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Crystallographic Studies of Metal–Peptide Complexes. II. Sodium Glycylglycylglycino Cuprate(II) Monohydrate

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The violet-pink complex sodium glycylglycylglycino cuprate (II) monohydrate is formed from glycylglycylglycine and cupric ions in aqueous alkaline solution. The crystals are monoclinic, space-group $I2/c$. There are eight formula units $C_6H_8N_3O_4CuNa.H_2O$ in a unit cell with dimensions

$$a=14{\cdot}328,\ b=10{\cdot}556,\ c=13{\cdot}175\ \text{Å},\ \beta=92°58'.$$

The structure has been determined and refined by three-dimensional X-ray Fourier and least-squares methods. It consists of dimers in which the copper atoms are 5-coordinated. Each of the two copper atoms in a dimer is bonded to the terminal amino nitrogen and the two peptide nitrogen atoms of one peptide, and to one of the carboxylic oxygen atoms of the other peptide molecule of the dimer. There is also a weaker bond between the copper atom and the third nitrogen atom of the second peptide molecule. Adjacent dimers are linked by hydrogen bonds into layers; adjacent layers are held mainly by electrostatic forces between sodium ions, water molecules and carboxyl oxygen atoms.

Introduction

The first paper of this series (Freeman, Robinson & Schoone, 1964) described the blue-green complex glycylglycylglycino copper(II) chloride 1·5-hydrate. This compound, to which we shall refer as CugggCl. $1\frac{1}{2}H_2O$, may be crystallized from an aqueous solution containing cupric chloride and the tripeptide. When such a solution is made alkaline, its colour changes to violet-pink. This colour change, the 'biuret reaction', is characteristic of polypeptides and proteins, and glycylglycylglycine is the shortest glycine-peptide to undergo it.

This structure has been determined as part of a systematic study of metal-peptide complexes. A preliminary account of it has been published (Cooper, Freeman, Robinson & Schoone, 1962).

Experimental

The crystals were grown by the method of Rising, Parker & Gaston (1934). Freshly precipitated cupric hydroxide was dissolved in a solution of glycylglycylglycine containing excess alkali. When the resultant violet solution was added to a large excess of a 2:1 alcohol–ether mixture and allowed to stand for some days, violet, flat six-sided prisms exhibiting the forms {100}, {001} and {011} were formed. Chemical analyses were inconclusive, probably because of decomposition of the substance before analysis.

$C_6H_8N_3O_4CuNa.H_2O$. F.W. 290·7.
Monoclinic:

$a=14{\cdot}328,\ b=10{\cdot}556,\ c=13{\cdot}175$ Å (all $\pm 0{\cdot}006$ Å).
$\beta=92°\ 58'\ (\pm 1')$, $U=1990$ Å^3, $Z=8$.
$D_m=1{\cdot}92$, $D_x=1{\cdot}94$, $\mu(\text{Cu } K\alpha)=39$ cm^{-1}.

Space group: $I2/c$ (C_{2h}^6) or Ic (C_s^4), from systematic absences. $I2/c$ confirmed by structure analysis.

The unit-cell dimensions were obtained from the quantities a^{*2}, b^{*2}, c^{*2} and $2\cos\beta^*a^*c^*$, which were fitted by least squares to the spacings of 9 $0kl$ and 9 $h0l$ reflexions. The spacings were measured on rotation photographs taken in a Straumanis-type camera with a radius of 5 cm.

The complete three-dimensional data were recorded with Cu $K\alpha$ radiation on Weissenberg multiple-film photographs about both the a and b axes. The crystals used had cross-sections $0{\cdot}165\times0{\cdot}066$ mm^2 (a-axis data) and $0{\cdot}08\times0{\cdot}05$ mm^2 (b-axis data) respectively. Intensities were estimated visually. Absorption corrections were applied to 30 intensities from the a-axis data, the only cases where the relative corrections differed from the mean for the layer by more than 5%. Of 2290 possible reflexions, 2100 were within the $\sin\theta$-range of the observations; 598 of these were unobservably weak and intensities were measured for 1502. The usual Lorentz and polarization factors were applied and the intensities were placed upon a common scale by correlations among the reflexions recorded more than once.

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Table 1. *Summary of refinement*

No. of cycles	Approximation	Temperature factors	Weights	F_{unobs}	Final R (%)	Computer	Program References
5	Diagonal	Single isotropic	189 inner F's only: $w=1$	$w=0$	17·1 (189F's)	ZEBRA	Schoone (1961)
6			418 inner F's only: $w=1$	$w=0$	13·0 (418F's)	ZEBRA	Schoone (1961)
3			1502 F_{obs}: $w=1$	598 F_{unobs}: $w=0$	15·4 (all F's)	ZEBRA	Schoone (1961)
3	Full matrix	Individual anisotropic	For $\|F\| \geq 20$, $\gamma/w=100/\|F\|$; for $\|F\|<20$, $\gamma/w=5$	F_{unobs} $=\frac{1}{2}F_{min}$: $w=1$	13·2 (all F's)	7090	Busing & Levy (1961)

Table 2. *Atomic coordinates in* $NaCuggg.H_2O$ *and their standard deviations (fractional standard deviations in parentheses)*

Atom	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Cu	0·55799(10)	0·56687(12)	0·65496(10)	0·0014 Å	0·0012 Å	0·0013 Å
Na	0·62645(29)	−0·01055(34)	0·59436(27)	0·0041	0·0036	0·0035
O(1)	0·57219(51)	0·19439(60)	0·60997(66)	0·0073	0·0064	0·0085
O(2)	0·28519(48)	0·49369(66)	0·59384(56)	0·0068	0·0070	0·0073
O(3)	0·36608(48)	0·90904(56)	0·73979(47)	0·0069	0·0059	0·0061
O(4)	0·40780(56)	0·74323(61)	0·82916(49)	0·0080	0·0064	0·0064
$O(5_w)$	0·58434(67)	−0·05196(73)	0·42786(55)	0·0095	0·0077	0·0071
N(1)	0·68921(53)	0·49954(73)	0·63523(63)	0·0077	0·0077	0·0081
N(2)	0·52335(60)	0·39825(71)	0·62271(61)	0·0087	0·0075	0·0078
N(3)	0·42031(62)	0·59701(70)	0·65182(61)	0·0089	0·0074	0·0079
C(1)	0·68815(65)	0·35857(84)	0·63563(80)	0·0093	0·0090	0·0103
C(2)	0·58489(81)	0·30908(84)	0·62172(70)	0·0109	0·0089	0·0090
C(3)	0·42480(67)	0·37098(79)	0·61147(73)	0·0095	0·0084	0·0093
C(4)	0·36989(68)	0·49457(83)	0·61790(67)	0·0100	0·0088	0·0086
C(5)	0·37360(75)	0·71624(87)	0·64768(67)	0·0106	0·0092	0·0087
C(6)	0·38205(65)	0·79511(82)	0·74491(69)	0·0092	0·0086	0·0089

Table 3. *Anisotropic thermal parameters and their standard deviations (in parentheses), all* $\times 10^5$

The temperature factor is $\exp -[B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	427(8)	482(12)	453(9)	−14(8)	26(6)	−53(7)
Na	530(23)	566(32)	472(22)	35(22)	31(17)	16(21)
O(1)	418(40)	437(55)	1058(64)	−28(38)	36(40)	−37(48)
O(2)	374(37)	713(66)	670(48)	14(42)	41(33)	−119(45)
O(3)	520(39)	492(53)	424(36)	98(37)	−39(30)	25(34)
O(4)	718(49)	568(57)	378(36)	108(42)	7(33)	−20(36)
$O(5_w)$	880(61)	947(79)	460(42)	−380(57)	−9(40)	41(46)
N(1)	297(38)	635(72)	620(52)	−62(44)	14(35)	−212(49)
N(2)	443(45)	512(62)	527(47)	27(47)	122(37)	−74(44)
N(3)	517(49)	493(63)	518(47)	−17(47)	126(38)	−81(42)
C(1)	297(44)	540(74)	699(66)	9(50)	16(43)	22(57)
C(2)	564(68)	530(75)	433(49)	139(59)	−29(45)	−41(49)
C(3)	327(44)	527(73)	555(55)	6(49)	1(38)	−115(50)
C(4)	400(51)	588(77)	444(50)	28(53)	74(39)	−76(50)
C(5)	584(59)	593(78)	390(49)	136(59)	25(44)	27(49)
C(6)	357(46)	566(75)	474(51)	69(51)	47(39)	−38(50)

Structure solution

After unsuccessful attempts to interpret Patterson projections and two-dimensional Fourier syntheses, the structure was solved in three dimensions *via* the Patterson function followed by a Fourier synthesis based upon the copper positions. The first cycle of least-squares refinement was carried out with only the 189 reflexions of lowest $\sin\theta$, the second cycle with 418 reflexions and subsequent cycles with the 1502 independent observed data. During this preliminary refinement (carried out on a ZEBRA computer with the diagonal matrix approximation (Schoone, 1961)), the structure remained essentially unaltered except for one atom which had been misplaced by 1·05 Å in the x direction. The single isotropic temperature parameter changed from $B=2$ to 3·03 Å^{-2}.

The correction of an atomic coordinate by 1·05 Å exceeds the largest change (0·6 Å) recorded by Cruickshank (1961) from his experience with the least-

Table 4. *Interatomic distances and inter-vector angles in* NaCuggg.H_2O, *and their standard deviations*

Code for superscripts

′ = atom at	$1-x$	y	$1\frac{1}{2}-z$	vi = atom at	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	z
″ = atom at	$1-x$	$1+y$	$1\frac{1}{2}-z$	vii = atom at	$\frac{1}{2}+x$	$\frac{1}{2}-y$	z
‴ = atom at	$1-x$	$-1+y$	$1\frac{1}{2}-z$	viii = atom at	$\frac{1}{2}+x$	$1\frac{1}{2}-y$	z
iv = atom at	$1-x$	$1-y$	$1-z$	ix = atom at	$-\frac{1}{2}+x$	$1\frac{1}{2}-y$	z
v = atom at	$1-x$	$-y$	$1-z$	x = atom at	$\frac{1}{2}-x$	$1\frac{1}{2}-y$	$1\frac{1}{2}-z$

Bond-angle standard deviations

Light atom–light atom–light atom	1·5°
Copper–light atom–light atom	1·2
Light atom–copper–light atom	0·7
Copper–light atom–copper	0·2

(*a*) Dimensions of peptide molecule

Present work						Pauling & Corey, 1953	
Bond	Length	$\sigma(l)$	Bond	Length	$\sigma(l)$	Bond	Length
N(1)–C(1)	1·49 Å	0·012 Å					
C(1)–C(2)	1·57	0·014	C(3)–C(4)	1·53 Å	0·013 Å	C(α)–C	1·53 Å
C(2)–O(1)	1·23	0·012	C(4)–O(2)	1·24	0·011	C=O	1·24
C(2)–N(2)	1·29	0·013	C(4)–N(3)	1·36	0·012	C–N	1·32
N(2)–C(3)	1·44	0·012	N(3)–C(5)	1·43	0·012	N–C(α)	1·47
			C(5)–C(6)	1·53	0·013		
			C(6)–O(3)	1·23	0·011		
			C(6)–O(4)	1·28	0·012		

Present work				Pauling & Corey, 1953	
Angle		Angle		Angle	
N(1)–C(1)–C(2)	110·0°				
C(1)–C(2)–O(1)	118·2	C(3)–C(4)–O(2)	118·7°	C(α)–C=O	121°
C(1)–C(2)–N(2)	113·4	C(3)–C(4)–N(3)	115·5	C(α)–C–N	114
O(1)–C(2)–N(2)	128·4	O(2)–C(4)–N(3)	125·9	O=C–N	125
C(2)–N(2)–C(3)	121·4	C(4)–N(3)–C(5)	116·6	C–N–C(α)	123
N(2)–C(3)–C(4)	109·2	N(3)–C(5)–C(6)	115·7	N–C(α)–C	110
		C(5)–C(6)–O(3)	118·9		
		C(5)–C(6)–O(4)	120·2		
		O(3)–C(6)–O(4)	120·9		

(*b*) Bonds involving the copper atom

Bond	Length	$\sigma(l)$	Angle		Angle	
Cu–N(1)	2·039 Å	0·008 Å	N(1)–Cu–N(2)	82·8°	Cu–N(1)–C(1)	109·8°
Cu–N(2)	1·891	0·008	N(2)–Cu–N(3)	84·1	Cu–N(2)–C(2)	121·2
Cu–N(3)	1·997	0·008	N(3)–Cu–O(4′)	95·4	Cu–N(2)–C(3)	117·0
Cu–O(4′)	1·933	0·007	O(4′)–Cu–N(1)	96·9	Cu–N(3)–C(4)	112·8
Cu–N(3′)	2·568	0·008	N(1)–Cu–N(3)	165·7	Cu–N(3)–C(5)	127·1
Cu · · · Cu′	3·077	0·002	N(2)–Cu–O(4′)	173·2	Cu–N(3)–Cu′	83·7
			N(1)–Cu–N(3′)	96·0	Cu′–N(3)–C(4)	105·2
			N(2)–Cu–N(3′)	110·9	Cu′–N(3)–C(5)	100·3
			N(3)–Cu–N(3′)	94·0	Cu–O(4′)–C(6′)	124·6
			O(4′)–Cu–N(3′)	76·0		

Table 4 (*cont.*)

(*c*) Hydrogen bonds

Bond	Equivalent bond	Length	$\sigma(l)$
N(1)–H · · · O(2^{iv})	O(2) · · · H–N(1^{iv})	3·06 Å	0·011 Å
N(1)–H · · · O(3^{viii})	O(3) · · · H–N(1^{ix})	2·99	0·010
H–O(5)–H · · · O(1^{v})	O(1) · · · H–O(5^{v})–H	2·72	0·012
H–O(5)–H · · · O(3^{iv})	O(3) · · · H–O(5^{iv})–H	2·80	0·010

Angle		Angle	
Cu—N(1)——C(1)	109·8°	C(2)–O(1) · · · · O(5^{v})	132·8°
Cu—N(1) · · · O(2^{iv})	106·1	C(4)–O(2) · · · N(1^{iv})	95·0
Cu—N(1) · · · O(3^{viii})	126·5	C(6)–O(3) · · · N(1^{ix})	119·7
C(1)–N(1) · · · O(2^{iv})	91·6	C(6)–O(3) · · · O(5^{iv})	121·2
C(1)–N(1) · · · O(3^{viii})	109·3	N(1^{ix}) · · · O(3) · · · O(5^{iv})	72·8
O(2^{iv}) · N(1) · · · O(3^{viii})	107·8	O(1^{v}) · · · O(5) · · · O(3^{iv})	113·2

(*d*) Contacts involving the sodium ion

Vector	Equivalent vector	Length	$\sigma(l)$
Na · · · O(1)	O(1) · · · Na	2·311 Å	0·008 Å
Na · · · O(2^{vii})	O(2) · · · Na^{vi}	2·281	0·008
Na · · · O(3‴)	O(3) · · · Na″	2·341	0·008
Na · · · O(5_w)	O(5_w) · · Na	2·287	0·008

Angle		Angle	
O(1) · · · Na · · · O(2^{vii})	105·5°	Na · · · O(1)——C(2)	151·9°
O(1) · · · Na · · · O(3‴)	104·8	Na · · · O(1) · · · O(5_w)	75·2
O(1) · · · Na · · · O(5_w)	101·1	Na^{vi} · · O(2)——C(4)	162·2
O(2^{vii}) · Na · · · O(3‴)	92·0	Na^{vi} · · O(2) · · · N(1^{iv})	99·9
O(2^{vii}) · Na · · · O(5_w)	103·0	Na″ · · O(3)——C(6)	107·8
O(3‴) · Na · · · O(5_w)	145·3	Na″ · · O(3) · · · O(5^{iv})	122·7
		Na″ · · O(3) · · · N(1^{ix})	108·1
		Na · · · O(5_w) · · O(1^{v})	117·1
		Na · · · O(5_w) · · O(3^{iv})	126·1

squares program on 'Pegasus' using a block-diagonal matrix approximation. It demonstrates the increase of the radius of convergence which is achieved by decreasing the resolution of least-squares data (see, *e.g.* Vand & Niggli, 1961). In this case, the data were simply cut off without applying even an artificial weighting or temperature parameter.

The refinement was completed on an IBM 7090 computer with the full-matrix program of Busing & Levy (1961). Anisotropic thermal parameters were computed and unobserved reflexions were included as $F_{\text{unobs}}=\frac{1}{2}F_{\text{min}}$. Details of the refinement, including the weighting functions applied to the observed and unobserved data, are shown in Table 1. The weights corresponded to

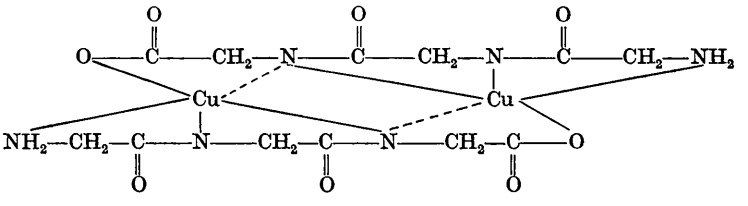
$$\begin{aligned} 10w^{-\frac{1}{2}} &= \sigma(F) = 0{\cdot}1|F| \quad \text{for } |F| \geq 20\,, \\ 10w^{-\frac{1}{2}} &= \sigma(F) = 2{\cdot}0 \quad \text{for } |F| < 20\,, \\ 10w^{-\frac{1}{2}} &= 5\sigma(F) = 10{\cdot}0 \quad \text{for } F_{\text{unobs}}\,, \end{aligned}$$

so that the relative weights of the unobserved F's were reduced. The final value of $[(\Sigma w_{hkl}\Delta^2_{hkl})/(m-n)]^{\frac{1}{2}}$ was 3·18, and the final reliability factor for *all* reflexions was $R=0{\cdot}132$.

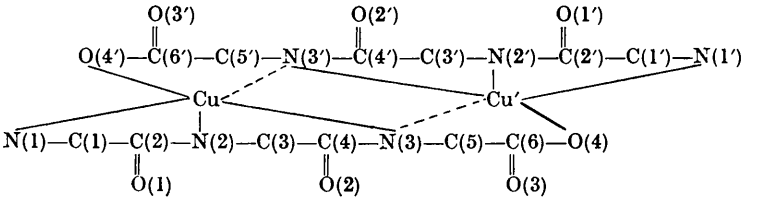
The atomic coordinates and their standard deviations are listed in Table 2, the thermal parameters in Table 3, the bond-lengths, interatomic contacts and inter-vector angles in Table 4, and the final calculated and observed structure-factors in Table 5. Part of the unit-cell contents is shown in Fig. 1.

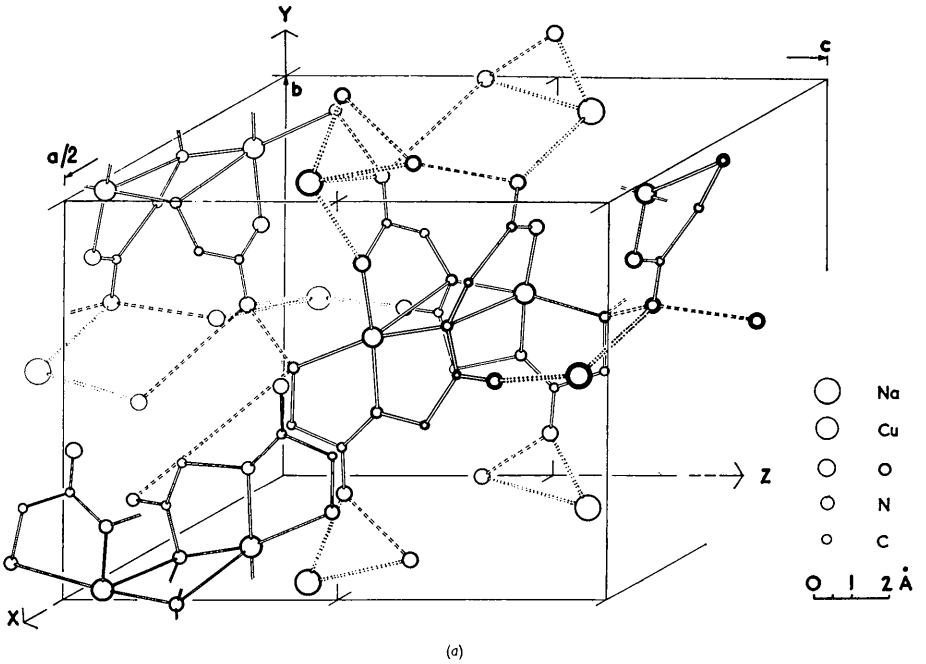
Description of structure

The complex is a dimer consisting of two copper atoms and two tripeptide molecules. The two halves of the dimer are related by a crystallographic twofold axis. Each peptide molecule binds one copper atom at its three nitrogen atoms, and the second copper of the dimer at one of its carboxyl oxygen atoms.

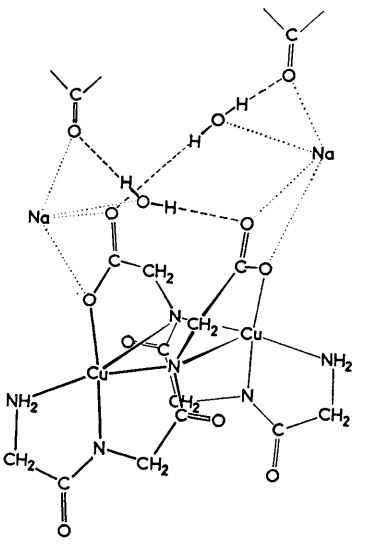


The labelling of the atoms in the complex follows the following scheme:





(a)



(b)

Fig. 1. (*a*) Part of unit-cell of sodium glycylglycylglycino cuprate(II) monohydrate. Dashed lines show hydrogen bonds, dotted lines represent electrostatic interactions with sodium ions. Origin in left bottom corner distant from observer. (*b*) One dimeric complex and its environment from (*a*).

Table 5. *Observed and calculated structure factors for sodium glycylglycylglycino cuprate*(II) *monohydrate*

Reflexions marked ● were unobservably weak; F_{obs} in these cases represents $\frac{1}{2}F_{min}$

Table 5 (*cont.*)

L (H K)	F_{calc}		F_{obs}
-9	26.13		28.62
-11	-20.77		27.82
-13	-6.32		7.81
-15	11.79		14.21
# 2	4		
0	-39.40		43.43
2	-35.29		37.83
4	36.45		45.23
6	5.61	●	2.40
8	-2.59	●	2.40
10	5.02		5.21
12	-3.60	●	2.40
14	-8.73		8.21
16	5.25	●	2.40
-2	20.40		20.61
-4	30.21		35.02
-6	6.36		8.01
-8	-24.43		25.82
-10	-10.54		10.41
-12	10.34		11.41
-14	7.24		7.81
-16	-2.86	●	2.40
# 3	4		
1	-36.24		28.42
3	50.27		55.24
5	-4.38		4.00
7	-55.14		57.64
9	11.60		12.41
11	27.64		29.22
13	-14.41		13.61
15	-3.02		4.20
-1	29.97		41.83
-3	50.85		45.43
-5	-50.46		52.84
-7	-32.09		33.02
-9	31.73		30.62
-11	-3.18	●	2.40
-13	-9.54		9.61
-15	11.82		12.81
# 4	4		
0	-40.59		49.43
2	-28.19		28.62
4	35.28		44.43
6	4.59		5.00
8	.72	●	2.60
10	-2.02	●	2.60
12	-8.30		8.61
14	.36	●	2.60
-2	17.42		19.21
-4	33.21		40.63
-6	-5.25		5.20
-8	-7.33		9.81
-10	-11.74		12.81
-12	5.97		6.40
-14	5.90		6.00
-16	-2.75	●	2.60
# 5	4		
1	1.89		4.60
3	48.99		55.64
5	-19.90		23.42
7	-25.36		27.22
9	28.21		31.02
11	-5.72		7.21
13	-13.13		12.81
15	5.53		6.00
-1	-34.57		35.22
-3	32.36		27.82
-5	-6.42		5.60
-7	-33.98		33.42
-9	18.57		15.61
-11	9.61		5.61
-13	-11.61		11.41
-15	5.12		4.00
# 6	4		
0	-6.39		9.41
2	31.01		33.82
4	7.30		8.61
6	.86	●	1.40
8	-8.57		7.41
10	-6.76		8.01
12	-.95	●	1.40
14	9.14		6.80
-2	-22.54		21.62
-4	-24.00		21.82
-6	4.34		3.00
-8	23.19		22.22
-10	6.98		6.80
-12	-7.41		8.01
-14	-4.52		5.50
# 7	4		
1	31.44		34.82
3	35.79		37.63
5	-36.61		41.23
7	1.85	●	2.40
9	31.62		31.42
11	-19.05		18.41
13	-10.60	●	12.01
-1	-71.67		74.05
-3	9.78		9.41
-5	34.31		33.22
-7	-23.42		24.02
-9	-3.62	●	2.40
-11	20.50		20.61
-13	-9.20		9.41
-15	-5.08		4.40
# 8	4		
0	24.52		27.42
2	17.25		19.01
4	-35.63		37.23
6	-9.80		9.21
8	15.19		16.81
10	5.39	●	2.60
12	1.77	●	2.60
14	-2.85	●	2.60
-2	-9.39		12.01
-4	-8.53		10.21
-6	6.38		7.21
-8	-5.32		5.80
-10	1.17	●	2.60
-12	2.61	●	2.60
-14	1.12	●	2.60
# 9	4		
1	30.33		29.42
3	9.63		10.41
5	-37.80		39.23
7	21.19		19.01
9	14.40		12.61
11	-13.47		9.61
13	-3.92	●	2.60
-1	-36.31		35.02
-3	-14.21		14.81
-5	37.71		36.63
-7	-11.68		12.01
-9	-8.72		9.41
-11	15.31		15.01
-13	-4.73	●	2.60
# 10	4		
0	11.92		18.01
2	10.15		10.01
4	-7.19		7.41
6	-10.25		5.00
8	5.22	●	2.80
10	2.27	●	2.80
12	4.33		5.00
-2	-23.12		21.62
-4	5.77	●	2.80
-6	15.73		14.41
-8	-6.60	●	2.80
-10	-10.09		9.81
-12	3.78	●	2.80
# 11	4		
1	12.01		13.61
3	-19.54		20.81
5	-8.81		7.21
7	22.73		20.81
9	-5.24	●	2.80
11	-7.69		4.40
-1	4.38	●	2.80
-3	-15.19		15.61
-5	19.67		19.81
-7	-.12	●	2.80
-9	-11.80		8.01
-11	4.04	●	2.80
-13	3.73	●	2.80
# 12	4		
0	-17.49		17.81
2	-6.43		4.00
4	14.96		14.01
6	7.24	●	2.80
8	-7.98		8.01
10	-1.91	●	2.80
-2	-5.53	●	2.80
-4	14.05		14.81
-6	12.04		13.81
-8	-3.30	●	2.80
-10	-10.14		8.41
-12	-1.55	●	2.80
# 13	4		
1	12.50		8.21
3	-23.91		26.82
5	8.01		7.41
7	8.55		6.00
9	-8.91		8.61
-1	12.88		14.41
-3	-17.31		16.61
-5	-.46	●	2.80
-7	17.90		16.41
-9	-11.73		12.01
-11	-5.19	●	2.80
# 14	4		
0	.61	●	2.80
2	3.39	●	2.80
4	3.19	●	2.80
6	-1.42	●	2.80
8	-7.89		5.60
-2	6.32		6.80
-4	-10.51		10.41
-6	-4.38	●	2.80
-8	5.65		16.41
-10	3.74	●	2.80
# 15	4		
1	3.96	●	2.80
3	-12.21		12.81
5	9.21		6.60
7	1.26	●	2.80
-1	13.18		13.81
-3	-11.59		12.81
-5	-9.71		8.01
-7	16.12		17.61
-9	-3.10	●	2.80
# 16	4		
0	2.83	●	2.80
2	-1.65	●	2.80
4	-.81	●	2.80
6	-.49	●	2.80
-2	3.19	●	2.80
-4	-4.87	●	2.80
-6	-2.83	●	2.80
# 17	4		
1	-6.34		5.00
3	.53	●	2.80
-1	10.98		11.21
-3	-2.32	●	2.80
-5	-8.61	●	2.80
# 0	5		
1	-89.62		94.97
3	-13.65		16.21
5	74.47		74.85
7	-15.48		15.61
9	-26.90		25.42
11	19.27		18.21
13	-7.59		6.60
15	-6.10		5.20
# 1	5		
0	-61.96		59.24
2	40.62		37.23
4	61.48		68.05
6	-18.85		19.61
8	-20.76		24.42
10	1.65	●	1.60
12	-6.54		9.61
14	6.01		8.21
-2	-40.44		35.23
-4	27.96		31.02
-6	1.47	●	1.60
-8	10.96		8.01
-10	8.66		9.41
-12	-11.57		11.61
-14	-9.29		9.21
# 2	5		
1	-90.92		89.66
3	40.72		39.23
5	46.64		44.23
7	-30.61		30.82
9	7.99		9.81
11	9.45		11.01
13	-15.17		15.41
15	-1.86	●	2.40
-1	-7.51		7.21
-3	54.56		53.04
-5	-37.54		36.23
-7	-.69	●	2.40
-9	33.38		35.62
-11	-15.91		15.61
-13	-5.72		8.01
-15	7.91		8.21
# 3	5		
0	-56.07		60.44
2	52.66		53.84
4	22.96		25.82
6	-29.39		28.62
8	-11.02		12.01
10	14.14		14.41
12	-1.98	●	2.40
14	2.31		7.21
-2	-23.03		22.62
-4	36.38		40.03
-6	2.97	●	2.40
-8	-22.98		22.62
-10	12.60		13.61
-12	9.68		8.61
-14	-8.65		9.41
# 4	5		
1	-17.23		14.21
3	45.29		49.83
5	-16.43		16.61
7	-25.41		26.82
9	30.26		29.42
11	.85	●	2.60
13	-11.20		13.01
15	3.12		4.60
-1	-50.07		52.84
-3	46.67		50.84
-5	-10.69		7.00
-7	-15.07		9.41
-9	32.35		29.62
-11	-.44	●	2.60
-13	-23.36		24.02
-15	6.42		6.80
# 5	5		
0	32.90		38.63
2	15.17		14.01
4	-32.66		33.02
6	-16.54		19.61
8	18.97		17.81
10	-.49	●	2.40
12	2.51		3.20
14	.92	●	2.40
-2	-5.31		4.00
-4	-2.51		5.40
-6	-3.97		3.20
-8	-19.59		19.61
-10	5.38		6.40
-12	16.31		15.21
-14	-1.02	●	2.40
# 6	5		
1	9.64		9.61
3	35.27		36.43
5	-38.92		40.63
7	-12.56		12.81
9	22.60		21.82
11	2.14		9.61
13	-5.17		6.00
-1	-47.75		49.83
-3	35.09		34.42
-5	26.58		24.02
-7	-38.25		33.42
-9	6.35		8.01
-11	16.23		16.41
-13	-17.25		15.61
# 7	5		
0	22.70		22.22
2	-16.79		14.81
4	-21.91		22.42
6	18.67		18.41
8	19.00		18.81
10	-16.56		16.41
12	-.59	●	2.40
14	3.10	●	2.40
-2	-23.27		26.42
-4	8.19		9.41
-6	27.03		27.42
-8	-7.30		6.40
-10	-20.82		20.01
-12	6.73		8.41
-14	4.38		4.40
# 8	5		
1	32.52		31.02
3	11.71		11.41
5	-37.35		34.62
7	4.37	●	2.50
9	11.98		11.01
11	-3.82	●	2.60
13	-1.24	●	2.60
-1	-24.64		23.22
-3	-7.25		10.01
-5	37.77		35.33
-7	-20.69		19.01
-9	-16.17		15.61
-11	12.85		13.81
-13	.39	●	2.60
# 9	5		
0	26.45		26.62
2	25.09		28.42
4	-22.65		22.82
6	-1.29	●	2.60
8	-1.14	●	2.60
10	1.51	●	2.60
12	1.15	●	2.60
-2	-31.39		31.02
-4	-20.41		21.01
-6	32.25		28.62
-8	1.29	●	2.60
-10	-16.93		16.81
-12	3.52	●	2.60
-14	5.39	●	2.60
# 10	5		
1	22.89		19.21
3	-11.02		10.41
5	-5.67		7.41
7	15.35		13.21
9	-5.03	●	2.60
11	-12.75		9.21
-1	-5.06	●	2.60
-3	-19.41		20.41
-5	18.40		19.21
-7	2.09	●	2.60
-9	-16.71		13.21
-11	6.52	●	2.60
-13	6.28		3.40
# 11	5		
0	5.17	●	2.60
2	7.81		6.60
4	1.91	●	2.60
6	2.37	●	2.60
8	-11.23		9.21
10	.44	●	2.60
-2	-4.65		11.21
-4	-19.60		15.41
-6	10.44		9.61
-8	7.91		8.21
-10	-3.13	●	2.60
-12	-3.51	●	2.60
# 12	5		
1	10.72		11.01
3	-11.06		10.31
5	4.85	●	2.60
7	9.00		6.30
9	-7.03	●	2.60
-1	1.53	●	2.60
-3	-12.97		13.61
-5	3.76	●	2.60
-7	7.09		6.60
-9	-11.23		9.81
-11	5.19	●	2.60
# 13	5		
0	-3.31	●	2.60
2	-22.15		22.02
4	10.60		7.00
6	2.07	●	2.60
8	-2.24	●	2.60
-2	20.76		23.62
-4	5.51	●	2.60
-6	-16.04		14.21
-8	1.07	●	2.60
-10	.94	●	2.60
# 14	5		
1	3.64	●	2.60
3	-10.97		10.21
5	2.36	●	2.60
7	6.76		4.00
-1	11.00		12.01
-3	-11.25		10.01
-5	-4.75	●	2.60
-7	10.30		10.01
-9	-2.10	●	2.60
# 15	5		
0	-4.60	●	2.60
2	-6.64		6.40
4	8.89		9.21
6	1.11	●	2.60
-2	2.33	●	2.60
-4	.64	●	2.60
-6	-3.43	●	2.60
-8	9.10		6.80
# 16	5		
1	-8.06		16.01
3	-8.13	●	2.40
5	6.98	●	2.60
-1	12.62		12.41
-3	.34	●	2.60
-5	-7.45		6.00
# 17	5		
0	-7.41		4.40
2	2.37	●	2.60
-2	1.99	●	2.60
-4	.05	●	2.60
# 0	6		
0	-29.56		22.42
2	50.45		51.64
4	-7.92		8.21
6	-58.59		60.64
8	9.45		13.61
10	41.81		36.03
12	-17.41		16.21
14	-6.86		7.21
# 1	6		
1	-44.10		45.83
3	-11.88		14.21
5	26.54		28.62
7	-22.55		22.22
9	-3.25		3.20
11	13.48		13.61
13	-.13	●	2.60
15	-3.82		5.00
-1	37.91		43.03
-3	43.38		40.23
-5	-37.93		37.83
-7	-3.19	●	1.60
-9	11.58		12.41
-11	-8.20		10.01
-13	-2.09	●	1.60
-15	6.41		4.60
# 2	6		
0	-70.58		69.05
2	14.35		12.61
4	15.45		17.81
6	-26.77		25.82
8	23.08		23.22
10	8.26		9.21
12	-10.15		12.41
14	-4.18		5.80
-2	10.05		13.61
-4	77.88		79.86
-6	-26.57		27.62
-8	-33.80		29.62
-10	23.96		26.22
-12	-4.98		4.50
-14	-6.14		7.81
# 3	6		
1	-17.37		15.61
3	17.00		19.01
5	-13.30		13.21
7	-17.61		15.61
9	15.64		15.01
11	5.18	●	2.40
13	-11.48		11.21
-1	14.72		12.01
-3	35.88		33.62
-5	-24.32		24.62
-7	-27.03		25.02
-9	15.79		13.81
-11	1.43	●	2.40
-13	-3.84		5.20
-15	4.41	●	2.40
# 4	6		
0	-7.64		5.60
2	21.53		22.02
4	-12.05		13.01
6	-8.04		6.80
8	24.27		26.22
10	-13.92		15.61
12	-5.61		7.81
14	7.42		7.21
-2	-55.81		56.04
-4	66.38		69.85
-6	22.28		24.02
-8	-42.31		47.43
-10	-10.63		10.81
-12	20.10		19.21
-14	-3.95		6.80
# 5	6		
1	-18.31		20.81
3	40.80		41.43
5	-5.98		4.60
7	-9.16		8.01
9	5.75		5.60
11	-3.03	●	2.40
13	-8.44		9.41
-1	-23.57		22.42
-3	25.16		26.42
-5	1.76	●	2.40
-7	-29.13		27.62
-9	18.20		19.01
-11	6.71		6.80
-13	-11.51		10.41
# 6	6		
0	30.47		28.42
2	27.93		27.82
4	-21.93		20.81
6	20.37		19.21
8	-4.56	●	1.40
10	-21.85		23.82
12	2.54	●	1.40
-2	-52.02		51.64
-4	-19.94		19.41
-6	38.76		37.03
-8	-7.32		7.21
-10	-8.08		9.41
-12	14.69		15.01
-14	-7.01		6.40
# 7	6		
1	1.26	●	2.40
3	34.23		33.22
5	1.00	●	2.40
7	-9.85		9.81
9	.40	●	2.40
11	-3.16	●	2.40
13	1.30	●	2.40
-1	-41.87		41.23
-3	2.54	●	2.40
-5	17.99		20.81
-7	-10.76		10.41
-9	3.64		5.80
-11	9.09		8.41
-13	-7.10		6.80
# 8	6		
0	24.51		27.62
2	7.94		8.41
4	-24.12		25.82
6	6.66		5.40
8	.22	●	2.60
10	.34	●	2.60
12	4.73		4.60
-2	-11.34		12.01
-4	-20.84		20.61
-6	27.60		28.82
-8	-12.93		10.41
-10	-10.91		11.01
-12	14.40		15.41
# 9	6		
1	25.55		25.82
3	.15	●	2.60
5	-6.14	●	2.60
7	1.91	●	2.60
9	1.33	●	2.60
11	-5.94	●	2.60
-1	-21.69		24.82
-3	-16.10		14.31
-5	13.07		14.21
-7	8.84		8.41
-9	-9.78		10.01
-11	6.41		6.40
-13	.53	●	2.60
# 10	6		
0	24.59		22.62
2	-7.11	●	3.20
4	-7.66	●	3.20
6	1.84	●	3.20
8	5.07	●	3.20
10	-3.03	●	3.20
-2	-10.98		8.21
-4	-20.58		19.81
-6	18.29		18.01
-8	11.65		7.81
-10	-19.11		18.01
-12	.21	●	3.20
# 11	6		
1	8.19		8.41
3	-13.81		16.41
5	-5.15	●	3.20
7	12.83		14.01
9	-2.03	●	3.20
11	-4.09	●	3.20
-1	.07	●	3.20
-3	-4.21	●	3.20
-5	13.26		11.41
-7	-.94	●	3.20
-9	-15.04		13.61
-11	6.39		4.20
# 12	6		
0	-5.02	●	3.20
2	-24.56		22.62
4	12.70		12.01
6	14.63		14.81
8	-6.76		8.01
10	-5.78	●	3.20
-2	11.63		11.21
-4	-1.26	●	3.20
-6	-2.74	●	3.20
-8	14.46		15.41
-10	-8.21		6.60
# 13	6		
1	-.10	●	3.20
3	-6.39		7.41
5	-5.07	●	3.20
7	8.14		6.60
9	-1.68	●	3.20
-1	7.12		7.21
-3	-5.18	●	3.20
-5	9.35	●	3.20
-7	-1.94	●	3.20
-9	-7.51		7.21
# 14	6		
0	-2.43	●	3.20
2	2.54	●	3.20
4	4.33	●	3.20
6	-4.19	●	3.20
-2	9.99	●	3.20
-4	-7.82	●	3.20
-6	-8.85	●	3.20
-8	7.39	●	3.20
# 15	6		
1	-2.92	●	3.20
3	-7.41		4.60
5	4.83	●	3.40
-1	9.73	●	3.20
-3	-1.74	●	3.20
-5	-4.61	●	3.20
-7	2.78	●	3.20
# 16	6		
0	-.59	●	3.20
2	-.29	●	3.20
-2	6.97	●	3.20
-4	-5.52	●	3.20
# 0	7		
1	16.03		17.31
3	-1.78	●	1.80
5	.61	●	1.80
7	2.61	*	1.80
9	2.77	*	1.80
11	-4.99		3.80
# 1	7		
0	-36.52		33.02
2	39.08		37.03
4	45.81		41.03
6	-45.76		45.33
8	-4.73	●	3.20
10	11.24		17.81
12	-7.83		4.20
14	-.05	●	1.60
-2	-15.07		14.21
-4	28.45		32.42
-6	-42.06		43.23
-8	17.63		19.81
-10	24.66		27.32
-12	-15.52		16.01
-14	-14.91		19.21
# 2	7		
1	-10.41		10.81
3	2.82	●	2.40
5	6.71		6.00
7	6.61		8.21
9	-.82	●	2.40
11	.91	●	2.40
13	-8.32		9.41
-1	-6.09		6.40
-3	-.10	●	2.40
-5	.26	●	2.40
-7	.14	●	2.40
-9	5.72		8.01
-11	3.94		5.80
-13	-6.75		7.41
# 3	7		
0	-38.91		43.23
2	71.29		71.05
4	-5.07		6.80
6	-29.92		28.02
8	3.03	●	3.40
10	14.41		15.41
12	-9.30		9.01
14	4.71	●	3.40
-2	-36.19		35.22
-4	33.04		31.42
-6	7.16		8.21
-8	-29.75		30.82
-10	17.24		18.81
-12	7.79		9.01
-14	-8.42		10.01
# 4	7		
1	-16.41		19.21
3	3.72	●	2.60
5	2.09	●	3.80
7	-5.09		6.60
9	3.65	●	2.60
11	5.08		5.60
13	-5.49		5.00
-1	16.86		21.62
-3	-.53	●	2.60
-5	-15.63		18.01
-7	-2.65	●	2.60
-9	20.99		24.02
-11	1.35	●	2.60
-13	-10.09		13.21
# 5	7		
0	25.94		27.42
2	35.24		33.02
4	-58.02		54.04
6	.57		3.40
8	32.84		33.82
10	-8.11		8.01
12	-11.01		10.21
-2	-33.73		32.62
-4	-.70	●	2.40
-6	32.70		33.62
-8	-33.70		35.83
-10	.59	●	2.40
-12	17.11		17.01
-14	-.16		3.40
# 6	7		
1	-14.94		15.01
3	-9.10		8.61
5	5.67		6.40
7	-6.31		7.21
9	6.02		6.00
11	-.40	●	1.40
13	2.08	●	1.40
-1	11.95		12.21
-3	23.75		24.82
-5	-14.59		14.41
-7	-8.59		9.21
-9	6.48		7.81
-11	1.89	●	1.40
-13	-2.05		3.00
# 7	7		
0	9.89		12.81
2	-25.87		24.82
4	-13.01		17.21
6	27.03		25.82
8	18.92		23.22
10	-24.65		26.22
12	.14	●	2.40
-2	-22.15		24.62
-4	19.93		19.61
-6	27.95		29.42
-8	-15.65		15.01
-10	-16.68		17.61
-12	11.25		12.21
# 8	7		
1	-8.25		8.21
3	-2.16	●	2.60
5	.74	●	2.60
7	.58	●	2.60
9	-.42	●	2.60
11	-1.41	●	2.60
-1	-4.56		6.40
-3	22.02		21.62
-5	3.46	●	2.60
-7	-9.46		11.61
-9	-8.42		8.41
-11	2.51	●	2.60
-13	3.44	●	2.60
# 9	7		
0	25.40		25.22
2	-5.01		5.80
4	-5.43	●	2.60
6	6.96		6.00
8	-3.19	●	2.60
10	-8.43		9.01
-2	-21.38		22.42
-4	-10.00		9.01
-6	20.18		20.81
-8	6.75		7.21
-10	-21.06		18.81
-12	7.04		7.21
# 0	8		
0	-13.74		12.41
2	18.46		19.61
4	-1.07	●	1.80
6	-26.14		25.42
8	1.99		5.60
10	26.23		26.62
12	-8.57	●	1.80
# 1	8		
1	14.17		15.21
3	14.62		18.21
5	-25.02		25.02
7	3.04		4.60
9	3.23	●	1.60
11	-2.89		8.41
13	2.03	●	1.60
-1	-5.22		5.60
-3	-17.13		18.41
-5	24.53		26.62
-7	-14.77		18.81
-9	-.55	●	1.60
-11	4.32		5.40
-13	3.72		4.00
# 2	8		
0	-46.80		46.63
2	25.00		26.62
4	15.08		15.01
6	-30.12		34.42
8	9.35		9.81
10	18.72		21.21
12	-8.93		10.01
-2	-13.16		13.61
-4	44.62		50.44
-6	4.45		6.40
-8	-19.45		20.01
-10	5.79		6.80
-12	-3.02	●	2.40
# 3	8		
1	4.63		4.60
3	-19.10		25.82
5	9.05		11.01
7	-9.29		9.81
9	4.64		3.20
11	-.79	●	2.40
13	5.33		7.00
-1	7.97		7.21
-3	23.14		23.82
-5	-15.34		17.61
-7	-12.15		13.01
-9	-2.21	●	2.40
-11	10.30		12.61
-13	-.02	●	2.40
# 4	8		
0	-8.27		9.01
2	45.33		51.04
4	-10.85		11.21
6	-33.78		37.63
8	24.83		24.42
10	1.97	●	2.60
12	-11.33		12.01
-2	-48.80		53.24
-4	35.95		40.03
-6	23.66		26.82
-8	-21.19		21.82
-10	-11.45		13.61
-12	8.01		10.21
# 5	8		
1	-5.16		6.00
3	-13.97		14.01
5	16.00		16.01
7	2.60	●	2.40
9	-6.73		8.01
11	-2.48	●	2.60
-1	5.28	●	2.40
-3	12.04		11.21
-5	-13.17		13.61
-7	7.93		9.01
-9	-8.13		8.21
-11	.78	●	2.40
-13	1.19	●	2.40
# 6	8		
0	30.72		33.62
2	29.55		29.22
4	-25.50		26.42
6	.30	●	1.40
8	12.88		14.01
10	-19.47		24.82
12	-3.16		2.80
-2	-36.06		36.43
-4	-14.41		13.81
-6	11.68		11.21
-8	2.63	●	1.40
-10	2.02	●	1.40
-12	3.73		3.00
# 7	8		
1	-14.10		15.21
3	.54	●	2.40
5	6.80		8.21
7	11.62	●	11.21
9	-14.29		15.01
11	-.34	●	2.40
-1	15.41		14.81
-3	-10.63		10.21
-5	-3.14	●	2.40
-7	5.17		6.60
-9	4.04		4.60
-11	-7.43		9.41
# 8	8		
0	29.28		29.22
2	-4.15	●	2.60
4	-31.12		28.82
6	18.37		18.41
8	6.44		7.00
10	-10.30	●	2.60
-2	1.54	●	2.60
-4	-14.86		15.41
-6	3.61		6.40
-8	-10.27		10.41
-10	2.82	●	2.60
-12	10.55	●	2.50
# 9	8		
1	-7.55		7.81
3	8.29		7.21
5	4.09		6.80
7	-3.94		6.00

Table 5 (*cont.*)

L	H	K	F_{calc}	F_{obs}
9			-4.04	6.00
-1			1.38	2.60
-3			-3.32	2.60
-5			1.31	2.60
-7			-5.10	5.60
-9			7.84	9.21
-11			-1.17	2.60
	0			
1			22.71	21.01
3			-11.65	10.81
5			-10.94	9.61
7			4.11	1.80
9			20.55	20.01
11			-15.72	13.21
	1			
0			-12.75	17.61
2			37.97	42.63
4			6.50	7.21
6			-19.93	21.89
8			.76	1.60
10			3.16	2.60
12			-9.15	13.21
-2			-14.65	18.21
-4			-4.27	1.60
-6			-.65	1.60
-8			3.63	1.60
-10			12.98	14.01
-12			-10.73	12.01
	2			
1			-10.71	9.21
3			2.28	2.40
5			5.39	2.40
7			17.00	19.01
9			-9.42	7.41
11			-11.43	12.41
-1			-18.41	19.61
-3			8.32	8.01
-5			19.21	20.01
-7			-.96	2.40
-9			-16.65	22.22
-11			5.18	6.60
	3			
0			-10.37	11.01
2			40.46	37.03
4			3.51	2.40
6			-31.63	30.82
8			14.69	13.81
10			3.53	5.00
12			-7.94	7.21
-2			-34.40	31.02
-4			22.73	23.62
-6			-2.29	2.40
-8			-12.86	13.61
-10			12.48	11.61
-12			6.25	2.40
	4			
1			-9.36	8.41
3			14.66	14.41
5			1.99	2.60
7			5.49	3.40
9			-17.82	17.61
11			.77	2.60
-1			-4.52	3.50
-3			-15.23	16.81
-5			17.95	21.82
-7			-1.93	2.60
-9			.60	2.60
-11			-3.93	5.40
	5			
0			11.84	12.21
2			13.84	12.21
4			-21.54	22.42
6			-5.53	5.60
8			20.54	20.01
10			-4.30	4.00
-2			-17.27	14.41
-4			11.13	10.21
-6			-4.24	2.40
-8			-10.57	10.21
-10			7.99	9.01
-12			10.11	12.01
	6			
1			8.97	8.41
3			-16.83	17.01
5			5.96	7.00
7			5.53	7.00
9			-6.95	6.40
11			-.60	1.40
-1			11.23	11.61
-3			-16.81	17.41
-5			-.18	1.40
-7			11.94	11.01
-9			-2.42	1.40
-11			-9.66	9.61
	7			
0			2.28	3.20
2			-13.31	12.21
4			-19.02	19.41
6			27.26	23.42
8			9.34	12.21
10			-13.97	12.01
-2			-1.89	5.80
-4			3.04	2.40
-6			15.64	14.41
-8			-7.34	14.21
-10			-4.21	4.20
	8			
1			.08	2.60
3			-23.07	21.01
5			14.10	14.21
7			-2.88	2.60
9			-1.94	2.60
-1			16.98	18.81
-3			3.79	2.60
-5			-19.21	19.61
-7			12.35	13.61
-9			-.72	2.60
	9			
0			-14.85	13.81
2			9.95	11.01
4			-19.28	19.41
6			10.39	10.01
8			7.74	9.41
10			-5.00	4.40
-2			4.09	2.60
-4			19.67	20.41
-6			5.40	6.80
-8			-26.70	26.82
-10			10.05	11.41
	10			
1			4.91	3.40
3			-20.95	19.81
5			5.14	5.20
7			14.86	15.21
9			-7.93	9.41
-1			9.15	9.41
-3			-10.12	9.21
-5			6.11	8.21
-7			11.23	12.21
-9			-13.91	14.81
	11			
0			7.44	7.21
2			2.34	3.40
4			-.22	1.40
6			5.27	6.60
8			-1.76	1.40
-2			-9.01	9.21
-4			-2.25	3.20
-6			4.45	4.60
-8			-6.63	6.80
-10			6.59	4.40
	12			
1			-9.79	10.01
3			-14.67	15.61
5			16.50	16.61
7			4.91	4.60
9			-13.76	10.81
-1			23.41	23.82
-3			-5.12	9.01
-5			-13.59	14.21
-7			12.94	13.81
-9			2.37	3.80
	13			
0			18.92	18.01
2			-5.86	8.01
4			-1.18	2.60
6			-.30	2.60
8			1.48	2.60
-2			-4.60	2.60
-4			-5.56	5.80
-6			-1.76	2.60
-8			4.03	4.40
	14			
1			-10.35	10.81
3			-2.30	2.60
5			12.69	14.21
7			-9.33	6.60
-1			17.90	16.21
-3			-.02	2.60
-5			-20.58	16.61
-7			5.45	4.40
	0			
1			21.75	22.22
3			9.64	9.61
5			-28.35	28.42
7			9.93	8.61
9			8.17	9.01
	1			
0			-4.80	3.00
2			13.54	13.61
4			2.38	1.60
6			-.90	1.60
8			-1.91	1.60
10			-5.66	1.60
-2			-4.96	1.60
-4			-7.77	7.00
-6			3.95	5.00
-8			3.66	3.80
-10			4.51	1.60
	2			
1			30.24	31.42
3			-13.11	13.61
5			-11.26	12.61
7			18.04	19.21
9			-4.01	3.20
-1			-9.20	9.81
-3			-29.33	29.02
-5			25.95	31.42
-7			10.80	11.21
-9			-19.30	17.61
	3			
0			6.51	5.60
2			2.45	2.40
4			.49	2.40
6			-1.92	2.40
8			5.15	4.60
-2			-9.05	9.61
-4			2.19	2.40
-6			-4.05	2.40
-8			-.93	2.40
	4			
1			28.78	28.42
3			-22.97	22.82
5			-.44	2.60
7			11.39	13.81
9			-6.48	2.60
-1			11.60	12.21
-3			-32.37	31.82
-5			-2.48	2.60
-7			22.71	22.62
-9			-10.53	12.61
	5			
0			9.84	9.01
2			-2.10	2.40
4			-8.61	7.81
6			1.50	2.40
8			6.23	5.80
-2			-.38	2.40
-4			1.59	2.40
-6			-9.57	9.41
-8			-2.92	2.40
	6			
1			-2.09	1.40
3			-20.23	18.21
5			10.06	11.01
7			6.65	5.40
-1			24.96	23.62
-3			-9.22	8.21
-5			-15.06	15.41
-7			13.03	12.81
	7			
0			-5.95	2.40
2			-3.46	2.40
4			-4.67	2.40
6			6.90	6.40
-2			5.08	5.20
-4			.34	2.40
-6			2.30	1.40
-8			-.61	2.40
	8			
1			-19.05	16.61
3			-5.16	6.40
5			10.41	9.61
-1			20.11	17.01
-3			5.74	4.60
-5			-12.55	12.41
-7			3.39	2.60
	9			
0			1.36	2.60
2			-.21	2.60
4			.68	2.60
-2			3.24	2.60
-4			-6.25	5.60
-6			1.36	2.60
	0			
0			14.83	14.81
2			-3.35	3.40
4			-8.75	9.21
6			3.85	4.40
8			.95	1.80
	1			
1			23.28	22.02
-3			-12.04	12.61
-5			14.44	14.21
-7			1.30	1.60
	2			
0			-1.22	2.40
2			-13.47	12.81
4			1.80	2.40
6			11.45	11.41
-2			5.73	6.60
-4			-1.42	2.40
-6			5.35	5.60
-8			1.61	2.40
	3			
1			17.04	20.41
3			-18.29	17.81
5			-10.95	10.01
7			17.88	16.81
-1			10.06	9.41
-3			-22.08	20.81
-5			9.51	10.21
-7			9.38	9.21
	4			
0			-2.82	2.60
2			-6.50	8.21
4			1.55	2.40
6			2.38	2.60
-2			7.03	9.01
-4			.09	2.60
-6			.94	2.60
	5			
3			-20.33	19.01
5			6.10	4.60
-1			16.20	14.21
-3			-17.01	14.41
	6			
4			3.51	4.00
-2			3.14	3.80
	7			
3			-3.95	3.00
-1			5.02	7.41
-3			-6.25	6.80
	8			
-2			6.02	5.60
	0			
1			3.08	2.80
	1			
0			12.33	12.21
2			-6.43	6.80
-4			-13.73	11.61
	2			
1			7.10	6.80
3			-4.12	3.80
-1			-4.63	4.60
-3			-4.94	5.20
	3			
2			-7.43	7.00
-2			6.08	6.80
	4			
-1			5.50	6.40
-3			-18.22	16.41

Table 6. *Deviations from least-squares planes in* $NaCuggg.H_2O$

Atoms included in calculation	Distances from plane (Å)					
Square of copper ligand atoms						
	N(1)	N(2)	N(3)	O(4′)	Cu	
N(1) N(2) N(3) O(4′)	−0·001	+0·001	−0·001	+0·001	+0·115	
N(1) N(2) N(3) O(4′) Cu	−0·023	−0·020	−0·024	−0·025	+0·092	
First peptide group						
	C(1)	C(2)	O(1)	N(2)	C(3)	Cu
C(1) C(2) O(1) N(2)	−0·002	+0·006	−0·003	−0·002	+0·004	+0·188
C(1) C(2) O(1) N(2) C(3) Cu	−0·039	+0·002	+0·053	−0·048	−0·020	+0·052
Second peptide group						
	C(3)	C(4)	O(2)	N(3)	C(5)	Cu
C(3) C(4) O(2) N(3)	+0·001	−0·005	+0·002	+0·002	−0·156	−0·388
C(3) C(4) O(2) N(3) Cu	+0·054	+0·013	−0·097	+0·124		−0·095
Carboxyl group						
	C(5)	C(6)	O(3)	O(4)		
C(5) C(6) O(3) O(4)	+0·002	−0·007	+0·003	+0·003		

The superscripts attached to atoms in various equivalent positions are shown at the head of Table 4. The oxygen of the water molecule has been labelled O(5), the subscript *w* being occasionally added.

The copper atoms are 5-coordinated. The atom Cu forms bonds to the nitrogen atoms N(1), N(2), N(3) of one peptide and to a carboxyl oxygen atom O(4′) of the other peptide molecule of the dimer. There is also a weaker bond between the copper Cu and nitrogen N(3′) of the second peptide molecule (Table 4(*b*)). This weakly bound atom N(3′) lies at the apex of a pyramid of which the corners of the approximately square base are occupied by the strongly bound ligand atoms N(1), N(2), N(3) and O(4′). The copper atom Cu lies near the centre of the square, but is displaced in the direction of N(3′) by 0·115 Å (Table 6 and Fig. 2).

The complex ion as a whole carries a double negative charge. This must be distributed mainly over the peripheral oxygen atoms O(1), O(2), O(3) and

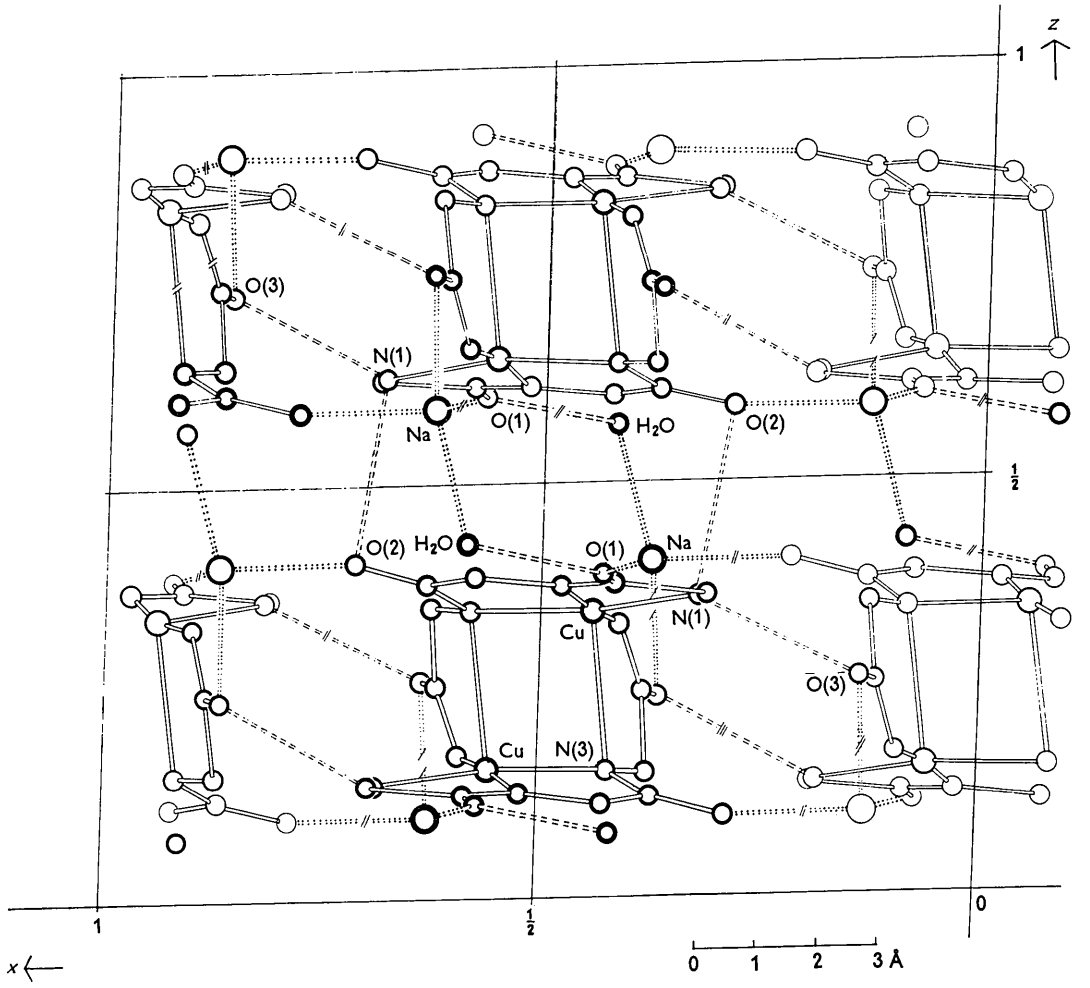


Fig. 2. Projection of unit-cell of sodium glycylglycylglycino cuprate(II) monohydrate along the y axis. Dashed and dotted lines represent hydrogen bonds and electrostatic interactions respectively. Breaks in these lines indicate that they join one atom to another in the unit-cell above/below it.

their symmetry-related equivalents. It is just these atoms which have short contacts with the sodium ions and which are the proton acceptors in the hydrogen-bond system. In fact, the sodium ion Na (Table 4(*d*)) is surrounded by a tetrahedron of oxygen atoms, of which two (O(1) at 2·31 Å and O(2^{vii}) at 2·28 Å) belong to two peptide groups, and one to a carboxyl group (O(3‴) at 2·34 Å). The fourth belongs to a water molecule (O(5_w) at 2·29 Å). We have not listed two other contacts (Na–O(5^{v}_{w})=3·09 Å and Na–O(4‴)=2·84 Å). If these are included, the environment of the sodium ion becomes a very irregular octahedron with O(3‴) much displaced in the direction of O(4‴). The water molecule H–O(5)–H forms hydrogen bonds 2·72 and 2·80 Å long with a carbonyl oxygen O(1^{v}) and a free carboxyl oxygen O(3^{iv}) (Table 4(*c*)). With respect to these two close neighbours and the sodium ion Na, the water molecule lies at the apex of a flat trigonal pyramid.

The complexes (Fig. 2) are packed in layers approximately parallel to (001). Stabilization within a layer is provided in the y direction by hydrogen-bonded bridges O(1^{v}) · · · H–O(5)–H · · · O(3^{iv}), and in the xz plane by hydrogen-bonds N(1)–H · · · O(3^{viii}). A sodium ion also links three complexes within a layer by interactions with atom-types O(2) in the x direction, O(1) in the y direction and O(3) in the z direction. Between adjacent layers there are only weak hydrogen bonds of the type N(1)–H · · · O(2^{iv}) (3·06 Å) in the z direction and weak attractions between sodium ions and water molecules. A repeated unit in this cross-linking system is a six-membered ring in the 'chair' configuration, consisting of atom types Na · · · O(1) · · · $H_2O(5)$ · · · Na · · · O(1) · · · $H_2O(5)$ (see centre of Fig. 2).

Dimensions of the peptide molecule

Before discussing the significance of our other results, we wish to comment on the length of the bond C(1)–C(2), whose value (1·57 Å, s.d. = 0·014) is

'probably significantly' different from the value for carbon–carbon single bonds (1·54 Å, average 1·53 Å in peptides). Originally we also considered it noteworthy that the bond C(2)–N(2) is shorter (1·29 Å) than in unchelated peptides (average 1·32 Å). Later we realized that the bonds corresponding to C(2)–N(2) in other copper-peptide complexes are characteristically shorter than 1·32 Å, but at the time of the refinement it seemed that the bond-lengths of both C(1)–C(2) and C(2)–N(2) were anomalous and that this could be caused by the misplacement of their common atom, C(2). To explore the possibility that the structure was refined to a false minimum of $\Sigma w(\Delta F)^2$, we over-corrected the position of C(2), keeping it in the plane of C(1), C(2), O(1) and N(2), and giving the bonds C(1)–C(2), C(2)–N(2), C(2)–O(1) respective lengths of 1·52, 1·34 and 1·23 Å. In two further cycles of full-matrix least-squares refinement, C(2) returned to its previous position and there were no significant changes in any other parameters. A final three-dimensional (F_o-F_c) Fourier map showed no significant features in the vicinity of C(2). We therefore conclude that C(1)–C(2) is elongated by a coincidence of errors in the data and weighting scheme. It follows that the standard deviation of this bond length, calculated in the usual way from the least-squares refinement, is too low. Our discussion of the other dimensional details of the structure is to be read with this reservation in mind.

The peptide molecule (Table 4(*a*)) generally reflects the combined effects of chelation and ring-strain. Each peptide molecule is involved in three five-membered and one four-membered ring:

CuN(1)C(1)C(2)N(2)Cu, CuN(2)C(3)C(4)N(3)Cu,
Cu′N(3)C(5)C(6)O(4)Cu′ and CuN(3)Cu′N(3′)Cu.

This situation is quite different from that in CugggCl.$1\frac{1}{2}H_2O$ (Freeman *et al.*, 1964), where the same tripeptide interacts with the metal atom only at the *N*-terminal glycine residue and at the terminal carboxyl group. In the present crystal, we find much larger deviations from the average dimensions of unchelated peptides (Pauling & Corey, 1953*a*, *b*; Hahn, 1957).

Although a tripeptide contains three amino acid residues, these form only two 'peptide groups', $-C_\alpha HR-CO-NH-C'_\alpha HR'-$. The terminal NH_2- and $-COO^-$ groups do not share in the peptide group resonance. The distribution of bond directions about N(1) is very nearly tetrahedral (Table 4(*c*)), provided only that the N–H bonds lie within about 15° of the N(1)···O(2^{iv}) and N(1)···O(3^{viii}) vectors. The bond N(1)–C(1) shows the slight elongation normally found in bonds from *N*-terminal amino groups when the nitrogen atom is sp^3 hybridized (Hahn, 1957).

At the other end of the peptide molecule, the carboxyl group is planar (Table 6). The characteristic difference between the lengths of its carbon–oxygen bonds (1·28, 1·23 Å) is not as great as in CugggCl.$1\frac{1}{2}H_2O$ (1·31, 1·21 Å), although the environments of the carboxyl groups in the two compounds are similar: In both compounds, one carboxyl oxygen atom forms a bond to the copper and the other forms hydrogen-bonds, about 3·0 and 2·8 Å long respectively, to a terminal amino nitrogen of a neighbouring complex and to a water molecule. In the present compound there is one additional close contact (between the 'free' carboxyl oxygen and the sodium ion). In CugggCl.$1\frac{1}{2}H_2O$ there is an additional hydrogen bond to the copper-bonded oxygen and the other oxygen is much closer to the copper atom.

The first peptide group, –C(1)C(2)O(1)N(2)C(3)–, contains the only approximately trigonal nitrogen atom in the molecule. Like the free peptide groups in CugggCl.$1\frac{1}{2}H_2O$, this chelated peptide group deviates from planarity (Table 6) although it is the N–Cu bond and not the N–C'_α bond which lies out of the plane of the rest of the group. The bond N(2)–Cu makes an angle of 5·7° with the plane of C(1), C(2), O(1), N(2) and C(3), and the configuration of the three bonds from N(2) is flatly pyramidal. We note that N(2) resembles the peptide nitrogen atom in glycylglycino copper(II) trihydrate (Strandberg, Lindqvist & Rosenstein, 1961).

In the second peptide group, –C(3)C(4)O(2)N(3)C(5)–, the nitrogen atom is bound to *two* copper atoms (Cu–N(3) = 1·99, Cu′–N(3) = 2·57 Å). The distribution of bond directions about N(3) is much distorted from tetrahedral regularity (extreme angles: Cu–N(3)–Cu′ = 84°, Cu–N(3)–C(5) = 127°), and both Cu and C(5) lie at significant distances from the plane through C(3), C(4), O(2) and N(3) (Table 6). Since the hybridization of the nitrogen orbitals must be far from sp^2, the peptide group resonance is considerably weakened and this is demonstrated by the elongation of the C(4)–N(3) bond (1·37 Å). A corresponding shortening of the C(4)–O(2) bond seems to be counteracted by participation of O(2) in a hydrogen-bond to N(1^{iv}). The bond N(3)–C(5) is shorter than normal N–C'_α bonds.

Van der Waals contacts

There are no abnormally short contacts. The closest non-bonded approach between two peptides (3·32 Å) occurs between O(2) and O(3^x): these two atoms are part of the polyhedron of oxygen atoms surrounding sodium ion Na^{vii}.

Geometry of the copper coordination

No sixth atom turned up near the copper peak in the Fourier syntheses upon which the structure analysis is based, and the final (F_o-F_c) synthesis contained no significant peak corresponding to an omitted atom. There is no doubt that the copper atom has a square pyramidal environment of five ligand atoms.

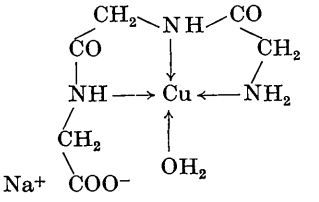
In the discussion of the structure of CugggCl.$1\frac{1}{2}H_2O$ (Freeman *et al.*, 1964) it was pointed out that the

apparent 5-coordination of copper in that compound might be caused by steric hindrance. The carboxyl group's second oxygen atom (itself presumed not to be bonded to the copper) would obstruct any sixth ligand atom. A similar geometry around a copper atom has since then been discovered in glutamato copper(II) dihydrate (Gramaccioli, 1963). A systematic search of inter-atomic vectors showed that steric hindrance is *not* responsible for the 5-coordination in the present complex. The copper has no non-bonded contacts shorter than 3·5 Å with atoms outside its own dimer. A hypothetical atom placed 2·57 Å from the copper along the continuation of N(3)–Cu (thus completing a distorted octahedron) admittedly would have some short contacts, but even the shortest of these would be 1·5 Å (with the atom C(3^{iv}) of a neighbouring dimer). Since the hydrogen-bond network which holds the crystal together is not particularly efficient, it seems improbable that the copper is prevented from binding a sixth ligand by any resultant reduction in the efficiency of packing or hydrogen-bonding. In view of (i) the absence of direct steric hindrance, (ii) the presence of a water-molecule elsewhere in the crystal but nowhere near the copper, and (iii) the easy availability of additional water molecules during the crystallization of the complex, we conclude that the 5-coordination of the copper atom is real.

The copper–ligand bonds fall smoothly into the pattern which is emerging from the increasing number of structure analyses of metal-peptide complexes (summarized by Freeman *et al.*, 1964). The bond Cu–N(2) is the shortest of the copper–nitrogen bonds since N(2) is not only deprotonated but is also the only approximately trigonal nitrogen atom in the ligand. The bond Cu–N(1) is longer than Cu–N(3), both because the distortion from a tetrahedral configuration is greater at N(3) and because N(3) loses a proton and acquires a formal negative charge before chelation takes place. As in CugggCl.$1\frac{1}{2}H_2O$, the fourth of the bonds to the closer ligand atoms, Cu–O(4′), is shorter (1·93 Å) than copper–(carboxyl) oxygen bonds are in peptide complexes where ring-strain may be present. The fifth bond from the copper atom, Cu–N(3′), is elongated (2·57 Å) by the Jahn–Teller effect usually found in copper(II) complexes. The elongation of the bonds to the ligand atoms in the 'polar' positions of octahedral copper(II) complexes may be simulated by assigning to copper a covalent radius of 1·64 Å (instead of 1·28 Å) in this direction.* If the tetrahedral covalent radius of nitrogen is 0·70 Å (Pauling, 1960*a*), then the length of a copper–nitrogen single-bond perpendicular to the square of the four closest ligands should be 2·34 Å. The relation $D(n)=D(1)-0{\cdot}6\log_{10}n$ (Pauling, 1960*b*) then yields a bond-order $n=0{\cdot}41$ for Cu–N(3′). There is no evidence for any partial bond-formation between the two copper atoms Cu and Cu′ of the dimer.

Chemical significance

Speculations concerning the structural reasons for the formation of coloured complexes in the 'biuret reaction' date back as far as 1912, when the formula



was suggested for the violet copper–glycylglycylglycine complex by Kober & Sugiura (1912). Kober & Haw (1916) deduced from the (then) known colours of other copper(II) compounds that purple copper–peptide complexes with $\lambda_{max}\simeq 540$ mμ had three Cu–N bonds and one Cu–OH_2 or Cu–OH^- bond. Following Gavrilow, Plekhan & Poddubnaya (1941), Plekhan (1952) attributed absorption at about 540 mμ to copper(II) with three coordinating N, one coordinating O and two covalently bonded O atoms. On the assumption that these relationships also applied to protein–copper complexes, Poroshin (1952) concluded that several proteins giving violet colours ($\lambda_{max}\simeq 560$ mμ) in the 'biuret reaction' formed three nitrogen–copper bonds per copper atom. At least for glycine–peptides, the present structure analysis supports this general conclusion. The other details of the structures proposed by Plekhan (1952) for metal–peptides and by Poroshin (1952) for metal–protein complexes, using the oxygen atoms of enolized amide groups as additional binding sites, have not been supported by subsequent structural evidence. The revised structural formulae of Plekhan & Russianova (1953), in which metal-binding occurred partly at amide nitrogen atoms without deprotonation, are reminiscent of Kober & Sugiura's original structure (see above). The realization that peptide nitrogen atoms can lose their protons in order to bind metal atoms stems from the potentiometric and spectral observations of Dobbie & Kermack (1955), extended by Rabin (1958) and by Gurd and his collaborators (Koltun, Roth & Gurd, 1962).

The most important result of this structure determination is therefore the confirmation that, at high *p*H and in the presence of copper(II) ions, the amide nitrogen atoms of a peptide are deprotonated and become binding sites for the metal. Metal-binding at

* The shortest distances listed by Orgel (1960) for bonds between copper(II) and chlorine or water ligands in 'polar' positions are: Cu–Cl, 2·64 Å (in $CsCuCl_3$) and Cu–OH_2, 2·30 Å (in Cu(acetate)$_2$.H_2O). Subtracting the covalent radii of chlorine and oxygen, respectively, we find $r_{Cu}=1{\cdot}65$ and $r_{Cu}=1{\cdot}64$ Å.

a peptide nitrogen atom has already been observed in the neutral complex glycylglycino copper(II) trihydrate by Strandberg, Lindqvist & Rosenstein (1961). There is no evidence for or against the dimerization of the glycylglycylglycino cuprate(II) complex in solution, but Koltun *et al.*, have noted the correspondence between their species 'CuGGG$^-$' and the structure reported in the present paper.

The second interesting feature of this structure is its demonstration of a way in which a metal atom may stabilize the relative positions of two peptide chains. In this case, the chains would be linked end-to-end at their carboxylic ends. While there are no short non-bonded contacts between adjacent complexes, inside a dimer the two peptide chains are brought into close proximity by their attachments to the same copper atoms. Thus the copper-bonded oxygen atom O(4) lies 2·90, 3·13 and 3·25 Å from the atoms N(3′), C(5′) and C(6′) respectively of the other peptide molecule. The shortest of these three distances is just equal to the sum of the van der Waals radii of the two atoms.

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