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The Crystal Structure of Copper Glutamate Dihydrate*

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The crystal structure of copper(II) glutamate dihydrate, $CuC_5H_7NO_4.2H_2O$, has been determined and refined by three-dimensional least-squares methods. The crystals are orthorhombic, space group $P2_12_12_1$, with $a=11\cdot084$, $b=10\cdot350$, $c=7\cdot238$ Å and four molecules per unit cell. Intensity data were collected visually from Weissenberg photographs about all three crystal axes; of 1087 reflections within the effective sphere of copper radiation all but 16 were strong enough to be measured. The final R index is 0·032; the standard deviations are about 0·004 Å for the light-atom positions.

The coordination about the copper atom is approximately square planar, involving two oxygen atoms and a nitrogen atom of glutamate groups and a water molecule; the Cu–O and Cu–N distances range from 1·97 to 2·00 Å. Two additional glutamate oxygen atoms at 2·30 and 2·59 Å complete a severely distorted octahedron. Five of the six available protons are involved in hydrogen bonding. The glutamate group is in an extended configuration and has normal bond distances and angles.

Introduction

The recent surge of interest in complexes of the transition metal elements with amino acids and peptides has prompted this investigation of the crystal structure of copper(II) glutamate dihydrate, $CuC_5H_7NO_4.2H_2O$.

Experimental

Crystals were readily grown by evaporation of an aqueous solution of glutamic acid and cupric nitrate. They are blue-green prisms, elongated along **c**, with principal faces {110} and {011}. A preliminary set of Weissenberg photographs indicated them to be orthorhombic with space group $P2_12_12_1$ (systematic absences: $h00$, $0k0$, and $00l$ with h, k or l odd). The unit-cell dimensions were obtained from a least-squares treatment of measurements on zero-level Weissenberg photographs taken about the three crystallographic axes; the film was held in the asymmetric position. A different crystal was used for each photograph. Absorption and eccentricity coefficients were included as parameters in the least-squares calculations, and weights were assigned inversely proportional to $\sin^2 2\theta$ (reflecting the expected pattern of uncertainties in the observational quantities $\sin^2\theta$). The resulting cell dimensions and their standard deviations are given in Table 1.

The density measured by flotation is 1·954 g.cm^{-3}; that calculated on the basis of four molecules of the dihydrate per unit cell is 1·957 g.cm^{-3}.

The differences between the cell dimensions for the three crystals (Table 1) are far greater than the experimental uncertainties, and are almost surely real. We have no explanation as to the source of the differences. The temperature of the room where the photographs were prepared was approximately constant, a check made during the preparation of the $hk0$ and $0kl$ photographs showing no variation exceeding 1° from the average temperature of 24·5°C. It is possible that the amount of water of crystallization varied slightly from one crystal to another; however, no deficiency in the occupancies of the sites of the water molecules was evidenced either by the density measurement or by the refinement of the structural parameters.

Table 1. *Unit-cell dimensions*

The cell dimensions and their standard deviations as determined by least-squares treatment of zero-level Weissenberg data for three different crystals are given in the first three columns; the values selected as the best average dimensions are given in the last column.

	No. 1	No. 2	No. 3	'Best'
a	11·0899 (1)		11·0781 (1)	11·084 (6)
b		10·3523 (4)	10·3468 (2)	10·350 (3)
c	7·2398 (1)	7·2358 (2)		7·238 (2)

(Cu $K\alpha_1$, 1·54051; Cu $K\alpha_2$, 1·54433)

For the determination and preliminary refinement of the structure, intensity data were collected from multiple-film equi-inclination Weissenberg photographs of layers 0–6 about **c**, using a needle-shaped crystal about 0·1 mm in diameter, and of the zero layer about **b**, using a rhomb-shaped crystal also about 0·1 mm in diameter. Copper radiation was used, and the intensities were estimated visually and corrected for Lorentz and polarization factors. No absorption or extinction corrections were made.

Prior to the final refinement of the structure, additional data were collected in a similar manner for layers 0–9 about the a and b axes. Data about all three axes were then processed through a subprogram of the CRYRM system on an IBM 7094 computer (Duchamp, 1964). This processing included the assignment of esti-

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mated standard deviations to the individual observations, evaluation of film and pack factors relating different photographs of the same layer line, correction for Lorentz and polarization effects, evaluation of relative scale factors for the 27 different sets of photographs, and, finally, the scaling together of these different photographs to give a single value of F^2, and its standard deviation, for each of the 1087 reflections within the effective sphere of copper radiation. Of these 1087 reflections, only 16 were too weak to be observed.

Determination and refinement of the structure

The trial structure was derived by the usual Patterson and Fourier methods based on the *hk*0 and *h*0*l* data; the Cu–Cu vectors were pronounced features of the Patterson projection onto (001). Preliminary refinement was by difference projections; the first three-dimensional structure-factor calculation led to an *R* index of 0·10.

The initial three-dimensional refinement was based on the data collected about the *c* axis only. Block-diagonal least-squares refinement, carried out on a Burroughs 220 computer using a program written by A. Hybl, reduced *R* to 0·052; anisotropic temperature factors were assigned to the heavy atoms, and the five hydrogen atoms of the carbon chain – whose positions could be assigned from structural considerations – were included in the structure factors but were not refined. The remaining hydrogen atoms were eventually located with the help of difference maps, and further refinement of the heavy-atom parameters led to an *R* index of 0·040. The results at this stage were presented at the International Congress in Rome (Gramaccioli, 1963).

Final refinement was carried out on an IBM 7094 computer, and was based on the complete set of intensities measured about all three axes (see *Experimental*). Refinement was by full-matrix least squares, using the orthorhombic subprogram of the CRYRM system (Duchamp, 1964). The quantity minimized was $\Sigma w (F_o^2 - 1/k^2F_c^2)^2$, with weights w taken equal to the reciprocals of the squares of the standard deviations in the individual values of F_o^2 as derived during the data-reduction process. For 38 of the strongest reflections presumed to suffer from extinction and 9 very weak reflections whose intensity estimations were doubtful, the weight was taken to be 0. Atomic form factors were taken from *International Tables for X-ray Crystallography* (1962), the values for Cu being corrected for the real part ($\Delta F'$) of the anomalous dispersion effect. A total of 162 parameters were adjusted: coordinates of all 24 atoms in the molecule, anisotropic temperature parameters of the 13 heavier atoms, isotropic temperature factors of the hydrogen atoms, and a scale factor *k*.

Considerable difficulty was encountered in locating the hydrogen atoms of the water molecules. Three-dimensional differences maps calculated at various stages of the refinement had pronounced maxima, of height about 0·5 e.Å^{-3}, at the positions expected for the hydrogen atoms of the carbon chain H(1)–H(5) and somewhat smaller maxima representing H(6) and H(7) of the amino group, but only indistinct maxima near the oxygen atoms of the water molecules. Nevertheless, coordinates were assigned to H(8)–H(11) by choosing maxima that were consistent with a reasonable hydrogen-bonding scheme; these coordinates as well as isotropic temperature factors of the hydrogen atoms were included in the final least-squares cycles. The final parameters include a negative temperature factor for H(1) and lead to some rather short N–H and O–H distances; nevertheless, the bond angles and hydrogen-bond arrangement are satisfactory and we are confident that the approximate positions of the hydrogen atoms are correctly assigned.

Convergence was first reached at an *R* index of 0·037. It was noted, however, that the observed values of the structure factors for the stronger reflections were systematically lower than the calculated values. Although this effect is symptomatic of extinction, it could also be the result of systematic errors in scaling – and, in particular, of too low a value for the film factor used to correlate intensities from adjacent films within the same pack. Our empirical value for this factor, averaged over all sets of films and adjusted for the angle of incidence of the diffracted beam, was 3·65 – appreciably lower than the value of about 3·9 usually found for this film (Eastman No-Screen Medical X-ray Film). Accordingly, the data were rescaled, using a value of 3·8 for the film factor, and further least-squares refinement was carried out. Disagreements among the stronger reflections, although still apparent, were much reduced and the refinement was considered complete when no heavy-atom parameter shifted by as much as 0·01 of its standard deviation, no hydrogen coordinate by as much as 0·1 e.s.d., and no hydrogen temperature factor by as much as 0·25 e.s.d.

The observed and calculated structure factors are listed in Table 2, the final heavy-atom parameters and their standard deviations in Table 3, and the hydrogen-atom parameters in Table 4. An electron-density projection onto (001), calculated at the conclusion of the refinement, is shown in Fig. 1.

Accuracy of the results

The final *R* index based on 1023 observed reflections of non-zero weight is 0·032; for none of the reflections too weak to be measured is F_c greater than the threshold value of F_o. The value of

$$\left(\frac{\Sigma\, w(F_o^2 - F_c^2)}{m-s}\right)^{\frac{1}{2}}$$

is 0·88. That this latter value is less than 1·0 suggests that the observational errors were over-estimated, perhaps because these errors were derived during the data-reduction process by comparing values of intensities scaled together on the basis of a film factor of 3·65 rather than of the final value 3·80.

Table 2. *Observed and calculated structure factors*

Within each group are the values of k, $10F_o$, $10F_c$, and α_c (the phase angle). A negative sign preceding $10F_o$ should be read 'less than'. Reflections indicated with an asterisk were assigned zero weight in the final least-squares cycles.

0 K 0			
0	----*	4882	0
2	555*	657	180
4	298	306	180
6	592*	626	0
8	234	234	180
10	176	171	0
12	45	43	180
1 K 0			
1	519*	600	90
2	161	166	90
3	220	239	270
4	36	36	90
5	732*	841	90
6	-26	3	270
7	131	125	90
8	80	83	90
9	235	228	270
10	34	37	270
11	195	187	90
12	58	53	270
13	139	135	270
2 K 0			
0	608*	1324	180
1	591*	736	0
2	265	286	0
3	409	430	180
4	174	177	0
5	25	19	0
6	593*	620	180
7	216	215	0
8	245	247	0
9	83	75	180
10	188	186	180
11	83	91	0
12	31	21	180
13	30	26	180
3 K 0			
1	44	49	270
2	622*	736	90
3	37	36	90
4	59	53	90
5	490	525	270
6	101	104	90
7	190	189	90
8	112	106	90
9	158	153	90
10	152	141	270
11	372	366	270
12	173	171	90
4 K 0			
0	498*	575	0
1	442	498	180
2	272	287	180
3	38	38	0
4	179	170	0
5	297	305	0
6	473	480	0
7	549	544	180
8	344	334	180
9	-34	0	180
10	139	128	0
11	74	69	180
12	136	136	0
5 K 0			
1	205	201	90
2	229	250	270
3	112	116	270
4	270	283	90
5	500	517	90
6	253	262	270
7	196	177	270
8	117	112	270
9	46	33	270
10	110	108	90
11	208	209	90
12	142	140	270
6 K 0			
0	454	491	180
1	701*	813	0
2	281	288	0
3	160	164	180
4	197	184	180
5	217	220	180
6	226	221	180
7	308	304	0
8	38	32	0
9	272	272	180
10	63	51	180
11	24	1	180
12	29	33	0
7 K 0			
1	233	229	270
2	137	152	90
3	170	176	90
4	569*	596	270
5	-27*	15	90
6	263	262	90
7	-31*	29	270
8	68	68	90
9	-31	14	90
10	239	248	270
11	118	127	270
8 K 0			
0	96	97	0
1	584*	651	180
2	67	57	0
3	250	237	0
4	266	248	180
5	199	201	0
6	172	170	0
7	278	276	180
8	84	84	0
9	221	228	0
10	28	33	180
11	46	63	180
9 K 0			
1	45	37	90
2	107	103	270
3	29	21	270
4	216	194	90
5	121	120	90
6	193	185	270
7	70	72	90
8	89	93	270
9	34	30	90
10	182	174	90
10 K 0			
0	32	13	0
1	326	329	0
2	290	297	180
3	62	72	0
4	35	32	180
5	152	151	180
6	141	144	0
7	204	198	0
8	96	103	180
9	129	122	180
11 K 0			
1	-33	0	90
2	258	252	90
3	208	210	270
4	317	329	270
5	78	81	270
6	153	152	90
7	94	90	90
8	34	34	90
12 K 0			
0	164	165	180
1	245	239	180
2	121	127	0
3	72	75	0
4	82	85	0
5	157	153	0
6	72	73	180
7	139	145	180
13 K 0			
1	101	97	270
2	207	198	270
3	155	154	90
4	79	82	90
5	109	106	270
14 K 0			
0	220	215	0
1	57	55	0
2	142	142	180
0 K 1			
1	370	392	270
2	773*	926	180
3	427	422	270
4	406	429	0
5	499	522	90
6	412	433	180
7	166	165	270
8	69	55	0
9	83	84	270
10	243	247	0
11	33	29	270
12	203	189	180
13	-22	2	270
1 K 1			
0	74	74	90
1	704*	760	278
2	812*	854	43
3	647*	668	117
4	597*	641	192
5	255	262	62
6	340	350	9
7	488	520	261
8	61	51	90
9	186	179	94
10	180	170	219
11	65	62	331
12	124	116	350
13	73	66	266
2 K 1			
0	145	153	270
1	750*	835	121
2	222	231	29
3	131	134	158
4	524	536	203
5	491	505	315
6	189	193	19
7	243	243	123
8	91	83	347
9	114	114	239
10	202	204	175
11	128	124	348
12	192	183	7
13	45	52	53
3 K 1			
0	564*	632	90
1	439	470	99
2	180	169	323
3	314	295	58
4	398	406	342
5	446	463	231
6	355	343	167
7	309	320	67
8	226	221	277
9	179	177	267
10	271	286	32
11	47	47	160
12	184	182	143
4 K 1			
0	479	505	270
1	105	109	278
2	350	371	169
3	240	248	56
4	331	346	13
5	371	389	182
6	324	325	206
7	158	159	231
8	154	148	148
9	215	218	42
10	89	82	349
11	118	117	197
12	130	126	174
5 K 1			
0	545*	606	270
1	675*	736	287
2	165	163	122
3	452	453	183
4	210	213	134
5	317	338	1
6	427	433	307
7	244	235	260
8	146	143	99
9	175	172	185
10	156	152	207
11	183	186	318
12	90	86	344
6 K 1			
0	243	251	90
1	489	496	32
2	267	268	301
3	436	458	171
4	240	233	215
5	332	327	321
6	346	349	38
7	153	157	121
8	184	183	322
9	49	39	206
10	37	39	12
11	138	142	347
7 K 1			
0	647*	721	90
1	215	197	96
2	413	421	256
3	297	293	26
4	164	154	23
5	285	285	180
6	341	332	89
7	168	170	24
8	156	160	265
9	70	76	316
10	73	67	86
11	120	133	171
8 K 1			
0	134	136	270
1	366	357	209
2	99	94	46
3	226	222	355
4	88	86	69
5	320	317	162
6	141	132	272
7	71	61	91
8	136	134	112
9	82	82	349
10	83	83	334
9 K 1			
0	366	387	270
1	231	202	60
2	59	50	151
3	253	250	168
4	164	159	319
5	285	278	10
6	293	293	250
7	118	112	193
8	174	193	88
9	80	81	211
10	49	54	270
10 K 1			
0	263	261	90
1	235	232	19
2	171	157	276
3	105	96	212
4	108	109	338
5	212	211	8
6	122	130	78
7	48	44	167
8	139	136	220
9	95	91	174
11 K 1			
0	229	218	90
1	98	90	248
2	186	183	320
3	106	100	344
4	149	153	168
5	95	96	116
6	205	194	83
7	75	71	282
8	93	103	253
12 K 1			
0	196	198	270
1	135	129	136
2	158	145	53
3	177	174	358
4	82	85	139
5	239	243	202
6	125	113	326
7	47	57	65
13 K 1			
0	249	245	270
1	151	140	76
2	134	125	151
3	107	101	203
4	104	102	22
5	59	63	9
14 K 1			
0	117	111	90
1	67	64	312
0 K 2			
0	515*	579	180
1	46	45	270
2	550	547	180
3	531*	576	90
4	377	365	180
5	727*	793	270
6	77	65	0
7	224	217	90
8	98	93	0
9	232	221	90
10	132	126	180
11	228	218	270
12	59	52	180
1 K 2			
0	649*	763	0
1	451	449	293
2	572*	600	132
3	121	127	61
4	416	414	235
5	584*	620	275
6	421	418	11
7	89	85	189
8	347	353	185
9	150	150	0
10	107	102	36
11	82	75	358
12	85	86	345
2 K 2			
0	172	169	0
1	157	152	133
2	278	251	37
3	708*	744	275
4	326	340	76
5	502	511	88
6	375	380	319
7	239	239	239
8	123	117	125
9	217	224	249
10	176	178	72
11	280	279	85
12	115	106	314
3 K 2			
0	662*	721	180
1	536	501	83
2	792*	850	325
3	352	349	225
4	220	205	325
5	66	68	151
6	302	305	196
7	301	290	39
8	235	225	3
9	146	143	199
10	121	116	192
11	120	119	87
12	72	71	273
4 K 2			
0	47	46	180
1	380	347	207
2	408	420	92
3	337	366	87
4	385	392	245
5	269	273	273
6	289	294	115
7	257	247	15
8	52	42	54
9	125	127	55
10	170	173	250
11	156	149	282
12	127	126	104
5 K 2			
0	590*	630	0
1	700*	791	202
2	238	241	116
3	202	202	74
4	222	230	224
5	310	318	334
6	241	239	26
7	255	252	184
8	169	170	144
9	141	142	319
10	66	65	289
11	29	31	231
12	92	102	103
6 K 2			
0	93	91	0
1	228	219	120
2	445	459	254
3	250	243	279
4	566*	575	70
5	201	195	112
6	202	190	332
7	76	64	254
8	110	113	241
9	152	152	329
10	153	152	80
11	64	62	87
7 K 2			
0	89	89	180
1	412	439	16
2	182	175	331
3	29	6	23
4	325	308	77
5	292	300	184
6	214	206	224
7	186	186	353
8	93	93	51
9	134	133	165
10	23	23	315
11	59	82	88
8 K 2			
0	130	125	0
1	118	115	68
2	334	329	102
3	-31	18	29
4	381	381	261
5	79	72	175
6	258	262	95
7	73	70	66
8	29	22	350
9	53	48	173
10	144	157	247
9 K 2			
0	-28*	0	180
1	341	334	172
2	173	177	107
3	156	161	302
4	174	176	282
5	109	106	5
6	76	72	155
7	321	307	204
8	97	102	105
9	129	131	11
10 K 2			
0	317	329	0
1	131	131	229
2	138	129	271
3	167	170	112
4	278	272	83
5	82	83	312
6	227	231	268
7	87	86	155
8	69	47	263
9	42	48	334
11 K 2			
0	108	101	0
1	245	246	15
2	81	80	205
3	125	130	144
4	55	50	109
5	75	78	157
6	68	64	348
7	147	141	21
8	48	66	207
12 K 2			
0	36	32	180
1	106	103	40
2	104	97	113
3	172	182	227
4	159	153	255
5	156	155	72
6	25	23	73
13 K 2			
0	165	157	180
1	166	157	163
2	137	135	55
3	108	105	301
4	48	49	159
0 K 3			
1	682*	757	90
2	374	344	0
3	277	274	270
4	187	169	0
5	295	282	270
6	80	83	180
7	563	555	90
8	263	264	180
9	177	170	270
10	188	194	0
11	60	60	90
12	58	56	180
1 K 3			
0	284	275	90
1	575	582	264
2	645	643	190
3	150	155	319
4	409	424	342
5	231	220	60
6	135	139	176
7	122	116	248
8	169	163	139
9	87	88	75
10	186	183	351
11	36	38	190
12	160	153	176
2 K 3			
0	436	440	270
1	630*	681	264
2	279	265	111
3	435	413	47
4	224	218	115
5	198	199	117
6	270	261	321
7	314	312	262
8	112	110	142
9	339	334	103
10	71	71	207
11	118	117	353
12	22	23	25
3 K 3			
0	138	125	90
1	353	354	48
2	408	409	319
3	373	370	198
4	610*	637	160
5	277	277	328
6	236	227	53
7	116	113	23
8	139	142	273
9	123	125	200
10	173	174	199
11	29	21	21
12	86	86	344
4 K 3			
0	761*	810	90
1	456	464	110
2	274	269	250
3	311	292	303
4	189	180	15
5	218	223	249
6	199	192	104
7	344	335	63
8	301	296	295
9	212	209	265
10	127	129	45
11	25	24	239
5 K 3			
0	307	309	270
1	133	136	203
2	296	298	144
3	246	240	6
4	289	285	38
5	330	334	139
6	160	159	212
7	108	104	355
8	74	69	153
9	114	111	25
10	148	150	7
11	128	134	161
6 K 3			
0	207	205	270
1	116	119	238
2	424	421	91
3	191	191	172
4	80	74	309
5	41	36	57
6	288	289	244
7	125	121	300
8	293	291	100
9	138	134	117
10	168	169	228
11	-29*	5	255
7 K 3			
0	296	294	90
1	94	90	51
2	184	172	279
3	407	405	195
4	346	341	232
5	221	215	335
6	84	83	75
7	42	30	194
8	78	78	262
9	153	153	170
10	54	53	134
8 K 3			
0	408	417	90
1	169	157	25
2	327	325	262
3	86	84	339
4	124	119	339
5	95	86	255
6	216	217	108
7	44	42	307
8	262	261	279
9	113	115	336
10	80	101	71
9 K 3			
0	98	99	270
1	160	165	173
2	238	242	116
3	324	313	347
4	-27	16	30
5	203	201	185
6	56	55	85
7	47	41	57
8	88	93	57
9	74	73	4
10 K 3			
0	317	318	270
1	189	198	132
2	255	298	118
3	102	104	222
4	-28*	18	99
5	107	114	339
6	206	203	294
7	122	128	165
8	143	143	92
11 K 3			
0	30	13	90
1	185	180	314
2	72	72	227
3	309	306	159
4	141	144	320
5	129	127	17
6	41	42	100
7	50	54	239
12 K 3			
0	124	123	90
1	140	135	255
2	117	115	277
3	129	121	38
4	87	85	234
5	51	55	95
13 K 3			
0	31	30	90
1	37	28	272
2	106	104	14
3	87	100	359
0 K 4			
0	118	123	180
1	66	57	270
2	365	376	0
3	254	255	270
4	226	218	0
5	130	132	90
6	299	300	180
7	124	125	90
8	241	237	0
9	178	184	270
10	-35	17	180
11	109	108	90
1 K 4			
0	263	267	180
1	220	218	288
2	356	358	17
3	701*	698	91
4	156	150	244
5	152	158	242
6	155	147	231
7	126	124	124
8	314	308	11
9	156	147	124
10	175	166	205
11	160	158	262
2 K 4			
0	324	324	0
1	241	240	207
2	526	504	167
3	447	433	110
4	192	190	207
5	257	265	345
6	284	285	312
7	75	74	62
8	271	257	170
9	89	84	12
10	88	89	296
11	62	54	269
3 K 4			
0	158	159	0
1	284	271	184
2	411	404	203
3	547	543	295
4	378	365	96
5	383	375	67
6	197	194	338
7	265	265	228
8	184	181	183
9	119	118	303
10	65	66	39
11	96	92	93
4 K 4			
0	178	185	180
1	412	408	32
2	321	320	308
3	453	443	264
4	121	121	70
5	185	175	123
6	150	137	235
7	96	97	32
8	226	233	10
9	153	154	211
10	72	67	141
11	-30	12	224
5 K 4			
0	202	201	180
1	123	116	18
2	254	248	83
3	174	173	138
4	402	395	269
5	199	193	277
6	252	246	115
7	160	154	20
8	160	161	357
9	228	235	134
10	137	132	274
11	56	69	282
6 K 4			
0	216	218	0
1	156	151	224
2	80	77	154
3	130	130	11
4	226	227	245
5	146	146	9
6	64	71	27
7	229	242	183
8	135	136	170
9	162	159	24
10	63	65	285
7 K 4			
0	111	109	180
1	242	244	187
2	226	227	243
3	143	149	313
4	252	251	62
5	110	112	22
6	130	135	275
7	161	165	177
8	61	61	182
9	168	168	340
10	137	174	79
8 K 4			
0	102	99	180
1	208	205	358
2	268	261	300
3	194	189	233
4	118	113	69
5	87	95	156
6	47	43	352
7	220	227	343
8	96	101	264
9	93	97	177
9 K 4			
0	67	72	0
1	244	238	1
2	301	296	95
3	79	80	157
4	232	237	282
5	94	101	96
6	137	143	61
7	142	143	8
8	31	30	55
10 K 4			
0	114	112	180
1	256	246	172
2	157	150	92
3	71	72	13
4	165	174	260
5	94	98	345
6	71	70	84
7	138	135	183
11 K 4			
0	120	121	180
1	111	108	213
2	177	167	303
3	94	91	81
4	169	165	106
5	154	160	298
6	45	44	235
12 K 4			
0	160	160	0
1	104	97	357
2	81	83	254
3	-19*	13	259
4	127	129	105
0 K 5			
1	248	247	90
2	261	258	0
3	105	106	90
4	424	428	180
5	109	103	270
6	365	365	0
7	105	107	270
8	84	78	0
9	31	34	270
10	149	143	180
11	17	16	270
1 K 5			
0	83	73	270
1	225	227	91
2	57	58	314
3	86	90	305
4	119	109	307
5	85	89	224
6	153	158	83
7	309	302	85
8	81	77	276
9	254	258	254
10	38	34	223
11	42	41	5
2 K 5			
0	65	59	270
1	164	164	186
2	487	476	175
3	256	257	0
4	600	588	2
5	113	101	172
6	168	161	178
7	53	54	325
8	64	61	201
9	64	67	313
10	168	165	354
11	74	80	208
3 K 5			
0	55	53	270
1	441	435	278
2	131	125	134
3	247	237	103
4	216	210	332
5	219	219	123
6	126	124	280
7	174	173	271
8	145	153	63
9	173	168	82
10	48	53	175
4 K 5			
0	105	93	270
1	244	240	6
2	433	430	348
3	308	308	182
4	303	289	184
5	242	242	18
6	83	74	118
7	111	114	148
8	42	30	49
9	73	66	174
10.	76	79	178
5 K 5			
0	277	294	90
1	162	154	66
2	256	249	285
3	94	97	227
4	40	35	63
5	154	157	283
6	180	186	120
7	198	190	108
8	212	210	273
9	94	88	300
10	55	60	115
6 K 5			
0	183	183	270
1	91	89	178
2	221	224	180
3	407	412	1
4	166	169	338
5	205	209	183
6	39*	29	117
7	51	48	314
8	50	49	95
9	127	128	335
7 K 5			
0	130	115	270
1	44	42	341
2	202	198	60
3	139	141	67
4	151	161	64
5	100	106	10
6	111	107	293
7	71	69	257
8	155	171	94
9	100	117	96
8 K 5			
0	32	35	90
1	88	84	349
2	102	100	155
3	396	408	167
4	41	36	111
5	222	224	350
6	48	46	76
7	43	42	157
8	79	87	175
9 K 5			
0	312	313	90
1	-29*	21	125
2	213	213	281
3	72	74	227
4	78	80	276
5	62	67	84
6	145	141	75
7	31	24	259
10 K 5			
0	66	58	270
1	97	92	193
2	75	73	319
3	287	274	358
4	92	95	158
5	166	165	184
6	48	52	19
11 K 5			
0	81	83	270
1	-22	10	16
2	177	170	102
3	104	97	284
4	29	30	199
12 K 5			
0	49	55	90
0 K 6			
0	68	69	0
1	234	227	90
2	166	164	180
3	112	113	270
4	-27*	9	180
5	180	181	90
6	185	177	0
7	74	75	270
8	258	269	180
9	80	83	270
10	31	34	0
1 K 6			
0	271	254	180
1	159	154	59
2	166	166	353
3	384	390	256
4	268	267	142
5	144	142	64
6	177	185	171
7	81	80	305
8	203	209	0
9	97	93	271
10	84	88	152
2 K 6			
0	192	187	180
1	147	146	307
2	377	375	7
3	80	82	56
4	48	42	265
5	176	184	216
6	152	152	141
7	71	71	280
8	205	207	17
9	92	91	155
3 K 6			
0	297	292	0
1	226	218	196
2	123	121	109
3	355	353	92
4	194	191	248
5	92	86	273
6	153	153	23
7	153	157	178
8	96	99	151
9	133	130	49
4 K 6			
0	286	275	0
1	324	318	145
2	198	191	187
3	277	271	291
4	96	95	121
5	85	72	86
6	72	67	329
7	136	138	138
8	192	191	218
9	81	87	340
5 K 6			
0	191	192	180
1	131	126	32
2	180	180	322
3	162	157	249
4	156	157	83
5	126	131	99
6	108	113	216
7	121	121	11
8	47	44	237
9	99	124	232
6 K 6			
0	72	64	180
1	163	163	3
2	178	182	95
3	129	130	152
4	77	82	289
5	103	108	228
6	61	58	148
7	112	118	4
8	111	114	351
7 K 6			
0	-28	8	180
1	241	259	180
2	168	178	78
3	156	157	38
4	183	181	282
5	110	117	323
6	59	53	139
7	146	147	153
8 K 6			
0	60	54	180
1	131	127	182
2	149	156	238
3	81	82	19
4	150	152	88
5	111	109	33
6	29	31	151
9 K 6			
0	123	120	0
1	89	87	343
2	236	233	251
3	57	59	213
4	159	156	108
5	65	71	219
10 K 6			
0	32	36	0
1	187	187	343
2	89	87	98
3	73	75	213
4	50	57	261
0 K 7			
1	369	376	270
2	106	111	180
3	129	122	90
4	38	33	0
5	40	38	90
6	36	29	180
7	172	166	270
8	98	98	180
1 K 7			
0	115	114	90
1	194	189	276
2	236	226	7
3	131	130	193
4	294	291	178
5	76	75	79
6	85	89	349
7	78	70	311
8	58	57	351
2 K 7			
0	199	197	90
1	160	157	81
2	196	204	254
3	78	81	252
4	78	77	211
5	134	142	243
6	84	78	84
7	182	182	94
8	36	32	235
3 K 7			
0	151	152	90
1	160	161	141
2	275	265	195
3	231	234	333
4	201	202	1
5	-31	30	216
6	89	94	140
7	39	22	125
8	67	65	227
4 K 7			
0	47	45	270
1	147	151	252
2	85	82	117
3	40	32	93
4	49	51	31
5	52	48	115
6	175	170	255
7	198	202	269
5 K 7			
0	89	86	270
1	55	66	5
2	197	191	25
3	152	151	159
4	117	124	194
5	162	167	10
6	125	130	349
7	114	115	241
6 K 7			
0	184	194	90
1	117	114	115
2	103	102	288
3	98	100	252
4	39	44	96
5	77	72	101
6	78	83	78
7 K 7			
0	71	68	90
1	100	98	164
2	131	131	238
3	167	167	4
4	84	87	253
5	194	211	191
8 K 7			
0	269	270	270
1	66	69	27
2	144	140	120
3	48	49	1
4	96	106	338
9 K 7			
0	90	92	270
1	133	143	357
2	40	42	102
0 K 8			
0	-28	0	180
1	235	242	270
2	-28	13	180
3	148	148	90
4	33	30	0
5	203	204	270
6	-20	18	0
1 K 8			
0	271	268	0
1	134	126	143
2	181	172	242
3	108	104	302
4	55	59	16
5	83	83	78
6	166	161	358
2 K 8			
0	139	137	180
1	139	136	69
2	56	58	259
3	204	205	275
4	88	94	109
5	205	208	105
6	92	96	242
3 K 8			
0	115	115	180
1	118	115	312
2	105	104	63
3	71	76	40
4	75	78	318
5	60	57	296
6	128	135	197
4 K 8			
0	-27	1	0
1	65	57	247
2	108	108	112
3	130	130	78
4	128	129	304
5	146	145	271
5 K 8			
0	164	173	0
1	115	114	154
2	96	95	198
3	56	58	250
4	41	44	55
6 K 8			
0	39	39	0
1	44	46	77
2	164	163	275
3	112	122	230
7 K 8			
0	85	95	180
1	116	133	356
0 K 9			
1	149	143	90
2	107	97	180
1 K 9			
0	47	45	270
1	126	126	290
2	57	56	201
3	83	95	49
2 K 9			
0	71	71	90
1	92	90	269
2	128	134	35
3 K 9			
0	93	93	90
1	135	147	91

Table 3. *The heavy-atom parameters and their standard deviations*

Values for the copper atom have been multiplied by 10^5; for other atoms, by 10^4. The temperature factor is in the form $T_i = \exp\{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)_i\}$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu	77933 (4)	31668 (5)	64970 (7)	315 (4)	455 (5)	786 (10)	3 (7)	−106 (10)	−26 (11)
C(1)	6595 (3)	5340 (3)	7780 (5)	43 (3)	39 (3)	71 (5)	−15 (5)	−15 (7)	21 (7)
C(2)	5611 (3)	4661 (3)	6699 (5)	33 (2)	48 (3)	70 (6)	3 (5)	0 (7)	3 (7)
C(3)	4630 (3)	4176 (4)	8015 (5)	31 (3)	58 (4)	95 (7)	3 (5)	10 (6)	20 (8)
C(4)	5067 (3)	3326 (4)	9573 (5)	34 (2)	66(4)	106 (6)	−2 (5)	0 (7)	48 (9)
C(5)	4046 (3)	2829 (4)	10756 (5)	35 (2)	50 (3)	97 (6)	−5 (5)	12 (7)	−1 (8)
N	6133 (3)	3583 (3)	5602 (4)	38 (2)	57 (3)	78 (5)	−5 (4)	−3 (6)	−22 (7)
O(1)	7666 (2)	4872 (3)	7683 (4)	36 (2)	58 (3)	113 (5)	−9 (4)	−20 (5)	−35 (6)
O(2)	6310 (2)	6286 (2)	8741 (4)	54 (2)	46 (2)	112 (5)	0 (4)	−29 (6)	−45 (6)
O(3)	4341 (2)	2214 (3)	12249 (4)	33 (2)	64 (3)	98 (5)	5 (4)	13 (5)	49 (6)
O(4)	2969 (2)	3006 (3)	10356 (4)	31 (2)	105 (4)	109 (5)	−5 (4)	9 (5)	57 (7)
O(5)	7691 (3)	1344 (3)	5632 (4)	87 (3)	46 (2)	113 (5)	−8 (5)	−48 (7)	20 (6)
O(6)	6559 (2)	0959 (3)	2343 (4)	42 (2)	65 (3)	113 (5)	10 (4)	−6 (6)	21 (6)

Table 4. *Coordinates and standard deviations of the hydrogen atoms*

	x	*y*	*z*	*B*
H(1)	0·528 (3)	0·522 (3)	0·583 (5)	−0·7 (6)
H(2)	0·419 (5)	0·481 (6)	0·839 (9)	4·1 (14)
H(3)	0·397 (5)	0·362 (6)	0·741 (8)	3·9 (14)
H(4)	0·563 (4)	0·393 (5)	1·039 (6)	1·2 (9)
H(5)	0·546 (5)	0·241 (5)	0·908 (8)	2·5 (12)
H(6)	0·635 (6)	0·361 (8)	0·476 (10)	6·1 (18)
H(7)	0·554 (5)	0·282 (5)	0·574 (8)	2·5 (12)
H(8)	0·781 (4)	0·084 (5)	0·610 (7)	2·2 (11)
H(9)	0·716 (6)	0·125 (8)	0·431 (10)	5·9 (18)
H(10)	0·699 (6)	0·123 (7)	0·197 (11)	6·2 (20)
H(11)	0·581 (4)	0·129 (4)	0·227 (7)	1·1 (9)

The standard deviations in the coordinates, derived from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle, correspond to positional uncertainties of about 0·0005 Å for the copper atom, about 0·003–0·004 Å for the C, N and O atoms, and about 0·04–0·08 Å for the hydrogen atoms. These uncertainties are unrealistically small for the hydrogen atoms of the amino group and the water molecules, H(6)–H(11), which were poorly represented on the difference maps and show a wide spread in the N–H and O–H distances (Table 5).

The corresponding standard deviations in the bond distances are about 0·004 Å for the Cu–N and Cu–O bonds and about 0·006 Å for the C–C, C–O and C–N bonds. In view of uncertainties in the corrections for thermal motion, which are especially large for the oxygen atoms, we feel that these uncertainties should be increased to, perhaps, 0·008 Å for all the bonds.

Discussion of the results

(i) *The molecular structure*

The structure as viewed down the *c* axis is shown in Fig. 2. The coordination about the copper atom is shown in Fig. 3, and the dimensions of the glutamate

Table 5. *Bond distances and angles involving the hydrogen atoms*

C(2)–H(1)	0·93 Å	C(1)–C(2)–H(1)	110°	C(3)–C(2)–H(1)	110°
		N—C(2)–H(1)	105		
C(3)–H(2)	0·86	C(2)–C(3)–H(2)	110	C(4)–C(3)–H(2)	113
C(3)–H(3)	1·03	C(2)–C(3)–H(3)	115	C(4)–C(3)–H(3)	103
		H(2)–C(3)–H(3)	99		
C(4)–H(4)	1·06	C(3)–C(4)–H(4)	105	C(5)–C(4)–H(4)	109
C(4)–H(5)	1·10	C(3)–C(4)–H(5)	113	C(5)–C(4)–H(5)	101
		H(4)–C(4)–H(5)	117		
N–H(6)	0·65	C(2)–N–H(6)	127	Cu–N–H(6)	89
N–H(7)	1·03	C(2)–N–H(7)	106	Cu–N–H(7)	113
		H(6)–N–H(7)	111		
O(5)–H(8)	0·63	Cu–O(5)–H(8)	126		
O(5)–H(9)	1·13	Cu–O(5)–H(9)	112	H(8)–O(5)–H(9)	120
O(6)–H(10)	0·61				
O(6)–H(11)	0·90	H(10)–O(6)–H(11)	121		

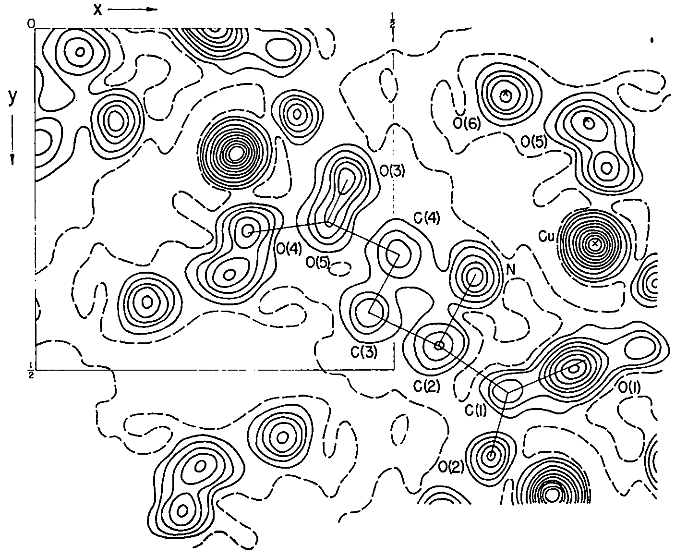

Fig. 1. The final electron-density map projected onto (001). Contours are at 4, 6, 8 · · · e.Å^{-2} for the light atoms and 4, 10, 15, 20 · · · for the copper atom; the 2 e.Å^{-2} contour is dashed.

group are given in Fig. 4. Distances and angles involving the hydrogen atoms are given in Table 5. Equations of, and deviations from, three planes of interest are given in Table 6.

The coordination about the copper atom is approximately square planar, the square comprising two oxygen atoms and a nitrogen atom of glutamate groups and a water molecule. The average distance from the copper atom to these four ligands is 1·99 Å, slightly longer than the normal single-bond distance of 1·92–1·95 Å (Pauling, 1960). A fifth atom, O(2), occupies an axial position at 2·30 Å from the copper atom; a sixth, O(4), at 2·59 Å and considerably displaced from the other axial position completes a severely distorted octahedron. The four nearest ligands – O(1), O(3), O(5) and N – are coplanar within 0·025 Å; the copper atom is displaced from this plane by 0·15 Å, in a direction toward the next nearest neighbor O(2) (Table 6).

There are no surprises in the dimensions of the glutamate group (Fig. 4). The lengths of the C(1)–O(1) and C(5)–O(3) bonds approach the values found in carboxylic acids and reflect the fact that these two oxygen atoms are strongly bonded to the copper atom. The two carboxyl groups are planar within 0·01 Å (Table 6). The nitrogen atom is tetra-coordinated and, within experimental error, tetrahedral; it lies only 0·06 Å from the plane of the nearest carboxyl group. The C(2)–C(3)–C(4) and C(3)–C(4)–C(5) angles are significantly larger than tetrahedral, as is usually observed in saturated carbon chains. And as has almost invariably been observed in amino acids and small peptides, the side chain [which begins at C(3)] is in a highly extended configuration.

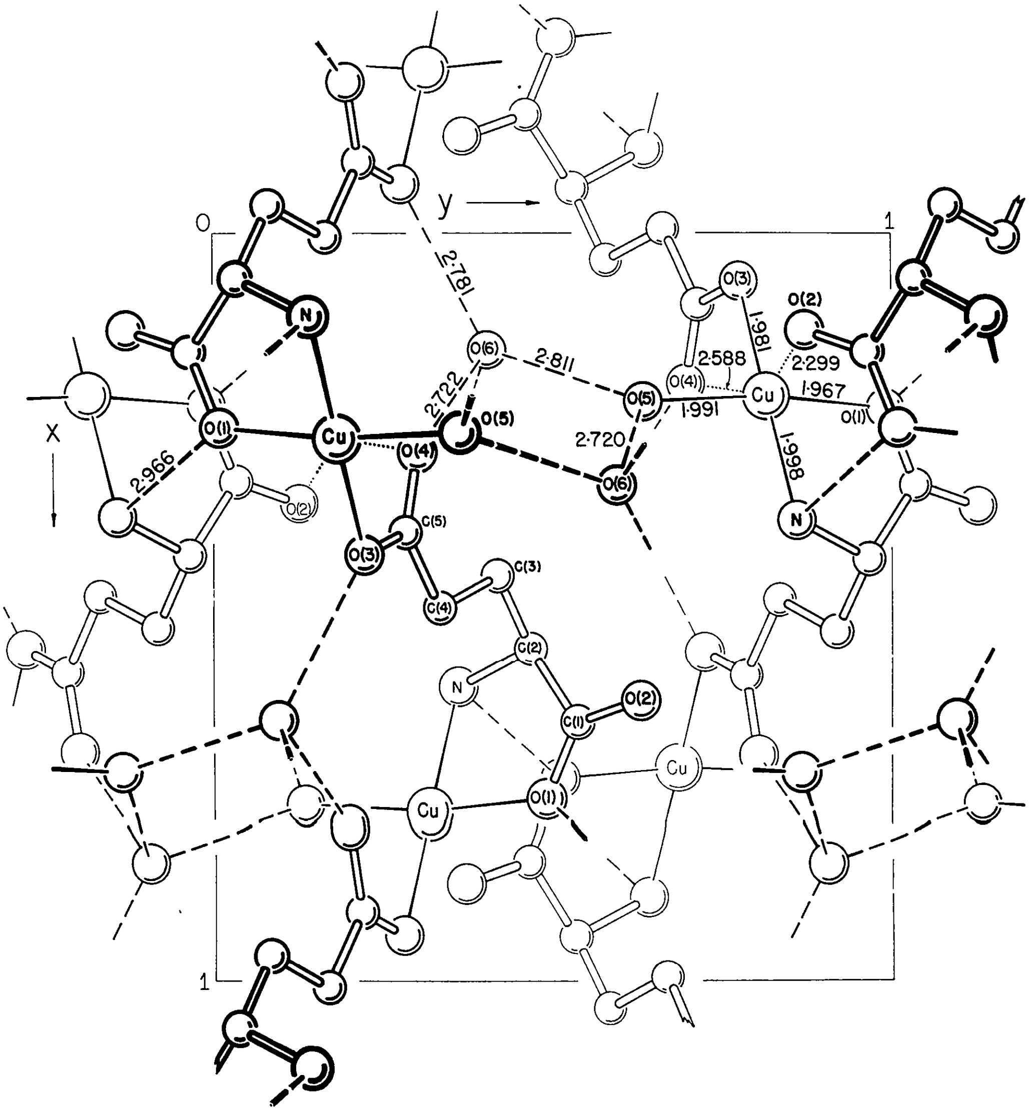

Fig. 2. The structure viewed down the *c* axis. Hydrogen bonds are indicated by dashed lines and the two long Cu···O interactions by dotted lines.

Table 6. *Some planes of interest*

The coefficients q_i are direction cosines relative to **a**, **b**, and **c**; *D* is the origin-to-plane distance. Atoms indicated with an asterisk were omitted from the calculation of the least-squares plane; the remaining atoms were given equal weights.

	Atom	Deviation
(1) Carboxyl group		
$q_1 = -0·1858$	C(1)	−0·010
$q_2 = -0·5986$	C(2)	0·003
$q_3 = 0·7791$	O(1)	0·004
$D = -0·2686$ Å	O(2)	0·004
	*N	−0·056
	*Cu	0·366
(2) Carboxyl group		
$q_1 = 0·0019$	C(4)	0·001
$q_2 = 0·8594$	C(5)	−0·005
$q_3 = 0·5111$	O(3)	0·002
	O(4)	0·002
$D = 6·5101$ Å	*C(3)	0·179
	*Cu′	0·121
(3) Copper ligands		
$q_1 = -0·4416$	N	−0·023
$q_2 = -0·3403$	O(1)	0·023
$q_3 = 0·8301$	O(5)	0·021
	O(3)′	−0·022
$D = -0·8759$ Å	*Cu	−0·151
	*O(2)′	−2·439
	*O(4)′	2·067

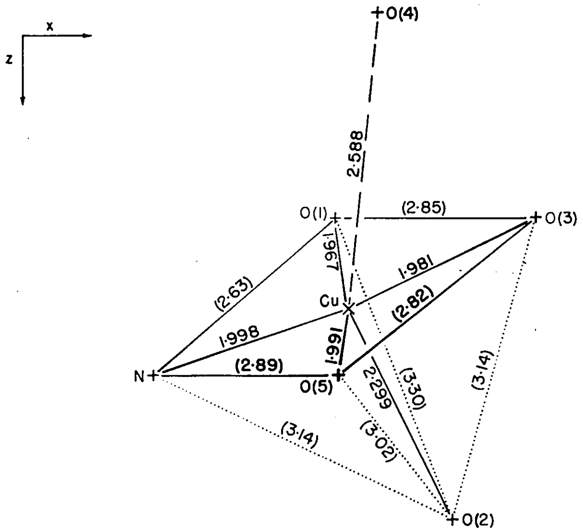

Fig. 3. The coordination about the copper atom.

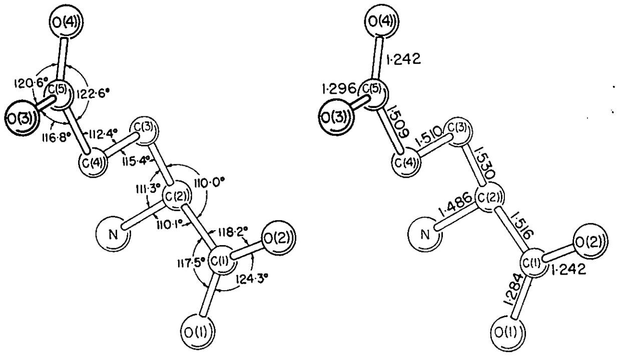

Fig. 4. Bond distances and angles within the glutamate group.

Of the six protons available for hydrogen bonding (two on the nitrogen atom and four on the two water molecules), five participate (Fig. 2). The four O–H···O distances of 2·72 to 2·81 Å and the N–H···O(1) distance of 2·97 are typical values and suggest moderately strong interactions. The second proton on the nitrogen atom, H(7), does not participate in hydrogen bonding, the nearest neighbors in this direction being an O(2) atom at 3·64 Å from the nitrogen atom and an O(3) atom at 3·44 Å.

The lengths and direction cosines of the principal axes of thermal vibration are given in Table 7. The thermal motions are relatively small and not highly anisotropic, reflecting the hardness of the crystals. The directions of maximum motion of O(1) and O(2) make angles of 12° and 29° with the normal to the plane of that carboxyl group, and the directions of maximum motion of C(3), C(4), O(3), and O(4) all lie within 12° from the normal to the second carboxyl group. The

Table 7. *Magnitudes and direction cosines, relative to the crystallographic axes, of the principal axes of the thermal ellipsoids*

	B_i	q_i^a	q_i^b	q_i^c
Cu	1·96	−0·090	−0·980	0·175
	1·77	−0·596	0·194	0·779
	1·42	0·798	0·035	0·602
C(1)	2·44	−0·795	0·485	0·364
	1·59	0·606	0·609	0·511
	1·25	−0·026	−0·627	0·778
C(2)	2·07	0·155	0·985	0·080
	1·60	−0·984	0·146	0·102
	1·46	0·087	−0·095	0·992
C(3)	2·66	0·116	0·895	0·430
	1·87	0·279	−0·445	0·851
	1·47	−0·953	−0·021	0·301
C(4)	3·29	−0·022	0·830	0·558
	1·75	0·186	−0·545	0·818
	1·66	−0·982	−0·122	0·143
C(5)	2·21	0·355	−0·843	0·405
	2·08	0·261	0·505	0·823
	1·61	−0·898	−0·187	0·399
N	2·56	0·122	−0·938	0·324
	1·89	−0·966	−0·038	0·255
	1·49	0·227	0·344	0·911
O(1)	2·95	−0·057	−0·721	0·690
	2·21	−0·634	0·560	0·533
	1·42	0·771	0·407	0·489
O(2)	3·15	−0·625	−0·386	0·679
	2·42	0·743	−0·560	0·366
	1·39	0·239	0·733	0·637
O(3)	3·22	0·128	0·830	0·543
	1·69	0·716	−0·455	0·528
	1·46	−0·686	−0·321	0·653
O(4)	4·79	−0·018	0·947	0·320
	2·05	0·329	−0·297	0·897
	1·47	−0·944	−0·122	0·306
O(5)	4·57	−0·933	0·103	0·344
	2·25	0·337	0·581	0·741
	1·77	0·124	−0·807	0·577
O(6)	2·99	0·175	0·886	0·429
	2·32	−0·543	−0·277	0·793
	1·91	0·822	−0·371	0·432

principal motion of O(5), a water molecule, is approximately perpendicular to the plane of the three atoms to which it is bonded – Cu, O(6), and O(6′). There is no indication of rigid-body motion of the glutamate group as a whole.

Further discussion of the details of the structure and its relationship to the nearly isostructural zinc compound is given in the following paper (Gramaccioli, 1966).

References

DUCHAMP, D. J. (1964). *Amer. Cryst. Assoc. Meeting*, Bozeman, Montana, paper B-14, p.29.
GRAMACCIOLI, C. M. (1963). *Acta Cryst.* **16**, A65.
GRAMACCIOLI, C. M. (1966). *Acta Cryst.* **19**, 600.
International Tables for X-ray Crystallography (1962). Vol. III, p.202–5, 214. Birmingham: Kynoch Press.
PAULING, L. (1960). *The Nature of the Chemical Bond.* 3rd ed. Ithaca: Cornell Univ. Press.

Acta Cryst. (1966). **21**, 600

The Crystal Structure of Zinc Glutamate Dihydrate*

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The crystal structure of zinc glutamate dihydrate, $ZnC_5H_7NO_4.2H_2O$, has been determined and refined by three-dimensional least-squares methods. The crystals are orthorhombic, space group $P2_12_12_1$, with $a=11{\cdot}190$, $b=10{\cdot}463$, and $c=7{\cdot}220$ Å. The final R index for 1035 reflections is 0·032; the standard deviations are about 0·004 Å for the light-atom positions.

Although the compound is nearly isostructural with the corresponding copper compound, the coordination about the zinc atom is a nearly regular square pyramid as compared with a square (with an additional ligand at a considerably greater distance) about the copper atom. The Zn–O and Zn–N distances range from 2·03 to 2·10 Å. This change in coordination has an appreciable effect upon the dimensions of one of the carboxyl groups; otherwise, the dimensions of the glutamate group are not significantly different from those found in copper glutamate. Hydrogen-bond lengths differ by as much as 0·05 Å between the two compounds.

Introduction

The determination of the structure of zinc glutamate (Zn.glu) was originally undertaken as a continuation of studies of the coordination of metal atoms with amino acids and peptides. Interest was further whetted when preliminary photographs showed that crystals of zinc glutamate dihydrate have the same space group, and very nearly the same cell dimensions, as the copper compound Cu.glu (Gramaccioli & Marsh, 1966; hereafter, GM) but that there are differences in intensity of corresponding reflections far greater than would be expected if the two compounds were truly isostructural. Very early in the analysis it became apparent that these differences in intensity were due primarily to differences in the coordinates of the metal atoms, rather than of the amino-acid or water molecules, and that as a result the coordination about zinc would be appreciably different from that about copper. In order to assure a good comparison between the two compounds, the same care has been taken with the present refinement as with that of the copper compound.

Experimental

White prismatic crystals of zinc glutamate dihydrate, $ZnC_5H_7NO_4.2H_2O$, form on slow evaporation of an aqueous solution of zinc oxide in glutamic acid; like the copper compound, they are elongated along **c** with principal faces {110} and {011}. Unit-cell dimensions were obtained as described by GM, based on measurements of 70 $0kl$ and $hk0$ reflections from two crystals; the results are summarized in Table 1. Once again, the difference between b values measured for the two crystals is much greater than the apparent experimental uncertainty, although the discrepancy is much less than that observed in Cu.glu. In view of this discrepancy, the e.s.d.'s of the final ('best') values include a lack-of-confidence factor of about 15.

The experimental density was not measured; that calculated on the basis of four molecules per unit cell is 1·937 g.cm^{-3}. Absence of reflections $h00$, $0k0$, and $00l$ with h, k or l odd indicates the space group $P2_12_12_1$.

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