15	109	131
K,L= 1 4		
-17	115	133
-16	39	36
-15•	0	3
-14	131	-119
-13	105	86
-12	49	-51
-11	239	237
-10	362	366
-9	83	67
-8	240	201
-7	111	93
-6	203	-136
-5	440	454
-4	62	-55
-3	382	388
-2•	25	6
-1	328	360
0	171	153
1	344	-361
2	315	-276
3	346	331
4	152	-125
5	173	168
6	79	76
7	58	42
8•	0	9
9	110	98
10	32	-37
11	141	138
12•	0	-16
13	111	105
14	75	74
15	41	52
K,L= 1 5		
-17	75	88
-16•	21	-32
-15	193	201
-14	100	80
-13	42	36
-12•	0	-4
-11•	0	-13
-10	90	-80
-9	262	259
-8	92	-87
-7	117	119
-6	191	-159
-5	267	263
-4	72	38
-3•	14	-4
-2	136	-138
-1	154	153
0	131	94
1	243	211
2	315	280
3•	0	0
4	102	-70
5	226	189
6	141	-109
7	269	235
8•	0	-27
9	233	222
10	92	61
11	113	96
12•	0	28
13	34	-46
14	65	-60
K,L= 1 6		
-17	57	71
-16•	0	13
-15	105	101
-14	78	-72
-13	145	152
-12•	0	-23
-11	151	171
-10	83	84
-9•	26	34
-8	36	27
-7	64	65
-6	203	-209
-5	106	109
-4•	0	-12
-3	467	580
-2	325	353
-1	154	150
0	169	151
1	102	83
2	117	-93
3	205	185
4	284	-241
5	407	359
6•	0	32
7	125	96
8	51	47
9	105	73
10	169	-130
11	126	103
12	72	-57
13	145	140
14	59	79
K,L= 1 7		
-16•	0	-24
-15	215	217
-14	90	85
-13	102	97
-12	147	145
-11•	0	-28
-10	78	-59
-9	159	157
-8	127	-114
-7	310	289
-6•	0	41
-5	258	257
-4	88	61
-3	160	143
-2	104	-100
-1	281	247
0	201	-181
1	235	228
2	101	82
3	60	-35
4	42	24
5•	0	6
6•	0	-20
7	147	149
8	139	133
9	138	131
10	73	58
11	139	134
12•	0	-5
13•	0	6
K,L= 1 8		
-16	51	55
-15	27	-31
-14	87	-95
-13	187	188
-12•	0	-23
-11	124	137
-10	91	93
-9	137	141
-8•	0	-11
-7	80	67
-6	39	-20
-5	72	76
-4	43	29
-3	210	213
-2	164	149
-1	139	115
0	52	31
1	63	-52
2	169	-151
3	222	219
4•	0	-17
5	135	116
6	82	67
7	164	160
8	135	124
9•	0	-1
10	94	-103
11	109	106
12	127	-155
K,L= 1 9		
-15	154	169
-14	49	41
-13	115	112
-12•	0	-4
-11	116	125
-10	39	-28
-9	27	35
-8	159	-155
-7	239	224
-6	109	100
-5	86	71
-4	210	224
-3	64	-57
-2	142	-149
-1	250	282
0	206	-190
1	354	383
2	57	-34
3	188	189
4•	0	-7
5	94	88
6	90	-89
7•	0	13
8•	0	-40
9	146	152
10	74	78
K,L= 1 10		
-15	52	42
-14•	0	-32
-13	110	100
-12	126	-110
-11	203	230
-10	51	51
-9	172	151
-8	29	26
-7	62	39
-6	128	-125
-5	144	135
-4	62	48
-3	224	231
-2	92	90
-1	93	96
0•	0	29
1	123	145
2•	0	29
3	103	108
4•	0	17
5	130	126
6	86	82
7•	0	29
8	52	46
9•	21	-16
10•	0	-32
K,L= 1 11		
-14	97	98
-13	92	83
-12	111	104
-11	60	48
-10•	0	5
-9	177	155
-8•	0	-29
-7	189	187
-6•	0	-20
-5	135	141
-4	111	109
-3	103	-100
-2	62	-59
-1	35	45
0	123	-122
1	114	117
2	116	114
3	158	153
4	101	92
5•	0	38
6	101	-102
7	85	90
8	119	-142
K,L= 1 12		
-13	50	49
-12	72	-65
-11	111	116
-10•	0	18
-9	179	175
-8	76	67
-7•	0	6
-6	135	-132
-5	132	122
-4	141	-143
-3	218	222
-2•	0	23
-1	54	56
0	56	-44
1	97	82
2•	0	-15
3	122	121
4•	0	5
5	168	189
6•	0	20
K,L= 1 13		
-11•	0	-2
-10•	0	-8
-9•	0	33
-8•	0	-12
-7	257	261
-6	127	124
-5	108	113
-4	84	88
-3	165	156
-2•	0	9
-1	90	83
0	62	-65
1	87	84
2•	0	30
3	80	86
4	93	105
5•	0	-3
K,L= 1 14		
-9	74	94
-8	76	85
-7•	0	20
-6•	0	-7
-5	91	86
-4	50	-47
-3	103	121
-2•	0	-6
-1	103	112
0	37	35
1	51	-53
2	52	-65
K,L= 2 0		
0	205	201
1	418	473
2	29	9
3	100	77
4	348	338
5	269	-245
6	82	65
7	144	-144
8	121	121
9	124	113
10	133	120
11	182	196
12	143	164
13•	0	-43
14	154	145
15•	0	-20
16	106	121
K,L= 2 1		
-16	47	49
-15	84	-83
-14	72	69
-13•	0	-16
-12•	24	33
-11	157	151
-10	68	48
-9	191	170
-8	276	239
-7	57	-37
-6	217	192
-5	320	-292
-4	292	294
-3	266	266
-2	345	323
-1	279	264
0•	0	42
1	76	-46
2	439	469
3	68	68
4	264	264
5•	0	-6
6	165	155
7	115	98
8	132	143
9	102	-95
10	130	121
11	74	-57
12	120	124
13	82	72
14	159	154
15	41	33
16	51	50
K,L= 2 2		
-16	73	73
-15	106	96
-14	131	114
-13	165	152
-12	114	109
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-9	177	-160
-8	195	182
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-6	392	364
-5	29	-21
-4	50	5
-3	282	-244
-2	134	121
-1	66	-59
0•	13	20
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2	365	319
3	322	341
4	323	348
5	301	-295
6	102	89
7	277	-285
8	68	-54
9	53	37
10	112	111
11	103	96
12	41	45
13	115	-110
14	151	162
15	97	-118
16	66	104
K,L= 2 3		
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-16	98	110
-15	44	-47
-14	138	138
-13	187	-176
-12	59	48
-11	67	79
-10	108	104
-9	127	102
-8	203	203
-7	130	-116
-6	67	-57
-5	291	-287
-4	138	134
-3	200	183
-2	90	-45
-1	397	409
0	280	274
1	287	-268
2	449	474
3	274	-237
4	362	390
5	98	79
6	148	130
7	64	50
8	110	115
9•	0	36
10	72	69
11	67	-51
12	135	130
13	101	86
14	68	74
15	36	38
K,L= 2 4		
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-15	97	90
-14	34	32
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-12	98	80
-11	37	-29
-10	111	102
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-8	337	324
-7	157	133
-6	302	284
-5	336	323
-4	288	294
-3	126	-116
-2	244	253
-1	136	-150
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1	39	39
2	161	140
3•	16	-15
4	278	274
5	122	98
6•	0	17
7	138	-116
8	126	119
9	126	120
10	132	129
11	161	151
12	62	51
13	93	-99
14	33	40
K,L= 2 5		
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-14	145	141
-13	88	-68
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-11	90	-85
-10	183	188
-9	224	228
-8	208	213
-7	99	-77
-6	197	202
-5	243	-238
-4	90	104
-3	104	96
-2	92	84
-1	186	162
0	101	-61
1	88	-79
2	144	139
3	270	-255
4	37	36
5	99	72
6	245	218
7	185	179
8	170	161
9	211	-198
10	235	248
11	128	-137
12	97	82
13•	0	-4
14•	0	24
K,L= 2 6		
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-14	101	99
-13	111	106
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-11	129	-131
-10•	0	11
-9	173	-200
-8	125	126
-7	118	125
-6	123	131
-5	111	112
-4	168	183
-3	97	-79
-2	398	451
-1	216	-180
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1	67	41
2	241	210
3	150	123
4	219	191
5	79	-48
6	65	40
7	100	-76
8	203	165
9•	0	-27
10	175	130
11	77	54
12	86	72
13•	0	2
K,L= 2 7		
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-14	122	122
-13	63	-66
-12	91	87
-11	98	92
-10	106	103
-9	155	150
-8	175	177
-7	136	115
-6	139	125
-5	220	-203
-4	252	248
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-2	198	179
-1	136	117
0	287	283
1•	0	-14
2	33	-34
3	126	-97
4	45	45
5	82	79
6	39	-13
7	242	227
8	84	84
9•	0	-20
10	176	154
11	142	-150
12	81	83
K,L= 2 8		
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-14	116	115
-13	152	148
-12	111	113
-11	98	102
-10	124	136
-9	187	-191
-8	150	157
-7•	0	22
-6•	0	-8
-5	180	162
-4•	0	11
-3	163	-137
-2	203	186
-1	115	-101
0	114	98
1•	21	-31
2	238	211
3	152	145
4	155	147
5	72	-61
6	159	167
7	149	-153
8	140	142
9•	0	26
10	130	126
11•	0	0
K,L= 2 9		
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-14	116	109
-13	147	-138
-12	139	128
-11•	0	-26
-10	194	226
-9	69	54
-8	147	141
-7	143	-166
-6	149	135
-5	50	-34
-4	42	25
-3•	0	18
-2	218	209
-1	173	165
0	231	212
1•	0	-2
2	175	161
3	224	-225
4	153	129
5	27	-45
6	78	68
7	75	51
8•	0	26
9•	0	16
10	58	79
11•	0	-14
K,L= 2 10		
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-13	152	137
-12	122	107
-11•	0	3
-10	138	116
-9	139	-116
-8	206	180
-7•	0	-45
-6•	0	-1
-5	187	171
-4	116	126
-3	130	139
-2	110	117
-1	118	-127
0	99	101
1	36	33
2	70	62
3	117	110
4	78	75
5•	0	-1
6	65	64
7	102	-106
8	87	98
9•	26	26
K,L= 2 11		
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-12	117	107
-11•	0	15
-10	79	74
-9	116	113
-8	152	141
-7	34	-32
-6	127	121
-5	202	-179
-4	81	85
-3•	0	13
-2	183	175
-1	66	67
0	123	123
1•	0	2
2	95	85
3	91	-89
4	167	170
5•	0	7
6	75	80
7	40	38
8	57	79
K,L= 2 12		
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-11	28	-33
-10	142	140
-9	123	-122
-8	73	75
-7•	0	3
-6	77	76
-5	32	29
-4	92	84
-3•	0	5
-2	123	122
-1	122	-124
0	67	55
1	88	-88
2	64	75
3	126	135
4	79	93
5•	0	12
6	104	128
K,L= 2 13		
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-9	121	122
-8	73	78
-7	144	152
-6	101	105
-5	31	-43
-4	111	105
-3	63	-82
-2	144	139
-1	116	122
0	34	40
1	31	-28
2	31	39
3	70	-84
4	100	140
K,L= 2 14		
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-7•	0	0
-6	132	144
-5	86	93
-4	153	175
-3	42	-41
-2	70	79
-1	81	-89
0	34	37
1•	0	8
K,L= 3 0		
1	363	344
2	245	-252
3	78	58
4	234	-227
5	60	-47
6	120	112
7	158	163
8•	0	-17
9	154	146
10	71	-62
11	114	117
12•	0	0
13	90	86

Table 3 (*cont.*)

H	FO	FC
14•	0	31
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K,L=	3	1
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-12	139	148
-11	142	145
-10	126	-112
-9•	0	14
-8•	0	22
-7•	0	12
-6	73	61
-5	305	309
-4•	26	-15
-3	416	388
-2	134	-125
-1	278	267
0	200	-167
1	109	-81
2	66	35
3	397	388
4	148	133
5	114	110
6	94	-77
7	79	75
8	143	145
9	57	52
10	138	135
11	232	264
12•	0	-3
13	243	246
14	116	-109
15•	0	12
K,L=	3	2
-16•	0	22
-15	189	200
-14	40	-32
-13	38	38
-12•	0	20
-11	79	72
-10	119	99
-9	163	142
-8	95	-68
-7	329	305
-6	165	-148
-5	178	180
-4•	0	12
-3	44	-26
-2	325	306
-1	375	390
0	92	73
1	320	314
2	129	-100
3	46	29
4	44	26
5	227	190
6	77	74
7	99	88
8	138	-145
9	205	214
10	128	-139
11•	0	5
12	72	-58
13	50	48
14•	0	5
15	85	105
K,L=	3	3
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-15	94	87
-14	91	89
-13	129	117
-12•	0	16
-11	142	140
-10	118	-112
-9	72	64
-8	67	-62
-7	45	44
-6	143	119
-5	248	227
-4	52	-45
-3	246	255
-2•	0	5
-1	135	-108
0	202	-183
1	171	171
2•	0	-3
3	177	182
4•	0	25
5	368	395
6	191	-198
7	80	73
8	107	-100
9	73	-69
10	118	104
11	108	100
12	96	82
13	112	115
14•	0	22
K,L=	3	4
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-15	91	94
-14	28	-37
-13	43	40
-12	33	-36
-11	82	-78
-10	114	106
-9	228	227
-8	93	73
-7	420	403
-6	94	-83
-5	244	208
-4	53	-44
-3	124	-110
-2	73	-53
-1	132	132
0	174	169
1	210	214
2	174	-179
3	169	159
4	200	199
5	73	72
6	218	218
7	295	315
8	46	-47
9	176	165
10	63	-64
11	51	53
12•	0	-7
13•	0	-8
14•	0	13
K,L=	3	5
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-15	49	-49
-14	160	163
-13	111	115
-12	82	72
-11	163	154
-10	106	-104
-9	171	180
-8	91	96
-7	165	166
-6	81	69
-5	277	286
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-3	231	216
-2	187	-177
-1•	0	-26
0	117	-89
1	59	56
2	104	91
3	218	206
4	27	27
5	245	235
6	78	-77
7	192	185
8	200	-170
9•	0	28
10	90	-66
11	117	117
12•	0	5
13	108	121
K,L=	3	6
-15	120	133
-14	69	-65
-13	44	55
-12	118	-102
-11	66	53
-10	86	-78
-9•	0	25
-8•	0	14
-7	338	330
-6•	0	13
-5•	0	13
-4	174	-163
-3	63	59
-2	99	82
-1	243	231
0•	0	-10
1	365	330
2	169	-152
3	116	93
4	49	-48
5	123	-103
6	183	147
7	91	62
8•	0	14
9	251	218
10•	0	-22
11•	0	8
12	29	27
K,L=	3	7
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-13	78	72
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-10	116	-118
-9•	0	9
-8	79	70
-7	124	-119
-6	276	268
-5	193	184
-4	137	123
-3	224	215
-2	104	-93
-1	264	275
0	62	-56
1	117	104
2	111	88
3	117	99
4•	0	21
5	139	128
6•	0	-28
7•	0	23
8•	0	-7
9•	0	71
10•	0	19
11	134	149
K,L=	3	8
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-13	147	151
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-11	89	69
-10	53	3
-9	190	194
-8•	0	16
-7	94	96
-6•	0	-32
-5	119	121
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-3	36	29
-2	36	-19
-1	221	222
0	74	53
1	282	292
2	136	-130
3	129	121
4•	0	-29
5•	0	-20
6•	0	-32
7	145	144
8•	0	15
9	159	175
10	60	-67
11	60	75
K,L=	3	9
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-13	104	107
-12•	0	-26
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-10	89	-94
-9	156	144
-8	148	-157
-7	57	-33
-6	79	55
-5	84	75
-4	78	68
-3	254	237
-2	82	-78
-1	96	81
0	55	55
1	55	31
2	117	109
3•	0	30
4•	0	10
5	184	186
6	86	-72
7	67	59
8	79	-84
9•	0	18
K,L=	3	10
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-12•	0	10
-11•	0	-26
-10	136	120
-9	111	90
-8	153	130
-7	204	212
-6	40	-26
-5	87	73
-4	81	-68
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-2	64	65
-1	76	54
0•	0	31
1	173	180
2	73	-54
3	81	66
4	91	-84
5•	0	3
6•	0	3
7	118	142
8•	0	20
K,L=	3	11
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-11	172	176
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-9	118	112
-8	77	-64
-7	105	94
-6	83	-59
-5	142	133
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-3	182	177
-2	89	-84
-1	168	168
0•	0	2
1	61	-49
2	41	37
3	129	142
4	54	47
5	145	168
6	40	-44
K,L=	3	12
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-9	82	76
-8	64	68
-7	132	138
-6	74	-72
-5	124	113
-4	78	-78
-3	67	-68
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0	79	85
1	152	167
2	56	-54
3	93	102
4	89	-98
5	54	69
K,L=	3	13
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-8	47	-43
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-6	73	83
-5	79	80
-4	45	-33
-3	134	138
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-1	57	56
0•	24	-29
1•	21	26
2	40	-45
K,L=	4	0
0	50	44
1•	0	0
2	155	159
3	219	-211
4	343	338
5	49	-42
6	62	53
7	69	64
8•	25	-24
9	53	54
10	88	78
11	43	-43
12	209	223
13•	0	-1
14•	0	-10
K,L=	4	1
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-6	164	146
-5	88	84
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-1	69	-65
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1	196	-186
2	179	166
3•	0	-14
4•	23	-19
5•	0	21
6	95	101
7	90	93
8	235	238
9	102	111
10	112	113
11•	0	-28
12	48	42
13	59	-57
14	91	103
K,L=	4	2
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-9•	23	31
-8	71	-62
-7	157	-143
-6	182	163
-5	112	103
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0	115	109
1•	0	4
2	148	146
3	38	-29
4	359	417
5•	0	7
6	212	227
7•	23	10
8	79	-72
9	96	-98
10	82	89
11•	0	-14
12	122	156
13•	0	-14
14	55	81
K,L=	4	3
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-8	293	305
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-6	131	129
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0	435	445
1	30	20
2	67	68
3	58	59
4	115	-104
5	70	-71
6	112	102
7	97	-97
8	135	145
9	46	-47
10•	0	20
11•	0	-18
12•	0	-10
13	89	92
K,L=	4	4
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-14	33	36
-13•	0	-12
-12	221	219
-11	109	97
-10	66	48
-9	67	59
-8	44	-28
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-6•	19	17
-5	60	-47
-4	282	284
-3	109	-93
-2	146	135
-1	88	-80
0•	0	14
1	56	43
2•	0	29
3	73	77
4	210	214
5	115	107
6	277	281
7	46	-41
8	91	83
9	79	-73
10	70	74
11	69	-62
12	179	207
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-8	206	217
-7•	0	-23
-6	291	327
-5	58	-60
-4	103	110
-3	111	-117
-2	189	194
-1	99	-94
0	298	292
1•	0	18
2	255	246
3	160	181
4	113	-113
5•	0	-19
6	171	180
7•	0	-20
8	248	242
9	109	-88
10	58	60
11	54	-46
12	55	-56
K,L=	4	6
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-10	119	111
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-8	96	-90
-7	60	37
-6	143	140
-5	84	87
-4	243	241
-3•	0	-18
-2	171	172
-1•	0	33
0	141	-129
1	51	-50
2	28	-38
3	85	-54
4	175	148
5•	0	-17
6	115	95
7•	0	-35
8	90	61
9	42	43
10•	0	-18
11•	0	10
K,L=	4	7
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-13	31	-40
-12•	0	-2
-11	60	-50
-10•	0	-15
-9•	0	-1
-8	68	55
-7	63	56
-6	183	198
-5	117	113
-4	97	82
-3	79	80
-2•	0	-18
-1	138	-138
0	317	313
1•	0	-4
2	159	168
3	94	-90
4	85	96
5•	0	-51
6	75	70
7•	0	0
8	252	228
9	34	43
10	129	142
K,L=	4	8
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-13•	0	8
-12	149	191
-11	49	-44
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-9	72	-59
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-7	54	-46
-6	78	85
-5•	25	-35
-4	289	323
-3•	0	-6
-2	166	180
-1•	0	29
0•	0	12
1•	0	-3
2	87	87
3•	0	25
4	173	178
5	72	-58
6	149	138
7•	0	-11
8	66	-66
9•	0	13
K,L=	4	9
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-12•	0	10
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-10	81	75
-9•	0	-11
-8	143	133
-7	77	-65
-6	121	107
-5	48	45
-4	39	-37
-3•	0	24
-2	48	-45
-1•	0	-2
0	152	148
1•	0	31
2	197	197
3•	0	14
4•	0	4
5	72	-64
6•	0	22
7•	0	-29
8	55	64
K,L=	4	10
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-11	59	54
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-8	79	62
-7	87	66
-6	55	-38
-5	88	-75
-4	202	197
-3•	0	-21
-2	180	189
-1	68	-54
0	67	54
1	55	-50
2	90	86
3•	0	-4
4	147	170
5•	0	-30
6	114	131
7•	0	7
K,L=	4	11
-10	40	18
-9	38	36
-8	195	204
-7	36	-46
-6	214	228
-5•	0	-38
-4•	0	-16
-3	39	-44
-2•	0	18
-1•	0	0
0	137	147
1•	0	29
2	133	148
3•	0	6
4	38	40
5•	0	3
K,L=	4	12
-9•	0	46
-8•	19	4
-7	55	-55
-6	72	75
-5	65	-57
-4	84	93
-3•	0	34
-2	94	108
-1	65	65
0	56	41
1•	0	23
2•	0	10
K,L=	5	0
1	188	188
2	144	140
3	79	86
4•	0	-14
5•	25	-19
6	121	-117
7	97	104
8•	0	20
9	154	154
10	85	77
11	67	60
12	40	37
K,L=	5	1
-13	77	80
-12•	0	26
-11	152	158
-10	139	143
-9	130	134
-8	59	58
-7•	0	-25
-6	106	-95
-5	80	67
-4•	0	-35
-3	162	155
-2	80	75
-1	134	123
0	97	90
1	46	38
2	193	-186
3	291	310
4•	0	17
5	172	191
6•	0	0
7	75	72
8•	23	7
9	55	48
10	104	-98
11	120	124
12•	0	-4
13	62	71
K,L=	5	2
-13•	0	3
-12•	0	27
-11	88	79
-10•	20	-9
-9	241	251
-8	115	-96
-7	200	195
-6•	0	-8
-5	33	24
-4•	0	0
-3	74	60
-2	204	-181
-1	232	222
0	118	115
1	196	180
2	196	194
3	78	75
4	100	-106
5	121	130
6	100	-105
7	120	118
8	85	-81
9	153	156
10	127	134
11•	0	-4
12	58	65
K,L=	5	3
-13	67	66
-12•	0	-23
-11	141	142
-10	74	64
-9	133	129
-8•	0	16
-7	68	67
-6	131	-132
-5	105	94
-4	36	22
-3	211	211
-2	250	265
-1	35	34
0	88	76
1•	0	-10
2•	22	24
3	33	50
4	150	-158
5	166	187
6•	0	19
7	61	51
8•	0	9
9•	0	26
10	108	-106
11	96	100
K,L=	5	4
-13	63	62
-12	94	93
-11•	24	-29
-10	33	-27
-9	108	95
-8•	0	5
-7	132	121
-6	102	97
-5	63	53
-4	30	21
-3	66	71
-2	214	-229
-1	215	235
0	108	-99
1	181	171
2	61	43
3	81	79
4•	0	-1
5	65	49
6	151	-143
7	213	188
8•	0	7
9	131	124
10•	26	23
11	52	51
K,L=	5	5
-13	132	161
-12•	0	-26
-11	126	130
-10	89	86
-9	48	44
-8•	0	43
-7•	0	18
-6	150	-141
-5	181	183
-4	94	-89
-3	269	273
-2	40	42
-1	138	142
0•	0	-12
1	65	54
2•	0	0
3	134	130
4	71	59
5	163	153
6	128	115
7	91	70
8	117	109
9•	0	0
10	113	-121
K,L=	5	6
-13	83	101
-12•	0	-17
-11	72	66
-10•	0	18
-9•	0	43
-8•	0	-49
-7	179	159
-6	272	236
-5	84	59
-4	113	102
-3	79	59
-2	86	-65
-1•	0	48
0	105	-81
1	109	99
2•	0	33
3	51	49
4•	0	28
5•	0	34
6	137	-111
7	150	115
8	71	-76
9	173	158
10•	0	60
K,L=	5	7
-12	102	-121
-11	121	132
-10	118	113
-9•	0	32
-8	83	67
-7•	0	-3
-6	155	-139
-5	183	179
-4•	0	-8
-3	192	202
-2	39	-36
-1	79	60
0	67	-45
1•	0	-26
2	136	-136
3	154	155
4	108	-104
5	176	184
6	109	96
7	82	78
8	64	55
K,L=	5	8
-11•	0	-13
-10	80	-102
-9	126	125
-8	68	-66
-7	149	150
-6•	0	-33
-5	182	172
-4	94	85
-3	108	102
-2•	0	-12
-1	111	110
0•	0	-3
1	133	109
2	105	106
3	117	106
4	78	74
5•	0	17
6	76	-82
7•	0	30
8•	0	-27
K,L=	5	9
-11•	0	94
-10	60	58
-9	88	86
-8•	0	22
-7•	0	16
-6	122	-110
-5	55	52
-4	42	-20
-3	181	168
-2	145	139
-1	61	49
0	42	44
1•	0	18
2	87	-82
3	135	119
4	144	-168
5	144	153
6•	0	14
K,L=	6	0
0	142	126
1	145	-120
2	93	67
3	192	-184
4	82	66
5	85	66
6•	0	13
7•	0	-1
8	88	91
9	66	-56
10	96	102
K,L=	6	1
-11	92	-100
-10	73	70
-9	98	-96
-8	30	29
-7	108	100
-6•	0	-8
-5	63	50
-4	109	107
-3	152	-149
-2	147	138
-1•	0	-14
0	122	122
1•	24	32
2	177	184
3	59	56
4	160	174
5	97	-99
6	122	131
7	140	-149
8	64	50
9	65	66
10	78	77
11•	0	90
K,L=	6	2
-11•	0	22
-10	103	93
-9	136	143
-8	155	157
-7	130	-119
-6	139	128
-5	137	-135
-4	123	112
-3•	22	-32
-2	159	149
-1	197	196
0	59	50
1	73	64
2	77	75
3	84	-90
4	46	30
5	83	78
6	73	67
7	74	64
8	86	86
9	106	-120
10	55	59
K,L=	6	3
-11•	0	-24
-10	47	40
-9	51	-46
-8	124	117
-7	148	144
-6	102	104
-5•	0	18
-4	131	113
-3	58	-51
-2	80	75
-1	108	-92
0•	0	-13
1	147	153
2•	0	18
3	76	75
4	147	146
5	135	-132
6	121	116
7	117	-119
8	114	129
9•	0	29
10	65	81
K,L=	6	4
-11	82	95
-10•	19	29
-9	98	107
-8	133	138
-7•	0	14
-6	145	133
-5	190	-167
-4	117	94
-3	28	-40
-2	126	103
-1	65	53
0	134	130
1	70	-67
2	135	121
3	162	-156
4	132	126
5•	0	17
6	69	70
7	70	70
8	78	70
9•	0	-30
K,L=	6	5
-11•	0	-19
-10	76	89
-9	70	-78
-8	66	61
-7•	0	22
-6	88	86
-5	89	82
-4	84	65
-3	77	-57
-2	97	81
-1	40	-45
0	58	60
1	42	42
2	110	106
3	170	168
4	102	111
5	85	-74
6	81	72
7	34	-53
8•	0	11
K,L=	6	6
-10	82	96
-9	87	90
-8	123	114
-7	31	-34
-6	85	80
-5	43	-44
-4	58	52
-3	45	48
-2	37	44
-1	198	174
0	103	109
1	98	-99
2	165	144

Table 3 (*cont.*)

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
3	174	-154	2	72	71	3	102	-110	3	118	114	2	154	-158'	2	115	115	3	83	72	4	52	47	K,L=	7	6
4	89	94	3•	0	-11	4	41	35	4	88	-103	3	40	34	3	123	133	4	53	-49	5	113	122	-6	44	53
5	60	48	4	77	77	K,L=	6	9	5	178	202	4•	0	-3	4•	24	11	5•	0	-2	6	42	-60	-5	117	139
6	64	63	5	57	52	-7•	0	1	6	100	-102	5	36	54	5	104	100	6•	0	37	K,L=	7	5	-4•	0	-5
7	33	24	6	30	24	-6	55	71	7	55	57	6•	0	13	6•	0	-10	7•	26	112	-7	96	129	-3	157	156
K,L=	6	7	K,L=	6	8	-5	107	115	8	29	-15	7	104	128	K,L=	7	3	K,L=	7	4	-6	33	-41	-2•	24	-20
-9	65	-76	-8	49	52	-4	95	96	K,L=	7	1	8•	0	24	-8	58	62	-7•	0	3	-5	69	77	-1	39	31
-8	99	105	-7•	0	2	-3	39	34	-8•	0	-16	K,L=	7	2	-7	167	203	-6	66	71	-4•	0	-2	0	42	-45
-7•	0	-7	-6	60	53	-2	151	166	-7	118	133	-7•	24	22	-6•	0	-11	-5	111	119	-3	33	-39	1	37	34
-6•	0	23	-5	107	-117	-1•	0	-35	-6	104	-98	-6	62	52	-5	28	34	-4•	20	-15	-2	42	44	2	49	42
-5	84	74	-4	76	81	0	61	65	-5	66	63	-5	133	140	-4	93	-91	-3	92	92	-1	107	121	3	37	35
-4	95	100	-3	29	44	1•	25	-33	-4	49	-35	-4•	0	-17	-3	27	-29	-2	150	-153	0•	0	13	K,L=	7	7
-3•	0	0	-2	149	151	2•	0	38	-3	48	-43	-3	144	155	-2•	25	28	-1	53	50	1	147	163	-3•	27	-34
-2	91	91	-1	117	121	3•	0	4	-2	81	76	-2•	0	-35	-1	107	108	0•	0	-9	2•	0	-10	-2•	21	34
-1	197	-199	0	109	109	K,L=	7	0	-1	121	110	-1•	0	-10	0•	25	-33	1•	0	22	3•	0	1	-1	67	76
0	70	67	1	75	-93	1•	0	-21	0•	0	31	0	100	90	1	174	178	2	31	39	4•	0	-6	K,L=	8	0
1	49	-44	2	100	110	2	62	-50	1	181	189	1	60	54	2	50	-38	3	134	145	5•	0	-19	0	108	164

computed at this stage, in which nine peaks corresponding to hydrogen atoms could be found. However, three hydrogen atoms to be attached to the N(1), O(4) and O(6) atoms were not observed. One more cycle of refinement was carried out without the contributions of hydrogen atoms to the structure factors. The final refinement reduced the R to 0·122 for all reflexions and 0·092 omitting the unobserved. The maximum shift in positional parameters in the last least-squares calculation was 0·0015 Å, about a quarter of the standard deviation. The final atomic coordinates and their standard deviations are listed in Table 1, the thermal parameters in Table 2. The calculated and observed structure factors are presented in Table 3. Large discrepancies between F_c and F_o of some low-order reflexions may be ascribed to omission of correction for absorption and extinction effects and neglect of the scattering form the hydrogen atoms.

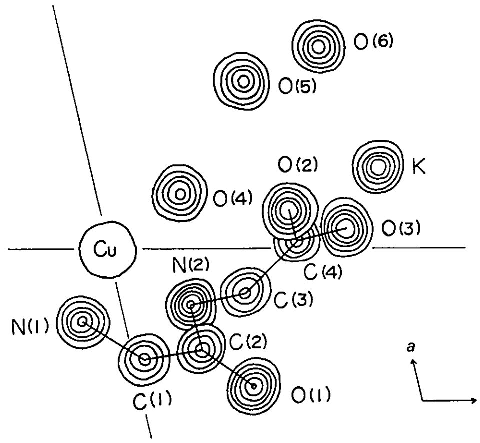

Fig. 1. A composite drawing of the final electron density map, viewed along the b axis. Contours are drawn at 3, 6, 9 e.Å^{-3}. . for light atoms, and at 10, 20, 30 e.Å^{-3}. . . for the potassium ion. Contours for the copper atom are omitted.

Fig. 1 shows a composite drawing of the final electron density map, viewed along the b axis. Omission of corrections for absorption results in atomic peaks higher than usual and smaller temperature factors. However, the general trend of the magnitudes of the thermal vibrations agrees with that expected. The trigonal nitrogen atom N(2) has the smallest thermal parameters, and the carboxyl oxygen atoms O(2) and O(3) the largest in the peptide molecule. The oxygen atoms of water molecules show the largest thermal motions in the crystal.

Discussion of the structure

The interatomic distances and angles are illustrated in Fig. 2, and are listed in Table 4. The estimated standard deviations of the bond lengths and angles are about 0·009 Å and 0·6° respectively.

Geometry of the copper coordination

The copper atom exhibits fourfold coordination. Two glycylglycine molecules related by a centre of symmetry coordinate to one copper atom through the

Table 4. *Bond lengths, angles and their standard deviations*

Bond	l	$\sigma(l)$	Angle	θ	$\sigma(\theta)$
N(1)-C(1)	1·46 Å	0·010 Å	N(1)-C(1)-C(2)	112°	0·6°
C(1)-C(2)	1·54	0·010	C(1)-C(2)-O(1)	116	0·6
C(2)-O(1)	1·26	0·009	C(1)-C(2)-N(2)	116	0·6
C(2)-N(2)	1·31	0·009	O(1)-C(2)-N(2)	128	0·7
N(2)-C(3)	1·46	0·009	C(2)-N(2)-C(3)	116	0·6
C(3)-C(4)	1·52	0·010	N(2)-C(3)-C(4)	116	0·6
C(4)-O(2)	1·28	0·009	C(3)-C(4)-O(2)	119	0·6
C(4)-O(3)	1·24	0·009	C(3)-C(4)-O(3)	117	0·6
			O(2)-C(4)-O(3)	124	0·7
Cu—N(1)	2·04	0·006	Cu—N(1)-C(1)	110	0·3
Cu—N(2)	1·97	0·006	Cu—N(2)-C(2)	116	0·3
Cu—O(4)	2·77	0·007	Cu—N(2)-C(3)	127	0·3
			N(1)-Cu—O(4)	85	0·2
			N(2)-Cu—O(4)	83	0·2
			N(1)-Cu—N(2)	83	0·2

terminal and peptide nitrogen atoms. Since the copper atom is located at a centre of symmetry, it is exactly on the plane made by the four ligand atoms. The bond distance Cu–N(1), 2·04 Å, is longer than Cu–N(2), 1·97 Å, and the difference of the two bond lengths is clearly significant. The environment around the amino nitrogen atom is close to tetrahedral, indicating an sp^3 distribution. On the other hand, the sum of angles around the N(2) atom is 359 °, which shows an sp^2 distribution. This situation may explain the difference of the two Cu–N bond lengths, as described by Strandberg, Lindqvist & Rosenstein (1961). It has been observed also in other peptide complexes that the copper–amino nitrogen bond is longer than the copper–peptide nitrogen bond (Strandberg, Lindqvist & Rosenstein, 1961; Freeman, Schoone & Sime, 1965; Freeman & Taylor, 1965).

There are two water molecules above and below the plane of the copper and the four nitrogen atoms. The two molecules which are also related to each other by a centre of symmetry lie on a line nearly normal to the plane. The distance between the copper atom and the oxygen atom of the water molecule, 2·77 Å, is too long for a usual covalent bond and the water molecules are very weakly associated with the copper atom; the shortest distance listed by Orgel (1960) for bond between copper(II) and the water ligand in the 'polar' position is 2·30 Å (in Cu(acetate)$_2$.H$_2$O). The vector Cu–O(4) makes an angle of 82 ° with the plane; the six atoms around the copper atom form a distorted octahedron.

Peptide molecule

The bond distances and angles in the peptide molecule are all normal within experimental error. The bond distance C(2)–O(1), 1·26 Å, seems a little longer than usual (1·24 Å, Pauling & Corey, 1953), though the difference is not significant; the O(1) atom accepts three hydrogen bonds and the bond might be lengthened.

The peptide group, –C(1)C(2)O(1)N(2)C(3)–, is planar within the limits of error. The best plane determined by least-squares calculation is described by equation (3) in Table 5. The amino nitrogen atom N(1) is 0·172 Å out of the plane, and the bond N(1)–C(1) makes an angle of 6·8 ° with the plane. The dihedral

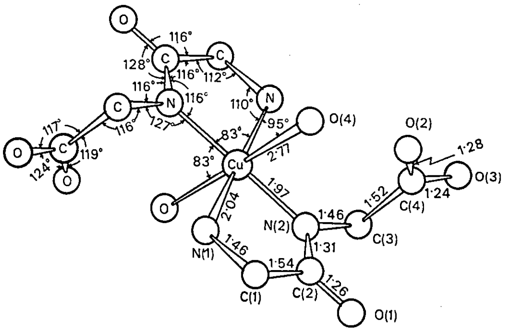

Fig. 2. Interatomic distances and angles in the bis(glycylglycinato)cuprate(II) anion.

Table 5. *The equations of the least-squares planes through atoms*

	Equation	Atom	Deviation
(1)	$0{\cdot}4148X+0{\cdot}7300Y+0{\cdot}5433Z=0$	Cu	0·000
		N(1)	0·000
		N(2)	0·000
		C(1)*	0·406
		C(2)*	0·302
		C(3)*	−0·088
(2)	$0{\cdot}5635X+0{\cdot}6511Y+0{\cdot}5085Z+0{\cdot}1644=0$	Cu	0·164
		N(1)	−0·109
		C(1)	0·085
		C(2)	0·014
		N(2)	−0·076
		O(1)*	0·011
		C(3)*	−0·129
(3)	$0{\cdot}5924X+0{\cdot}6038Y+0{\cdot}5334Z+0{\cdot}2257=0$	C(1)	0·003
		C(2)	0·009
		O(1)	−0·006
		N(2)	−0·013
		C(3)	0·008
		Cu*	0·226
		N(1)*	−0·172
(4)	$0{\cdot}8634X-0{\cdot}4583Y-0{\cdot}3802Z+1{\cdot}5506=0$	C(3)	0·003
		C(4)	−0·009
		O(2)	0·003
		O(3)	0·003
		N(2)*	−0·005
where	$X=ax+cz\cos\beta,\ Y=by,\ Z=cz\sin\beta.$		

* Atoms not included in the least-squares calculation.

angle between the peptide plane and that of four ligand atoms is 12·8°. The five-membered chelate ring, CuN(1)C(1)C(2)N(2), is therefore not planar, the deviations of the atoms from the plane (2) being shown in Table 5.

The carboxyl group, -C(3)C(4)O(2)O(3), and the N(2) atom are coplanar within the limits of error. The dihedral angle between the peptide group and the carboxyl group is 90·2°. The oligopeptides so far analyzed generally take a conformation such that peptide group and carboxyl group are approximately orthogonal or parallel with each other.

Hydrogen bonds

The complex anions in the crystal are held by hydrogen bonds as seen in Figs. 3 and 4. Six hydrogen atoms of water molecules and the N(1) atom have been assigned to form hydrogen bonds. The distances and angles around the three water molecules and the N(1) atom are listed in Table 6. Bond angles around the N(1) atom show a reasonable tetrahedral environment. The water molecules, O(4) and O(6), link two peptide molecules, and another, O(5), links three peptide molecules.

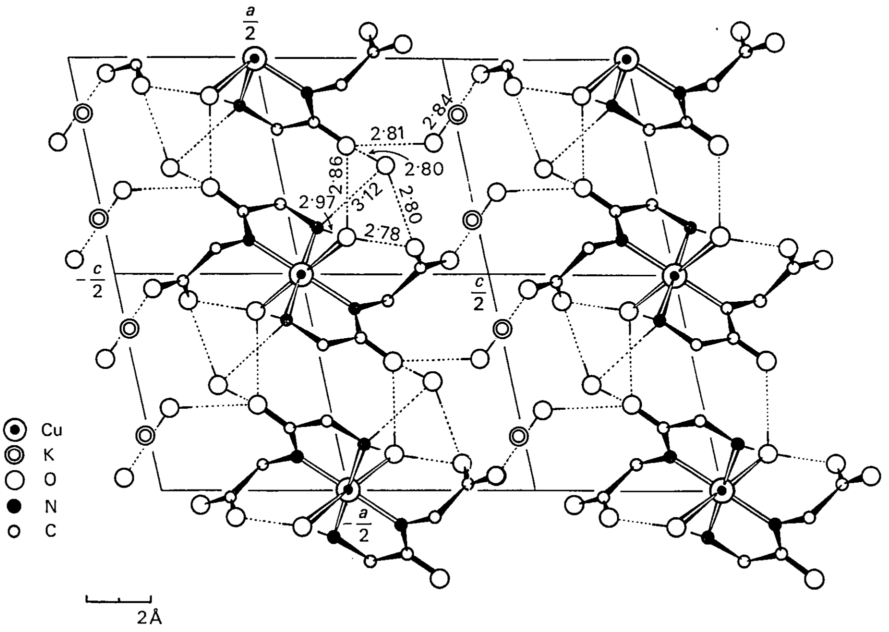

Fig. 3. The structure viewed along the *b* axis. Hydrogen bonds are indicated by broken lines. Proton donation in a hydrogen bond is represented by a short full line at the appropriate end of the bond. Coordination bonds are shown by ═══.

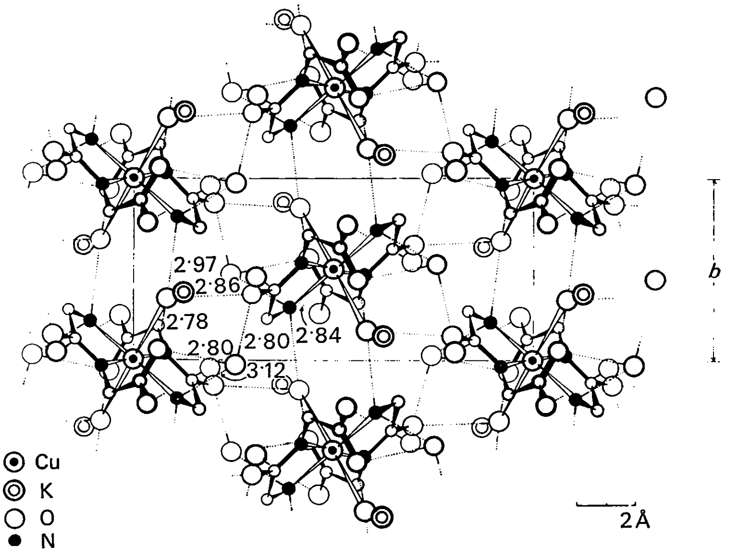

Fig. 4. The structure viewed along the *c* axis.

Table 6. *Environment of water molecules and amino nitrogen atom*

The asymmetric units are denoted as follows:

Coordinates			superscript	Coordinates			superscript
x	y	z	none	$-x$	$-y$	$1-z$	v
$-x$	$-y$	$-z$	i	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$1-z$	vi
$\frac{1}{2}+x$	$\frac{1}{2}-y$	z	ii	$-x$	$1-y$	$-z$	vii
$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$1-z$	iii	$-x$	$1-y$	$1-z$	viii
x	$1+y$	z	iv				

Atom	Neighbour atom	Distance		Angle
O(4)–H···	O(2)	2·78 Å	O(2)—O(4)–O(1$^{\text{ii}}$)	99°
O(4)–H···	O(1$^{\text{ii}}$)	2·86	O(1$^{\text{ii}}$)—O(4)–N(1$^{\text{vii}}$)	80
O(4)···H–	N(1$^{\text{vii}}$)	2·97	O(2)—O(4)–N(1$^{\text{vii}}$)	147
	Cu	2·77	Cu—O(4)–O(2)	83
			Cu—O(4)–O(1$^{\text{ii}}$)	116
			Cu—O(4)–N(1$^{\text{vii}}$)	127
O(5)–H···	O(2)	2·80	O(2)—O(5)–O(1$^{\text{ii}}$)	100
O(5)–H···	O(1$^{\text{ii}}$)	2·80	O(2)—O(5)–N(1$^{\text{i}}$)	74
O(5)···H–	N(1$^{\text{i}}$)	3·12	O(1$^{\text{ii}}$)—O(5)–N(1$^{\text{i}}$)	95
	K(1$^{\text{iii}}$)	2·81	O(2)—O(5)–K(1$^{\text{iii}}$)	108
			O(1$^{\text{ii}}$)—O(5)–K(1$^{\text{iii}}$)	116
			N(1$^{\text{i}}$)—O(5)–K(1$^{\text{iii}}$)	144
O(6)–H···	O(1$^{\text{ii}}$)	2·81	O(1$^{\text{ii}}$)—O(6)–O(3$^{\text{vi}}$)	114
O(6)–H···	O(3$^{\text{vi}}$)	2·84	O(1$^{\text{ii}}$)—O(6)–K(1)	110
	K(1)	2·75	O(1$^{\text{ii}}$)—O(6)–K(1$^{\text{vi}}$)	117
	K(1$^{\text{vi}}$)	2·83	O(3$^{\text{vi}}$) –O(6)–K(1)	112
			O(3$^{\text{vi}}$) –O(6)–K(1$^{\text{vi}}$)	92
			K(1)—O(6)–K(1$^{\text{vi}}$)	110
N(1)–H···	O(4$^{\text{vii}}$)	2·97	O(4$^{\text{vii}}$)–N(1)–O(5$^{\text{i}}$)	102
N(1)–H···	O(5$^{\text{i}}$)	3·12	O(4$^{\text{vii}}$)–N(1)–C(1)	94
	C(1)	1·46	Cu—N(1)–C(1)	110
	Cu	2·04	O(5$^{\text{i}}$)—N(1)–C(1)	110
			Cu—N(1)–O(5$^{\text{i}}$)	111
			O(4$^{\text{vii}}$)–N(1)–Cu	128

Environment of potassium ions

Each potassium ion is surrounded by six oxygen atoms. Three of these, O(5$^{\text{vi}}$), O(6) and O(6$^{\text{iii}}$), belong to water molecules and the other three, O(2), O(3$^{\text{iv}}$), O(3$^{\text{v}}$), are carboxyl oxygen atoms. The distances between the potassium ion and the oxygen atoms are listed in Table 7. These six oxygen atoms make a distorted octahedron, though the distortion is larger than that around the copper atom. The situation around the potassium ions is illustrated in Fig. 5. Two octahedra related to each other by the centre of symmetry have two oxygen atoms in common to share an edge, and those by screw axis hold an apex in common. Thus they extend in a two-dimensional network parallel to (001). The weak electrostatic interactions between the potassium ion and the oxygen atoms seem to play an auxiliary role to hold the complex anions together.

Table 7. *Interatomic distances and intervector angles of the potassium octahedra*

Distances			
K(1)–O(2)	2·74 Å	K(1)–O(3$^{\text{iv}}$)	2·78 Å
K(1)–O(3$^{\text{v}}$)	2·83	K(1)–O(5$^{\text{vi}}$)	2·81
K(1)–O(6)	2·75	K(1)–O(6$^{\text{iii}}$)	2·83
Angles			
O(2) —K(1)–O(3$^{\text{iv}}$)	109°	O(2) —K(1)–O(3$^{\text{v}}$)	87°
O(2) —K(1)–O(5$^{\text{vi}}$)	147	O(2) —K(1)–O(6)	98
O(2) —K(1)–O(6$^{\text{iii}}$)	68	O(3$^{\text{iv}}$)–K(1)–O(3$^{\text{v}}$)	92
O(3$^{\text{iv}}$)–K(1)–O(5$^{\text{vi}}$)	104	O(3$^{\text{iv}}$)–K(1)–O(6)	97
O(3$^{\text{iv}}$)–K(1)–O(6$^{\text{iii}}$)	172	O(3$^{\text{v}}$) –K(1)–O(5$^{\text{vi}}$)	91
O(3$^{\text{v}}$) –K(1)–O(6)	167	O(3$^{\text{v}}$) –K(1)–O(6$^{\text{iii}}$)	81
O(5$^{\text{vi}}$)–K(1)–O(6)	78	O(5$^{\text{vi}}$)–K(1)–O(6$^{\text{iii}}$)	80
O(6) —K(1)–O(6$^{\text{iii}}$)	91		

The computations in the present analysis were carried out on the NEAC 2101, NEAC 2206 of this University and the HITAC 5020 of the Computing Center of the University of Tokyo. The computing programs of HITAC 5020 were written by one of the authors (T.A.). The authors wish to thank Professor Akitsugu Nakahara for supplying the crystals.

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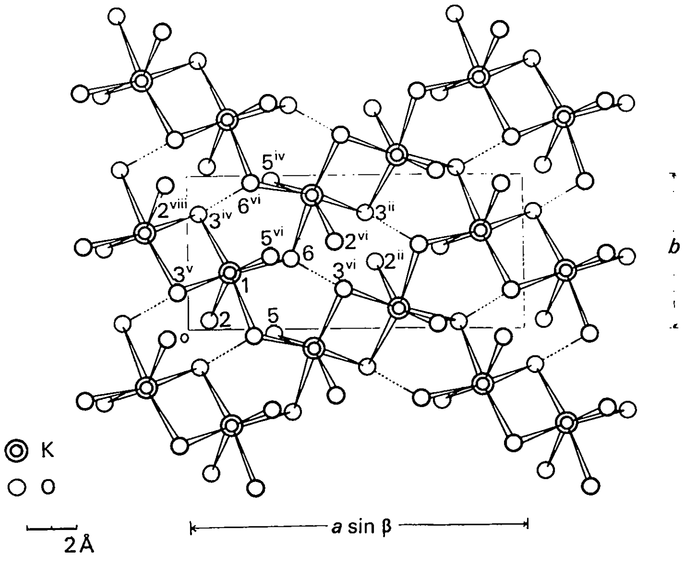

Fig. 5. The potassium ion–oxygen atom interaction, viewed along the c axis. Broken lines represent hydrogen bonds. For Roman numerals associated with atoms, see Table 6.

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The Ordered Structure of Ti_3O

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The ordered Ti_3O structure has been redetermined with the use of transmission electron diffraction in an electron microscope. This structure consists essentially of a close-packed hexagonal arrangement of titanium atoms with every second layer of octahedral interstices normal to the c axis vacant. One third of the oxygen sites in the occupied layers are empty and these vacancies have an ordered arrangement in the direction of the c axis. The space group is $P312$ (no. 149) and the unit-cell dimensions are: $a = 5{\cdot}1418$, $c = 14{\cdot}308$ Å.

Oxygen dissolves in the octahedral interstices of the titanium lattice up to 34 at.% (Ehrlich, 1941; Bumps, Kessler & Hansen, 1953). As there is one octahedral site for each titanium atom in the close-packed hexagonal structure, only half of the available interstitial sites are occupied at the limiting composition, Ti_2O. X-ray diffraction studies of Ti_2O (Andersson, Collen, Kuylenstierna & Magnéli, 1957) have indicated the existence of an ordered structure of the anti-CdI_2 type in which the oxygen atoms occupy alternate layers of octahedral sites normal to the c axis and, as a result of ordering, the titanium atoms surrounding the oxygen atoms are forced slightly apart in the **c** direction.

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