Fig. 3. A view of the structure along a^* .

molecules is evident in Fig. 3 which is a view along a^* ; the angle between the planes of molecules in adjacent stacks, related by the twofold axis, is 48° . The perpendicular distance between the planes of adjacent molecules within a given stack is 3.45 \AA , only about 0.1 \AA more than that in graphite.

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Crystallographic Studies of Metal-Peptide Complexes.

III. Disodium Glycylglycylglycylglycino Cuprate(II) Decahydrate

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The structure of the pink complex disodium glycylglycylglycylglycino cuprate(II) decahydrate has been determined by X-ray diffraction methods from three-dimensional intensity data recorded on Weissenberg films and estimated visually. The structure (without hydrogen atoms) has been refined by full-matrix least-squares with anisotropic temperature factors to an *R* index of 0.092. The environment of the copper(II) atom is approximately square-planar, the copper being coordinated by the four nitrogen atoms of one peptide molecule. The discrete glycylglycylglycylglycino cuprate(II) ions are extensively hydrogen bonded to water molecules. Both sodium ions exhibit distorted octahedral coordination, the octahedra sharing a face of three water molecules.

Introduction

This is the third in a series of papers describing a crystallographic study of complexes between metals and small peptides (Freeman, Robinson & Schoone, 1964;

Freeman, Schoone & Sime, 1965). From the study of a number of these complexes it is hoped to establish possible stereochemical relationships for metal-protein interaction. Disodium glycylglycylglycylglycino cuprate(II) decahydrate is the first complex to be studied in this series where there exists the possibility of fourfold coordination of a metal ion by nitrogen atoms of the same peptide molecule. Koltun, Roth & Gurd (1963)

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have recently presented evidence, from pH titration and spectrophotometric measurements, that the metal ion is coordinated to the terminal amino and three peptide nitrogen atoms, accompanied by the ionization of the three peptide hydrogen atoms. It was expected that the two negative charges on the Cu^{GGGG²⁻}* ion in this complex would produce some interesting changes in the normally constant peptide-group dimensions.

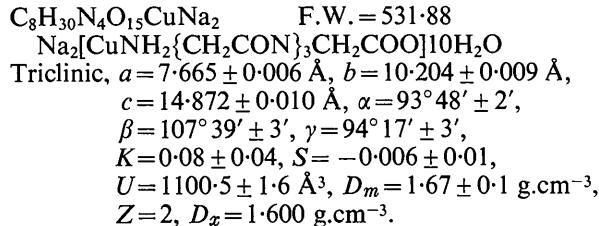
A preliminary account of this structure analysis has been published (Freeman & Taylor, 1964).

Experimental

The preparation of crystals of a pink complex between copper(II) and GGGG* from alkaline solution was reported by Rising, Parker & Gaston (1934). By chemical analysis they established the empirical formula as Na₂CuC₈H₁₀N₄O₅.2H₂O.

Pink solutions of the complex were readily obtained by a similar procedure. Moist, freshly prepared cupric hydroxide (10⁻³ mole) and solid GGGG (10⁻³ mole) were mixed and heated for thirty minutes on a steam bath. Some of the GGGG dissolved, to give a deep blue solution, presumably of a neutral complex. When a solution containing 2 × 10⁻³ mole of sodium hydroxide was added to this mixture, all the GGGG immediately dissolved to give a pink solution. The compound crystallized as long, pink needles with rectangular cross-section from a solution containing acetone, ethanol, and water. Not enough crystals were obtained for chemical analysis, and this crystallization could not be successfully repeated†.

Crystal data for the Delaunay reduced cell are:



Space group $P\bar{1}$ (C_1^1).

The unit-cell parameters were obtained from 79 high sin θ values measured on three zero-level photographs. The $0kl$ data were recorded on a double radius camera using the Straumanis method of film mounting, and the $h0l$ and $hk0$ data on normal radius, platinum-calibrated Weissenberg photographs. The six unit-cell parameters and two parameters K and S were fitted to

* Cu^{GGGG²⁻} is written for the glycylglycylglycylglycine cuprate(II) ion and GGGG for the glycylglycylglycylglycine molecule.

† Since the completion of this work Mr R. L. Sinclair has prepared the substance reproducibly by adding excess cupric hydroxide to GGGG (0.1 g) and sodium hydroxide (0.1 g) in water (0.75 ml). Undissolved cupric hydroxide is filtered off and absolute alcohol is added until a faint cloudiness just appears. Pink crystals appear if the solution is allowed to stand in a stoppered tube for 48 hours.

the data by least-squares. K and S are coefficients of terms which allow for systematic errors and are defined by $\Delta\theta_{abs} = K \cos^2 \theta$, and $\Delta\theta_{ecc} = S \sin 2\theta$ (Buerger, 1942).

The density was measured by flotation in methylene bromide-ethanol mixtures. This density was measured after the intensity data had been recorded. At this stage the only crystals available were of very poor quality, and so coated with extraneous material that the value of the density is not considered to be accurate.

The intensity data were recorded on equi-inclination Weissenberg photographs with unfiltered CuK X-radiation. One crystal of dimensions 0.160 × 0.050 × 0.106 mm³ was used to collect data from layers $h=0-6$, and another, 0.210 × 0.030 × 0.060 mm³ to collect layers $k=0$ and 1. Data were obtained for 4319 of the 5000 unique reflexions within the Cu $K\alpha$ limit. The intensities were estimated visually. 629 were too weak to measure and were given a value of one-third of the minimum observable intensity (Hamilton, 1955). Absorption corrections were calculated by the method outlined by Busing & Levy (1957). A least-squares method equivalent to that described by Hamilton, Rolllett & Sparks (1965) was used to calculate the scale factors required to correlate the intersecting layers of data.

Statistical tests to distinguish between $P1$ and $P\bar{1}$ gave ambiguous results.

The solution of the structure

The routine application of the heavy-atom method was complicated by the lack of knowledge of the empirical formula, the space group, and the accurate density. The formula weight calculated from the observed density indicated that the compound was not the same as that prepared by Rising, Parker & Gaston (1934). It did indicate, however, that provided there was at least one tetrapeptide molecule associated with one copper atom there could only be two copper atoms in the unit cell. In view of these uncertainties the structure was solved in space group $P1$.

Table 1. Observed and calculated structure factors

Each group of reflexions is headed by

$h\ k$

and for each reflexion the data are presented in the order

$l \ 10F_c \ 10|F_0|$

The symbol following $|F_0|$ indicates the weight that was given to the reflexion during the least-squares refinement.

Symbol	Weight of $ F_0 $
none	$1.0/\sigma^2$
V	$2.0/\sigma^2$
W	$2.5/\sigma^2$
X	$1.5/\sigma^2$
Y	$16/ F_{2\min} $
Z	Zero

Y also denotes an unobservably weak reflexion.

Standard deviations in $|F_0|$ used in least-squares refinement

$ F_0 $	0	2.5	10.0	20.0	35.0	50.0	95.0
$\sigma F_0 $	0.40	0.35	0.57	1.05	1.90	3.00	35.00

Table 1. Observed and calculated structure factors

#	0	0	-11	137	133	-5	91	99	0	1	-11	-14	168	159 ^x	-15	122	123	13	76	82 ^w	8	113	129	-6	38	34	11	-38	26	10 ^y							
1	-433	590V	-9	194	200	-4	290	257	-9	-59	53	-12	166	160	-13	39	57	17	38	43V	10	179	169	-4	-76	63	12	23	10Y								
2	561	549V	-9	-418	412	-3	-165	188	-8	-71	72	-11	45	63	-12	102	98	1	1	2	11	-186	170	-3	-25	29	0	2	-8								
3	-485	453V	-7	99	131	-2	195	213	-7	-210	202	-19	-507	476	-10	137	153	1	1	2	12	-153	141	-1	-14	22	-14	61	63	-12	-60	66					
4	-485	521V	-7	125	125	-2	-250	254	-6	-21	45	-8	-26	21V	-9	-32	96	-15	121	112	14	-217	200X	-2	-2	104	112	-12	-12	-60	66						
5	-46	20V	-5	176	201	0	132	138	-5	-13	51	-7	-96	90	-1	213	213	-17	-77	82	15	-104	91X	1	-1	-85	-22	22	-12	-12	-60	66					
6	-463	497V	-4	-558	530	1	255	259	-4	-85	87	-4	93	93	-7	255	259	-16	16	18 ^y	1	6	2	57	69	-11	-192	208	-10	-5	167						
7	232	242V	-3	169	131	2	55	61	-3	-223	227	-6	-253	253	-7	103	103	-16	16	18 ^y	1	6	2	57	69	-11	-192	208	-10	-5	167						
8	161	143V	-2	-104	103	3	23	25	-2	-94	92	-4	-391	390	-5	439	487	-14	-125	137	1	6	2	57	69	-11	-192	208	-10	-5	167						
9	-81	12V	-1	-175	203	-7	65	61	-1	-104	106	-3	-39	39	-13	-94	94	-17	55	52	1	6	2	57	69	-11	-192	208	-10	-5	167						
10	-870	866	-8	-196	190	-3	-196	190	-3	-9	23Y	-4	-246	296	-13	-94	94	-17	55	52	1	6	2	57	69	-11	-192	208	-10	-5	167						
11	62	91V	1	330	384	-6	-190	193	-1	-76	74	-2	-564	513	-3	-486	405	-12	-216	212	-16	19	14Y	6	-151	163	-7	-118	142	-12	-12	-60	66				
12	-238	261V	-2	-515	541	-6	79	95	-2	44	24Y	-1	-204	200	-1	-250	250	-17	19Y	19Y	1	6	2	57	69	-11	-192	208	-10	-5	167						
13	-238	23V	-2	-515	51	-6	-12	12	-3	-48	24Y	-1	-215	234	-1	-567	537	-10	-265	271	-14	-66	77	1	6	2	57	69	-11	-192	208	-10	-5	167			
14	-139	29V	-4	-31	31	8	-12	12	-4	-48	24Y	-1	-215	234	-1	-567	537	-10	-265	271	-14	-66	77	1	6	2	57	69	-11	-192	208	-10	-5	167			
15	190	197V	5	158	173	10	-95	121	5	4	23Y	-2	-367	361	1	450	490	-5	-316	399	-13	-118	127	1	6	2	57	69	-11	-192	208	-10	-5	167			
16	-204	210V	6	342	367	11	145	157	6	-123	125	-4	-303	303	-2	-200	275	-7	-285	252	-11	11	127	1	6	2	57	69	-11	-192	208	-10	-5	167			
17	141	154V	8	154	191	13	123	130	8	74	63	-4	-320	320	-5	-332	325	-10	-334	325	-11	-118	127	1	6	2	57	69	-11	-192	208	-10	-5	167			
18	-196	101V	9	-344	405	0	12	123	9	43	45	-6	-35	36	-5	-16	69	-4	-184	226	-5	-176	190	-10	14	12Y	-1	239	278	-10	-5	167					
19	0	1	10	64	83	0	9	10	-70	61	7	476	465	6	430	440	-3	-173	252	-7	-250	244	-9	-27	14Y	0	-104	142	-12	-12	24						
20	0	1	10	-16	178	0	9	10	-109	104	4	-104	104	-1	-104	104	-1	-104	104	-1	-104	104	2	-104	104	0	2	-76	83								
21	-31	25V	-13	-107	115	-4	-13	46	63	-11	-35	30	11	-66	65	10	-24	23Y	0	-378	363	-6	67	76	1	6	2	57	69	-11	-192	208	-10	-5	167		
22	-149	164V	14	172	192	-12	-91	113	-11	-35	30	11	-66	65	10	-24	23Y	1	38	55	-3	-163	192	5	102	112	6	-38	47								
23	115	132V	14	172	192	-12	-91	113	-10	-160	145	12	-176	176	11	-103	115	12	-176	172	12	-43	161	5	124	74	-1	23	5	-63	69						
24	49	74V	14	33	47	-10	-176	191	-9	109	107	14	-133	132	13	-101	109	14	-133	132	13	-14	140	5	124	74	-1	23	5	-63	69						
25	-202	177V	0	5	-115	123	-7	-83	21Y	-13	-137	130	14	-198	195	15	-238	235	11	-177	175	12	-220	223	10	-10	123	-1	12	-27	13Y						
26	-65	177V	0	5	-115	123	-7	-83	21Y	-13	-137	130	14	-198	195	15	-238	235	11	-177	175	12	-220	223	10	-10	123	-1	12	-27	13Y						
27	56	63V	-15	-106	113	-1	-390	357	-1	51	72	-3	-99	99	-10	-25	21Y	14	-44	42	15	-32	22Y	1	12	-14	15Y	-11	-156	157							
28	-249	495V	-9	155	162	3	-87	95	4	41	49	-5	-234	239	-13	-135	140	16	-175	172	12	-182	180	13	-125	127	0	-13	14Y	-11	-156	157					
29	613	321V	4	362	366	3	-87	95	4	41	49	-5	-234	239	-13	-135	140	16	-175	172	12	-182	180	13	-125	127	0	-13	14Y	-11	-156	157					
30	-728	611V	6	146	161	4	-122	125	5	-122	125	6	-153	156	-13	-153	156	16	-175	172	12	-182	180	13	-125	127	0	-13	14Y	-11	-156	157					
31	-407	399V	-5	-63	96	6	60	53	-14	-145	149	-12	-123	125	-10	-534	499	1	3	1	7	1	-247	237	5	-394	379X	-3	-130	144	-12	-12	36				
32	-49	47V	4	211	183	-7	-136	151	8	166	173	-5	-11	24	-9	-336	328Y	1	1	7	1	7	1	-17	27Y	6	-432	429	-4	-177	182	2	-2	-7			
33	-91	132V	5	93	94	8	25	25	9	-133	146	-13	-376	375	-1	-202	202	-11	-131	115	1	-141	144	-4	-137	144	8	-74	67	-1	23	5	-63	69			
34	-70	90V	5	70	70	9	-95	95	10	132	145	-12	-176	176	-1	-212	212	-12	-192	192	1	-137	137	-5	-137	137	8	-74	67	-1	23	5	-63	69			
35	-525	525V	10	18	26Y	-7	-97	92	10	116	111	-5	-121	121	-1	-212	212	-12	-192	192	1	-137	137	-5	-137	137	8	-74	67	-1	23	5	-63	69			
36	-247	222V	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127		
37	-277	333V	-5	37	37	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127					
38	108	124V	6	108	124	-10	-24	24	-5	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127					
39	-115	111V	6	-115	111	-10	-17	17	-5	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127					
40	-151	155V	14	-35	33	-9	-35	47	1	1	-8	-1	-8	-1	-1	-8	-1	-1	-8	-1	-1	-8	-1	-1	-8	-1	-1	-8	-1	-1	-8	-1					
41	-151	155V	14	-35	33	-9	-35	47	1	1	-8	-1	-8	-1	-1	-8	-1	-1	-8	-1	-1	-8	-1	-1	-8	-1	-1	-8	-1	-1	-8	-1					
42	-210	230V	10	-153	153	-10	-17	17	-5	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127	-11	-125	127					
43	-341	351V	5	-1	247	405	-1	-10	10	-10	10	-10	-267	270	-16	-23	26	13	-102	100	1	-1	1	-6	67	1	-1	1	-6	67	1	-1	1	-6	67	1	
44	-35	81	-7	42	47	0	11	11	-1	-23	25	-17	-1	-39	516	-15	-39	42	14	10	24Y	1	1	1	-6	67	1	-1	1	-6	67	1	-1	1	-6	67	1
45	-493	533V	6	273	312	-1	-123	125	-1	-123	125	-1	-123	125	-1	-123	125	-1	-123	125	-1	-123	125	-1	-123	125	-1	-123	125	-1	-123	125					
46	-41	33	-103	103	-10	-37	44	-1	-8	8	-1	-123	1																								

CRYSTALLOGRAPHIC STUDIES OF METAL-PEPTIDE COMPLEXES

Table 1. (cont.) Observed and calculated structure factors

-11	29	303	-18	99	103V	13	-66	64	-13	92	85	6	65	62	10	-228	231	12	235	241	6	-157	149	10	64	66X	0	-118	54			
-10	20	303	-15	134	145V	14	-140	93	-13	122	120	R	52	50	11	-24	16Y	13	-119	121	7	156	161	11	-55	103	1	-103	54			
-9	76	79	-15	-117	130V	15	-195	91X	-12	-147	158	3	-10	13	-124	120	13	-51	46	9	-118	115	12	43	32	2	-1	35	36			
-7	108	129	-13	129	94V	2	4	-10	-104	101	-1	-17	103	3	-1	11	106	105	11	-95	94	-16	73	72	4	-11	4	-11	4			
-5	-79	90	-12	-130	135V	-18	-60	56	-9	42	32	-11	-123	113	5	-5	-19	76	55	13	-140	129	-15	-110	101	-8	-32	10Y				
-4	756	714	-11	41	-17	22	13Y	-8	-22	17Y	-4	-48	52	-17	-79	67	-18	3	13	-114	105	-14	-91	82	-7	-111	86	-1				
-3	-142	130	-10	-121	107	-15	-78	40	-7	150	163	-8	-11	14Y	-16	21	12Y	-17	-47	44Y	-13	-76	61	-6	-142	108	-1					
-2	309	313	-5	-415	394	-14	-92	103	-5	-247	253	-7	-91	99	-15	-121	121	-15	19Y	17Y	3	-12	126	-5	-15	121	-1					
-1	105	129	-7	234	255	-13	-118	129	-4	-353	367	-6	-9	157	-14	15	15Y	-17	-25	25Y	-26	25Y	-1	-154	99	-1						
0	346	373	-6	-119	114V	-12	240	259	-3	-33	21	-10	-45	49	-12	164	161	-13	-14	121	-17	-62	56	-9	-181	163	-2	-94	92			
2	453	444	-5	-134	119	-17	-103	120	-1	-205	221	-1	-17	17Y	-3	-37	45	-11	158	145	-12	435	406Y	-16	-129	130	-8	-45	64	-1	-20	16Y
3	289	545	-3	1390	1202	-10	-177	195	0	-45	45	-10	-178	191	-10	-203	191	-270	270Y	18	-182	169	-10	-252	197	-1	-157	90	-1			
4	103	113	-2	-1719	1205	-6	-328	317	1	-10	17Y	-1	-178	191	-10	-203	191	-270	270Y	18	-182	169	-10	-252	197	-1	-157	90	-1			
5	130	146	-1	-149	145	-7	-232	234	-5	-20	55	-1	-180	193	-9	-29	106	-9	-232	218Y	-5	-64	93	-1	-160	165	-3	-25	14Y			
7	-25	29	-7	-57	55V	-5	-517	505	4	-24	94	-6	-94	97	-6	-226	214	-7	232	232	11	76	69	-5	-155	154	-1	-154	99			
9	95	103	2	-343	329V	-4	-233	274	-5	-94	97	-5	-153	188	-6	-204	239	-7	232	232	11	76	69	-5	-155	154	-1	-154	99			
10	83	92	3	-493	412V	-3	-99	102	6	-255	210	-5	-21	15Y	-3	-266	239	-4	-256	245Y	-9	-251	243	-1	-216	216	-1	-150	154			
11	-54	60	4	-561	518V	-1	-19	51	54	-6	-183	205	-2	-449	445	-3	-51	54Y	-7	-244	234	1	-211	211	-1	-150	154	-1				
12	14	24	5	-561	518V	-1	-19	51	54	-6	-183	205	-2	-449	445	-3	-51	54Y	-7	-244	234	1	-211	211	-1	-150	154	-1				
13	168	166	6	-245	254V	0	-63	67X	9	-135	139	7	-133	143	-1	-41	51	-2	241	251	-6	-302	292	3	-163	174	-10	-61	44			
14	-131	133	7	-332	326V	1	-165	155	10	-251	224	4	-41	41	0	-10	20	-10	-203	191	-270	270Y	18	-182	169	-10	-252	197	-1			
15	114	115	8	-179	195V	2	-326	351	11	-11	9Y	9	47	57	2	-202	191	1	-37	37V	-3	-252	232	6	-75	73	-1	-154	99			
16	-165	139	9	-404	419V	-1	-15	53	52	-7	-101	110	-7	-67	77	-11	-220	193	10	-154	152Y	6	-147	130	-1	-157	90	-1				
17	-109	106	-19	54	43V	4	-99	99	9Y	-6	65	65	-5	-40	34	13	-35	38	11	74	58Y	7	-137	129	-1	-155	154	-1				
18	-109	107	-19	52	43V	5	-111	117	11	-7	95	98	-3	-171	170	14	-32	47	14	-111	112Y	12	-172	173	-11	-225	217	6	-85	76		
19	-296	293	-16	-53	52V	2	5	-202	218	-2	-110	111	3	-3	4	15	-29	25Y	11	-13	13Y	-12	-41	55	-1	-157	151	7	-77	67		
20	-172	-15	9	26	-1	-14	-17	156	5	-72	630	-1	-14	-17	156	5	-30	24	17	-71	72Y	3	0	13	-3	-157	154	-1	-157	90		
21	-449	453	-14	322	339V	-16	-41	3C	-1	-239	250	0	-220	240	-17	-71	72Y	3	0	13	-41	45Y	-7	-229	236	4	-9	-1				
22	-116	159	15	-240	261V	-16	-129	122	1	-155	149	-2	-249	245	-16	-65	62	-19	19	11Y	3	4	-6	-37	42	-1	-157	90	-1			
23	-400	424	14	-277	265V	8	-173	175	-12	-122	123	-11	-15	12Y	7	-149	171	6	-19	171	-23	147	130	-1	-157	90	-1					
24	-15	136	15	-17	19Y	9	-15	15	11	-71	65	-10	-10	14Y	8	-114	105	6	-248	248	-1	-157	90	-1	-157	90	-1					
25	-15	75	16	105	113V	10	-202	256	-10	-57	57	-10	-10	14Y	9	-158	149	6	-248	248	-1	-157	90	-1	-157	90	-1					
26	-56	65	-11	-348	340V	-15	-43	37	-2	-81	78	3	-9	17Y	-14	-53	56	-6	-248	248	-1	-157	90	-1	-157	90	-1					
27	-342	341	-10	-491	465V	-16	-87	87	3	-359	354	4	-41	115	-13	-179	174	-10	-15	15Y	12	-157	151	-1	-157	90	-1					
28	-519	566	-1	-402	371V	-13	-109	109	4	-202	240	-5	-65	66	-10	-10	14Y	-15	-103	103	1	-157	90	-1	-157	90	-1					
29	-243	238	-7	-209	244V	-11	-176	189	6	-203	243	-7	-91	93	-11	-15	13Y	-15	-227	210	-1	-157	90	-1	-157	90	-1					
30	-135	201	-6	-204	236V	-12	-153	153	1	-203	243	-7	-91	93	-11	-15	13Y	-15	-227	210	-1	-157	90	-1	-157	90	-1					
31	-51	111Y	9	-31	31Y	-9	-59	45	8	-79	90	11	-116	94	-6	-40	44	-5	-29	29V	1	-117	117	-1	-157	90	-1					
32	-578	290	-2	-134	225V	-6	-147	156	5	-202	218	-1	-14	14Y	-16	-71	72Y	-12	-157	154	-1	-221	207	-1	-157	90	-1					
33	-463	491	-1	-219	219V	-5	-112	114	-1	-9	RY	-14	-57	57	-14	-25	25	-7	1	-157	154	-1	-157	90	-1	-157	90	-1				
34	-313	304	0	-112	122V	-4	-62	62	-1	-42	43	-5	-57	57	-14	-25	25	-7	1	-157	154	-1	-157	90	-1	-157	90	-1				
35	-475	473	-1	-207	219V	-4	-193	235	-1	-80	73	-13	-31	20	-1	-942	500	-1	-35	37V	-1	-37	34	-5	-51	63	-1	-104	103	-1		
36	-15	139	15	-246	253V	-1	-144	144	-1	-34	34	-12	-54	60	0	-127	137	-3	-39	37V	-1	-35	37V	-1	-106	103	-1	-157	90			
37	-12	72	1	-209	264V	-6	-234	242	-5	-44	45	-15	-125	111	-1	-235	242	-14	-35	37V	-1	-35	37V	-1	-106	103	-1	-157	90			
38	-12	73	2	-207	265V	-6	-234	242	-5	-44	45	-15	-125	111	-1	-235	242	-14	-35	37V	-1	-35	37V	-1	-106	103	-1	-157	90			
39	-124	138	-6	-106	134	-7	-207	227	-4	-21	14Y	-14	-27	25	-7	-9	257	12	-37	35	-13	-62	65	-1	-157	90	-1					
40	-454	497	-5	-403	483V	-15	-156	157	-3	-165	157	-8	-116	153	-5	-50	53	-1	-164	163	-1	-157	90	-1	-157	90	-1					
41	-44	39	4	-121	97	9	-235	235V	-1	-141	14Y	-11	-116	119X	-5	-50	53	-1	-164	163	-1	-157	90	-1	-157	90	-1					
42	-571	595	-1	-242	242V	-2	-147	147	-1	-41	42	-5	-116	119X	-5	-50	53	-1	-164	163	-1	-157	90	-1	-157	90	-1					
43	-124	137	7	-242	242V	-2	-147	147	-1	-41	42	-5	-116	119X	-5	-50	53	-1	-164	163	-1	-157	90	-1	-157	90	-1					
44	-124	137	7	-242	242V	-2	-147	147	-1	-41	42	-5	-116	119X	-5	-50	53	-1	-164	163	-1	-157	90	-1	-157	90	-1					
45	-124	137	7	-242	242V	-2	-147	147	-1	-41	42	-5	-116	119X	-5	-50	53	-1	-164	163	-1	-157	90	-1	-157	90	-1					
46	-124	137	7	-242	242V	-2	-147	147	-1	-41	42	-5	-116	119X	-5	-50</td																

Table 1. (cont.) Observed and calculated structure factors

0	113	122	8	-93	98	9	-111	138	-11	54	50	-7	89	84	-5	-174	167	7	147	158V	-11	229	217	0	-27	17Y	-2	-91	85			
0	299	241	9	-63	69	10	-253	262	-6	-106	99	-6	-72	74	-4	216	219	8	210	222V	-10	-129	122	1	90	72	-1	-56	57			
2	377	74	10	-12	12	11	-164	144	-9	220	237	-5	-86	92	-2	-51	305	5	-55	64	-9	141	163	2	-46	59	0	-72	85			
3	246	228	11	-38	45	12	164	144	-1	141	157	-3	-125	119	-1	44	48	11	-83	91V	-7	213	194	3	116	98	1	-1	2			
4	-198	207	12	-141	147	13	15	12	12Y	-7	311	300	-3	-125	119	-1	44	48	11	-83	91V	-6	-146	154	6	-9	4	3	-55	56		
5	233	231	13	33	15Y	-6	-20	29Y	-2	-124	131	0	244	236	12	28	16Y	-6	-146	154	6	-9	4	3	-55	56						
6	5	6Y	14	-143	106	4	4	3	-5	189	199	-1	2	24	-1	-56	65	-5	100	102	-5	1	24Y	4	-99	111						
7	16	21Y	-4	-1	-18	-57	53	-3	-53	57	1	-13	20Y	3	-158	159	-5	1	-153	217	-10	-47	49	4	-41	38						
8	-128	139	4	-1	-17	53	22Y	-2	-17	28Y	2	84	99	-5	-142	145	5	-335	319	-15	-18	222	-8	-67	18Y	7	164	170				
9	122	130	-16	125	121V	-10	-153	159	-5	-167	145	-1	167	161	4	31	36	-30	31	0	236	242X	-6	126	133	8	-136	143				
10	30	30Y	-16	-17	120	-10	-153	159	-5	-167	145	-1	167	161	4	31	36	-30	31	0	236	242X	-6	126	133	8	-136	143				
11	82	82	-16	-17	120	-10	-153	159	-5	-167	145	-1	167	161	4	31	36	-30	31	0	236	242X	-6	126	133	8	-136	143				
12	33	13Y	-16	-17	120	13	63	73	1	15	159	-5	-161	145	4	41	42	7	151	159	-1	-146	154	0	-150	116						
13	-33	8Y	-15	-55	65	-13	-88	100	2	88	93	-6	-13	16Y	8	-27	30Y	-1	-10	73	12	-12	52	62	4	343	333X	-2	44	60		
4	-5	-14	-26	26Y	-12	215	240	3	-170	190	8	-138	120	12	-41	36	-10	-234	222Y	-10	-17	21Y	-1	-17	50	46						
-16	-79	70	-11	-9	23Y	-9	-446	414	6	166	180	5	-5	-8	-20	44Y	-9	-190	178Y	7	-154	167X	1	-18	20Y	-15	125	129				
-15	66	79	-10	-301	276V	-8	153	137	7	-172	181	6	-13	16Y	10	-73	12	-12	52	62	4	343	333X	-2	44	60						
-14	56	56	-246	244V	-7	-378	392	8	156	150	-13	-10	94	5	-5	-8	-20	44Y	9	-163	172X	2	-29	36	4	-123	141					
-13	59	163	-14	-17	135	13	101	135	-6	-161	145	9	-54	68	-11	-105	103	-17	-45	45	14	-10	41	30	4	-12	144	175				
-12	43	43V	-7	-472	447V	-5	-495	467	-11	-105	103	-17	-45	53	-7	-236	207Y	9	-98	94	3	-37	78	1	-14	4	23Y					
-11	10	29Y	-6	-674	604	-4	-10	37	-13	114	127	-11	-7	12	-5	-291	29Y	5	-5	-28	14Y	-10	-111	131	0	-9	70	1	-20	20Y		
-10	-54	58	-5	883	794	-3	-205	226	-7	-15	22	-7	-20Y	-15	-22	20Y	-5	-332	309Y	5	-5	6	-8	6	-9	70	1	-1	21	36		
-9	66	56	-5	-381	342V	-3	-205	226	-15	-15	22	-5	-10	15	-10	-292	233V	-16	-105	75	-12	-97	71	-7	-36	38						
-8	-44	27Y	-3	291	21V	-1	-19	30	14	-63	49	-7	-43	49	1	-15	91	10Y	-2	-292	233V	-16	-105	75	-12	-97	71	-7	-36	38		
-7	-71	83	-7	-17	167	0	-149	140	-13	-66	21Y	5	-142	145	5	-335	319	-17	-18	22Y	-1	-10	73	16	-11	78	76	-6	-12	19Y		
-6	180	178	-1	-562	412V	1	-292	271	-12	73	71	-5	-105	119	-11	-150	172	0	44	67	-6	-14	39	19Y	-11	-10	43	48	-10	-210	211	
-5	-103	99	0	-34	244	-2	-216	225	-11	-122	229	-4	-29	25Y	-10	-45	5C	1	-107	119Y	-9	-107	100	-10	-10	40	44	-1	-10	40		
-4	-57	57X	-3	-90	37V	3	-10	20	-10	-10	20	-5	-10	20	-5	-10	20	-5	-10	20	-5	-10	20	-5	-10	20	-5	-10	20			
-3	-394	354	-2	-334	309V	4	-205	209	-5	-156	153	-5	-90	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-2	280	239	3	198	209V	5	165	153	-5	-156	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-160	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6	-155	153	-7	-155	153	-5	-91	104	-1	-30	37	-7	-350	329	-12	-12	120Y	-9	-153	129	-6	-57	78	-1	-21	36
-1	-164	149	4	83	105V	6																										

Table 1. (cont.) Observed and calculated structure factors

-13	2	23Y	-1	-54	70	#	6	4	-4	192	103	-1	-119	118	-6	-105	110	-11	-35	32Y	3	-85	101	-5	127	136	-5	94	69				
-13	39	23Y	0	34	70	#	6	4	-4	193	104	-10	-119	122	-6	-105	110	-11	-35	32Y	4	-85	102	-4	-151	163	-5	-129	138				
-11	-49	35	1	-57	51	-2	16	-128	86	-2	192	104	-9	-113	123	-4	-10	102	-10	-93	105	4	-85	102	-4	-12	65	-5	-20	41			
-10	-36	50	2	-331	304	-15	-16	76	71	-1	-169	179	-8	-143	142	-3	-61	54	-8	-147	145	6	-80	79	-2	-166	181	-5	-27	99			
-9	199	157Y	3	214	213	-15	-105	103	0	832	224X	-7	73	92	-2	-39	15Y	-7	-50	33Y	7	-46	98	-2	-103	125	-5	-27	99				
-8	-42	47Y	4	166	176	-14	-5	21Y	1	167	171	-6	-22	22	-1	-41	14Y	-7	-50	33Y	7	-46	98	-2	-103	125	-5	-27	99				
-7	72	20Y	5	53	52	-2	16	12	12	23Y	3	-31	40	-4	-97	90	-7	-1	-4	89	95	-8	-1	-133	142	-1	-13	13Y					
-6	-46	50Y	6	52	52	-2	16	12	12	23Y	3	-31	40	-4	-97	90	-7	-1	-4	89	95	-8	-1	-133	142	-2	-28	26					
-5	199	173Y	7	181	183	-11	-111	103	4	-123	132X	-3	-91	90	-7	-1	-4	-44	46	-3	-1	-24Y	3	-44	59	-9	-9	0					
-4	-219	180Y	8	104	107	-10	-13	23Y	5	13	43	-2	-97	92	-16	94	101	-2	-22	20Y	11	-14	27	13Y	4	-60	69	-3	-13	13Y			
-3	13	193Y	9	108	104	-9	-10	13	23Y	6	100	109	-1	-11	21Y	-1	-11	34Y	-12	-98	110	6	8	1	-12	-86	57	-10	-34	22Y			
-2	-237	195Y	10	-70	33X	-7	-22	22Y	7	91	86	0	-173	151	-13	-11	21Y	-1	-11	34Y	-12	-98	110	6	8	1	-12	-86	57	-10	-34	22Y	
-1	198	191Y	0	-245	225Y	-7	-22	22Y	6	-15	191	#	6	6	2	-87	98	-12	22Y	2	-6	34Y	-11	-17	180	-10	-15	27	-3	-10	-34	22Y	
1	198	82Y	1	-25	43	-5	-23	43	6	-15	61	54	-4	-16	16	-10	-11	72	50	80	-9	-35	40	-14	12	14Y	-9	14	23Y	-10	-34	22Y	
2	-192	20Y	-17	79	78	-15	61	54	-1	7	16Y	9	99	90	-10	-11	72	50	80	-9	-35	40	-14	12	14Y	-9	14	23Y	-10	-34	22Y		
3	-35	23Y	16	-49	43	3	-202	198	-14	7	16Y	9	99	90	-9	-57	67	5	95	103	-8	56	64	-13	-59	76	-5	-11	24Y	-7	-21	24Y	
4	-144	142Y	19	-95	103	-2	-219	204X	13	35	44	-8	-128	137	6	-144	145	6	-61	69	-12	67	78	-7	-21	24Y	-6	-36	26Y	-7	-21	24Y	
5	218	225Y	-14	-114	113	-1	-206	194X	-12	-111	105	6	-7	-19	33	7	95	95	-5	-25	22Y	-10	-99	113	-5	-10	26Y	-7	-21	24Y			
6	22	225Y	-13	106	105	-1	-206	195X	-1	-111	105	6	-6	-14	33	-1	-11	34Y	-12	-98	110	6	8	1	-12	-86	57	-10	-34	22Y			
7	-140	149Y	-12	-104	104	-2	-132	144	-10	142	137	-11	37	57	45	-4	122	135	7	1	-3	-23	22Y	-8	97	105	-3	-66	86	-7	-21	24Y	
8	-21	197Y	-12	-104	104	-2	-132	144	-10	142	137	-11	37	57	45	-4	122	135	7	1	-3	-23	22Y	-7	-31	22Y	-7	-21	24Y	-7	-21	24Y	
9	-171	169Y	-10	-125	177	-3	-7	24Y	-9	94	95	-10	-68	98	-3	-43	90	-17	-21	22Y	-7	-31	22Y	-7	-21	24Y	-7	-21	24Y	-7	-21	24Y	
10	55	92Y	-9	119	138	4	-98	130	-7	94	96	-23Y	-1	-11	21Y	-10	173	160	-17	-21	21Y	-7	-31	22Y	-7	-21	24Y	-7	-21	24Y	-7	-21	24Y
#	6	2	-5	-56	225	6	-63	63	-5	95	95	-7	-123	129	0	-5	75	-15	76	92	-1	-53	70	-4	98	97	1	-64	77	-2	39	36	
-17	32	15Y	-17	-193	191	7	7	43	54	-4	-133	108	-6	-129	136	1	-32	42	-14	-54	65	2	171	174	-3	-103	99	1	-62	63	-9	1	1
16	34	45Y	-4	-167	153	13	15Y	71	71	5	-15	163	-13	-135	145	3	-50	50	-14	14	14Y	1	-53	70	-4	-21	21Y	-7	-31	22Y	-7	-21	24Y
15	-50	80	-3	-167	153	13	15Y	71	71	5	-15	163	-13	-135	145	3	-50	50	-14	14	14Y	1	-53	70	-4	-21	21Y	-7	-31	22Y	-7	-21	24Y
14	-5	22Y	-3	-200	225X	6	5	0	10	23Y	-2	157	157	4	-6	20Y	-10	63	94	6	-90	95	0	-21	21Y	-2	88	97	-10	-9	52		
-13	-137	152Y	-1	119	109	-16	-59	48	-1	-19	22Y	-1	15	19Y	6	-17	19Y	9	-173	162	6	122	92	1	-39	41	-12	-11	11Y				
-12	31	51	0	216	219	-11	-56	62	-1	-19	21Y	0	104	106	7	-28	15Y	-7	91	113	8	8	0	2	31	16Y	-10	-21	24Y				
-11	-20	20Y	1	119	109	-16	-59	48	-1	-19	21Y	4	88	86	8	-17	17Y	-7	102	121	6	59	65	-14	-72	77	-8	-31	16Y				
-10	129	150	2	118	115	-13	-53	53	-1	-19	21Y	4	88	86	8	-17	17Y	-7	102	121	6	59	65	-14	-72	77	-8	-31	16Y				
-9	-180	197	3	17	24Y	-12	16	22Y	5	-106	119	5	91	72	6	7	0	-5	23Y	13	-55	64	-9	-1	-1	-5	-28	38	-7	-21	24Y		
-8	-25	20Y	4	212	218	-11	-53	53	6	-14Y	6	-1	-19	21Y	-10	-17	21Y	-12	-20Y	20Y	9	-1	-1	-4	-3	17Y	-7	-21	24Y				
-7	5	45	23Y	-10	76	95	#	6	7	-1	-17	48	43	-3	-16	20Y	-2	101	103	-10	-14	29Y	-12	50	54	-4	-12	44	-7	-21	24Y		
-6	-20	20Y	5	45	23Y	-10	76	95	#	6	7	-1	-17	48	43	-3	-16	20Y	-2	101	103	-10	-14	29Y	-12	50	54	-4	-12	44	-7	-21	24Y
-5	99	109	6	137	137	-8	-77	97	-7	105	112	-14	33	12Y	-9	-45	24Y	-1	-32	23Y	-9	-56	93	-11	-26	35	-3	-9	44	-7	-21	24Y	
-4	-117	103	7	90	77	-8	-77	97	-7	105	112	-14	33	12Y	-9	-45	24Y	-1	-32	23Y	-9	-56	93	-10	-54	63	-3	-9	44	-7	-21	24Y	
-3	-108	111X	8	-77	97	-7	-105	112	-13	-34	12Y	-8	-149	125	-13	-74	75	-10	-51	74	-7	-28	41	-9	-11	11Y	0	-37	44	-7	-21	24Y	
-2	107	106	9	-79	72X	-5	-97	99	-12	-121	140	-12	70	74	-12	-31	31Y	2	35	59	-8	-9	77	0	-37	44	-7	-21	24Y				

The positions of two copper atoms were obtained from a three-dimensional Patterson synthesis. Four small peaks surrounding the copper atom-copper atom vector indicated the orientation of the coordination square of at least one of these atoms. A three-dimensional Fourier synthesis was computed with phases based on the contributions to the structure factors from two copper atoms and four nitrogen atoms surrounding one of them. All the observed data were included in the computation, the terms being weighted to minimize the errors in electron density due to errors in phase angle (Rossmann & Blow, 1961).

All the atoms in the structure were identified in this and one more Fourier synthesis. The presence of a centre of symmetry was also established. The *R* index at this stage was 0.27. The scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon, nitrogen, oxygen and Cu⁺ and that of Freeman (1959) for Na⁺. The curve for Cu⁺ was used instead of that for Cu²⁺, consistent with the principle (Pauling, 1948) that the partial ionic character of the metal-ligand bonds reduces the electrical charge on the central metal ion in a complex to +1 or less. To allow for the real part of the anomalous scattering by copper, 2.1 electrons were subtracted over the whole sin θ range before the temperature factor was applied (Dauben & Templeton, 1955).

Values of $\sigma(|F_0|)$ for weighting the refinement were found from the independent observations used to calculate $|F_0|$. A similar method has been described by Ibers (1956). The data were divided into three groups: those where $|F_0|$ was derived from more than one observation, those where there was only one observation, and those that were too weak to be measured.

For each of the reflexions in the first group, the population variance (*i.e.* the variance of a single observation) was estimated from the sample variance. This

estimate is likely to be more accurate than the range estimate recommended by Ibers (1956) (Tippett, 1925; Davies & Pearson, 1934). The standard errors of these individual variances are high so that an average of them was used. The mean variance for a range of $|F_0|$ was plotted against $|F_0|$, a smooth curve drawn through the points, and the appropriate variances read off (see legend to Table 1).

The variance of the mean $|F_0|$ rather than the population variance is required for least-squares weighting. This was obtained from the relation $\sigma^2(|F_0|) = \sigma^2(|F_0|)/n$. The variances needed for the second group of reflexions were given by $\sigma^2(|F_0|)$ ($n=1$ in the above equation). The variance of reflexions in the third group was obtained by the method outlined by Hamilton (1955). In some cases where two or more observations were not considered to be independent, non-integral values for n were used. A complete list of the weights used is given in the legend to Table 1.

Four cycles of full-matrix least-squares refinement using isotropic temperature factors lowered *R* to 0.14 and $\sum w(\Delta F)^2$ to 3.5. Large systematic trends in ΔF with the *h* index indicated that the atoms of the approximately planar CuGGGG²⁻ ion had their major component of anisotropic thermal motion normal to the plane. Accordingly the refinement was continued with anisotropic thermal parameters.

With the full-matrix least-squares program and computer available (see last paragraph) only 205 of the 271 variables could be refined in the same cycle. Different but overlapping blocks of parameters were therefore refined in successive cycles. (i) The scale factor and the parameters of the copper atom were refined in every cycle. (ii) All or none of the positional parameters of a particular atom were included in the same refinement cycle. (iii) All or none of the thermal parameters of a particular atom were included in the same refinement cycle. (iv) All thermal parameters were var-

ied in the first cycle since the changes in these were expected to be far larger than the changes in the positional parameters. (v) All positional parameters were varied in every cycle after the first, and the thermal parameters were chosen so that each of them was varied at least every second cycle.

The *R* index fell to 0.097 after the first cycle, then more slowly through three more cycles to 0.092. With few exceptions, the shifts in the parameters had decreased to less than one-half of their standard deviations. Consequently, the refinement was terminated. The final parameters and standard deviations are presented in Table 2. The final scale factor, applied to the F_c , was 1.0372 with a standard deviation of 0.0033.

Description of the structure

Arabic numerals have been used to distinguish between atoms of the same type and Roman numerals to distinguish between atoms in different asymmetric units. The Arabic numerals have been assigned sequentially, beginning at the *N*-terminus of the peptide molecule. The oxygen atoms of water molecules are numbered from six to fifteen.

The asymmetric units are denoted as follows:

Coordinates	Superscript
$x \quad y \quad z$	none
$1-x \quad 1-y \quad 1-z$	i

Coordinates	Superscript
$x \quad -1+y \quad z$	none
$1-x \quad -y \quad 1-z$	ii
$-1+x \quad y \quad z$	iii
$-x \quad 1-y \quad 1-z$	iv
$-1+x \quad -1+y \quad z$	v
$x \quad y \quad -z$	vi
$x \quad 1+y \quad z$	vii
$1-x \quad 1-y \quad 2-z$	viii
$1+x \quad y \quad z$	ix
$2-x \quad 1-y \quad 2-z$	x
$1+x \quad y \quad 1+z$	xi
	xii

The structure consists of layers of discrete CuGGGG²⁻ anions alternating with layers of sodium ion–water molecule octahedra, the layers being parallel to (001). The approximately planar CuGGGG²⁻ anions within the layers do not lie parallel to (001). They are inclined 25° to this plane and are linked edge to edge by hydrogen bonding through water molecule O(15) to form infinite chains parallel to the *b* axis. The ions in neighbouring chains have no bonded contacts with each other (Fig. 1).

One GGGG molecule is coordinated to one copper atom as a tetradentate chelate with its four nitrogen atoms as ligand atoms, thus forming three five-membered chelate rings. The four Cu–N bonds range from 1.912 to 2.028 Å in length. The CuGGGG²⁻ ion [the

Table 2. Final atomic parameters

All values are $\times 10^4$. Standard deviations from the least-squares refinement are in parentheses.
Temperature factor = $\exp\{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)\}$.

Atom	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu	3203(07)	6508(06)	5299(06)	123(2)	44(1)	21(1)	-15(1)	7(1)	-4(0)
*Na(1)	5475(26)	1458(21)	8782(22)	222	53	39	-9	-20	-3
*Na(2)	1805(21)	6059(19)	9914(19)	133	58	33	-14	10	O(3)
*C(1)	1590(63)	8335(50)	3967(53)	207	48	38	-20	-13	-2
*C(2)	812(49)	6933(45)	3539(43)	108	54	28	-5	15	-O(4)
*C(3)	894(50)	4608(44)	3832(43)	130	46	26	-19	3	-6
C(4)	1849(48)	3876(44)	4676(41)	104(9)	49(3)	25(2)	-7(4)	13(3)	-6(2)
C(5)	4031(49)	4225(42)	6289(42)	128(9)	42(3)	26(2)	-11(5)	3(3)	-3(2)
C(6)	5134(47)	5435(45)	6921(41)	91(8)	62(4)	24(2)	-17(5)	11(3)	-8(2)
C(7)	5955(51)	7736(45)	7169(43)	139(9)	55(4)	26(2)	-37(5)	17(3)	-14(2)
C(8)	5245(48)	8285(43)	7957(41)	110(9)	50(4)	26(2)	-1(5)	2(3)	0(2)
*N(1)	3182(53)	8337(43)	4843(44)	219	51	35	-13	-5	-4
*N(2)	1461(42)	6017(38)	4065(37)	127	49	26	-6	1	-5
*N(3)	2960(43)	4649(38)	5398(36)	141	50	22	-19	-0 ₂	-2
*N(4)	4865(41)	6574(36)	6586(34)	117	52	19	-21	5	-6
O(1)	-403(38)	6792(35)	2725(33)	153(8)	64(3)	29(1)	-6(4)	-4(2)	2(2)
O(2)	1547(42)	2632(32)	4631(34)	224(9)	39(3)	32(2)	-23(4)	-8(3)	-5(2)
O(3)	6246(39)	5223(36)	7715(32)	160(8)	69(3)	25(1)	-5(4)	-13(2)	-1(2)
O(4)	3829(37)	7744(38)	8076(36)	129(7)	74(3)	41(2)	-27(4)	26(3)	-10(2)
O(5)	6206(37)	9290(35)	8462(34)	145(7)	59(3)	36(2)	-18(4)	12(3)	-20(2)
O(6)	2760(40)	1229(39)	7503(36)	156(8)	80(4)	36(2)	3(4)	9(3)	3(2)
O(7)	4957(47)	3644(52)	9264(55)	161(9)	113(5)	81(3)	43(6)	-2(4)	-20(3)
O(8)	2564(40)	8316(38)	9620(35)	161(8)	78(4)	34(2)	13(4)	17(3)	3(2)
O(9)	2606(53)	1631(43)	9721(42)	313(12)	71(4)	41(2)	-34(6)	-1(4)	2(2)
O(10)	7805(49)	2946(48)	8410(41)	256(11)	109(5)	43(2)	3(6)	46(4)	2(3)
O(11)	8547(40)	6081(40)	9496(36)	158(8)	76(4)	36(2)	-13(4)	-11(3)	4(2)
O(12)	2280(44)	5348(40)	8471(36)	230(10)	73(4)	32(2)	-18(5)	12(3)	-6(2)
O(13)	667(42)	8740(41)	6978(40)	183(9)	76(4)	43(2)	-6(5)	-4(3)	-13(2)
*O(14)	9797(40)	9825(47)	8533(40)	133	114	44	-16	5	-8
*O(15)	3510(46)	959(39)	5768(41)	246	64	48	20	36	-4

* The thermal parameters of these atoms were not refined in the final refinement cycle.

Table 3(a). Interatomic distances (\AA) and angles ($^\circ$) of the glycylglycylglycylglycino cuprate(II) ion

	Present work		Average in peptides		
Cu—N(1)	2.028(5)	Cu—N(2)	1.923(4)	Cu—N(3)	1.912(4)
N(1)—C(1)	1.490(8)	N(2)—C(3)	1.458(6)	N(3)—C(5)	1.444(6)
C(1)—C(2)	1.523(7)	C(3)—C(4)	1.527(7)	C(5)—C(6)	1.527(7)
C(2)—O(1)	1.276(6)	C(4)—O(2)	1.267(6)	C(6)—O(3)	1.272(6)
C(2)—N(2)	1.290(7)	C(4)—N(3)	1.316(6)	C(6)—N(4)	1.301(6)
				C(8)—O(4)	1.246(6)
				C(8)—O(5)	1.268(6)
	Present work		Average in peptides		
Cu—N(1)—C(1)	108.8(3)	N(2)—C(3)—C(4)	108.9(3)	N(3)—C(5)—C(6)	108.6(3)
N(1)—C(1)—C(2)	111.5(3)	C(3)—C(4)—N(3)	113.9(3)	C(5)—C(6)—N(4)	116.7(3)
C(1)—C(2)—N(2)	114.9(3)	C(3)—C(4)—O(2)	119.7(3)	C(5)—C(6)—O(3)	116.6(3)
C(1)—C(2)—O(1)	117.7(3)	O(2)—C(4)—N(3)	126.4(3)	O(3)—C(6)—N(4)	126.7(3)
O(1)—C(2)—N(2)	127.4(3)	O(2)—C(4)—N(3)	125.8(3)	C(6)—N(4)—C(7)	117.3(3)
C(2)—N(2)—C(3)	125.4(3)	C(4)—N(3)—C(5)	118.9(3)	C(6)—N(4)—Cu	115.3(2)
C(2)—N(2)—Cu	119.0(3)	C(4)—N(3)—Cu	115.3(2)	Cu—N(4)—C(7)	127.1(2)
Cu—N(2)—C(3)	115.5(3)	Cu—N(3)—C(5)	82.8(2)	N(3)—Cu—N(1)	84.0(2)
N(1)—Cu—N(2)	83.5(2)				

Table 3 (b). Intervector angles for the hydrogen bonded contacts of the glycylglycylglycylglycino cuprate(II) ion

Atoms	Angle*
Cu — N(1)—H · · · O(15 ^j)	111.5°
Cu — N(1)—H · · · O(15 ^{viii})	133.6
C(1) — N(1)—H · · · O(15 ^j)	104.5
C(1) — N(1)—H · · · O(15 ^{viii})	103.7
O(15 ^j) · H—N(1)—H · · · O(15 ^{viii})	90.7
C(1) — N(1) — Cu	108.8
C(2) — O(1) · · · H—O(6 ^v)	111.9
C(2) — O(1) · · · H—O(10 ⁱ)	96.8
C(2) — O(1) · · · H—O(12 ^v)	133.9
O(6 ^v)—H · · · O(1) · · · H—O(10 ⁱ)	113.0
O(6 ^v)—H · · · O(1) · · · H—O(12 ^v)	107.0
O(10 ⁱ)—H · · · O(1) · · · H—O(12 ^v)	89.8
C(4) — O(2) · · · H—O(13 ^v)	120.5
C(4) — O(2) · · · H—O(15)	128.0
O(13 ^v)—H · · · O(2) · · · H—O(15)	109.4
C(6) — O(3) · · · H—O(10)	132.5
C(6) — O(3) · · · H—O(11)	151.5
O(10)—H · · · O(3) · · · H—O(11)	75.9
C(8) — O(4) · · · H—O(8)	125.6
C(8) — O(4) · · · H—O(12)	143.0
C(8) — O(4) · · · H—O(13)	111.8
O(8)—H · · · O(4) · · · H—O(12)	73.0
O(8)—H · · · O(4) · · · H—O(13)	86.4
O(12)—H · · · O(4) · · · H—O(13)	100.1
C(8) — O(5) · · · H—O(9 ^{ix})	102.4
C(8) — O(5) · · · H—O(14)	120.1
C(8) — O(5) xxxxxxx Na(1 ^{viii})	131.9
O(9 ^{ix})—H · · · O(5) · · · H—O(14)	89.6
O(9 ^{ix})—H · · · O(5) xxxxxxx Na(1 ^{viii})	103.2
O(14)—H · · · O(5) xxxxxxx Na(1 ^{viii})	100.0

xxxx is not a hydrogen bond.

* Subtended by atoms other than hydrogen.

carboxyl group C(8), O(4) and O(5) excepted] is close to planar. There are several significant deviations from the least-squares plane of these atoms, but the most remarkable one is that of N(1) which is nearly 0.25 Å away (plane 1, Table 4). The copper atom exhibits fourfold, approximately square-planar, coordination. The fifth and sixth 'octahedral' positions are vacant, the atoms nearest to these positions all being further than 3.65 Å from the copper atom. The four copper atom–nitrogen atom bonds are not coplanar but are

Table 4(a). Coefficients for best (least-squares) planes
Each plane is represented by $lX + mY + nZ + p = 0$ where X , Y and Z are coordinates in Å, referred to orthogonal axes*

Plane	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>
1	0.917930	-0.050559	-0.393508	3.67810 Å
2	0.901160	-0.082735	-0.425518	4.01351
3	0.924557	-0.068801	-0.374781	3.61062
4	0.927410	-0.066111	-0.368156	3.55018
5	0.925832	-0.106302	-0.362678	3.71053
6	0.903541	-0.024073	-0.427825	3.66153
7	0.926578	-0.070519	-0.369433	3.58339
8	0.904818	-0.060396	-0.421493	4.02246
9	-0.427456	0.654180	-0.623963	2.10007

* The coordinates X , Y , Z are obtained from the fractional non-orthogonal coordinates x , y , z by the transformation:

$$\begin{aligned} X &= 7.6650x - 0.7623y - 4.0598z \\ Y &= 10.1755y - 1.3286z \\ Z &= 14.1093z \end{aligned}$$

Table 4(b). Distances (\AA) from the planes listed in Table 4(a)

Atom	1	2	3	4	5	6	7	8	9
Cu	0.041	-0.046	0.003	0.007	(-0.029) [†]	(-0.069)	(0.004)	(0.124)	
N(1)	(0.243)	0.114			0.046				
N(2)	0.064	0.056	-0.006		-0.048	0.015			
N(3)	0.000		-0.001	-0.002	0.040		0.004		
N(4)	-0.035			-0.016	-0.039			-0.012	(-0.004)
C(1)	-0.034	-0.113				-0.015			
C(2)	0.001	-0.010				0.009			
C(3)	0.060		0.008			-0.012	0.000		
C(4)	0.008		-0.003				-0.003		
C(5)	-0.052			-0.009			-0.002	0.011	
C(6)	-0.032			0.020				-0.011	
C(7)	0.030							0.013	
C(8)									-0.001
O(1)	-0.053					0.002			0.004
O(2)	-0.010						0.002		
O(3)	0.013							-0.001	
O(4)									-0.001
O(5)									-0.001

[†] A distance in parentheses indicates that the atom was not included in the least-squares computation.

arranged so that the copper atom is near the centre of an extremely flattened tetrahedron (plane 5, Table 4). The chelate ring Cu,N(1),C(1),C(2),N(2) is not planar but the other two are planar within the limits of experimental error (planes 2, 3 and 4, Table 4).

The three peptide groups $\text{C}\alpha\text{--CO--N--C}'\alpha$ and the carboxyl group are each planar (planes 6, 7, 8 and 9, Table 4). Despite the coplanarity of the atoms of the chelate rings, the copper atom is significantly out of the planes of the peptide groups containing N(2) and N(4).

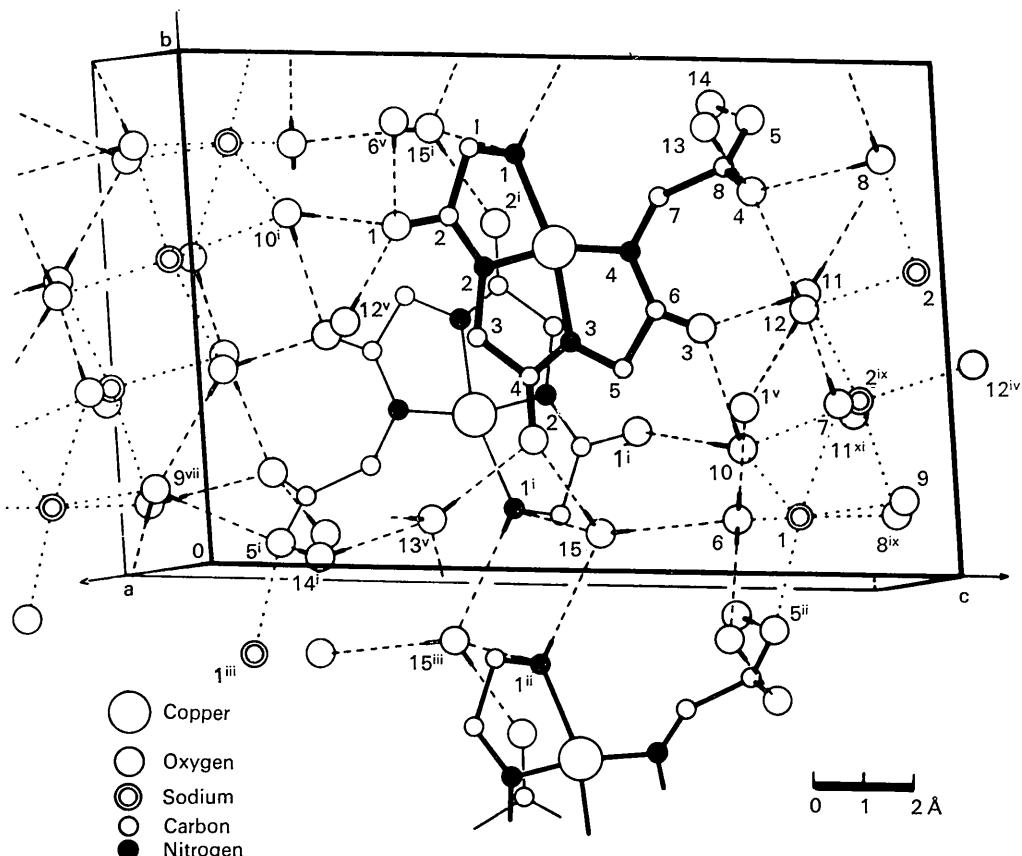


Fig. 1. The structure of disodium glycylglycylglycylglycino cuprate(II) decahydrate viewed along the normal to the (100) plane. Hydrogen bonds are dashed and sodium ion–water molecule contacts dotted. Proton donation in a hydrogen bond is represented by a short full line at the appropriate end of the bond.

The carboxyl group is twisted so that it makes an angle of 79·6° with the mean plane (plane 1, Table 4) of the remaining atoms of the CuGGGG²⁻ ion.

The bond lengths and angles in the ligand are listed in Table 3(a) and illustrated in Fig. 4.

Na(1) is surrounded by a distorted octahedron of five water molecules and the carboxyl oxygen atom O(5), while Na(2) is surrounded by a more regular octahedron of six water molecules (Figs. 2 and 3). The relevant interatomic distances and angles are listed in

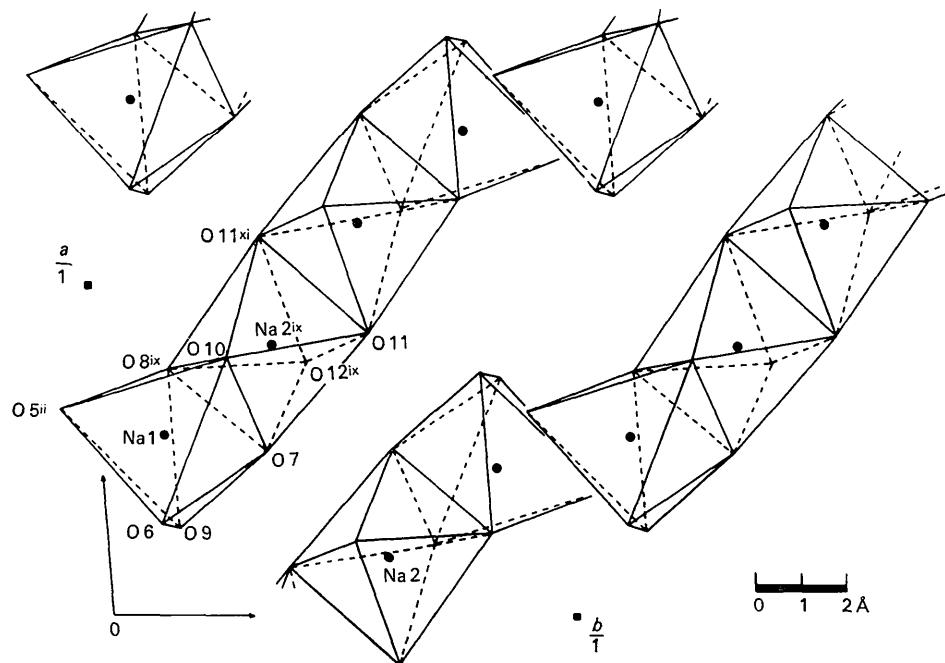


Fig. 2. The sodium ion–water molecule polyhedra viewed along the normal to the (001) plane. Both full and broken lines represent polyhedron edges.

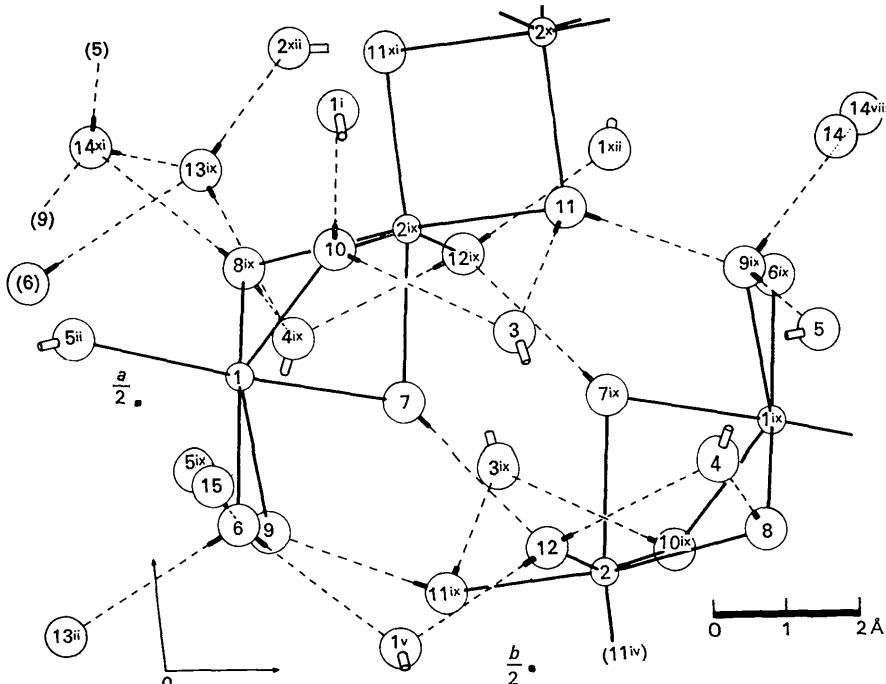


Fig. 3. Bonding associated with the sodium ion–water molecule polyhedra. The region near the origin in Fig. 2 is shown in more detail. Full lines represent electrostatic interactions and broken lines hydrogen bonds. Proton donation in a hydrogen bond is represented by a short full line at the appropriate end of the bond. Small circles represent sodium ions and large circles oxygen atoms.

Table 5. Environment of water molecules

— H indicates proton donation to the hydrogen bond from the water molecule and H— donation from the neighbour atom.

Water molecule	Proton assignment	Neighbour atom	Distance (σ)	Angle neighbour-water-neighbour	
O(6)	H—	O(15)	2.809(6) Å	O(15), Na(1)	111.2°
		Na(1)	2.339(5)	O(15), O(1 ^v)	103.8
	— H	O(1 ^v)	2.779(6)	O(15), O(13 ⁱⁱ)	87.8
	— H	O(13 ⁱⁱ)	2.829(6)	Na(1), O(1 ^v)	119.6
O(7)				Na(1), O(13 ⁱⁱ)	119.4
		Na(1)	2.395(6)	O(1 ^v), O(13 ⁱⁱ)	109.4
	*	Na(2 ^{ix})	2.397(6)	Na(1), Na(2 ^{ix})	85.8
	— H	O(9)	2.883(7)	Na(1), O(9)	67.2
O(8)				Na(1), O(12)	133.3
		O(12)	2.822(6)	Na(2 ^{ix}), O(9)	120.7
				Na(2 ^{ix}), O(12)	134.7
				O(9), O(12)	98.6
O(9)		Na(1 ^{ix})	2.381(4)	Na(1 ^{ix}), Na(2)	85.3
		Na(2)	2.433(5)	Na(1 ^{ix}), O(4)	122.9
	— H	O(4)	2.794(6)	Na(1 ^{ix}), O(14 ^{iv})	134.3
	— H	O(14 ^{iv})	2.868(6)	Na(2), O(4)	98.1
O(10)		Na(1)	2.950(6)	Na(2), O(14 ^{iv})	121.2
	H—	O(11 ^{ix})	2.857(7)	O(4), O(14 ^{iv})	92.0
	— H	O(5 ^{ix})	2.825(6)	Na(1), O(11 ^{ix})	128.9
	— H	O(14 ^{vi})	2.780(7)	Na(1), O(5 ^{ix})	110.5
O(11)		Na(1)	2.471(6)	Na(1), O(14 ^{vi})	101.2
		Na(2 ^{ix})	2.550(5)	O(11 ^{ix}), O(5 ^{ix})	90.1
	— H	O(1 ⁱ)	2.984(7)	O(11 ^{ix}), O(14 ^{vi})	116.0
	— H	O(3)	2.807(6)	O(5 ^{ix}), O(14 ^{vi})	108.9
O(12)		Na(2 ^{ix})	2.434(5)	Na(1), Na(2 ^{ix})	81.0
		Na(2 ^x)	2.385(5)	Na(1), O(1 ⁱ)	145.3
	— H	O(3)	2.743(6)	Na(1), O(3)	109.7
	— H	O(9 ^{ix})	2.857(7)	Na(2 ^{ix}), O(1 ⁱ)	128.9
O(13)		Na(2)	2.360(5)	Na(2 ^{ix}), O(3)	88.9
	H—	O(7)	2.822(6)	O(1 ⁱ), O(3)	90.3
	— H	O(1 ^v)	2.732(6)	Na(2 ^{ix}), Na(2 ^x)	91.9
	— H	O(4)	2.814(6)	Na(2 ^{ix}), O(3)	122.3
O(14 ^{iv})	H—	O(6 ^{viii})	2.829(6)	Na(2 ^{ix}), O(9 ^{ix})	114.1
	H—	O(14 ^{iv})	2.780(6)	Na(2 ^{ix}), O(2 ^v)	92.8
	— H	O(2 ^v)	2.702(6)	Na(2 ^{ix}), O(9 ^{ix})	120.9
	— H	O(4)	2.785(6)	O(3), O(9 ^{ix})	111.9
O(15)	H—	O(8)	2.868(6)	Na(2), O(7)	95.6
	H—	O(9 ^{viii})	2.797(7)	Na(2), O(1 ^v)	125.3
	— H	O(5 ^{iv})	2.734(6)	Na(2), O(4)	99.3
	— H	O(13)	2.780(6)	O(7), O(1 ^v)	86.4
				O(7), O(4)	112.6
				O(1 ^v), O(4)	130.2
				O(6 ^{viii}), O(14 ^{iv})	74.3
				O(6 ^{viii}), O(2 ^v)	137.3
				O(6 ^{viii}), O(4)	85.2
				O(14 ^{iv}), O(2 ^v)	129.6
				O(14 ^{iv}), O(4)	94.1
				O(2 ^v), O(4)	121.1
				O(8), O(9 ^{viii})	73.1
				O(8), O(5 ^{iv})	120.1
				O(8), O(13)	85.1
				O(9 ^{viii}), O(5 ^{iv})	131.2
				O(9 ^{viii}), O(13)	113.0
				O(5 ^{iv}), O(13)	114.8
				N(1 ⁱ), N(1 ⁱⁱ)	89.3
				N(1 ⁱ), O(2)	91.6
				N(1 ⁱ), O(6)	134.2
				N(1 ⁱⁱ), O(2)	113.0
				N(1 ⁱⁱ), O(6)	118.1
				O(2), O(6)	107.7

* Not a hydrogen-bond.

Tables 5 and 6. The octahedra surrounding Na(1) and Na(2^{ix}) have three water molecules in common [O(7), O(8^{ix}), and O(10)] and therefore may be said to share a face. This unit is related to another across a centre of symmetry, so that the octahedra surrounding adjacent atoms of type Na(2) share an edge of two water molecules [O(11) and O(11^{xii})]. These short chains of four octahedra extend obliquely across the sodium ion-water molecule layer, being linked at each side of the layer to a CuGGG²⁻ ion *via* its carboxyl oxygen atom O(5) (Fig. 2).

Table 6. *Interatomic distances and intervector angles of the sodium octahedra*

Distances from Na(1)			Distances from Na(2 ^{ix})		
Atom	D(Å)	σ (Å)	Atom	D(Å)	σ (Å)
O(5 ⁱⁱ)	2.376	0.004	O(11)	2.434	0.005
O(6)	2.339	0.005	O(11 ^{xii})	2.385	0.005
O(7)	2.395	0.006	O(7)	2.397	0.006
O(8 ^{ix})	2.381	0.004	O(8 ^{ix})	2.433	0.005
O(9)	2.950	0.006	O(12 ^{ix})	2.360	0.005
O(10)	2.471	0.006	O(10)	2.550	0.005

Other distances		
Atoms	D(Å)	σ (Å)
O(7)-O(8 ^{ix})	3.076	0.007
O(7)-O(10)	2.946	0.007
O(8 ^{ix})-O(10)	3.358	0.007

Angles subtended at Na(1) by		Angles subtended at Na(2 ^{ix}) by	
Atoms	Angle	Atoms	Angle
O(5 ⁱⁱ), O(6)	93.5°	O(11), O(11 ^{xii})	88.1°
O(5 ⁱⁱ), O(7)	174.1	O(11), O(7)	92.4
O(5 ⁱⁱ), O(8 ^{ix})	94.0	O(11), O(8 ^{ix})	169.2
O(5 ⁱⁱ), O(9)	115.4	O(11), O(12 ^{ix})	99.0
O(5 ⁱⁱ), O(10)	105.3	O(11), O(10)	86.4
O(6), O(7)	92.1	O(11 ^{xii}), O(7)	163.9
O(6), O(8 ^{ix})	159.3	O(11 ^{xii}), O(8 ^{ix})	98.2
O(6), O(9)	77.3	O(11 ^{xii}), O(12 ^{ix})	103.5
O(6), O(10)	109.1	O(11 ^{xii}), O(10)	91.0
O(7), O(8 ^{ix})	80.2	O(7), O(8 ^{ix})	79.1
O(7), O(9)	64.3	O(7), O(12 ^{ix})	92.4
O(7), O(10)	74.5	O(7), O(10)	73.0
O(8 ^{ix}), O(9)	82.1	O(8 ^{ix}), O(12 ^{ix})	88.2
O(8 ^{ix}), O(10)	87.4	O(8 ^{ix}), O(10)	84.7
O(9), O(10)	138.6	O(12 ^{ix}), O(10)	164.7

No attempt was made to find the positions of hydrogen atoms but their presence in hydrogen bonds has been inferred by considering interatomic distances and angles. Eight of the thirty hydrogen atoms present are bonded to carbon atoms and do not form hydrogen bonds. Nineteen hydrogen atoms of water molecules and two bonded to N(1) have been assigned to hydrogen bonds. One hydrogen atom of water molecule O(7) does not seem to be involved in a hydrogen bond. The

only two atoms apart from O(12) which could be hydrogen bonded to O(7) are O(9) (2.833 Å) and O(3) (3.242 Å). A hydrogen bond to O(9) would be directed along the O(7)-O(9) edge of the Na(1) coordination polyhedron and is therefore unlikely (Templeton, 1960). Such a bond would also disrupt the very reasonable tetrahedral environment proposed for O(9). A bond to O(3) would be too long and O(3) is not in a favourable orientation to the O(7)-O(12) vector.

The CuGGG²⁻ ion makes twelve acceptor and two donor hydrogen bonds with neighbouring water molecules, ranging from 2.695 Å to 2.997 Å in length (Table 5). O(1) and O(4) each make three hydrogen bonds and O(2), O(3) and O(5) each make two. The environments of O(1), O(4) and O(5) are approximately tetrahedral [O(5) has an interaction with Na(1) and those of O(2) and O(3) are approximately trigonal planar. N(1ⁱ) is hydrogen bonded to O(15) and O(15ⁱⁱⁱ). Intervector angles for these hydrogen bonds are listed in Table 3(b).

There are no direct links between neighbouring peptide chains but there are many links *via* one or two water molecules. Water molecule O(15) links three peptide chains. Every water molecule [except O(7)] is attached to atoms of the CuGGG²⁻ ion and is bound to four neighbouring atoms arranged at the corners of a more or less distorted tetrahedron.

Discussion

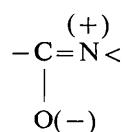
The copper atom–amide nitrogen atom bond lengths are similar to those found in other metal-peptide structures, but they are not equal. The difference between the lengths of Cu–N(3) and Cu–N(4) of 0.032 Å (s.d. 0.006 Å) is probably significant. It should be noted that the short Cu–N(3) bond is complemented by a C(4)–N(3) bond which is longer than the two other examples of this type of bond (Table 3).

The non-planarity of the four nitrogen ligand atoms is not caused by direct steric interference from other elements of the structure since all non-bonded contacts of these atoms are at normal van der Waals lengths or longer, and the environment of each atom is similar on both sides of the planar anion. The non-planarity is possibly caused by the strain which results from closing the five-membered chelate rings. The first ring [Cu, N(1), C(1), C(2), N(2)] has a tetrahedrally hybridized nitrogen atom in place of the trigonal one in the other two rings. The strain is therefore greatest in the first ring which is buckled so that N(1) is 0.24 Å from the plane of the other four atoms. In this connected system, this deviation causes N(1) to be out of the plane of N(2), N(3) and N(4).

Rings corresponding to the first ring of this compound also occur in glycylglycino copper(II) trihydrate (Strandberg, Lindqvist & Rosenstein, 1961) and sodium glycylglycylglycino cuprate(II) hydrate (Freeman, Schoone & Sime, 1965). In both these compounds this ring is non-planar. Calculations have shown that the tetrahedrally hybridized nitrogen atoms are 0.196 Å

and 0.206 Å out of the plane of the other four atoms of the rings in the two crystallographically distinct examples in the first compound, and 0.210 Å out of the plane in the second compound.

There are some indications of a correlation between the lengths of the peptide C—N and C=O bonds. The C—N bond-lengths (C(4)—N(3), 1.316 Å; C(6)—N(4), 1.301 Å; C(2)—N(2), 1.290 Å) run in the reverse order to the corresponding C=O bond-lengths (C(4)—O(2), 1.267 Å; C(6)—O(3), 1.272 Å; C(2)—O(1), 1.276 Å). While the difference between the two extreme C=O bond-lengths is only on the threshold of significance, the trend in these bonds parallels the number of hydrogen bonds (two, two, three) in which the carbonyl oxygens are acceptors. The hydrogen bonds possibly stabilize the contribution of



to the resonance hybrid and so contribute to the shortening of the C—N and the lengthening of the C=O bonds. A similar situation was found in cytosine monohydrate by Jeffrey & Kinoshita (1963).

The environment of the copper atom in this complex is similar to that of the copper in potassium bis-biureto cuprate(II) tetrahydrate (Freeman, Smith & Taylor, 1961). In both complexes the copper(II) atoms are square-planar coordinated by four nitrogen ligand atoms, of which three are deprotonated in the present complex, and four in the other. The similarity of the

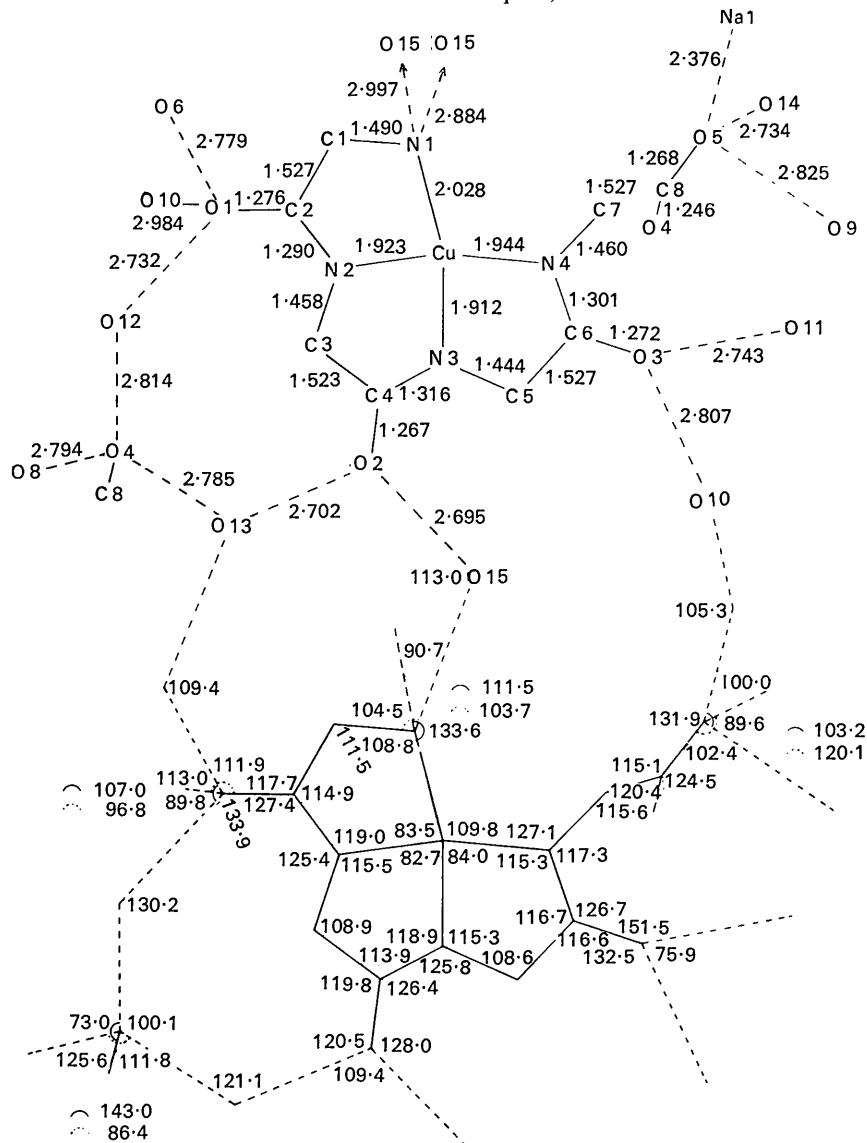


Fig. 4. Interatomic distances (above) and intervector angles (below) of the glycylglycylglycylglycino cuprate(II) anion and its contacts. This diagram is not to scale though the general relationship between atomic positions has been retained. Roman superscripts have been omitted.

ligand fields results in a similarity of the colours (pink) of the crystals. The structure of the complexes appears to persist in solution, for the solution spectra also resemble each other,

$\lambda_{\text{max}}(\text{CuGGGG}^{2-}) = 520 \text{ m}\mu$ (Koltun *et al.*, 1963);
 $\lambda_{\text{max}}(\text{Cu(biu)}_2^{2-}) = 505 \text{ m}\mu$ (Ferguson, private communication in Freeman, Smith & Taylor, 1961],

and the solution spectrum of Cu(biu)_2^{2-} is almost identical with the crystal spectrum (Ferguson, private communication).

In the solid state this structure, therefore, supports the deductions made by Koltun, Roth & Gurd (1963) from the results of pH titration and spectrophotometric studies, that the hydrogen atoms of the three peptide nitrogen atoms are ionized in alkaline solution. It also supports the structure proposed for the oxytocin complex of copper(II) by Breslow (1961), since her conclusions included a consideration of the similarity between the spectra of the copper-GGGG and the copper-oxytocin complexes.

In the crystalline metal-peptide complexes examined to this date, every terminal amino nitrogen atom is bonded to the copper(II) ion, indicating that this may be an essential requirement for chelation of a peptide chain to copper(II). This view is supported by Breslow's (1961) observation that complex formation with de-amino-oxytocin (in which the free amino group is substituted by hydrogen) occurs only at pH's higher than 12 and then only slightly.

The calculations for this analysis were made on the SILLIAC with programs devised by Dr F. M. Lovell, Dr J. G. Sime and M.R.T., and on the IBM 7090 computer at the Weapons Research Establishment, Salisbury, with programs ORXLS, ORXFE, and ORFLS (Busing & Levy, 1959a, b; Martin, Busing & Levy, 1962). The research was undertaken during the tenure of an Australian Institute of Nuclear Science and Engineering Post-Graduate Research Studentship by M.R.T., and was supported by Grant GM10867 from the Division of General Medical Sciences, U.S. Public Health Service.

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