Acta Cryst. (1964). **17**, 719

Crystallographic Studies of Metal–Peptide Complexes. I. Glycylglycylglycinocopper(II) Chloride Sesquihydrate

BY H. C. FREEMAN, G. ROBINSON* AND J. C. SCHOONE†

School of Chemistry, University of Sydney, Sydney, Australia

(*Received* 7 *June* 1963)

A blue-green complex, glycylglycylglycinocopper(II) chloride sesquihydrate, has been crystallized from an aqueous solution containing equimolar proportions of glycylglycylglycine and cupric chloride. The boat-shaped crystals are monoclinic, space-group $C2/c$, with 8 formula units in a cell with dimensions

$$a=21{\cdot}36,\ b=6{\cdot}72,\ c=15{\cdot}64\ \text{Å};\ \beta=98°\ 15'.$$

The metal atom is bonded to the terminal nitrogen and to the oxygen atom of the first peptide residue. In the crystal, the terminal carboxyl group is coordinated to a second copper atom, so that the structure consists of infinite –Cu–peptide–Cu–peptide– chains. These are cross-linked by a hydrogen-bond network making efficient use of the water molecules and chloride ions. The copper atoms are 5-coordinated. The configuration of the ligand atoms is tetragonal pyramidal: the 'top' of the pyramid is occupied by a water molecule and the corners of the base by the terminal nitrogen and peptide oxygen of one peptide chain, a carboxylic oxygen of another peptide, and a chloride ion.

Introduction

This structure determination is the first in a program of crystallographic studies of metal-peptide complexes which has been initiated in this laboratory. The complexes are being studied in an effort to gain a detailed understanding of the steric relationships involved in metal-protein interaction. A preliminary report of this structure has been published (Cooper, Freeman, Robinson & Schoone, 1962).

Experimental

Blue-green crystals of glycylglycylglycinocopper(II) chloride sesquihydrate were grown by allowing a concentrated aqueous solution containing equimolar proportions of cupric chloride and glycylglycylglycine to stand for some days. The results of chemical analysis were: Calc., C=22·94, N=13·38, H=4·17%; Found, C=22·76, N=13·89, H=4·19%.

The crystals had a distorted boat shape: two parallel faces were planar, while the two other faces were distinctly curved and met at the 'bow' and 'stern' of the boat. The sides of the boat were not perpendicular to the top and bottom faces. The crystallographic b axis was parallel to the length of the boat.

Oscillation and calibrated Weissenberg photographs gave the following data:

$C_6H_{10}N_3O_4CuCl\cdot 1\frac{1}{2}H_2O$ F.W.=314·19

Monoclinic: $a=21{\cdot}36$, $b=6{\cdot}72$, $c=15{\cdot}64$ Å; $\beta=98°\ 15'$; $U=2221{\cdot}8$ Å^3, $D_m=1{\cdot}81$ g.cm^{-3}. $Z=8$. $D_x=1{\cdot}88$ g.cm^{-3}.

Systematic absences: hkl with $h+k=2n+1$; $h0l$ with $l=2n+1$.

Space group: $C2/c$ or Cc, from systematic absences; $C2/c$ (C_{2h}^6) confirmed by structure analysis.

Three-dimensional intensity data about the b and c axes were collected by the multiple-film equi-inclination Weissenberg method. A total of 2379 reflexions, of which 632 were too weak to be measured, were estimated visually. Copper $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å) was used for all photographs.

The crystal from which the b-axis data were collected was 0·24 mm long and had a cross-section of 0·20 × 0·21 mm^2. For the c-axis data, an irregular crystal fragment had a maximum dimension of 0·19 mm parallel to the rotation axis and a cross-section of approximately 0·12 × 0·13 mm^2. Absorption corrections were not made ($\mu=52{\cdot}4$ cm^{-1}). The Lorentz-polarization-Tunell corrections were applied to the two sets of three-dimensional data, which were then correlated and placed upon a common scale.

Solution of the structure

The statistical $N(z)$ test of Howells, Phillips & Rogers (1950), applied to the $h0l$ to $h3l$ data, indicated that

* Present address: Department of Chemistry, University of Manchester, England.

† Permanent address: Crystallography Laboratory, Catharijnesingel 51/2, Utrecht, Netherlands.

the space group was centrosymmetric. The copper and chlorine positions were readily obtained from the three-dimensional Patterson function, which was also consistent with the centrosymmetric space group $C2/c$.

In the first three-dimensional electron density synthesis, a reflexion was included only when $|F_c|$ was greater than one-eighth of the maximum possible copper and chlorine contributions. A second Fourier synthesis sufficed to define the structure completely. One atom, corresponding to the oxygen atom of a water molecule, was discovered on the twofold axis. This discovery added $\frac{1}{2}H_2O$ to the formula and accounted for a discrepancy between the chemical

Table 1. *Details of the refinement*

No. of cycles	Matrix approximation	Temperature factors	Final R (all F's)	Weighting scheme	Treatment of F_{unobs}	Machine	Program reference
2	Diagonal	Single isotropic	0·17	$\sqrt{w}=1$	Omitted	ZEBRA	Schoone (1961)
5	3×3 positional and 6×6 vibrational matrices for each atom	Individual anisotropic	0·132	$F^*=8F_{min}$ If $\lvert F_o\rvert \le \lvert F^*\rvert$, $\sqrt{w}=\lvert F_o\rvert/\lvert F^*\rvert$. If $\lvert F_o\rvert > \lvert F^*\rvert$, $\sqrt{w}=\lvert F^*\rvert/\lvert F_o\rvert$.	$F_{unobs}=\frac{1}{2}F_{min}$	DEUCE	Rollett (1961)
2	Full matrix	Individual anisotropic	0·119	$\sqrt{w}=1/\sigma(F_o)$ from $\lvert\Delta F\rvert/\lvert F_o\rvert$ plot	$F_{unobs}=\frac{1}{2}F_{min}$	IBM 7090	Busing & Levy (1961)

Table 2. *Final atomic parameters and their standard deviations*

Atom	x/a	y/b	z/c	σ_x	σ_y	σ_z
Cu	0·16424	−0·05413	0·72219	0·0013 Å	0·0015 Å	0·0012 Å
Cl	0·23099	−0·11087	0·84405	0·0024	0·0027	0·0022
C(1)	0·21077	−0·05071	0·56025	0·0088	0·0109	0·0081
C(2)	0·14973	0·07428	0·55631	0·0085	0·0104	0·0083
C(3)	0·07001	0·26045	0·46569	0·0096	0·0102	0·0099
C(4)	0·07828	0·48602	0·45461	0·0096	0·0099	0·0091
C(5)	0·04280	0·77080	0·36624	0·0098	0·0093	0·0091
C(6)	0·09400	0·80975	0·31098	0·0094	0·0102	0·0086
N(1)	0·23238	−0·09675	0·64956	0·0075	0·0087	0·0070
N(2)	0·13085	0·16103	0·48253	0·0077	0·0081	0·0070
N(3)	0·04070	0·55828	0·38852	0·0070	0·0086	0·0067
O(1)	0·11953	0·07956	0·61747	0·0058	0·0067	0·0053
O(2)	0·11303	0·58224	0·50480	0·0083	0·0089	0·0070
O(3)	0·09461	0·99459	0·28420	0·0062	0·0058	0·0058
O(4)	0·13230	0·68964	0·29388	0·0070	0·0073	0·0066
$O(5_w)$	0·12147	−0·36168	0·68339	0·0073	0·0076	0·0067
$O(6_w)$	0·00000	0·29531	0·25000	0·0000	0·0104	0·0000

Mean values of coordinate s.d.'s (σ):
Copper 0·0013, oxygen 0·0068, carbon 0·0094, chlorine 0·0024, nitrogen 0·0079 Å.

Table 3. *Final anisotropic thermal parameters b_{ij} and their standard deviations (in parentheses)**

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu	0·00160(03)	0·01611(034)	0·00205(05)	0·00074(10)	0·00037(02)	0·00023(13)
Cl	0·00179(06)	0·02376(078)	0·00224(09)	0·00071(17)	0·00007(06)	0·00079(21)
C(1)	0·00191(22)	0·01723(234)	0·00234(34)	0·00154(74)	0·00029(22)	−0·00082(90)
C(2)	0·00152(20)	0·01544(248)	0·00256(36)	0·00016(67)	−0·00035(21)	−0·00093(85)
C(3)	0·00179(24)	0·01530(258)	0·00363(44)	0·00057(65)	0·00032(27)	0·00146(89)
C(4)	0·00176(23)	0·01725(290)	0·00277(39)	−0·00048(63)	−0·00012(25)	−0·00002(84)
C(5)	0·00221(25)	0·01026(226)	0·00330(43)	−0·00087(65)	0·00109(26)	0·00220(81)
C(6)	0·00166(23)	0·01593(261)	0·00234(37)	−0·00088(67)	0·00003(23)	−0·00020(81)
N(1)	0·00180(19)	0·02176(259)	0·00246(32)	0·00170(59)	0·00042(19)	0·00142(74)
N(2)	0·00195(20)	0·01385(207)	0·00231(32)	0·00051(53)	0·00029(20)	0·00092(66)
N(3)	0·00183(19)	0·01441(190)	0·00250(31)	−0·00004(61)	0·00010(20)	0·00138(75)
O(1)	0·00168(14)	0·01700(176)	0·00213(24)	0·00135(46)	0·00061(15)	0·00049(58)
O(2)	0·00384(26)	0·02465(249)	0·00331(32)	−0·00282(68)	−0·00125(24)	0·00252(76)
O(3)	0·00183(16)	0·01176(179)	0·00269(26)	−0·00067(38)	0·00073(16)	0·00085(51)
O(4)	0·00233(19)	0·01697(190)	0·00354(32)	0·00092(52)	0·00100(20)	−0·00057(63)
$O(5_w)$	0·00264(20)	0·01982(201)	0·00361(32)	−0·00092(53)	0·00045(20)	−0·00043(67)
$O(6_w)$	0·00189(24)	0·01774(272)	0·00438(49)	0·00000(—)	−0·00042(27)	0·00000(—)

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

Table 4. *Observed and calculated* structure factors for glycylglycylglycinocopper(II) sesquihydrate*

The scale factor $k=1\cdot752$ (s.d. $=0\cdot007$) has been applied to the F_c to bring them to the arbitrary scale of the F_o

h	k	l	F_o	kF_c
6	0	0	43.0	-35.2
8			120.0	119.6
10			87.0	-80.5
12			35.0	41.7
14			19.0	-13.0
16			53.0	-52.9
18			74.0	70.5
20			35.0	-36.0
22			<4.0	5.9
24			33.0	26.0
26			17.0	19.1
2	0	2	59.0	78.6
4			150.0	177.4
6			21.0	6.4
8			72.0	-69.8
10			56.0	60.9
12			136.0	-143.6
14			65.0	64.0
16			48.0	46.6
18			56.0	-54.7
20			54.0	-51.2
22			<3.0	7.9
24			<3.0	-6.8
26			<3.0	-1.4
-2			100.0	110.3
-4			129.0	-134.0
-6			221.0	-255.4
-8			<6.0	32.8
-10			<8.0	16.0
-12			87.0	-92.6
-14			29.0	29.0
-16			65.0	63.4
-18			62.0	-63.3
-20			63.0	61.2
-22			22.0	-18.0
-24			33.0	-31.7
-26			17.0	11.9
0	0	4	93.0	-98.8
2			58.0	57.1
4			192.0	-229.1
6			122.0	128.9
8			89.0	84.1
10			76.0	-75.0
12			104.0	104.1
14			21.0	18.4
16			34.0	-26.0
18			34.0	30.6
20			51.0	45.0
22			69.0	-62.1
24			<4.0	9.5
26			5.0	-7.5
-4			198.0	-223.8
-6			149.0	162.6
-8			167.0	-166.7
-10			120.0	121.3
-12			117.0	116.9
-14			18.0	18.8
-16			15.0	3.8
-18			<4.0	-.2
-20			42.0	-37.4
-22			<3.0	.2
-24			51.0	48.9
-26			42.0	-39.6
0	0	6	73.0	62.6
2			82.0	-73.7
4			165.0	170.0
6			223.0	-236.3
8			45.0	-46.5
10			46.0	40.1
12			25.0	-23.4
14			62.0	-58.5
16			83.0	78.9
18			27.0	26.0
20			58.0	-55.8
22			38.0	33.5
24			16.0	-15.6
-2			56.0	-43.9
-4			112.0	-132.6
-6			51.0	-57.0
-8			272.0	271.0
-10			28.0	-34.3
-12			85.0	-93.5
-14			65.0	65.7
-16			44.0	-45.0
-18			57.0	-55.0
-20			16.0	14.0
-22			21.0	21.1
-24			44.0	-46.7
-26			32.0	28.1
0	0	8	30.0	30.0
2			125.0	123.3
4			85.0	-80.7
6			55.0	56.9
8			74.0	70.5
10			62.0	-58.2
12			73.0	-68.8
14			37.0	34.3
16			30.0	-26.0
18			50.0	48.1
20			21.0	17.4
22			14.0	-14.8
-2			56.0	-64.4
-4			136.0	134.3
-8			46.0	-53.3
-10			32.0	32.6
-12			48.0	49.9
-14			119.0	-118.9
-16			74.0	68.2
-18			<3.0	.7
-20			48.0	-45.4
-22			29.0	26.1
-24			35.0	33.5
0	0	10	15.0	-6.7
2			28.0	23.7
4			32.0	-25.7
6			44.0	43.5
8			39.0	-34.2
10			63.0	62.7
12			26.0	-20.9
14			92.0	-97.3
16			53.0	52.8
18			<4.0	-8.0
20			15.0	-15.4
-2			103.0	100.8
-4			217.0	-247.1
-6			31.0	32.9
-8			70.0	68.6
-10			31.0	-36.2
-12			46.0	-37.5
-14			42.0	40.4
-16			48.0	-45.2
-18			<4.0	53.5
-20			49.0	53.5
-22			20.0	-20.5
-24			<4.0	6.7
0	0	12	55.0	-57.1
2			32.0	31.5
4			20.0	13.9
6			37.0	-33.1
8			106.0	110.1
10			32.0	-29.2
12			26.0	-24.6
14			24.0	23.3
16			14.0	16.0
18			14.0	-19.6
-2			90.0	-91.6
-4			129.0	136.6
-6			38.0	-38.6
-8			43.0	-41.1
-10			82.0	82.0
-12			<2.0	-1.8
-14			31.0	-27.7
-16			18.0	17.0
-18			30.0	26.6
-20			34.0	-30.8
-22			33.0	32.3
-24			19.0	-24.6
0	0	14	60.0	61.6
2			72.0	-74.0
4			13.0	-18.0
6			31.0	30.3
8			39.0	-36.8
10			32.0	31.9
12			<2.0	-1.3
14			19.0	-17.6
16			18.0	-19.3
-2			42.0	-42.2
-4			<3.0	-8.2
-6			32.0	31.1
-8			51.0	51.1
-10			96.0	-95.0
-12			58.0	56.5
-14			12.0	9.9
-16			51.0	-46.8
-18			<2.0	1.1
-20			8.0	12.2
-22			9.0	-10.0
0	0	16	51.0	-50.1
2			74.0	79.4
4			40.0	-38.1
6			28.0	-31.2
8			28.0	27.4
10			34.0	37.4
12			39.0	-41.5
-2			18.0	18.0
-4			12.0	11.0
-6			17.0	17.5
-8			<4.0	-7.8
-10			29.0	30.7
-12			56.0	-58.2
-14			<4.0	9.0
-16			28.0	31.2
-18			26.0	-25.9
0	0	18	49.0	55.0
2			47.0	-45.6
4			15.0	-15.2
6			20.0	19.7
8			17.0	15.7
-2			<4.0	-6.7
-4			23.0	-24.6
-6			36.0	31.5
-8			32.0	-32.2
-10			<3.0	-2.7
-12			15.0	14.1
-14			<2.0	-2.4
-16			16.0	-30.2
-2	0	20	<3.0	3.8
-4			26.0	29.6
-6			30.0	-38.7
-8			18.0	27.5
5	1	0	112.0	120.5
7			<4.0	11.5
9			22.0	-23.4
11			<4.0	-6.0
13			105.0	119.3
15			105.0	-116.6
17			24.0	26.2
19			29.0	26.6
21			14.0	-15.1
23			<3.0	-5.6
25			14.0	11.7
3	1	1	47.0	36.2
5			106.0	-106.7
7			14.0	-18.2
9			12.0	-14.4
11			35.0	-31.0
13			85.0	-88.7
15			52.0	46.3
17			16.0	-17.0
19			<4.0	10.6
21			<3.0	6.3
23			13.0	12.8
25			22.0	-20.7
-3			52.0	67.0
-5			67.0	-97.2
-7			30.0	35.1
-9			30.0	-25.1
-11			34.0	27.7
-13			45.0	-51.1
-15			20.0	22.0
-17			55.0	-63.8
-19			22.0	-20.0
-21			24.0	18.7
1	1	2	184.0	-180.0
3			52.0	49.6
5			62.0	67.1
7			58.0	-63.8
9			57.0	57.9
11			57.0	-50.8
13			62.0	-63.0
15			100.0	106.8
17			<4.0	-7.3
19			23.0	-21.7
21			<3.0	9.4
23			28.0	26.8
25			24.0	-25.5
-1			40.0	-62.5
-3			126.0	168.3
-5			37.0	-56.1
-7			97.0	110.4
-9			100.0	106.7
-11			89.0	-96.1
-13			71.0	-77.3
-15			100.0	111.7
-17			35.0	-32.2
-19			20.0	-18.8
-21			33.0	34.5
-23			32.0	-33.3
-25			9.0	-8.6
1	1	3	118.0	104.3
3			166.0	149.8
5			<4.0	-10.3
7			91.0	89.6
9			17.0	-19.7
11			<3.0	2.1
13			18.0	-12.0
15			27.0	-22.0
17			18.0	16.5
19			12.0	13.2
21			<3.0	-6.0
23			<4.0	-7.7
25			25.0	26.1
-1			36.0	-26.8
-3			126.0	-141.4
-5			95.0	109.2
-7			45.0	39.1
-9			71.0	-73.2
-11			32.0	32.0
-13			16.0	13.5
-15			20.0	-22.9
-17			<3.0	-1.2
-19			38.0	39.2
-21			<3.0	-6.6
-23			13.0	15.1
-25			<2.0	-.3
1	1	4	10.0	-2.9
3			90.0	-85.7
5			66.0	-66.3
7			164.0	166.3
9			126.0	126.0
11			<3.0	0
13			42.0	44.1
15			52.0	-49.6
17			49.0	-46.9
19			58.0	57.7
21			<4.0	-6.3
23			<2.0	-3.5
25			19.0	17.6
-1			110.0	81.9
-3			12.0	-13.4
-5			168.0	161.8
-7			40.0	-36.0
-9			200.0	-199.3
-11			124.0	127.1
-13			18.0	-18.2
-15			28.0	-26.5
-17			20.0	-16.5
-19			22.0	20.1
-21			50.0	-34.8
-23			60.0	38.5
-25			<4.0	-8.7
-27			19.0	-14.8
1	1	5	164.0	-145.2
3			97.0	-88.1
5			125.0	111.3
7			<3.0	4.3
9			56.0	49.0
11			62.0	-54.4
13			9.0	-1.1
15			24.0	-20.7
17			24.0	22.6
19			33.0	-29.5
21			<4.0	8.0
23			<4.0	-5.5
25			14.0	-12.1
-1			16.0	-7.1
-3			25.0	27.7
-5			106.0	-86.7
-7			89.0	-77.7
-9			75.0	75.9
-11			42.0	-40.2
-13			43.0	43.7
-15			27.0	-25.5
-17			<5.0	5.4
-19			19.0	-15.6
-21			21.0	23.8
-23			22.0	-21.5
-25			<2.0	.7
1	1	6	151.0	-137.4
3			173.0	159.8
5			123.0	119.6
7			178.0	-175.7
9			59.0	49.1
11			59.0	50.8
13			<3.0	-1.3
15			44.0	-44.6
17			39.0	40.7
19			60.0	-60.3
21			21.0	21.9
23			16.0	16.0
-1			37.0	35.7
-3			12.0	21.7
-5			45.0	-45.3
-7			42.0	38.6
-9			64.0	63.0
-11			167.0	-175.1
-13			50.0	50.7
-15			46.0	47.4
-17			15.0	-20.0
-19			<5.0	-10.4
-21			50.0	49.1
-23			31.0	-29.8
1	1	7	52.0	51.8
3			18.0	6.6
5			28.0	-25.2
7			26.0	17.7
9			<4.0	-2.9
11			37.0	31.5
13			14.0	14.2
15			<5.0	8.0
17			23.0	-23.4
19			35.0	34.9
21			<3.0	-1.2
-1			127.0	-118.3
-3			29.0	19.9
-5			100.0	86.2
-7			65.0	56.3
-9			51.0	-50.8
-11			63.0	73.0
-13			21.0	19.1
-15			19.0	-18.2
-17			22.0	-22.0
-19			<2.0	-1.0
-21			17.0	17.5
1	1	8	110.0	121.2
3			59.0	-55.1
5			109.0	-96.0
7			89.0	79.4
9			56.0	52.1
11			52.0	-46.8
13			32.0	27.3
15			<3.0	-2.9
17			20.0	-20.9
19			19.0	18.4
21			16.0	-16.6
23			13.0	-10.5
-1			122.0	-117.9
-3			<3.0	-1.4
-5			74.0	61.5
-7			50.0	-46.7
-9			70.0	-69.4
-11			51.0	55.1
-13			25.0	-25.8
-15			16.0	12.8
-17			72.0	79.0
-19			66.0	-64.6
-21			18.0	-14.4
-23			29.0	25.6
1	1	9	65.0	-83.9
3			30.0	27.7
5			<3.0	3.9
7			11.0	-12.2
9			54.0	-45.9
11			41.0	39.3
13			48.0	-45.6
15			<5.0	-9.7
17			14.0	12.0
19			<4.0	3.2
-1			23.0	20.4
-3			13.0	11.3
-5			<3.0	4.0
-7			50.0	39.6
-9			21.0	-13.8
-11			42.0	-38.1
-13			23.0	-25.8
-15			14.0	10.0
-17			37.0	-34.5
-19			26.0	25.3
-21			13.0	-11.2
1	1	10	87.0	-87.6
3			19.0	14.3
5			21.0	20.9
7			35.0	-29.5
9			70.0	-65.3
11			108.0	106.1
13			41.0	-38.2
15			8.0	22.5
17			12.0	12.9
19			11.0	-19.4
21			14.0	-10.2
-1			89.0	82.7
-3			30.0	22.3
-5			121.0	-108.1
-7			88.0	81.4
-9			<5.0	-9.6
-11			13.0	13.6
-13			31.0	26.2
-15			8.0	7.4
-17			57.0	-56.4
-19			55.0	55.3
-21			14.0	-13.8
-23			22.0	-22.6
1	1	11	17.0	17.7
3			22.0	-19.3
5			12.0	7.7
7			26.0	18.3
9			57.0	51.8
11			41.0	-38.0
13			14.0	15.3
15			15.0	-14.2
17			<4.0	4.3
19			<4.0	-5.7
-1			<5.0	8.3
-3			27.0	22.7
-5			35.0	32.1
-7			75.0	-65.6
-9			37.0	33.6
-11			12.0	-10.2
-13			<3.0	1.3
-15			20.0	-15.2
-17			35.0	33.8
-19			11.0	-11.9
-21			17.0	14.6
-23			14.0	10.3
1	1	12	27.0	24.9
3			57.0	53.6
5			61.0	-58.5
7			<4.0	-3.3
9			16.0	16.8
11			58.0	-58.0
13			27.0	26.7
15			21.0	21.1
17			12.0	-11.7
19			10.0	-15.0
-1			89.0	-89.1
-3			14.0	39.2
-5			108.0	101.4
-7			105.0	-93.5
-9			25.0	19.8
-11			<5.0	8.5
-13			14.0	-10.4
-15			<3.0	-1.8
-17			31.0	25.3
-19			52.0	-48.5
-21			<2.0	2.9
-23			22.0	21.8
1	1	13	18.0	-17.8
3			20.0	-16.9
5			42.0	39.3
7			32.0	-33.6
9			<6.0	-8.8
11			30.0	26.9
13			<3.0	2.6
15			12.0	-11.4
-1			28.0	-29.2
-3			14.0	13.3
-5			<5.0	-6.9
-7			15.0	9.4
-9			34.0	-31.1
-11			<6.0	11.4
-13			21.0	19.5
-15			20.0	-21.0
-17			<4.0	-5.9
-19			23.0	22.2
1	1	14	51.0	50.7
3			41.0	-41.8
5			61.0	62.2
7			45.0	-42.4
9			17.0	-14.8
11			21.0	19.0
13			<5.0	7.8
15			24.0	-24.5
-1			31.0	25.2
-3			41.0	-37.1
-5			<5.0	-8.3
-7			46.0	43.4
-9			46.0	-40.8
-11			30.0	-27.0
-13			79.0	72.1
-15			49.0	-46.8
-17			17.0	-15.8
-19			22.0	16.7
1	1	15	34.0	-33.3
3			22.0	24.3
5			26.0	-24.2
7			19.0	20.7
9			<6.0	-4.7
11			<5.0	9.0
13			<5.0	-9.4
15			17.0	22.0
-1			<3.0	-.9
-3			36.0	34.5
-5			18.0	14.7
-7			12.0	-10.8
-9			<2.0	1.6
-11			21.0	20.3
-13			33.0	-32.8
-15			27.0	26.8
-17			<3.0	-5.5
1	1	16	<3.0	-1.4
3			63.0	59.7
5			29.0	-27.2
7			<3.0	3.8
9			<4.0	7.7
11			<3.0	-2.1
13			16.0	-19.2
-1			52.0	-52.2
-3			20.0	22.1
-5			<5.0	-8.5
-7			17.0	-17.2
-9			<6.0	13.8
-11			<5.0	5.7
-13			44.0	-45.5
-15			51.0	50.0
-17			12.0	-10.3
1	1	17	<3.0	-.1
3			10.0	-7.9
5			<3.0	-.4
7			<4.0	-12.1
9			<2.0	-1.0
-1			18.0	15.5
-3			11.0	-13.8
-5			24.0	23.9
-7			18.0	-16.3
-9			15.0	-16.9
-11			<5.0	-5.6
-13			22.0	22.5
-15			25.0	-23.3
1	1	18	<5.0	6.5
3			24.0	-24.5
5			<5.0	5.7
7			18.0	19.1
-1			28.0	28.8
-3			64.0	-63.7
-5			25.0	26.9
-7			14.0	11.6
-9			17.0	-17.6
-11			<5.0	11.2
-13			26.0	26.9
-15			17.0	-21.5
1	1	19	<5.0	4.1
3			<5.0	4.9
5			10.0	13.2
-1			15.0	-14.6
-3			22.0	22.1
-5			8.0	-13.0
-7			<4.0	-4.0
-9			<4.0	8.1
-11			<3.0	-3.6
0	2	0	151.0	179.4
2			117.0	-111.7
4			69.0	-64.8
6			31.0	42.6
8			27.0	-37.5
10			24.0	-26.8
12			75.0	73.9
14			41.0	-38.3
16			66.0	-62.3
18			40.0	40.3
20			<5.0	-8.0
22			27.0	-22.9
24			18.0	17.5
26			<3.0	4.2
0	2	1	124.0	-133.7
2			233.0	264.7
4			65.0	-64.1
6			121.0	-116.0
8			28.0	18.2
10			154.0	176.2
12			60.0	-67.2
14			21.0	-20.7
16			30.0	27.3
18			14.0	-13.5
20			<6.0	9.5
22			<4.0	-.5
24			<3.0	-1.4
26			6.0	-6.9
-2			49.0	44.5
-4			86.0	[illegible]
-6			57.0	42.2
-8			26.0	24.7
-10			<6.0	6.9
-12			35.0	-41.3
-14			24.0	22.2
-16			62.0	62.5
-18			56.0	-57.2
-20			35.0	32.8
-22			<1.0	-5.6
-24			<4.0	5.0
-26			7.0	-7.6
0	2	2	53.0	-53.7
2			38.0	-23.8
4			67.0	[illegible]
6			25.0	-32.1
8			35.0	29.0
10			51.0	50.9
12			62.0	-65.3
14			35.0	29.7
16			43.0	38.6
18			24.0	-27.4
20			<5.0	-7.0
22			24.0	21.7
24			11.0	-7.8
-2			148.0	-134.9
-4			<4.0	-3.6
-6			77.0	-76.9
-8			97.0	101.1
-10			52.0	52.5
-12			59.0	-97.3
-14			30.0	32.5
-16			29.0	26.6
-18			43.0	-38.9
-20			31.0	28.9
-22			<4.0	10.3
-24			12.0	-11.0
-26			12.0	11.7
0	2	3	52.0	53.8
2			3.0	-.4
4			110.0	-121.6
6			40.0	46.0
8			46.0	42.7
10			111.0	-114.6
12			71.0	66.0
14			[illegible]	7.0
16			[illegible]	[illegible]
18			17.0	-14.8
20			15.0	13.6
22			27.0	-24.6
24			16.0	13.3
-2			52.0	-54.0
-4			111.0	-108.2
-6			119.0	125.1
-8			73.0	-73.6
-10			30.0	28.4
-12			19.0	17.3
-14			31.0	-28.5
-16			25.0	-23.8
-18			52.0	54.9
-20			23.0	-22.8
-22			25.0	-22.7
-24			<4.0	8.7
-26			<4.0	-3.4
0	2	4	41.0	47.3
2			6.0	13.7
4			92.0	-96.3
6			39.0	40.5
8			15.0	10.3
10			58.0	-54.5
12			54.0	51.0
14			<3.0	1.6
16			60.0	-60.1
18			20.0	19.6
20			11.0	7.6
22			28.0	-27.7
24			14.0	10.9
-2			81.0	-74.5
-4			39.0	-31.4
-6			65.0	63.3
-8			126.0	-138.9
-10			26.0	23.8
-12			69.0	67.8
-14			53.0	-58.6
-16			29.0	-27.1
-18			26.0	25.3
-20			<3.0	-2.2
-22			<3.0	3.9
-24			16.0	16.8
-26			21.0	-21.9
0	2	5	13.0	14.2
2			49.0	-50.1
4			141.0	146.4
6			131.0	-123.3
8			26.0	-19.3
10			61.0	60.0
12			<4.0	5.1
14			31.0	-25.9
16			14.0	9.9
18			24.0	23.9
20			22.0	-20.7
22			33.0	32.4
24			22.0	-23.9
-2			54.0	-41.4
-4			124.0	115.3
-6			54.0	-49.6
-8			94.0	93.8
-10			100.0	-90.5
-12			23.0	18.0
-14			70.0	68.6
-16			31.0	-30.6
-18			34.0	-30.6
-20			18.0	16.7
-22			27.0	24.7
-24			40.0	-42.8
-26			28.0	28.8
0	2	6	79.0	-77.7
2			67.0	-67.1
4			146.0	151.1
6			39.0	-34.1
8			41.0	-42.3
10			49.0	48.9
12			22.0	16.7
14			26.0	-21.3
16			37.0	38.9
18			<3.0	1.3
20			22.0	-20.5
-2			85.0	82.3
-4			43.0	-40.4
-6			39.0	-31.6
-8			126.0	131.8
-10			<5.0	-8.9
-12			53.0	-54.6
-14			41.0	41.0
-16			16.0	14.9
-18			13.0	12.8
-20			28.0	29.0
-22			<4.0	-5.3
-24			21.0	-18.8
0	2	7	<3.0	-1.3
2			122.0	123.1
4			95.0	-101.3
6			35.0	30.1
8			48.0	-40.1
10			<5.0	-7.0
12			<5.0	4.8
14			28.0	26.9
16			58.0	-54.1
18			<3.0	2.0
20			26.0	26.5
22			16.0	-19.2
-2			53.0	-51.2
-4			9.0	9.3
-6			29.0	27.1
-8			45.0	-46.1
-10			<3.0	.3
-12			40.0	35.4
-14			66.0	-67.5
-16			23.0	22.8
-18			<5.0	-3.4
-20			<4.0	-6.2
-22			<4.0	-2.4
-24			15.0	16.3
-26			17.0	-18.5
0	2	8	14.0	17.5
2			43.0	43.4
4			121.0	-124.8
6			23.0	-23.8
8			73.0	68.0
10			33.0	-34.7
12			15.0	-16.3
14			<4.0	7.4
16			21.0	-19.4
18			<5.0	12.4
20			14.0	13.7
22			16.0	-15.2
-2			62.0	-55.4
-4			57.0	53.1
-6			21.0	19.5
-8			56.0	-51.0
-10			36.0	34.5
-12			17.0	16.1
-14			62.0	-64.1
-16			33.0	29.8
-18			<3.0	-.5
-20			39.0	-38.4
-22			17.0	15.3
0	2	9	[illegible]	-39.4
2			26.0	18.7
4			59.0	54.4
6			15.0	10.2
8			56.0	-55.0
10			36.0	38.2
12			39.0	36.2
14			57.0	-58.8
16			33.0	31.6
18			<4.0	-4.9
20			<3.0	3.3
-2			67.0	66.1
-4			101.0	-91.7
-6			62.0	58.5
-8			18.0	13.5
-10			34.0	-30.5
-12			45.0	-43.2
-14			75.1	76.6
-16			30.0	-27.8
-18			<4.0	-9.1
-20			26.0	25.9
0	2	10	2.0	.6
2			23.0	-24.5
4			44.0	48.3
6			32.0	30.0
8			65.0	-64.5
10			29.0	27.1
12			15.0	13.6
14			31.0	-29.6
16			28.0	25.4
18			<2.0	1.5
20			17.0	-16.6
-2			99.0	95.9
-4			60.0	-56.8
-6			<3.0	1.7
-8			61.0	59.1
-10			25.0	-24.3
-12			18.0	-16.9
-14			<5.0	-8.6
-16			33.0	-33.2
-18			32.0	29.0
-20			34.0	36.1
-22			22.0	-24.3
0	2	11	23.0	24.5
2			<4.0	10.9
4			21.0	19.6
6			75.0	-76.4
8			47.0	47.1
10			<4.0	5.1
12			<3.0	-1.5
14			<3.0	3.5
16			19.0	-19.2
18			10.0	12.0
-2			102.0	-102.7
-4			81.0	61.4
-6			62.0	-58.2
-8			11.0	-10.9
-10			37.0	32.6
-12			<3.0	-3.6
-14			18.0	-18.9
-16			16.0	17.5
-18			17.0	17.0
-20			30.0	-34.7
-22			21.0	23.8
0	2	12	35.0	-33.7
2			26.0	26.9
4			18.0	-28.9
6			<3.0	-2.7
8			58.0	60.4
10			22.0	-19.8
12			32.0	-32.3
14			17.0	15.3
16			<3.0	-1.5
18			19.0	-18.5
-2			31.0	-25.3
-4			76.0	73.1
-6			50.0	-43.9
-8			59.0	-52.4
-10			21.0	13.5
-12			20.0	-20.3
-14			17.0	-12.5
-16			39.0	44.0
-18			<4.0	3.9
-20			24.0	-23.6
-22			21.0	21.8
0	2	13	23.0	24.7
2			35.0	-37.0
4			<3.0	1.3
6			37.0	35.7
8			56.0	-53.3
10			26.0	26.3
12			<3.0	2.7
14			<3.0	7.0
16			9.0	-6.7
-2			22.0	-18.9
-4			33.0	-30.6
-6			<4.0	-5.7
-8			48.0	44.9
-10			20.0	-17.3
-12			31.0	30.1
-14			17.0	-14.6
-16			10.0	-10.0
-18			<5.0	6.6
-20			20.0	20.1
-22			23.0	-27.5
0	2	14	48.0	45.5
2			35.0	-33.7
4			<3.0	-4.2
6			17.0	14.4
8			22.0	-24.6
10			25.0	23.5
12			30.0	30.2
14			9.0	-10.4
-2			<6.0	-10.2
-4			33.0	-36.0
-6			16.0	14.3
-8			15.0	17.9
-10			31.0	-27.8
-12			39.0	43.0
-14			20.0	16.6
-16			29.0	-29.8
-18			23.0	24.4
-20			16.0	12.7
0	2	15	73.0	-80.4
2			54.0	55.5
4			<5.0	7.9
6			26.0	-28.4
8			<4.0	-4.1
10			<3.0	4.1
12			<3.0	-7.3
-2			24.0	25.1
-4			24.0	24.6
-6			22.0	20.8
-8			56.0	-57.5
-10			43.0	44.8
-12			21.0	-20.9
-14			<3.0	1.1
-16			<2.0	1.7
-18			18.0	-18.9
0	2	16	33.0	-33.5
2			14.0	11.9
4			13.0	-11.0
6			18.0	-18.7
8			<5.0	8.4
10			<3.0	-.4
12			22.0	[illegible]
-2			<4.0	9.7
-4			31.0	30.1
-6			14.0	-13.6
-8			<5.0	8.4
-10			23.0	23.5
-12			36.0	-42.0
-14			<3.0	5.2
-16			28.0	29.8
-18			12.0	-15.2
0	2	17	43.0	47.6
2			[illegible]	-15.6
4			16.0	17.1
6			13.0	-13.1
8			<4.0	9.6
-2			29.0	[illegible]
-4			<3.0	-5.7
-6			19.0	18.1
-8			<3.0	-4.8
-10			10.0	-17.8
-12			13.0	11.6
-14			<2.0	-.5
-16			15.0	[illegible]
0	2	18	53.0	55.7
2			14.0	-13.5
4			21.0	-22.8
6			13.0	13.9
-2			[illegible]	7.5
-4			17.0	-17.1
-6			17.0	[illegible]
-8			19.0	-20.1
-10			10.0	-10.8
-12			[illegible]	[illegible]
0	2	19	[illegible]	[illegible]
-2			<4.0	-5.1
-4			8.0	9.2
-6			30.0	-34.4
-8			27.0	26.6
1	3	0	35.0	45.4
3			90.0	-63.9
5			[illegible]	-1.7
7			[illegible]	76.1
9			[illegible]	[illegible]
11			57.0	[illegible]
13			[illegible]	[illegible]
15			[illegible]	[illegible]
17			<3.0	4.9
19			26.0	33.0
21			24.0	[illegible]
23			<2.0	[illegible]
25			12.0	3.5
1	3	1	61.0	-60.2
3			119.0	116.8
5			81.0	-71.1
7			31.0	-25.3
9			68.0	65.9
11			15.0	19.6
13			78.0	-73.0
15			82.0	78.1
17			17.0	-19.3
19			<3.0	[illegible]
21			<3.0	3.3
23			9.0	13.4
25			17.0	[illegible]
-1			[illegible]	[illegible]
-3			205.0	155.0
-5			70.0	-54.2
-7			22.0	17.4
-9			<6.0	12.1
-11			32.0	25.4
-13			70.0	-66.4
-15			78.0	74.2
-17			33.0	-27.5
-19			<3.0	-.3
-21			17.0	20.1
-23			8.0	-12.6
-25			6.0	-6.6
1	3	2	200.0	-171.2
3			88.0	77.2
5			19.0	16.5
7			77.0	-78.6
9			13.0	12.9
11			9.0	-11.7
13			15.0	-15.4
15			<3.0	1.2
17			<3.0	7.9
19			11.0	-10.4
21			19.0	22.3
23			8.0	-9.9
25			<3.0	-8.5
-1			42.0	-40.1
-3			123.0	92.0
-5			72.0	52.3
-7			74.0	-70.9
-9			40.0	36.5
-11			21.0	-22.9
-13			<3.0	-4.0
-15			<3.0	4.2
-17			31.0	-30.7
-19			<3.0	9.8
-21			<3.0	7.4
-23			15.0	-20.0
-25			3.0	-12.2
1	3	3	73.0	58.4
3			141.0	-113.6
5			94.0	-64.8
7			143.0	149.8
9			87.0	-80.3
11			40.0	-36.9
13			41.0	40.1
15			17.0	-18.6
17			<5.0	-8.1
19			11.0	11.8
21			10.0	-12.9
23			16.0	-16.2
-1			123.0	96.7
-3			112.0	-97.1
-5			76.0	57.2
-7			8.0	6.0
-9			96.0	-92.6
-11			48.0	49.9
-13			<6.0	-10.1
-15			49.0	-46.3
-17			21.0	19.3
-19			21.0	23.8
-21			38.0	-41.7
-23			16.0	14.9
1	3	4	80.0	72.8
3			60.0	-57.1
5			32.0	26.2
7			12.0	15.8
9			10.0	-7.2
11			<6.0	-12.0
13			60.0	54.9
15			49.0	-50.4
17			<5.0	-12.5
19			31.0	29.3
21			<4.0	2.8
23			<3.0	3.5
-1			52.0	34.3
-3			21.0	6.1
-5			70.0	58.8
-7			25.0	-26.5
-9			30.0	-27.8
-11			30.0	31.6
-13			<5.0	.3
-15			35.0	-37.7
-17			38.0	35.8
-19			<4.0	-7.6
-21			<3.0	-3.5
-23			11.0	10.6
1	3	5	77.0	-77.0
3			<4.0	6.6
5			101.0	96.1
7			69.0	-67.6
9			53.0	50.5
11			25.0	-22.2
13			<4.0	7.8
15			<3.0	3.3
17			40.0	37.3
19			50.0	-54.5
21			19.0	19.7
23			<4.0	7.1
-1			95.0	76.4
-3			120.0	100.3
-5			91.0	-82.7
-7			52.0	-45.4
-9			79.0	72.5
-11			89.0	-65.1
-13			62.0	61.0
-15			<6.0	-10.5
-17			<4.0	-6.0
-19			<3.0	-.4
-21			52.0	54.2
-23			35.0	-39.6
1	3	6	75.0	-70.2
3			48.0	43.5
5			13.0	17.6
7			29.0	-24.6
9			<3.0	-1.9
11			28.0	31.5
13			48.0	-45.8
15			<3.0	12.0
17			<3.0	-2.4
19			16.0	-16.8
21			<3.0	-5.6
-1			<3.0	4.0
-3			35.0	33.6
-5			88.0	-78.2
-7			35.0	31.4
-9			24.0	-20.9
-11			40.0	-31.3
-13			17.0	-19.5
-15			33.0	36.2
-17			18.0	-17.3
-19			18.0	20.0
-21			<3.0	3.1
-23			22.0	-25.2
1	3	7	49.0	52.5
3			45.0	-38.7
5			10.0	-12.0
7			69.0	65.0
9			57.0	-58.4
11			14.0	-13.5
13			[illegible]	[illegible]
15			<5.0	11.8
17			44.0	[illegible]
19			31.0	35.3
21			<5.0	-13.0
-1			128.0	[illegible]
-3			21.0	[illegible]
-5			39.0	36.3
-7			41.0	-41.5
-9			96.0	[illegible]
-11			87.0	75.7
-13			<4.0	-6.0
-15			<4.0	-4.0
-17			29.0	30.3
-19			<5.0	-10.1
-21			[illegible]	-12.7
-23			[illegible]	13.8
1	3	8	24.0	-25.2
3			<3.0	1.3
5			[illegible]	-28.4
7			54.0	[illegible]
9			12.0	[illegible]
11			11.0	11.0
13			[illegible]	[illegible]
15			18.0	-16.1
17			[illegible]	[illegible]
19			11.0	12.3
21			[illegible]	15.8
-1			<2.0	1.5
-3			17.0	41.8
-5			[illegible]	43.1
-7			104.0	-94.0
-9			<5.0	[illegible]
-11			[illegible]	[illegible]
-13			<4.0	-1.7

* Correction: For $F(\overline{18},0,10)$, kF_c is $-6\cdot1$, not $53\cdot5$

Table 4 (*cont.*)

h	k	l	F_o	kF_c
-15			<4.0	-8.3
-17			26.0	22.8
-19			<3.0	-7.2
-21			13.0	-15.9
1	3	9	71.0	-64.4
3			<3.0	3.4
5			11.0	11.6
7			17.0	-17.4
9			32.0	-31.8
11			79.0	76.5
13			43.0	-47.3
15			13.0	10.7
17			24.0	29.8
19			<3.0	1.2
-1			96.0	86.4
-3			<4.0	-8.0
-5			70.0	-64.7
-7			81.0	75.0
-9			19.0	15.1
-11			44.0	-40.3
-13			38.0	38.2
-15			51.0	52.8
-17			52.0	-59.5
-19			17.0	17.9
1	3	10	<3.0	.8
3			17.0	-20.6
5			23.0	24.5
7			58.0	-60.1
9			<5.0	-5.3
11			17.0	12.6
13			<5.0	6.1
15			<4.0	-5.7
17			16.0	15.5
19			16.0	-18.2
-1			26.0	24.5
-3			29.0	-23.6
-5			52.0	-45.3
-7			44.0	45.8
-9			29.0	27.2
-11			45.0	-42.5
-13			29.0	26.1
-15			15.0	-19.7
-17			<3.0	-2.3
-19			<3.0	-.8
-21			<3.0	1.2
-23			13.0	-18.7
1	3	11	31.0	30.6
3			<4.0	-3.4
5			24.0	-16.9
7			14.0	-11.4
9			24.0	24.1
11			60.0	-71.5
13			24.0	26.4
15			<3.0	1.7
17			16.0	2.0
19			16.0	-7.1
-1			27.0	-27.2
-3			27.0	26.4
-5			55.0	47.7
-7			100.0	-94.9
-9			54.0	62.3
-11			<5.0	6.7
-13			33.0	-32.6
-15			37.0	-30.3
-17			36.0	43.7
-19			30.0	-37.6
-21			<3.0	-6.3
1	3	12	<3.0	9.3
3			<3.0	3.5
5			44.0	-9.0
7			27.0	25.3
9			<4.0	-5.4
11			14.0	-17.3
13			<3.0	-2.3
15			19.0	21.4
17			9.0	-16.0
-1			36.0	-27.1
-3			79.0	71.9
-5			<4.0	8.1
-7			47.0	-43.5
-9			46.0	-8.7
-11			41.0	38.5
-13			19.0	-22.4
-15			<4.0	4.6
-17			<3.0	10.2
-19			14.0	-16.3
1	3	13	<3.0	-3.0
3			34.0	-37.8
5			73.0	79.8
7			13.0	-9.8
9			18.0	-19.1
11			<5.0	9.3
13			<5.0	-6.9
15			<3.0	-7.7
-1			44.0	43.9
-3			<6.0	10.1
-5			37.0	-36.5
-7			18.0	19.0
-9			34.0	-33.9
-11			<4.0	-7.9
-13			28.0	31.4
-15			10.0	-15.4
-17			10.0	-14.6
-19			15.0	22.0
1	3	14	<3.0	-4.0
3			<3.0	-2.4
5			<5.0	12.8
7			<5.0	-.8
9			26.0	-35.4
11			18.0	22.0
13			<3.0	5.1
-1			36.0	43.5
-3			32.0	-36.6
-5			21.0	-29.5
-7			<3.0	5.2
-9			<4.0	1.0
-11			<5.0	4.4
-13			<4.0	9.5
-15			16.0	-16.9
-17			8.0	-12.6
-19			14.0	21.5
1	3	15	18.0	-26.6
3			54.0	59.1
5			26.0	-35.0
7			9.0	14.3
9			<4.0	8.5
11			<3.0	1.4
13			6.0	-17.4
-1			34.0	-37.6
-3			14.0	19.2
-5			<5.0	-5.3
-7			37.0	-44.8
-9			<5.0	5.1
-11			35.0	41.5
-13			31.0	-35.6
-15			30.0	36.5
1	3	16	<2.0	-1.8
3			9.0	12.7
5			<4.0	11.6
7			<5.0	-5.4
9			15.0	19.2
11			10.0	-24.8
-1			<3.0	-28.1
-3			<3.0	6.4
-5			<6.0	9.7
-7			<6.0	-13.5
-9			34.0	30.6
-11			11.0	-17.3
-13			<3.0	-4.2
-15			7.0	12.6
1	3	17	<4.0	-7.0
3			13.0	-20.0
5			6.0	14.6
7			<3.0	4.5
-1			9.0	14.0
-3			38.0	-41.9
-5			24.0	30.9
-7			<6.0	14.5
-9			8.0	-8.4
-11			<3.0	4.6
-13			23.0	33.3
1	3	18	<4.0	4.2
3			22.0	-33.9
5			5.0	12.2
-1			9.0	15.0
-3			<4.0	-1.6
-5			6.0	-12.9
-7			<3.0	2.3
-9			<3.0	-5.3
-11			12.0	22.5
2	4	0	74.0	78.8
4			11.0	-18.5
6			20.0	20.1
8			67.0	-86.7
10			10.0	13.1
12			42.0	41.5
14			<4.0	-2.7
16			12.0	-12.5
18			<4.0	-9.6
20			16.0	16.8
22			9.0	-9.8
24			10.0	16.5
0	4	1	113.0	-120.2
2			52.0	50.7
4			25.0	25.4
6			65.0	-64.4
8			37.0	38.6
10			50.0	53.3
12			62.0	-63.3
14			19.0	19.3
16			25.0	27.4
18			45.0	-42.6
20			17.0	-7.5
22			15.0	15.6
24			20.0	-23.1
-2			24.0	24.8
-4			64.0	-55.5
-6			58.0	-57.0
-8			42.0	39.8
-10			24.0	22.4
-12			79.0	-61.7
-14			20.0	20.3
-16			54.0	58.5
-18			40.0	-35.9
-20			<4.0	5.6
-22			<3.0	.7
-24			12.0	-10.8
0	4	2	6.0	-13.3
2			24.0	25.6
4			84.0	87.9
6			61.0	-62.5
8			10.0	7.6
10			26.0	-22.6
12			<5.0	8.5
14			<5.0	-4.4
16			26.0	23.5
18			15.0	-13.3
20			10.0	-12.3
22			<4.0	-8.2
-2			54.0	-49.5
-4			18.0	-9.9
-6			19.0	-10.2
-8			21.0	-16.1
-10			<4.0	-3.6
-12			31.0	-33.0
-14			46.0	46.9
-16			<5.0	-1.3
-18			<4.0	7.6
-20			16.0	-17.1
-22			<3.0	1.9
-24			10.0	-6.1
0	4	3	77.0	73.6
2			15.0	11.0
4			118.0	-117.6
6			47.0	46.5
8			40.0	39.0
10			43.0	-48.2
12			60.0	59.9
14			<6.0	11.3
16			24.0	-24.1
18			30.0	29.3
20			18.0	19.5
22			23.0	-20.4
-2			75.0	-65.2
-4			28.0	-23.6
-6			116.0	-113.0
-8			49.0	-49.6
-10			<6.0	8.9
-12			81.0	80.9
-14			27.0	-26.6
-16			7.0	-9.4
-18			34.0	34.2
-20			25.0	-26.0
-22			15.0	-17.4
-24			16.0	-18.5
0	4	4	59.0	61.7
2			44.0	-41.9
4			10.0	2.8
6			11.0	8.3
8			<5.0	6.3
10			18.0	-14.1
12			<4.0	2.2
14			32.0	31.4
16			17.0	-12.5
18			28.0	28.3
20			16.0	-16.7
22			<3.0	5.2
-2			33.0	-35.9
-4			34.0	30.4
-6			68.0	-62.4
-8			10.0	8.5
-10			23.0	22.3
-12			64.0	62.9
-14			15.0	-15.2
-16			<4.0	-.7
-18			<4.0	-3.6
-20			16.0	-18.9
-22			<3.0	6.1
0	4	5	<6.0	-14.8
2			74.0	-74.8
4			68.0	66.6
6			43.0	-43.9
8			46.0	-46.1
10			<6.0	-1.7
12			<5.0	-8.8
14			<5.0	-9.8
16			27.0	25.9
18			23.0	-23.4
20			<4.0	-9.3
22			29.0	34.1
-2			106.0	100.9
-4			27.0	-23.9
-6			92.0	-91.0
-8			114.0	114.1
-10			10.0	-11.5
-12			50.0	-49.1
-14			15.0	10.3
-16			15.0	-16.4
-18			29.0	-30.1
-20			17.0	18.1
-22			<3.0	3.0
0	4	6	73.0	-75.8
2			54.0	59.4
4			27.0	19.3
6			18.0	15.1
8			69.0	-72.7
10			14.0	-7.9
12			<6.0	-10.0
14			19.0	14.3
16			16.0	16.7
18			10.0	-11.7
20			10.0	9.8
-2			31.0	25.4
-4			35.0	-40.2
-6			33.0	34.4
-8			6.0	8.9
-10			11.0	10.7
-12			<4.0	-.9
-14			18.0	-17.2
-16			<4.0	-9.8
-18			20.0	-19.3
-20			21.0	23.4
-22			19.0	-22.8
0	4	7	27.0	26.4
2			85.0	95.2
4			52.0	-52.8
6			45.0	46.0
8			18.0	21.8
10			47.0	-45.2
12			<5.0	5.5
14			26.0	25.9
16			33.0	-35.0
18			<3.0	1.4
20			23.0	26.2
-2			68.0	-73.6
-4			50.0	48.8
-6			63.0	56.8
-8			59.0	-58.2
-10			17.0	-18.4
-12			22.0	16.9
-14			25.0	-25.8
-16			21.0	22.8
-18			<3.0	7.9
-20			20.0	-23.3
0	4	8	<2.0	-1.6
2			15.0	11.4
4			18.0	15.1
6			18.0	18.8
8			26.0	29.6
10			45.0	-46.6
12			<5.0	6.1
14			18.0	-16.8
16			<5.0	9.6
18			<4.0	-.5
20			14.0	18.3
-2			<3.0	4.1
-4			<4.0	-2.3
-6			21.0	16.0
-8			39.0	-39.0
-10			26.0	27.6
-12			15.0	-12.9
-14			<4.0	4.7
-16			<4.0	-6.4
-18			<3.0	4.8
-20			11.0	-10.4
-22			11.0	13.4
0	4	9	<3.0	-5.3
2			34.0	-38.0
4			35.0	35.4
6			14.0	13.4
8			52.0	-56.5
10			51.0	55.8
12			19.0	18.1
14			46.0	-48.8
16			<3.0	5.0
-2			55.0	51.9
-4			99.0	-95.5
-6			29.0	-27.0
-8			54.0	54.5
-10			32.0	-33.0
-12			31.0	-28.4
-14			44.0	50.7
-16			21.0	-18.2
-18			<3.0	-6.1
-20			16.0	17.6
-22			9.0	-7.4
0	4	10	<5.0	11.3
2			34.0	-35.1
4			48.0	53.0
6			<4.0	4.5
8			<4.0	-9.2
10			<4.0	-2.2
12			<3.0	-.6
14			<3.0	4.5
16			12.0	-15.0
-2			53.0	-46.8
-4			<3.0	3.1
-6			38.0	-34.4
-8			45.0	42.7
-10			12.0	-15.3
-12			24.0	20.3
-14			<4.0	-10.8
-16			19.0	-15.5
-18			13.0	12.6
0	4	11	<10.0	11.2
2			27.0	29.9
4			18.0	-23.3
6			25.0	-24.7
8			48.0	52.2
10			14.0	-12.8
12			<4.0	-12.3
14			29.0	34.1
-2			74.0	-64.4
-4			38.0	37.7
-6			26.0	-20.0
-8			18.0	18.8
-10			60.0	56.0
-12			32.0	-28.1
-14			28.0	-24.9
-16			38.0	44.0
-18			<4.0	7.2
-20			26.0	-32.2
0	4	12	41.0	-46.3
2			12.0	17.3
4			19.0	-21.7
6			31.0	31.4
8			<4.0	-4.5
10			<4.0	9.3
12			15.0	-13.2
14			<3.0	8.0
-2			<3.0	-3.3
-4			15.0	11.7
-6			26.0	24.4
-8			<5.0	11.4
-10			<5.0	-1.6
-12			<4.0	-1.9
-14			<4.0	-7.5
-16			21.0	23.8
-18			14.0	-17.1
0	4	13	18.0	20.0
2			53.0	-56.1
4			<5.0	8.8
6			14.0	17.0
8			37.0	-37.7
10			<5.0	10.3
12			<4.0	4.6
14			14.0	-18.9
-2			18.0	16.9
-4			20.0	-19.4
-6			20.0	22.9
-8			15.0	12.9
-10			29.0	-32.5
-12			16.0	17.0
-14			13.0	10.9
-16			25.0	-33.6
0	4	14	3.0	1.7
2			14.0	-13.1
4			<4.0	-10.3
6			<5.0	6.6
8			<4.0	1.8
10			<4.0	-8.9
12			<6.0	10.6
-2			29.0	30.0
-4			23.0	-26.5
-6			17.0	19.4
-8			<4.0	-1.4
-10			16.0	17.4
-12			18.0	-20.7
-14			<3.0	-5.3
-16			14.0	-17.4
0	4	15	27.0	-25.3
2			40.0	46.2
4			<4.0	1.0
6			26.0	-29.0
8			14.0	15.6
10			7.0	9.1
-2			11.0	11.9
-4			13.0	17.4
-6			13.0	-14.3
-8			10.0	-9.7
-10			35.0	40.2
-12			29.0	-36.7
-14			13.0	-10.5
-16			16.0	23.2
0	4	16	<3.0	2.8
2			19.0	-20.6
4			21.0	26.6
6			<3.0	-3.5
8			6.0	9.4
-2			14.0	-15.4
-4			32.0	37.4
-6			14.0	-19.7
-8			<4.0	8.2
-10			<4.0	-10.5
-12			9.0	-10.0
0	4	17	21.0	26.3
2			9.0	-8.1
4			<3.0	-.2
-2			23.0	-30.4
-4			9.0	-19.8
-6			30.0	41.3
-8			<4.0	-10.7
-10			22.0	-35.7
1	5	0	<3.0	-4.2
3			26.0	29.6
5			42.0	-41.3
7			9.0	-5.6
9			14.0	-14.1
11			43.0	42.0
13			50.0	-49.9
15			<3.0	-3.4
17			21.0	-24.3
19			15.0	16.4
21			<2.0	2.9
1	5	1	25.0	-34.7
3			74.0	77.1
5			36.0	-34.4
7			48.0	-48.4
9			42.0	43.1
11			44.0	-48.1
13			35.0	-35.0
15			29.0	28.3
17			14.0	14.2
19			12.0	-14.3
21			21.0	27.4
-1			5.0	9.3
-3			46.0	49.1
-5			40.0	-30.7
-7			18.0	-14.7
-9			78.0	79.0
-11			28.0	-27.6
-13			44.0	-43.8
-15			22.0	18.9
-17			19.0	-16.6
-19			19.0	-18.7
-21			13.0	15.2
1	5	2	8.0	-4.8
3			21.0	22.5
5			15.0	13.8
7			39.0	37.7
9			9.0	10.1
11			19.0	-19.2
13			8.0	11.8
15			<3.0	-4.1
17			<3.0	10.3
19			11.0	-12.3
21			5.0	8.2
-1			10.0	3.4
-3			51.0	-46.3
-5			56.0	42.2
-7			18.0	16.9
-9			21.0	16.8
-11			42.0	-41.6
-13			<3.0	-2.1
-15			<3.0	6.4
-17			23.0	27.6
-19			11.0	12.5
1	5	3	65.0	66.0
3			68.0	-68.1
5			40.0	37.1
7			93.0	97.8
9			49.0	-52.7
11			48.0	-48.2
13			27.0	34.3
15			22.0	-23.1
17			15.0	-15.6
19			17.0	17.2
21			6.0	-6.5
-1			30.0	24.9
-3			50.0	-41.4
-5			6.0	5.3
-7			<3.0	-.4
-9			54.0	-49.9
-11			49.0	45.0
-13			11.0	-10.7
-15			50.0	-52.6
-17			33.0	36.6
-19			12.0	12.6
-21			10.0	-12.7
1	5	4	14.0	13.2
3			56.0	-56.3
5			17.0	-23.4
7			23.0	-21.5
9			70.0	78.5
11			10.0	-9.8
13			19.0	-19.3
15			30.0	-28.4
17			22.0	22.5
19			<3.0	-1.9
-1			13.0	-10.9
-3			11.0	2.6
-5			9.0	-3.2
-7			28.0	-24.7
-9			<3.0	6.2
-11			20.0	-18.1
-13			28.0	28.5
-15			12.0	-9.1
-17			<3.0	9.6
-19			18.0	-21.4
-21			10.0	10.5
1	5	5	82.0	-85.4
3			38.0	39.7
5			40.0	34.7
7			9.0	-6.1
9			18.0	13.0
11			28.0	28.2
13			32.0	-35.4
15			13.0	15.4
17			<3.0	4.4
19			24.0	-27.0
-1			<2.0	.9
-3			27.0	26.9
-5			97.0	-86.3
-7			31.0	26.0
-9			36.0	33.5
-11			33.0	-29.4
-13			17.0	11.6
-15			28.0	30.6
-17			27.0	-31.0
-19			<3.0	6.8
-21			25.0	28.1
1	5	6	24.0	20.4
3			15.0	-14.5
5			29.0	-26.0
7			28.0	31.3
9			17.0	-18.7
11			15.0	13.0
13			<4.0	-.7
15			31.0	34.0
17			23.0	-27.7
19			6.0	5.6
-1			15.0	13.4
-3			16.0	13.4
-5			26.0	-21.6
-7			45.0	38.8
-9			<4.0	3.3
-11			37.0	36.5
-13			37.0	-43.6
-15			<4.0	2.2
-17			<3.0	4.6
-19			22.0	26.1
-21			14.0	-18.1
1	5	7	22.0	23.9
3			46.0	-47.3
5			28.0	-30.5
7			65.0	67.7
9			18.0	-15.7
11			28.0	-29.2
13			36.0	28.7
15			<3.0	.8
17			11.0	-14.4
-1			38.0	-33.1
-3			28.0	-23.6
-5			62.0	55.5
-7			11.0	-10.4
-9			14.0	13.5
-11			32.0	33.6
-13			18.0	-19.8
-15			19.0	-22.0
-17			30.0	34.8
-19			14.0	-15.8
-21			17.0	-18.9
1	5	8	28.0	-26.6
3			<3.0	-6.0
5			24.0	-21.3
7			20.0	19.1
9			12.0	-8.7
11			<4.0	-1.5
13			15.0	-13.7
15			<3.0	-4.9
17			<2.0	3.1
-1			38.0	30.7
-3			<3.0	-.8
-5			25.0	22.8
-7			14.0	15.1
-9			28.0	-29.0
-11			21.0	-19.9
-13			14.0	12.2
-15			14.0	14.1
-17			17.0	-22.4
-19			<2.0	1.3
1	5	9	36.0	-35.1
3			36.0	-36.6
5			42.0	49.3
7			34.0	-37.2
9			<4.0	-6.8
11			24.0	23.3
13			21.0	-24.9
15			<3.0	-5.2
17			8.0	13.5
-1			45.0	46.3
-3			31.0	28.8
-5			44.0	-44.3
-7			49.0	47.0
-9			19.0	18.2
-11			51.0	-55.5
-13			18.0	20.1
-15			<3.0	-1.8
-17			22.0	-25.1
-19			6.0	6.5
1	5	10	34.0	37.3
3			<4.0	-6.0
5			<4.0	2.7
7			25.0	-27.2
9			31.0	35.7
11			<3.0	-5.2
13			18.0	22.8
15			17.0	-19.3
-1			<3.0	5.1
-3			<3.0	-7.6
-5			<4.0	1.9
-7			24.0	-22.0
-9			14.0	12.6
-11			<4.0	-5.8
-13			21.0	23.9
-15			17.0	-19.5
-17			13.0	17.0
-19			5.0	-7.5
1	5	11	30.0	33.5
3			14.0	11.9
5			29.0	-33.3
7			21.0	25.7
9			14.0	15.8
11			17.0	-21.5
13			<3.0	-4.0
-1			34.0	-31.7
-3			14.0	14.6
-5			26.0	22.0
-7			32.0	-33.6
-9			11.0	11.0
-11			9.0	11.3
-13			41.0	-47.5
-15			10.0	11.2
-17			22.0	26.1
1	5	12	12.0	9.7
3			21.0	-21.6
5			<4.0	-4.0
7			8.0	9.0
9			8.0	-10.3
11			<3.0	5.0
-1			<3.0	2.0
-3			<4.0	-5.4
-5			31.0	-31.2
-7			28.0	30.9
-9			13.0	-11.2
-11			<4.0	-5.1
-13			8.0	-7.7
-15			21.0	24.0
1	5	13	24.0	-26.3
3			30.0	-36.3
5			26.0	28.8
7			7.0	8.8
9			<3.0	-3.8
11			10.0	13.4
-1			52.0	54.0
-3			22.0	-23.9
-5			15.0	-15.4
-7			13.0	12.8
-9			<4.0	-4.8
-11			15.0	-16.6
-13			15.0	21.4
1	5	14	7.0	-8.7
3			11.0	14.8
5			16.0	-22.0
7			8.0	10.3
-3			<3.0	3.0
-5			<3.0	-2.2
-7			9.0	-8.8
-9			<3.0	4.1
-11			13.0	20.2
1	5	15	<3.0	-.1
3			11.0	14.3
5			13.0	-19.0
-1			24.0	-27.2
-3			21.0	26.2
-5			7.0	9.5
-7			22.0	-27.5
-9			12.0	17.8
-11			7.0	6.4
1	5	16	<4.0	2.9
3			<5.0	-9.2
-1			<4.0	5.5
-3			<5.0	-5.1
-5			<3.0	-1.0
-7			8.0	-11.1
0	6	0	39.0	-43.0
2			26.0	25.0
4			<7.0	-16.6
6			<7.0	-18.8
8			<7.0	4.5
10			39.0	37.7
12			<7.0	-3.8
14			<6.0	6.9
16			<6.0	8.3
18			22.0	-21.4
0	6	1	28.0	-27.0
2			<5.0	-4.3
4			50.0	54.5
6			61.0	-66.3
8			36.0	33.6
10			23.0	25.5
12			<7.0	-6.3
14			<6.0	-1.7
16			<6.0	7.1
18			12.0	-12.1
-2			31.0	31.2
-4			42.0	41.2
-6			47.0	-47.6
-8			6.0	4.9
-10			27.0	25.7
-12			22.0	-20.1
-14			20.0	19.8
-16			<6.0	.7
-18			<6.0	-6.8
-20			<5.0	7.6
0	6	2	<4.0	-3.5
2			<5.0	4.1
4			<6.0	-.1
6			<6.0	-3.6
8			<7.0	-7.7
10			31.0	-29.7
12			<6.0	15.7
14			<6.0	6.8
16			<5.0	5.5
18			<5.0	3.7
-2			45.0	-46.5
-4			20.0	23.1
-6			54.0	56.1
-8			<6.0	-1.8
-10			<7.0	-20.6
-12			<6.0	6.7
-14			<6.0	-3.4
-16			15.0	-12.9
-18			<6.0	8.7
0	6	3	38.0	41.1
2			<5.0	.3
4			51.0	-53.7
6			27.0	30.4
8			<6.0	-3.8
10			26.0	-26.4
12			15.0	16.7
14			13.0	15.9
16			26.0	-29.3
18			15.0	-13.8
-2			50.0	-49.0
-4			<6.0	-10.1
-6			31.0	28.6
-8			<7.0	-14.1
-10			30.0	-30.6
-12			35.0	31.7
-14			30.0	-30.3
-16			<6.0	14.9
-18			<6.0	11.8
0	6	4	16.0	23.8
2			<6.0	-7.0
4			<6.0	6.5
6			16.0	-24.0
8			<7.0	-14.8
10			15.0	17.1
12			23.0	-23.5
14			16.0	-15.0
16			<6.0	11.2
-2			<6.0	15.8
-4			<6.0	13.8
-6			30.0	-30.0
-8			25.0	23.6
-10			<8.0	-15.0
-12			<8.0	-16.1
-14			<7.0	7.1
-16			<6.0	3.7
-18			16.0	-14.1
0	6	5	65.0	-41.9
2			<6.0	3.9
4			<6.0	5.6
6			<7.0	-5.2
8			<6.0	-8.1
10			26.0	31.0
12			<6.0	-10.3
14			<6.0	-15.1
16			36.0	37.3
-2			84.0	80.4
-4			30.0	-24.9
-6			<6.0	-11.0
-8			25.0	19.6
-10			<4.0	-2.0
-12			<6.0	-7.4
-14			31.0	31.9
-16			<5.0	-.1
-18			21.0	-24.5
0	6	6	<3.0	3.7
2			38.0	42.0
4			25.0	-29.7
6			21.0	21.9
8			<7.0	9.3
10			<7.0	-11.8
12			<6.0	-10.3
14			21.0	22.8
16			<6.0	-3.7
-2			38.0	-34.4
-4			13.0	-19.4
-6			31.0	28.0
-8			19.0	-17.4
-10			<6.0	3.7
-12			<6.0	2.1
-14			18.0	-16.2
-16			<4.0	-.2
-18			12.0	17.7
0	6	7	21.0	20.1
2			14.0	14.8
4			23.0	-21.8
6			<6.0	-7.5
8			<7.0	10.0
10			39.0	-41.5
12			21.0	23.0
14			<6.0	9.2
16			12.0	-19.0
-2			33.0	-37.7
-4			28.0	26.8
-6			<5.0	2.7
-8			32.0	-33.8
-10			18.0	19.1
-12			<5.0	6.3
-14			23.0	-21.1
-16			<6.0	-2.5
-18			12.0	14.3
0	6	8	26.0	-24.1
2			32.0	-32.6
4			19.0	16.0
6			12.0	16.0
8			<5.0	-6.4
10			<5.0	2.0
12			14.0	7.9
-2			18.0	15.9
-4			<6.0	4.2
-6			<7.0	13.0
-8			<6.0	-5.0
-10			15.0	-13.3
-12			<5.0	2.2
-14			28.0	30.2
0	6	9	22.0	24.1
2			15.0	-19.1
4			23.0	29.2
6			<5.0	8.0
8			22.0	-26.0
10			24.0	28.5
-2			<5.0	10.1
-4			18.0	-13.8
-6			15.0	-15.3
-8			45.0	48.7
-10			40.0	-45.5
-12			13.0	-1.2
-14			20.0	24.1
0	6	10	19.0	19.7
2			<6.0	13.2
4			<6.0	-6.4
6			27.0	-31.0
8			<6.0	11.8
-2			42.0	-39.2
-4			17.0	17.8
-6			<7.0	13.4
-8			<7.0	6.2
-10			<6.0	-10.0
-12			<5.0	-1.5
0	6	11	22.0	-25.8
2			28.0	33.6
4			22.0	-25.3
-2			<5.0	-8.9
-4			<6.0	12.8
-6			15.0	-16.4
-8			24.0	-32.0
-10			31.0	34.3
-12			<5.0	-2.3
0	6	12	<5.0	1.2
2			<5.0	-4.6
4			<6.0	1.7
6			13.0	13.3
8			14.0	-16.1
-2			<5.0	9.6
-4			<6.0	-13.0
-6			24.0	21.7
-8			<5.0	5.0
-10			24.0	-26.6
0	6	13	13.0	17.4
2			21.0	-25.1
4			14.0	16.0
6			<5.0	2.1
-2			<5.0	.3
-4			25.0	-26.1
-6			21.0	24.2
-8			<6.0	9.4
1	7	0	<3.0	-11.0
3			34.0	32.1
5			<4.0	-9.9
7			<5.0	-15.0
9			25.0	24.1
11			<4.0	.2
13			12.0	-9.1
15			10.0	13.1
1	7	1	15.0	-16.8
3			19.0	19.6
5			19.0	-19.0
7			18.0	-22.2
9			30.0	34.3
-1			<3.0	9.0
-3			<4.0	4.6
-5			<5.0	-6.8
-7			16.0	-18.6
-9			32.0	33.8
-11			24.0	-22.8
1	7	2	32.0	33.7
3			16.0	-17.1
5			<6.0	-12.4
7			<7.0	13.1
9			<6.0	-7.9
11			<5.0	-3.0
13			<4.0	-2.5
-1			18.0	-17.5
-3			28.0	-29.5
-5			18.0	19.2
-7			17.0	22.1
-9			21.0	-27.9
-11			<5.0	-4.7
-13			<4.0	1.4
1	7	3	34.0	33.1
3			<4.0	-9.4
5			<5.0	6.6
7			<5.0	-4.3
9			<4.0	-12.2
11			<4.0	3.1
13			19.0	20.8
-1			21.0	-23.0
-3			<4.0	-10.6
-5			24.0	28.6
-7			19.0	15.9
-9			26.0	-29.3
-11			<4.0	11.6
1	7	4	<3.0	-6.7
3			<4.0	5.5
5			<4.0	-10.2
7			<5.0	-.6
9			26.0	27.8
11			<4.0	7.1
13			21.0	-23.9
-1			22.0	24.7
-3			18.0	16.4
-5			30.0	-31.1
-7			<5.0	-4.9
-9			27.0	26.8
-11			<5.0	-14.9
-13			<4.0	-3.8
-15			14.0	15.1
1	7	5	22.0	-25.1
3			14.0	22.1
5			<5.0	-10.8
7			<4.0	-3.2
9			<4.0	-3.1
11			18.0	21.5
13			14.0	-32.3
-1			<5.0	9.8
-3			27.0	25.7
-5			29.0	-32.1
-7			<6.0	12.3
-9			<6.0	-10.6
-11			<5.0	-9.1
-13			<5.0	-8.6
-15			20.0	22.9
1	7	6	22.0	28.7
3			12.0	-14.5
5			20.0	-19.8
7			18.0	16.4
9			<4.0	-.9
11			16.0	-17.6
-1			23.0	-21.9
-3			27.0	-29.3
-5			29.0	26.3
-7			<5.0	-7.5
-9			17.0	-14.2
-11			12.0	12.1
-13			<3.0	1.5
1	7	7	23.0	27.1
3			<4.0	4.2
5			19.0	-21.8
7			13.0	12.1
9			<3.0	1.4
-1			<4.0	-10.3
-3			25.0	-25.0
-5			25.0	24.5
-7			13.0	-16.9
-9			<4.0	.9
-11			<4.0	6.3
1	7	8	<4.0	-8.7
3			15.0	-17.5
5			<6.0	9.9
7			<5.0	-10.5
9			<4.0	6.3
-1			32.0	24.8
-3			<5.0	11.1
-5			16.0	-16.9
-7			18.0	14.8
-9			<5.0	4.9
-11			12.0	-9.8
-13			14.0	18.0
1	7	9	10.0	-12.9
3			<5.0	-11.1
5			24.0	29.2
7			23.0	-31.2
-1			<4.0	-2.0
-3			12.0	14.7
-5			<6.0	-11.8
-7			<5.0	5.8
-9			<4.0	6.0
-11			13.0	-13.0
1	7	10	19.0	23.5
3			<4.0	11.4
5			16.0	-21.9
7			<4.0	.5
-1			<5.0	-7.8
-3			<6.0	-13.1
-5			12.0	15.0
-7			11.0	-7.2
-9			<4.0	-1.9
1	7	11	16.0	20.5
3			<5.0	8.9
-1			<6.0	-12.5
-3			<7.0	11.7
-5			<6.0	7.9
0	8	0	24.0	-21.4
2			<4.0	7.6
4			21.0	20.7
6			32.0	-37.2
8			13.0	-1.4
10			<6.0	12.1
0	8	1	<5.0	-7.8
2			<5.0	-8.9
4			<6.0	13.4
6			17.0	-16.2
8			15.0	15.0
-2			<5.0	-4.5
-4			<5.0	.4
-6			15.0	-19.2
0	8	2	14.0	13.5
2			6.0	9.4
4			18.0	-16.9
6			19.0	22.5
8			10.0	-13.6
10			<6.0	-14.2
-2			<6.0	-12.8
-4			<7.0	-.9
-6			<6.0	13.6
-8			<5.0	-7.2
0	8	4	13.0	-16.2
2			13.0	16.5
4			15.0	12.6
6			13.0	-25.5
8			18.0	-11.8
-2			16.0	16.8
-4			<6.0	-7.2
-6			<5.0	-11.8
0	8	5	15.0	-15.7
2			12.0	15.7
4			10.0	-1.2
6			<6.0	-10.9
-2			<5.0	18.5
-4			<6.0	-6.1
-6			<7.0	5.7
-8			<6.0	-.7
0	8	6	21.0	21.0
2			17.0	7.0
4			<5.0	-1.7
-2			10.0	-25.6

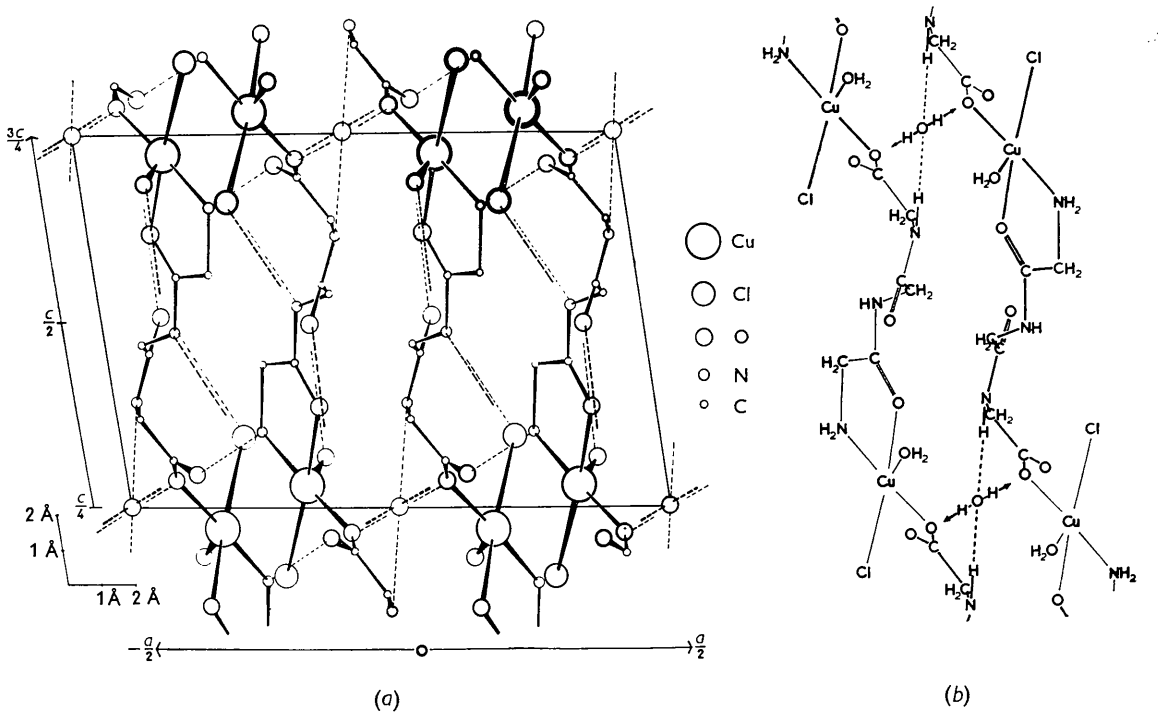


Fig. 1. (*a*) Projection of part of glycylglycylglycinocopper(II) sesquihydrate structure along the *b* axis. (*b*) Atomic arrangement in the two central chains of (*a*).

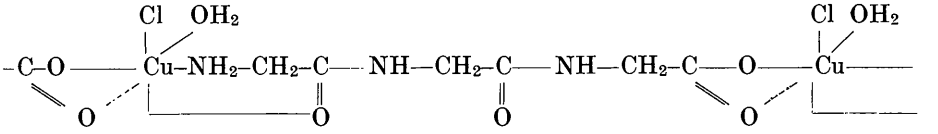
analysis and the composition calculated for a monohydrate. The scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon, nitrogen, oxygen, chlorine and Cu^+. The *f* curve for Cu^+ was used instead of that for Cu^{2+}, consistently with the principle (Pauling, 1948, 1960) 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 anomalous scattering by copper, 2·1 electrons were subtracted over the whole $\sin\theta$ range before the temperature factor was applied (Dauben & Templeton, 1955).

At this stage the agreement index *R* for the reflexions with non-zero intensities was 0·24. The structure was refined by the least-squares method in three stages. Details of the refinement are shown in Table 1.

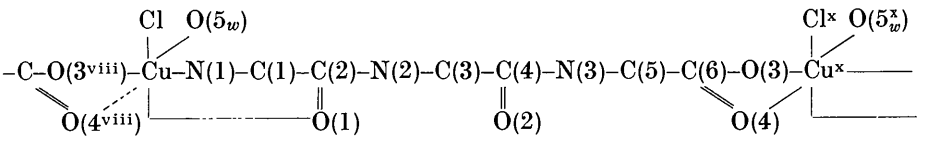
The final positional parameters together with their standard deviations are given in Table 2, and the thermal parameters in Table 3. The final observed calculated structure factors are listed in Table 4, and the unit-cell is shown diagrammatically in Fig. 1.

Discussion of the structure

In the structure the peptide chain ist attached to two copper atoms — to one through the nitrogen and oxygen of the first glycine residue and to the other through the negatively charged oxygen atom of the terminal carboxyl group:



The atoms of each type have been numbered sequentially along the chain, water-oxygen atoms being labelled with subscript *w*:



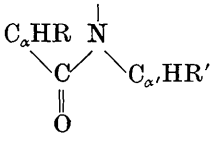
To facilitate the discussion of the interactions between atoms of adjacent asymmetric units, equivalent atoms have been identified as follows:

Superscript	Atomic coordinates	
None	x, y, z	(see Table 2)
′	$x, y+1, z$	
″	$x, y-1, z$	
‴	$\bar{x}, \bar{y}, 1-z$	
iv	$\frac{1}{2}-x, \frac{1}{2}-y, 1-z$	
v	$\bar{x}, y, \frac{1}{2}-z$	
vi	$\bar{x}, y-1, \frac{1}{2}-z$	
vii	$x, \bar{y}, \frac{1}{2}+z$	
viii	$x, 1-y, \frac{1}{2}+z$	
ix	$x, \bar{y}, z-\frac{1}{2}$	
x	$x, 1-y, z-\frac{1}{2}$	
xi	$\bar{x}, y+1, \frac{1}{2}-z$	

Geometry of the peptide molecule

The most important characteristics which are common to those peptides whose structures have been accurately determined are:

(i) The approximate constancy of the linear and angular dimensions of the peptide group,



(ii) The planarity of the peptide group; and

(iii) The *trans* configuration of the C=O and N–H bonds.

Variety in peptide structures is achieved by rotation about the C_α–C and N–$C_{\alpha'}$ bonds.

The bond lengths and angles of the tripeptide molecule in the copper complex are listed in Table 5, where they are also compared with the average values found in non-chelated peptides (Pauling & Corey, 1953; Hahn, 1957). The tripeptide really contains only two non-terminal peptide groups, C(1)C(2)O(1)N(2)C(3) and C(3)C(4)O(2)N(3)C(5); their dimensions show no significant deviations from the average values.

The unexceptional values of the peptide group dimensions make it surprising that these groups do not also possess the expected planarity. The atoms C_α–C–O–N in each group are, indeed co-planar within the limits of accuracy (planes I and III in Table 6). The $C_{\alpha'}$-atom of each group, however, lies several standard deviations away from the least-squares plane through the other atoms. If planes are fitted to all five atoms C_α–CO–N–$C_{\alpha'}$, then in each case there are several atoms with significant deviations (planes II and IV in Table 6). In other words, the N–$C_{\alpha'}$ bonds do not lie in the planes of the amide groups.

This effect does not seem to be explained by anything unusual which happens at the peptide nitrogen atoms. The non-coplanarity of the bonds about peptide nitrogen atoms which are electron donors in ligand–metal bonds has been noted earlier (Cooper *et al.*,

Table 5. *Bond lengths and angles in tripeptide molecule*

Present work						Pauling & Corey (1953)	
Bond	Length	$\sigma(l)$	Bond	Length	$\sigma(l)$	Bond	Length
N(1)–C(1)	$1{\cdot}44_0$ Å	0·012 Å					
C(1)–C(2)	$1{\cdot}54_4$	0·013	C(3)–C(4)	$1{\cdot}53_8$ Å	0·014 Å	C(α)–C	1·53 Å
C(2)–O(1)	$1{\cdot}22_8$	0·011	C(4)–O(2)	$1{\cdot}19_0$	0·013	C=O	1·24
C(2)–N(2)	$1{\cdot}30_4$	0·012	C(4)–N(3)	$1{\cdot}30_7$	0·012	C–N	1·32
N(2)–C(3)	$1{\cdot}45_1$	0·013	N(3)–C(5)	$1{\cdot}47_1$	0·012	N–C(α)	1·47
			C(5)–C(6)	$1{\cdot}51_1$	0·013		
			C(6)–O(3)	$1{\cdot}31_1$	0·011		
			C(6)–O(4)	$1{\cdot}20_6$	0·012		

Present work						Pauling & Corey (1953)	
Angle θ		$\sigma(\theta)$	Angle θ		$\sigma(\theta)$	Angle θ	
C(1)–N(1)–Cu	111·3°	1·1°					
C(2)–O(1)–Cu	112·6	1·1					
N(1)–C(1)–C(2)	107·9	1·4					
C(1)–C(2)–O(1)	121·3	1·6	C(3)–C(4)–O(2)	122·1°	1·6°	C(α)–C=O	121°
C(1)–C(2)–N(2)	115·4	1·5	C(3)–C(4)–N(3)	112·8	1·5	C(α)–C–N	114
O(1)–C(2)–N(2)	123·2	1·7	O(2)–C(4)–N(3)	125·0	1·7	O=C–N	125
C(2)–N(2)–C(3)	121·3	1·5	C(4)–N(3)–C(5)	120·7	1·5	C–N–C(α)	123
N(2)–C(3)–C(4)	111·1	1·4	N(3)–C(5)–C(6)	110·7	1·4	N–C(α)–C	110
			C(5)–C(6)–O(3)	112·8	1·4		
			C(5)–C(6)–O(4)	125·5	1·7		
			O(3)–C(6)–O(4)	121·7	1·6		

Table 6. *Least-squares planes through peptide and carboxyl groups*

No.	Atoms to which plane was fitted	Equation of plane
I	C(1) C(2) O(1) N(2)	$0{\cdot}48456X+0{\cdot}80704Y+0{\cdot}33747Z-4{\cdot}2297=0$
II	C(1) C(2) O(1) N(2) C(3)	$0{\cdot}46086X+0{\cdot}83124Y+0{\cdot}31088Z-3{\cdot}9520=0$
III	C(3) C(4) O(2) N(3)	$0{\cdot}81055X-0{\cdot}15462Y-0{\cdot}56490Z+3{\cdot}9707=0$
IV	C(3) C(4) O(2) N(3) C(5)	$0{\cdot}81355X-0{\cdot}16332Y-0{\cdot}55809Z+3{\cdot}9454=0$
V	C(5) C(6) O(3) O(4)	$0{\cdot}51060X+0{\cdot}25513Y+0{\cdot}82110Z-6{\cdot}0176=0$

$lX+mY+nZ+p=0$, where $X=ax+cz\cos\beta$, $Y=by$, $Z=cz\sin\beta$.

Atom	Deviation from Plane I	Deviation from Plane II	Atom	Deviation from Plane III	Deviation from Plane IV	Atom	Deviation from Plane V
C(1)	−0·006 Å	−0·044 Å	C(3)	−0·006 Å	0·004 Å	C(5)	0·003 Å
C(2)	0·022	0·037	C(4)	0·021	0·017	C(6)	−0·010
O(1)	−0·008	0·000	O(2)	−0·008	−0·011	O(3)	0·003
N(2)	−0·008	0·057	N(3)	−0·007	−0·024	O(4)	0·004
C(3)	−0·168	−0·050	C(5)	0·044	0·013		

1962), but N(2) and N(3) in the present complex are not involved in metal bonding.

It is therefore likely that these deviations from planarity are produced to accomodate strains in other parts of the molecule, as may be the case in *N,N'*-diglycylcystine (Yakel & Hughes, 1952).

Apart from the equations of the least-squares planes through the peptide groups and the distances of the individual atoms from these planes, Table 6 contains the same information concerning the carboxyl group C(5)C(6)O(3)O(4). From the equations of the planes, the angles between their normals are as follows:

Plane 2:	C(3)C(4)O(2)N(3)	C(5)C(6)O(3)O(4)
Plane 1		
C(1)C(2)O(1)N(2)	94° 26′	40° 15′
C(3)C(4)O(2)N(3)	—	84° 52′

In the approximate perpendicularity of the adjacent peptide groups and of the second peptide and terminal groups, the tripeptide resembles glycylphenylalanylglycine, for which Marsh & Glusker (1961) report a peptide–peptide dihedral angle of 126° and for which we calculate a peptide–carboxyl interplanar angle of 99°. In L-leucyl-L-prolylglycine, the only other tripeptide whose structure is accurately known (Leung & Marsh, 1958), the angle between the peptide-group planes is 102°, but the carboxyl group lies close to the plane of the prolyl–glycyl peptide group. The other compounds with which relevant comparisons may be made are all dipeptides. Marsh & Glusker (1961) have pointed out that in all these reported structures the carboxyl groups are either approximately coplanar with, or approximately perpendicular to, the adjacent peptide groups. The choice between these configurations seems to depend on a molecule's environment.*

* *Note added in proof.*— At the suggestion of the Referee we note that the shortest non-bonded intermolecular contacts are O(2)–C(1′) (3·27 Å), O(2)–C(2′) (3·46 Å), O(3)–N(2′) (3·28 Å), O(3)–C(3′) (3·46 Å) between a peptide and its neighbour in the y direction, and N(1)–Cl($\frac{1}{2}-x$, $y+\frac{1}{2}$, $\frac{3}{2}-z$) (3·35 Å). The shortest contacts between different parts of the same tripeptide molecule occur betweens atoms of adjacent C=O groups: C(2)–C)4) (3·44 Å), C(4)–C(6) (3·18 Å), C(4)–O(4) (3·22 Å), O(2)–C(6) (3·37 Å), O(2)–O(4) (3·46 Å).

Details of the tripeptide structure

We shall leave a comprehensive comparison between the bond lengths and angles in peptides and metal–peptide complexes to be made in a later paper in this series. The general agreement between the dimensions of the tripeptide in this copper complex and the averages taken from a number of peptides has already been stressed. The following remarks are therefore restricted to a number of special features.

The terminal H_3N^+–C bond in the zwitterionic form of a peptide is usually appreciably longer than the other N–C_α bonds. Hahn (1957) concluded from a review of all the known examples that the difference was real and that it could be attributed to the sp^3 hydridization of the orbitals of the terminal nitrogen atom. His compilation include β-glycylglycine (Hughes & Moore, 1949) where N(1)–C(1) is 1·51 Å and N(2)–C(3) is 1·48 Å, the atoms being labelled consistently with the present paper. In α-glycylglycine (Biswas, Hughes, Sharma & Wilson, private communication) the corresponding bond lengths are 1·497 and 1·462 Å respectively. Since 1957, Leung & Marsh (1958) have reported N–C_α bond lengths of 1·49 (terminal), 1·45 and 1·45 Å (non-terminal) in L-leucyl-L-prolylglycine; and Marsh & Glusker (1961) have found values of 1·46 (terminal), 1·46 and 1·46 Å (non-terminal) in glycylphenylalanylglycine. The last set of values is the only one which does not follow the general trend, but it occurs in a structure which it was not possible to refine to high precision.

All of this is a preamble to the fact that the bond N(1)–C(1) of the copperglycylglycylglycine complex is *shorter* (1·44 Å) than the bonds N(2)–C(3) and N(3)–C(5), (1·45 and 1·47 Å). The differences between the three bonds are not significant, but the difference between 1·44 Å and Hahn's (1957) standard value, 1·49 Å, is significant.

In seeking an explanation for the shortness of this bond we note that the covalent bonds Cu–N(1) and N(1)–C(1) are at an angle of 111·3° (Table 5). Two hydrogen atoms are attached to N(1). One of these hydrogen atoms is involved in the hydrogen bond N(1)–H $\cdots$ O(4^{vi}), whose direction makes angles of

Table 7. *Environment of the copper atom in* Cu(glyglygly)Cl·$1\frac{1}{2}H_2O$

Bond	l	σ_l	Angle	θ	$\sigma(\theta)$
Cu–N(1)	$1{\cdot}99_0$ Å	0·008 Å	N(1)–Cu–O(1)	84·2°	0·4°
Cu–O(1)	$1{\cdot}98_7$	0·007	O(1)–Cu–O(3^{viii})	90·4	0·4
Cu–O(3^{viii})	$1{\cdot}93_0$	0·007	Cl–Cu–O(3^{viii})	92·9	0·3
Cu–Cl	$2{\cdot}24_2$	0·003	Cl–Cu–N(1)	91·8	0·4
Cu–O(5_w)	$2{\cdot}30_4$	0·007	N(1)–Cu–O(3^{viii})	174·5	0·9
Cu · · · O(4^{viii})	$2{\cdot}81_7$	0·007	O(1)–Cu–Cl	161·5	0·6
Angle	θ	$\sigma(\theta)$	Angle	θ	$\sigma(\theta)$
O(5_w)–Cu–N(1)	90·9°	0·5°	O(5_w)–Cu–O(4^{viii})	140·8°	0·6°
O(5_w)–Cu–O(1)	93·6	0·4	Cl–Cu–O(4^{viii})	88·3	0·3
O(5_w)–Cu–O(3^{viii})	90·8	0·4	N(1)–Cu–O(4^{viii})	126·2	0·6
O(5_w)–Cu–Cl	104·5	0·4	O(1)–Cu–O(4^{viii})	79·6	0·3
			O(3^{viii})–Cu–O(4^{viii})	51·1	0·2

128·4° and 119·8° with N(1)–Cu and N(1)–C(1), respectively. The sum of the three inter-bond angles is 359·5°. We have no evidence where the hydrogen atoms attached to N(1) are, but it is likely that one of them lies so that N(1)–H is within about 10° of the line N(1) · · · O(4^{vi}). The fourth bond to the second hydrogen atom must then complete a much distorted tetrahedral distribution. We suggest that the distortion is an accident of the packing and of the hydrogen-bond system and that its effect is to cancel the elongation of the N–C_α bond which would be expected for an sp^3-hybridized nitrogen atom.

The two peptide nitrogen atoms, N(2) and N(3), each act as donor in one hydrogen bond — N(2) to Cl^{ix} and N(3) to $H_2O(6_w)$. Their amide N–C bonds are equal in length (N(2)–C(2) = $1{\cdot}30_4$, N(3)–C(4) = $1{\cdot}30_7$ Å), but the expected trigonal bond distribution about N(2) is less distorted (sum of inter-bond angles = 360°) than that about N(3) (sum = 354°).

Two other hydrogen bonds link the carboxylic oxygen atoms O(3) and O(4) to the two water molecules $H_2O(5'_w)$ and $H_2O(6'_w)$, respectively. The carbon–oxygen bond lengths in the carboxyl group, 1·31 and 1·21 Å, correspond to 20% and 80% double-bond character (Hahn, 1957); the bond angles are in agreement with this description. The copper–oxygen bond therefore strongly stabilizes the resonance form in which C(6)–O(3) is a single bond. A similar, though not quite so pronounced, stabilization is found in the terminal carboxyl groups of bisglycinocopper(II) hydrate, in the triglycine-copper complex formed in alkaline solution and, to an even smaller extent, in glycylglycinocopper(II) trihydrate (for references see Table 8).

Environment of the copper atom

The copper atom exhibits fivefold coordination. It is attached to N(1) and O(1), the nitrogen and oxygen atoms of the first glycine residue of one peptide chain, to the carboxyl oxygen O(3^{viii}) of a second peptide chain, to a chloride ion and to the oxygen O(5_w) of a water molecule. This water oxygen atom lies at the apex of a pyramid of which the other four ligand atoms form the approximately planar base.

The distribution of atoms around the copper atom is summarized in Fig. 2 and Table 7. It is seen that the copper atom lies slightly (0·14 Å) out of the plane of the base of the pyramid, in the direction of the water oxygen atom. Nor are the four closest ligand atoms truly coplanar: the angles N(1)–Cu–O(3^{viii}) and O(1)–Cu–Cl are 174·5° and 161·5°, respectively. The equation of the least-squares plane through atoms Cu, N(1), O(1), O(3^{viii}) and Cl is

$$0{\cdot}30759X + 0{\cdot}93512Y + 0{\cdot}17588Z - 2{\cdot}3481 = 0$$

(where X, Y, Z, are the same orthogonalized coordinates in Å, as in Table 6), and the deviations of the atoms from this plane are:

O(3^{viii})		Cl
−0·100 Å		+0·160 Å
	Cu	
	−0·142 Å	
O(1)		N(1)
+0·191 Å		−0·109 Å .

At first sight, the tetragonal-pyramidal environment of the copper atom places glycylglycylglycinocopper(II)

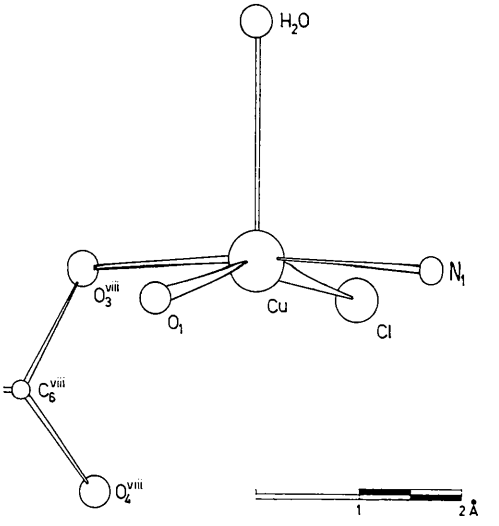


Fig. 2. Environment of copper atom in glycylglycylglycino-sesquihydrate structure.

Table 8. *Copper-ligand bond lengths in peptide complexes*

Compound	Cu–N(amino)	Cu–N(peptide)	Cu–O(peptide)	Cu–O⁻(carboxyl)	Cu–OH_2	$\sigma(l)$	Ref.
$K_2Cu(biu)_2.4\,H_2O$	— —	1·932 Å 1·938	— —	— —	— —	0·007– 0·008 Å	1
$Cug_2.H_2O$	2·021 Å 1·984	— —	— —	1·947 Å* 1·957*	2·42 Å —	0·008– 0·010	2
$Cugg.3\,H_2O$	2·018 2·045	1·867 1·880	— —	1·971* 1·988*	2·39 2·30	0·010– 0·012	3
$NaCuggg.H_2O$	2·034	1·893	—	1·932†	—	—	4
$CugggCl.1\frac{1}{2}H_2O$	1·990	—	1·987 Å	1·930†	2·304	0·007– 0·008	5

* Cu–O bond is part of chelate ring. † Carboxyl group is bonded to Cu to which rest of peptide is *not* chelated.

Symbols: biu = biuret, g = glycine, gg = glycylglycine, ggg = glycylglycylglycine.

References:
1. Freeman, Smith & Taylor (1961).
2. Tomita & Nitta (1960); Freeman & Snow (unpubl.).
3. Strandberg, Lindqvist & Rosenstein (1961).
4. Freeman, Schoone & Sime (unpubl.).
5. Present work.

hydrate in the growing class of structures with 5-coordinate copper(II). This classification appears all the more appropriate since two closely related metal-peptide complexes — glycylglycinocopper(II) trihydrate (Strandberg, Lindqvist & Rosenstein, 1961) and sodium glycylglycylglycino cuprate(II) hydrate (Cooper *et al.*, 1962) — have also been found to contain tetragonal-pyramidally 5-coordinated metal atoms.

The compounds in this class were last listed by Barclay & Kennard (1961), who pointed out that the tetragonal-pyramidal arrangement of ligands — with and without association of the complexes into bimolecular units — is now as characteristic of copper(II) as are its better established square-planar, distorted octahedral and tetrahedral configurations.

It is, however, possible that the 5-coordination of copper in the present tripeptide complex is simply due to steric hindrance. The geometry of the carboxyl group places the second oxygen atom, O(4^{viii}), at a distance of 2·82 Å from the copper atom. Although neither this distance nor the Cu · · · O(4^{viii}) direction corresponds to a possible bond, the location of O(4^{viii}) effectively prevents the approach of any sixth ligand to the copper atom.

In Table 8, the recent accurate determinations of the lengths of metal–ligand bonds in copper-peptide complexes are summarized. The values for bisglycinocopper(II) hydrate and for glycylglycinocopper(II) trihydrate in each case occupy two lines: in the first case the asymmetric unit contains two crystallographically independent glycine molecules, and in the second case two complete complexes.

The structures of bis-β-aminobutyratocopper(II) dihydrate (Bryan, Poljak & Tomita, 1961) and of bis-β-alaninocopper(II) hexahydrate (Tomita, 1960) have been omitted from the tabulated comparison since the chelate rings in these compounds are six- and not five-membered and since the bond lengths were based only on two-dimensional data.

The bond from the copper atom to the terminal amino group in the present triglycine complex is shorter (1·990 Å, s.d. = 0·007) than four of the five listed similar bonds by amounts (0·028–0·055 Å) which have 'probable' significance by the usual tests; the difference between its length and the mean of all six values (2·014 Å, s.d. = 0·010) is also 'probably significant' ($t_o = 2·0$). As a group these bonds are significantly longer than the known examples of copper–nitrogen bonds involving approximately sp^2-hybridized peptide nitrogen atoms (Table 8, column 2). An explanation of this effect in terms of the hybridization of the nitrogen orbitals has been noted by Strandberg *et al.* (1961). The fact that the Cu–NH_2 bond in the present case is apparently shorter than similar bonds in the other cited compounds is therefore consistent with the deviations from sp^3-tetrahedral towards sp^2-trigonal bond directions at nitrogen N(1), which have been noted above.

This structure contains two bonds from copper atoms to oxygen atoms of the peptide. The bond Cu–O(1) is the first recorded bond from copper to a peptide oxygen atom. The other bond, Cu–O(3^{viii}), is one of the two Cu–O(carboxyl) bonds in Table 8 which are not members of chelate rings, the second example being the terminal oxygen–copper bond in the other triglycine complex. Both these Cu–O⁻ bonds are shorter than the corresponding bonds in the glycine and glycylglycine complexes. In these last two complexes the Cu–O⁻ bond-lengths are presumably increased to accomodate the Cu–O–CO–CH_2–N– chelate rings.

The copper coordination is completed by bonds to the chlorine atom and water molecule. The length of the former bond (2·24 Å) is close to the sum (2·27 Å) of the relevant covalent radii. The sum of the corresponding ionic radii is 2·62 Å.

Table 9

(*a*) Hydrogen-bonded contacts X · · · H · · · Y in Cu(glyglygly)Cl. $1\frac{1}{2}$ H_2O

Atom X	Atom Y	d_{X-Y}	Atom X	Atom Y	d_{X-Y}	$\sigma(d)$
N(1)–H	O(4^{iv})	$2{\cdot}96_5$ Å	O(4)	H–N(1^{iv})	$2{\cdot}96_5$ Å	0·011 Å
N(2)–H	Cl^{ix}	$3{\cdot}27_2$	Cl	H–N(2^{vii})	$3{\cdot}27_2$	0·008
N(3)–H	O(6_w)	$2{\cdot}83_3$	O(6_w)	H–N(3)	$2{\cdot}83_3$	0·010
			O(6_w)	H–N(3^{v})		
O(2)	H–O($5'_w$)	$2{\cdot}79_8$	O(5_w)–H	O($2''$)	$2{\cdot}79_8$	0·011
O(3)	H–O($6'_w$)	$2{\cdot}85_2$	O(6_w)–H	O(3″)	$2{\cdot}85_2$	0·009
			O(6_w)–H	O(3^{vi})		
O(4)	H–O(5_w^{ix})	$2{\cdot}78_8$	O(5_w)–H	O(4^{vii})	$2{\cdot}78_8$	0·010

(*b*) Bond angles at hydrogen-bond donors and acceptors

Angle	θ	$\sigma(\theta)$	Angle	θ	$\sigma(\theta)$
Cu–N(1)–C(1)	111·3°	1·1°	C(6)–O(4) · · · O(5^{ix})	131·9°	1·5°
Cu–N(1) · · · O(4^{iv})	128·4	0·8	C(6)–O(4) · · · N(1^{iv})	137·6	1·6
C(1)–N(1) · · · O(4^{iv})	119·8	1·2	N(1^{iv}) · · · O(4) · · · O(5_w^{ix})	90·5	0·5
C(2)–N(2)–C(3)	121·3	1·5	Cu–O(5_w) · · · O($2''$)	110·5	0·6
C(2)–N(2) · · · Cl^{ix}	113·1	1·1	Cu–O(5_w) · · · O(4^{vii})	123·4	0·7
C(3)–N(2) · · · Cl^{ix}	125·5	1·2	O($2''$) · · · O(5_w) · · · O(4^{vii})	120·0	0·7
C(4)–N(3)–C(5)	120·7	1·5	N(3) · · · O(6_w) · · · N(3^{v})	102·9	0·6
C(4)–N(3) · · · O(6_w)	117·3	1·2	O(3″) · · · O(6_w) · · · O(3^{vi})	89·9	0·4
C(5)–N(3) · · · O(6_w)	116·1	1·1	N(3) · · · O(6_w) · · · O(3″)	99·6	0·5
			N(3^{v}) · · · O(6_w) · · · O(3^{vi})		
C(4)–O(2) · · · O($5'_w$)	132·6	1·3	N(3) · · · O(6_w) · · · O(3^{vi})	135·7	0·7
			N(3^{v}) · · · O(6_w) · · · O(3″)		
Cu^{x}–O(3)–C(6)	113·6	1·1			
Cu^{x}–O(3) · · · O($6'_w$)	109·6	0·6	Cu–Cl · · · N(2^{vii})	100·6	0·8
C(6)–O(3) . . . O($6'_w$)	133·7	1·3			

Hydrogen-bond network

In Table 9 we have listed the hydrogen-bonded interactions, together with the inter-bond angles at all donor and acceptor atoms. We have already mentioned the probable influence of these links upon the relative orientations of the functional groups of the peptide. What is equally remarkable is the network which links any one complex (for example, the non-superscripted one) to no less than eight others through fourteen hydrogen bonds:

O(2) · · · O($5'_w$)–Cu′ and	
O(3) · · · O($6'_w$) · · · N(3′)	to complex(′)
Cu–O(5_w) · · · O($2''$) and	
N(3) · · · O(6_w) · · · O(3″)	to complex(″)
O(4) · · · N(1^{iv}) and	
N(1) · · · O(4^{iv})	to complex(^{iv})
N(3) · · · O(6_w) · · · N(3^{v}) and	
O(3) · · · O($6'_w$) · · · O(3^{v})	to complex(^{v})
N(3) · · · O(6_w) · · · O(3^{vi})	to complex(^{vi})
Cl · · · N(2^{vii}) and	
Cu–O(5_w) · · · O(4^{vii})	to complex(^{vii})
N(2) · · · Cl^{ix} and	
O(4) · · · O(5_w^{ix})–Cu^{ix}	to complex(^{ix})
O(3) · · · O($6'_w$) · · · N(3^{xi})	to complex(^{xi})

Most of these interactions are illustrated in Figs. 1 and 3. It is apparent that three non-peptide atoms — O(5_w), Cl and O(6_w) — are important in the hydrogen-bond network.

The water-molecule $H_2O(5_w)$ is coordinated to the copper atom and must be the donor in its two hydrogen-bonded contacts with the peptide oxygen O(2″) and the 'free' carboxyl oxygen O(4^{vii}). The sum of the inter-vector angles at O(5_w) is 354°, so that this water molecule more closely resembles the trigonal H_2O in bis-glycinocopper(II) hydrate (Snow & Freeman, unpublished) than the two copper-bonded tetrahedral H_2O's in glycylglycinocopper(II) trihydrate (Strandberg *et al.*, 1961).

There is a second link between the two complexes joined by the O(5_w)–H · · · O(4^{vii}) bond. This is the weak hydrogen bond between the chlorine atom Cl and the second peptide nitrogen N(2^{vii}). The atom N(2) also has a close contact with O(2) of the same molecule (2·28 Å). The relative positions of the atoms preclude this from being a hydrogen bond (angles: C(2)–N(2)–O(2) = 111°; C(3)–N(2)–O(2) = 56°; C(4)–O(2)–N(2) = 58°). In any case, the sole hydrogen atom attached to N(2) is already used in the bond to the chlorine atom.

Finally, the water molecule $H_2O(6_w)$ lies on a two-fold axis and acts as a link between two peptide nitrogens N(3) and two copper-bonded carboxyl oxygens O(3) belonging to *four* different peptide chains. O(6_w) acts as the hydrogen donor in the bonds to the oxygen atoms and as the acceptor in the bonds to the nitrogen atoms. The configuration about O(6_w) is a distorted tetrahedron, with inter-hydrogen-bond angles between 90° and 136°. There is another pair of

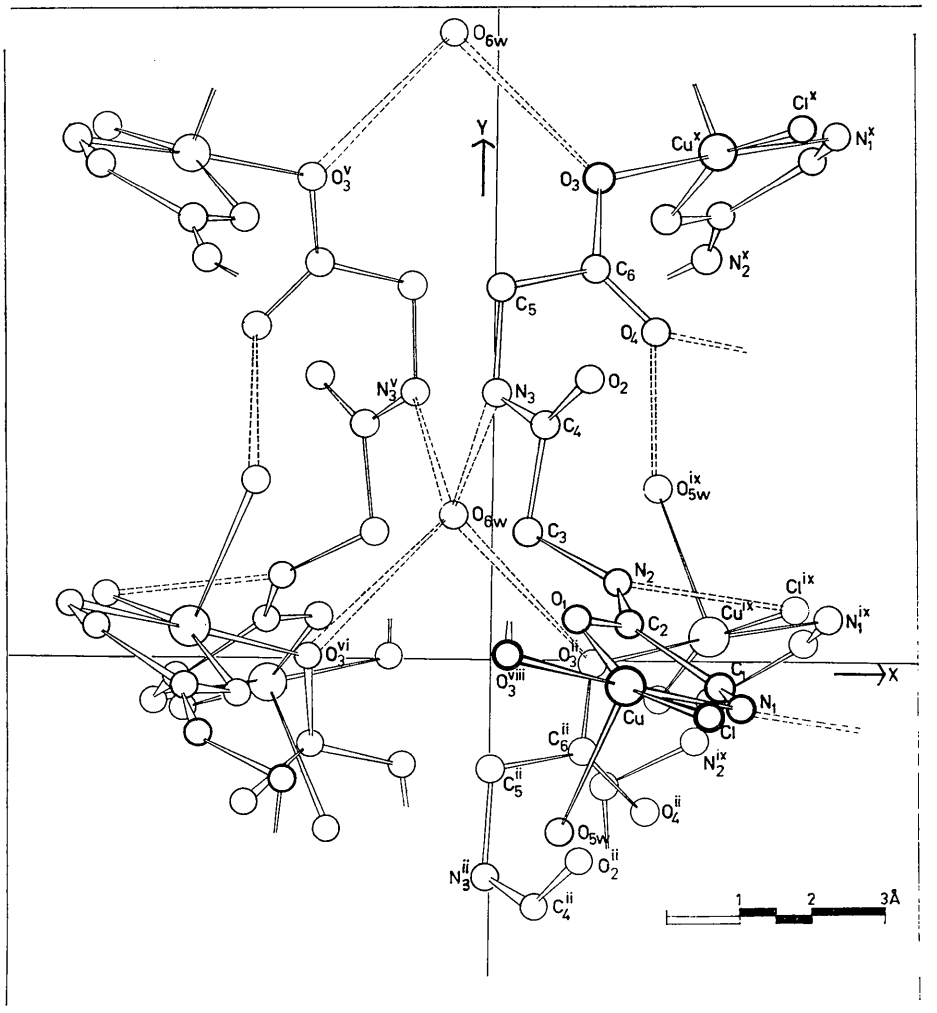


Fig. 3. Hydrogen bonds in glycylglycylglycinocopper(II) sesquihydrate: Normal projection of part of unit cell on (001) plane.

reasonably close contacts (2·964 Å) to the water molecules $H_2O(5'''_w)$ and $H_2O(5^{ix}_w)$, but these contacts would not be hydrogen bonds (angle $O(5'''_w)$–$O(6_w)$–$O(5^{ix}_w)$ = 162·7°) even if the hydrogen-bonding capacity of $O(6_w)$ were not already satisfied.

Chemical significance

This structure analysis provides the first solid-state evidence that, in non-alkaline solution, copper–peptide binding occurs predominantly at the terminal amino nitrogen and first peptide oxygen atoms. Spectral studies and potentiometric titrations (Dobbie & Kermack, 1955; Murphy & Martell, 1957; Rabin, 1958; Koltun, Roth & Gurd, 1963) and proton magnetic resonance measurements (Li, Scruggs & Becker, 1962) at pH≤6 are all consistent with this view, although not all these authors have been as explicit as Rabin (1958) in specifying the oxygen, and not the nitrogen, atom as the binding site on the first peptide residue.

The binding of a second copper atom at the carboxyl group has not been expected on the basis of other measurements. In this bond the carboxyl group behaves as though it were a side-chain of a peptide.

The structure can be added to the growing list of well established cases of 5-coordinated copper(II), although this coordination number may in this instance be due to steric hindrance in the sixth octahedral coordination position.

The structure-factors, Fourier syntheses and molecular dimensions for this work were calculated on the Sydney University computer SILLIAC, using mainly programs written and supervised by Dr F. M. Lovell. The least-squares refinement was carried out successively on three computers. We are grateful that this was possible through the cooperation of Mr T. Prentice, Standard Telephones & Cables Ltd., Sydney (ZEBRA); Drs G. Ferguson, J. G. Sime and S. Sutherland, University of Glasgow (DEUCE); and Mr P. Goddard, Weapons Research Establishment, Salisbury, South Australia (IBM 7090). The preparation in

Sydney of data for the 7090 computer was supervised by Dr J. G. Sime.

This investigation was supported by a research grant A–3460 (later GM 10867) from the Institute for Arthritis and Metabolic Diseases, United States Public Health Service, and by the award of an Alexander Boden Fellowship at Sydney University to one of us (J.C.S.).

References

BARCLAY, G. A. & KENNARD, C. H. L. (1961). *J. Chem. Soc.* p. 3289.
BERGHUIS, J., HAANAPPEL, J. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
BRYAN, R. F., POLJAK, R. J. & TOMITA, K. (1961). *Acta Cryst.* **14**, 1125.
BUSING, W. L. & LEVY, H. (1961). *Computing methods and the phase problem in X-ray crystal analysis.* p. 146. Pergamon Press.
COOPER, T., FREEMAN, H. C., ROBINSON, G. & SCHOONE, J. C. (1962). *Nature, Lond.* **194**, 1237.
DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.
DOBBIE, H. & KERMACK, W. O. (1955). *Biochem. J.* **59**, 246, 257.
FREEMAN, H. C., SMITH, J. E. W. L. & TAYLOR, J. C. (1961). *Acta Cryst.* **14**, 407.
HAHN, T. (1957). *Z. Kristallogr.* **109**, 438.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
HUGHES, E. W. & MOORE, W. J. (1949). *J. Amer. Chem. Soc.* **71**, 2618.
KOLTUN, W. L., ROTH, R. H. & GURD, F. R. N. (1963). *J. Biol. Chem.* **238**, 124.
LEUNG, Y. C. & MARSH, R. E. (1958). *Acta Cryst.* **11**, 17.
LI, N. C., SCRUGGS, R. L. & BECKER, E. D. (1962). *J. Amer. Chem. Soc.* **84**, 4650.
MARSH, R. E. & GLUSKER, J. P. (1961). *Acta Cryst.* **14**, 1110.
MURPHY, C. B. & MARTELL, A. E. (1957). *J. Biol. Chem.* **226**, 37.
PAULING, L. (1948). *J. Chem. Soc.* p. 1461.
PAULING, L. (1960). *Nature of the chemical bond*, 3rd ed. p. 172. Ithaca: Cornell Univ. Press.
PAULING, L. & COREY, R. B. (1963). *Proc. Nat. Acad. Sci. Wash.* **39**, 253; *Nature Lond.* **171**, 59.
RABIN, B. R. (1958). *Metals and enzyme activity.* (ed. Crook, E. M.) p. 21. Cambridge Univ. Press.
ROLLETT, J. S. (1961). *Computing methods and the phase problem in X-ray crystal analysis.* p. 87. Pergamon Press.
SCHOONE, J. C. (1961). See Rogers, D. *Computing methods and the phase problem in X-ray crystal analysis.* p. 5. Pergamon Press.
STRANDBERG, B., LINDQVIST, I. & ROSENSTEIN, R. D. (1961). *Z. Kristallogr.* **116**, 266.
TOMITA, K. & NITTA, I. (1960). *Bull. Chem. Soc. Japan*, **34**, 286.
TOMITA, K. (1960). *Bull. Chem. Soc. Japan*, **34**, 297.
YAKEL, H. L. & HUGHES, E. W. (1952). *J. Amer. Chem. Soc.* **74**, 6302.

Acta Cryst. (1964). **17**, 730

The Crystal Structure of Sodium Bromide Dihydrate

BY WILLIAM R. HAAF* AND G. B. CARPENTER

Department of Chemistry, Brown University, Providence 12, *Rhode Island, U.S.A.*

(*Received* 21 *June* 1963)

$NaBr.2H_2O$ is monoclinic, $P2_1/c$, $Z=4$, with $a=6{\cdot}575$, $b=10{\cdot}456$, $c=6{\cdot}776$ Å and $\beta=113{\cdot}38°$. The structure agrees very well with that determined independently by Culot, Piret & Van Meersche (1962); the differences are attributed chiefly to different absorption errors.

Introduction

The crystal structure of sodium bromide dihydrate has been investigated in order to study the role of hydrogen bonding in alkali halide hydrates and to make possible a more detailed analysis of the infrared absorption of the solid (Schiffer & Hornig, 1961). During the final stages of refinement, we learned that Culot, Piret & Van Meersche (1962) had just completed determination of the same structure. Comparison of the two independent studies shows several interesting features.

Structure determination

Details of the present work are described in a thesis (Haaf, 1963). $NaBr.2H_2O$ is monoclinic, space group $P2_1/c$, with 4 formula units per cell. The cell dimensions are $a=6{\cdot}575$ (0·002), $b=10{\cdot}456$ (0·005), $c=6{\cdot}776$ (0·002) Å and $\beta=113{\cdot}38$ (0·02)°. The values in parentheses are standard deviations measuring internal consistency only; the systematic error may be two or three times as large. These results agree well

* Present address: General Electric Research Laboratory, The Knolls, Schenectady, New York, U.S.A.