trächtlich grösser sind (2,678 bis 2,844 Å) als die beiden zuvor diskutierten, führt direkt zu einem weiteren Wassermolekül. Damit ergibt sich zusammenfassend das Vorliegen der Wasserstruktur als Diaquooxonium-Kation, $H_7O_3^+$, das zusammen mit dem organischen Anion die Kristallstruktur aufbaut.

Über die Auffindung des $H_7O_3^+$-Ions durch eine Kristallstrukturanalyse ist bisher nur einmal in der Literatur berichtet worden. Lundgren & Olovsson (1968) bestimmten für $HBr.4H_2O$ die Struktur

$$(H_7O_3^+)\,(H_9O_4^+)\,(Br^-)_2\,.\,H_2O$$

und entdeckten damit erstmalig gleich zwei der höheren hydratisierten Oxoniumionen. Für die beiden kurzen O···O-Abstände im $H_7O_3^+$-Ion erhielten sie 2,465 und 2,498 Å und für den eingeschlossenen Winkel 113,6° (Standardabweichungen 0,014 Å und 0,5°).

Die Verknüpfung im grossen der Kationen und Anionen durch die Wasserstoffbrücken ist sehr komplex, wovon Fig. 3 einen Eindruck geben soll. Die einzigen intermolekularen Anion–Anion–Wasserstoffbrücken,

O(2)–H(2)···O(52) und O(71)–H(71)···O(51),

erzeugen zweidimensional unbegrenzte Bausammenhänge parallel (010) von ineinandergreifenden und seitlich miteinander verknüpften Spiralsystemen um die Schraubenachsen parallel zur *a*-Achse. Die Kationen verstärken diese Verknüpfung und verbinden benachbarte Bauzusammenhänge, wodurch letztenendes ein dreidimensionales Netzwerk entsteht.

Die Autoren danken Herrn Dipl.-Ing. D. Nockenberg für Programmierarbeiten, dem Rechenzentrum der Technischen Universität Braunschweig und dem Deutschen Rechenzentrum in Darmstadt für Rechenzeit und dem Fonds der Chemischen Industrie und der Stiftung Volkswagenwerk für Förderung. Ihr besonderer Dank gilt der Deutschen Forschungsgemeinschaft für Leihgaben und Personalmittel, ohne die diese Arbeit nicht hätte durchgeführt werden können.

Literatur

HANSON, H. P., HERMAN, F., LEA, I. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.

LUNDGREN, J.-O. & OLOVSSON, I. (1968). *J. Chem. Phys.* **49**, 1068.

MOOTZ, D., ALTENBURG, H., FAYOS, J. & WUNDERLICH, H. (1969). *Acta Cryst.* A**25**, S105.

MOOTZ, D. & WUNDERLICH, H. (1970). *Acta Cryst.* B**26**, 1820.

OKAYA, Y. (1966). *Acta Cryst.* **21**, 726.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

SUNDARALINGAM, M. & JENSEN, L. H. (1965). *Acta Cryst.* **18**, 1053.

Acta Cryst. (1970). B**26**, 2054

The Crystal Structure of Ethylenebidiguanide Copper(II) Chloride Monohydrate

BY M. MATTHEW* AND N. R. KUNCHUR

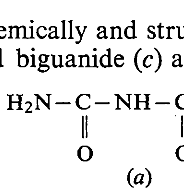
Chemistry Department, University of Western Ontario, London, Ontario, Canada

(*Received* 24 *April* 1967 *and in revised form* 18 *February* 1970)

The crystal structure of ethylenebidiguanide copper(II) chloride monohydrate has been determined from Patterson and Fourier syntheses with use of three-dimensional photographic data and refined by a least-squares method. The *R* index is 0·084 for all the observed reflexions. The space group is $P2_1/c$ and the cell constants are $a=6{\cdot}97$, $b=11{\cdot}88$, $c=18{\cdot}50$ Å, $\beta=103{\cdot}5°$ and $Z=4$. The two halves of the copper complex ion are independently planar and the angle between the two plane normals is 4·6°. The complex ions are held together by a network of hydrogen bonds through two chlorine ions and the oxygen atoms of the water molecules. The Cu–N distances vary between 1·933 and 1·989 Å.

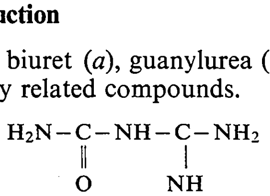
Introduction

Chemically and structurally biuret (*a*), guanylurea (*b*), and biguanide (*c*) are closely related compounds.



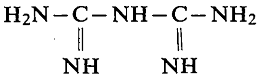
$$H_2N-\underset{\underset{O}{\|}}{C}-NH-\underset{\underset{O}{\|}}{C}-NH_2$$

(*a*)



$$H_2N-\underset{\underset{O}{\|}}{C}-NH-\underset{\underset{NH}{|}}{C}-NH_2$$

(*b*)



$$H_2N-\underset{\underset{NH}{\|}}{C}-NH-\underset{\underset{NH}{\|}}{C}-NH_2$$

(*c*)

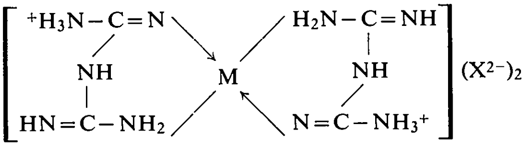
Compound (*b*) is derived from biuret by substitution of one oxygen atom with an imino group and (*c*) by substituting both the oxygen atoms with two imino groups. During the last quarter of century, a considerable amount of work has been done on the chemistry of these compounds in order to explain their important

---

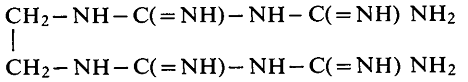
* Present address: Department of Chemistry, University of Florida, Gainesville, Florida 32601, U.S.A.

physiological and potential chemotherapeutic properties.

All these compounds behave as bases, acids or zwitterions and this property enhances their chelating capacity as can be seen in the numerous coloured chelate compounds they form with various transition metals. The compounds of biguanides with Cu(II) and Ni(II) have been studied although their structures have formed a subject of controversy. Various proposals have been offered for their structures (Tschugaeff, 1907; Ley & Muller, 1907; Slotta & Tschesche, 1929; Träube & Glaubitte, 1930; Ray & Saha, 1937). Only the structure proposed by Ray & Saha seems to be reasonable. They suggest that the metal replaces the hydrogen of the terminal imino group and that the amino group on the other terminal donates a lone pair of electrons to the metal atom to form a coordinate bond:

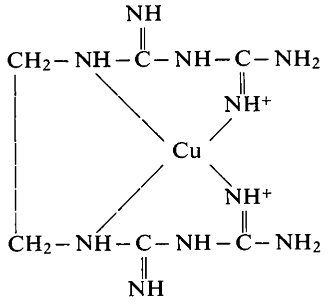


Among the various substituted biguanides, ethylenebidiguanide is one of the most interesting compounds that chelate metals. Chakrovorty & Ray (1944) confirmed this compound to be a true bidiguanide and proposed the following symmetrical structure which seems to be quite plausible.



$$\begin{array}{l} CH_2-NH-C(=NH)-NH-C(=NH)\ NH_2 \\ | \\ CH_2-NH-C(=NH)-NH-C(=NH)\ NH_2 \end{array}$$

Assuming that the above structure has a *cis* configuration, Chakravorty & Ray proposed a *cis*-planar structure for the bisethylenebidiguanide Cu(II) complex



A detailed structure analysis of the preceding compound was undertaken to verify the structures proposed and obtain precise dimensions of the coordination compound.

Experimental

Crystal data

Copper ethylenebidiguanide chloride, monohydrate: $CuC_6N_{10}OH_{18}Cl_2$
Molecular weight: 380·63
Monoclinic, space group: $P2_1/c$.
Cell dimensions: $a = 6{\cdot}97 \pm 0{\cdot}01$, $b = 11{\cdot}88 \pm 0{\cdot}02$
$c = 18{\cdot}50 \pm 0{\cdot}03$ A°, $\beta = 103{\cdot}5^\circ \pm 0{\cdot}3^\circ$

The cell dimensions and the values for their estimated standard deviations were determined from rotation and Weissenberg photographs).
Volume of the unit cell = 1489 $Å^3$
Number of molecules per unit cell, $Z = 4$
$D_c = 1{\cdot}705$ g.cm^{-3}, $D_m = 1{\cdot}73$ g.cm^{-3}
Absorption coefficient for X-rays with $\lambda = 1{\cdot}542$ Å, $\mu = 57{\cdot}0$ cm^{-1}.
Total number of electrons in the unit cell: $F(000) = 780$.

Collection of intensity data

For collection of intensity data a crystal ground into a sphere of diameter of 0·22 mm was used. Data were

Table 1. *The final fractional coordinates of non-hydrogen atoms and their estimated standard deviations*

	x/a	$\sigma(x)$	y/b	$\sigma(y)$	z/c	$\sigma(z)$
Cu	0·2523	0·001 Å	0·0393	0·002 Å	0·0108	0·001 Å
Cl(1)	0·6663	0·003	0·0325	0·004	0·3474	0·003
Cl(2)	0·7634	0·003	0·3628	0·003	0·2752	0·003
N(1)	0·1961	0·008	0·8856	0·011	0·0336	0·008
N(2)	0·1650	0·008	0·8063	0·010	0·9107	0·008
N(3)	0·2326	0·007	0·0058	0·010	0·9053	0·007
N(4)	0·3061	0·007	0·1929	0·010	0·9821	0·007
N(5)	0·3661	0·008	0·2766	0·010	0·1030	0·008
N(6)	0·2832	0·008	0·0835	0·010	0·1167	0·008
N(7)	0·1425	0·009	0·6897	0·011	0·0082	0·009
N(8)	0·1853	0·008	0·8848	0·010	0·7983	0·008
N(9)	0·3506	0·008	0·3892	0·011	0·0020	0·008
N(10)	0·3643	0·008	0·2041	0·010	0·2205	0·008
C(1)	0·1684	0·009	0·7969	0·012	0·9864	0·009
C(2)	0·1976	0·008	0·9072	0·013	0·8727	0·009
C(3)	0·3369	0·010	0·2828	0·014	0·0264	0·010
C(4)	0·3396	0·009	0·1807	0·012	0·1453	0·009
C(5)	0·2793	0·009	0·0984	0·013	0·8599	0·009
C(6)	0·2676	0·010	0·2101	0·013	0·8998	0·010
O(1)	0·8771	0·009	0·4513	0·010	0·1285	0·009

recorded from layers $k=0\rightarrow7$ and $h=0$ with nickel filtered Cu $K\alpha$ radiation on an integrating Weissenberg camera with multiple film technique. By this procedure the size and shape of all reflexions recorded on the film were identical and thus the errors in the measurements of the intensity of the reflexions due to contraction and expansion of some reflexions were eliminated. A calibrating strip was prepared by integrating a suitable reflexion. The integrating limits used in taking the intensity photographs and preparing the calibration strip were the same so that the size of the spots in both cases was identical. This strip was used for measuring the intensity of the reflexions by visual comparison. 1515 reflexions out of 2109 in the range of observation had non-zero intensities. Intensities were corrected for absorption and the usual Lorentz and polarization factors. Values for absolute scale and temperature factors were obtained for all layers of photographs from a Wilson plot. The scale factors for layers $k=0\rightarrow7$ were improved by correlating the overlapping reflexions in the layer $h=0$. Every unobserved reflexion was assigned a value equal to half of the minimum F_o.

Structure determination

All observed reflexions were used to compute a three-dimensional Patterson synthesis. There are four formula units of the compound in one unit cell so that there are one copper and two chlorine atoms per asymmetry unit. The coordinates of these atoms were obtained by interpretation of the Patterson map. A three-dimensional electron density Fourier synthesis was computed using the signs from copper and the two chlorine atoms. This synthesis revealed the positions of all (excluding hydrogen) atoms. The atomic coordinates were refined by three successive electron density Fourier syntheses using calculated signs and observed F values. The disagreement index R for all observed reflexions at this stage was 0·17.

The next stage of refinement of the structure consisted of six cycles of full-matrix least-squares refinement using the program written by Busing, Martin & Levy (1962). The parameters refined were three positional and six thermal parameters for each atom and an overall scale factor. The scattering factors used were those of Watson & Freeman (1961) for Cu^{2+}, Dawson (1960) for Cl^- and Freeman (1959) for carbon, nitrogen and oxygen atoms. The following weighting scheme was used.

$$W=\sigma|F|=0\cdot1|F_o| \text{ for } |F_o|\geq30\cdot0$$
$$W=\sigma|F|=3\cdot0 \text{ for } |F_o|\leq30\cdot0$$

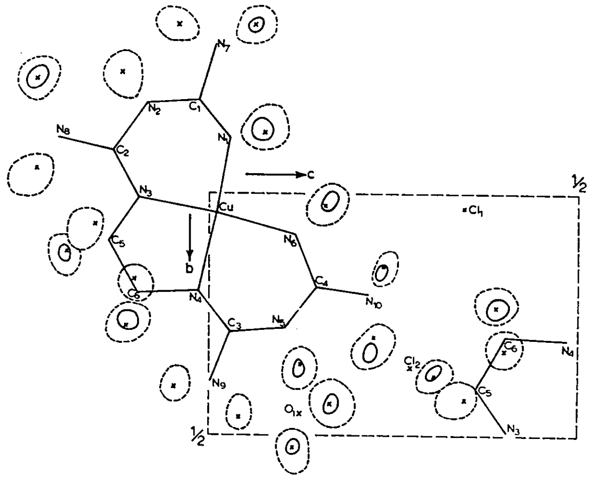


Fig. 1. The final composite three-dimensional electron density difference map projected along the a axis. The contours are drawn at 0·3 and 0·6 e.Å^{-3}. The assumed positions of the hydrogen during the last least-squares refinement are indicated by crosses.

Table 2. *Anisotropic thermal parameters* β_{ij}

All values are multiplied by 10^4. Standard deviations are written in parentheses. The expression used for the temperature factor is $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	155 (2)	29 (1)	13 (1)	−2	12	−1
Cl(1)	252 (5)	32 (2)	16 (1)	−12	15	1
Cl(2)	171 (4)	35 (2)	18 (1)	−1	13	−4
N(1)	181 (13)	22 (7)	14 (2)	35	18	4
N(2)	168 (12)	24 (6)	16 (2)	9	12	−1
N(3)	141 (11)	17 (6)	10 (1)	14	9	−2
N(4)	144 (11)	22 (7)	9 (1)	11	14	−1
N(5)	171 (12)	30 (7)	11 (1)	−7	11	−4
N(6)	146 (12)	26 (9)	15 (2)	−6	13	−2
N(7)	188 (15)	36 (8)	22 (2)	4	14	0
N(8)	186 (13)	38 (7)	11 (1)	18	14	0
N(9)	195 (14)	16 (6)	17 (2)	−13	11	3
N(10)	166 (12)	34 (7)	12 (1)	15	13	−5
C(1)	111 (12)	32 (9)	16 (2)	−10	11	−2
C(2)	100 (12)	12 (8)	15 (2)	7	12	3
C(3)	133 (16)	31 (9)	17·(2)	−6	12	−1
C(4)	100 (12)	43 (9)	14 (2)	−2	16	1
C(5)	148 (14)	25 (7)	11 (2)	−5	12	−7
C(6)	175 (15)	45 (9)	11 (2)	−14	15	2
O(1)	267 (15)	64 (8)	21 (2)	−7	22	−4

The unobserved reflexions were excluded from refinement. The atomic shifts for all positional parameters in the final cycle of refinement were less than one-tenth of their estimated standard deviations and hence the refinement was considered to be completed. The final disagreement index R was 0·084 for observed reflexions only.

A three-dimensional electron density difference Fourier synthesis was computed at this stage in order to locate hydrogen atoms. Eleven out of eighteen hydrogen atoms could be located at peak heights of 0·5–0·6 electrons. The rest of the hydrogen atom. could be fixed in positive regions of the difference map There was no change in the disagreement index R after including the hydrogen positions. The difference map showing hydrogen atoms is given in Fig. 1. The final positional parameters and their estimated standard deviations are given in Table 1 and 3, thermal parameters in Table 2 and the observed and calculated structure factors in Table 4.

Table 3. *The fractional coordinates of the hydrogen atoms*

	x/a	y/b	z/c
H(1)	0·200	0·870	0·082
H(2)	0·146	0·650	0·062
H(3)	0·167	0·637	0·960
H(4)	0·125	0·750	0·884
H(5)	0·229	0·762	0·775
H(6)	0·250	0·900	0·775
H(7)	0·220	0·125	0·816
H(8)	0·416	0·075	0·850
H(9)	0·125	0·200	0·900
H(10)	0·380	0·250	0·892
H(11)	0·335	0·400	0·995
H(12)	0·375	0·450	0·033
H(13)	0·416	0·350	0·120
H(14)	0·375	0·300	0·225
H(15)	0·312	0·150	0·241
H(16)	0·271	0·038	0·160
H(17)	0·916	0·437	0·175
H(18)	0·980	0·535	0·116

Description and discussions of the structure

To facilitate the description of the structure, the symmetry related atoms have been identified by a

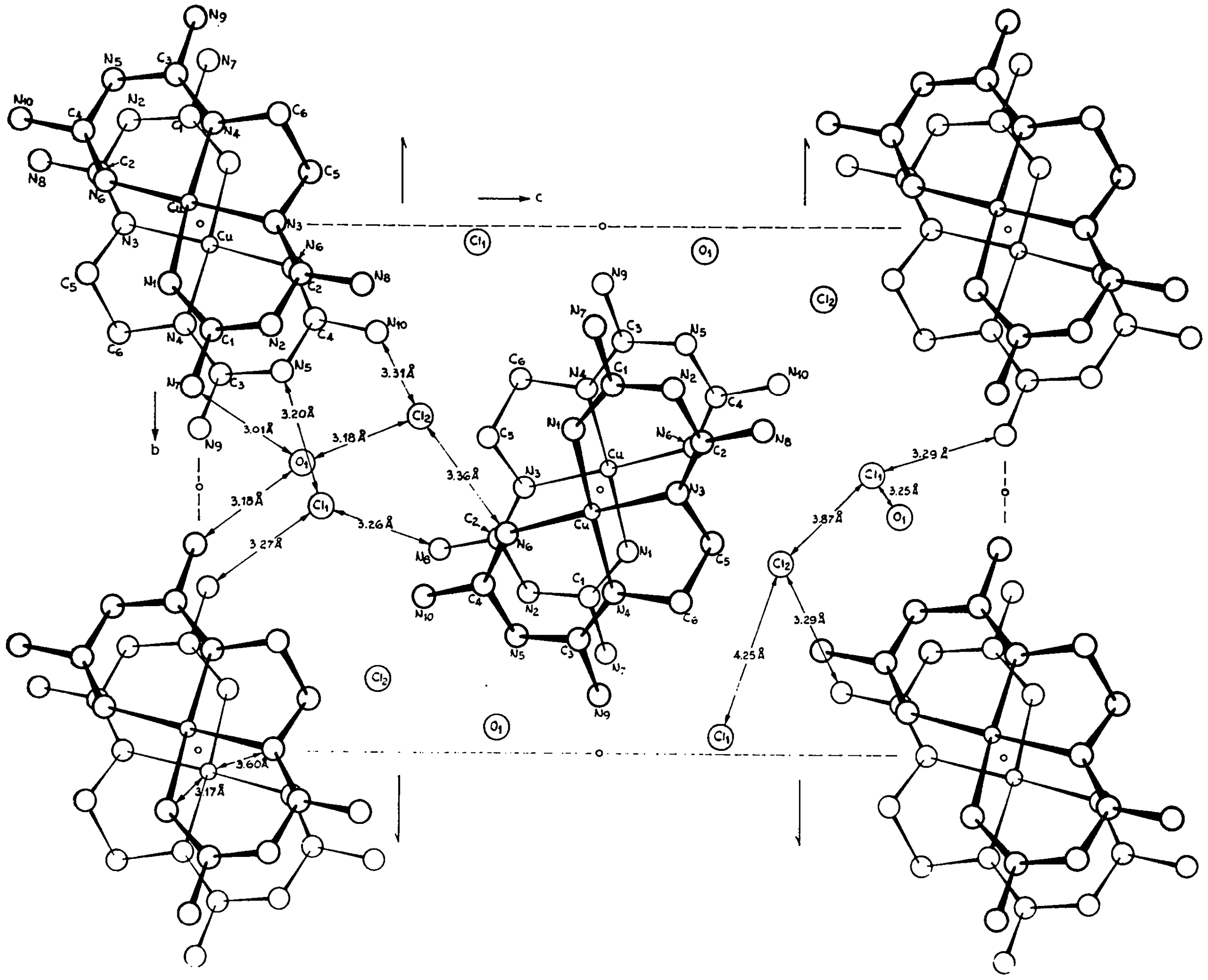


Fig. 2. A projection of the structure along the *a* axis. Distances are given in Å.

Table 4. *The observed and calculated structure factors*

The three columns in each group contain the values, reading from left to right l, $10F_o$ and $10F_c$. A negative F_o indicates an unobserved reflexion which was not included in the least-squares refinement.

L	FO	FC
H= 0, K= 0		
2	998	1388
4	640	620
6	1098	1233
8	1772	1954
10	913	912
12	339	312
14	748	632
16	353	-332
18	199	165
20	108	127
H= 0, K= 1		
1	1297	1294
2	494	-535
3	665	707
4	116	-100
5	794	742
6	324	285
7	291	-220
8	176	141
9	1143	1143
10	-51	-60
11	365	326
12	349	-290
13	114	105
14	116	107
15	-51	64
16	214	-167
17	155	127
18	-51	-54
19	108	-97
20	-51	-76
21	-51	2
H= 0, K= 2		
0	458	509
1	-49	21
2	211	239
3	336	-317
4	405	-390
5	515	539
6	940	1043
7	158	-159
8	480	499
9	-49	49
10	164	-140
11	-49	-77
12	295	300
13	135	-149
14	383	346
15	115	-135
16	223	226
17	295	-318
18	-49	43
19	-49	-36
20	160	170
21	350	-354
H= 0, K= 3		
1	-50	-22
2	148	162
3	1468	1776
4	295	-296
5	170	215
6	255	190
7	528	347
8	80	-97
9	297	277
10	247	-206
11	925	894
12	653	-628
13	140	-111
14	237	210
15	305	282
16	281	-246
17	341	310
18	442	-432
19	-50	42
20	303	-262
21	-50	53
H= 0, K= 4		
0	244	210
1	229	-276
2	726	839
3	260	-254
4	447	-411
5	-48	-57
6	328	355
7	286	-267
8	298	264
9	403	-378
10	231	235
11	403	-394
12	525	518
13	428	-410
14	-47	-47
15	302	-283
16	-47	-98
17	-47	-95
18	-47	-10
19	232	-265
20	206	211
21	305	-351
H= 0, K= 5		
1	191	198
2	160	-157
3	761	778
4	382	-363
5	158	124
6	587	-625
7	-47	-28
8	122	112
9	317	297
10	860	-878
11	546	585
12	466	-451
13	298	271
14	325	-314
15	-47	62
16	107	-136
17	-47	17
18	516	-538
19	-47	50
20	292	-275
21	86	91
H= 0, K= 6		
0	183	199
1	554	-582
2	-47	4
3	219	207
4	315	320
5	296	-268
6	-47	2
7	466	-453
8	-47	-102
9	676	-639
10	-47	18
11	-47	21
12	315	298
13	149	-172
14	177	166
15	787	-762
16	237	-256
17	-47	-88
18	-47	21
19	305	-307
H= 0, K= 7		
1	118	-144
2	-47	102
3	95	-106
4	359	-339
5	-47	61
6	376	-374
7	441	-416
8	118	-118
9	-47	43
10	401	-375
11	200	-182
12	237	-217
13	-47	-34
14	279	-268
15	202	-208
16	216	-215
17	-47	-49
18	365	-353
H= 0, K= 8		
0	256	-250
1	-47	-19
2	512	-515
3	451	-433
4	-47	-7
5	97	118
6	451	-416
7	512	-489
8	313	-320
9	520	-474
10	107	-112
11	-47	11
12	198	-198
13	470	-492
14	122	-150
15	405	-406
16	152	-129
17	175	-173
18	-47	71
H= 0, K= 9		
1	198	-164
2	432	436
3	335	-344
4	386	-374
5	305	-316
6	105	-154
7	290	-299
8	305	-303
9	168	-167
10	-47	2
11	302	-319
12	589	-571
13	141	-139
14	-47	7
15	-47	-99
16	275	-262
17	149	-140
18	256	-290
H= 0, K= 10		
0	-47	71
1	-47	119
2	-47	64
3	-47	90
4	305	-292
5	183	194
6	275	-254
7	405	-409
8	107	-84
9	130	-123
10	-47	68
11	-47	121
12	-47	-95
13	-47	-58
14	172	-190
15	198	-238
H= 0, K= 11		
1	-47	-5
2	152	150
3	558	-583
4	-47	-34
5	715	-732
6	237	-264
7	-47	63
8	124	164
9	305	-328
10	-47	-107
11	179	-154
12	126	-142
13	217	-227
14	-47	-10
15	61	-106
H= 0, K= 12		
0	753	-747
1	328	-361
2	309	-315
3	-47	-28
4	558	-599
5	-47	29
6	466	-429
7	-47	57
8	290	-306
9	-47	-68
10	141	-172
11	-47	-55
12	206	-229
H= 0, K= 13		
1	283	-278
2	-47	-5
3	436	-455
4	-47	28
5	275	-279
6	-47	-4
7	-47	-66
8	206	215
9	210	-220
10	-47	-104
11	214	-198
H= 0, K= 14		
0	334	-294
1	-47	-50
2	325	-336
3	-47	52
4	76	-97
5	-47	62
6	504	-524
7	-47	41
8	240	-236
H= 1, K= 0		
0	332	-323
2	88	-66
4	424	422
6	940	-1056
8	782	-740
10	599	-629
12	-47	22
14	773	-753
16	-52	65
18	241	-232
20	465	-480
H= 1, K= 1		
0	162	-131
1	432	412
2	629	-588
3	407	399
4	338	300
5	644	-668
6	146	-139
7	160	-109
8	451	-417
9	565	-544
10	-52	-29
11	519	-528
12	114	-136
13	114	-90
14	147	142
15	241	-183
16	147	-133
17	374	-353
18	-52	-11
19	478	-439
20	-52	-87
21	-52	28
H= 1, K= 2		
0	156	127
1	217	-224
2	278	-277
3	146	-156
4	264	-272
5	125	101
6	403	-456
7	1087	-1047
8	679	-646
9	240	254
10	-49	-29
11	389	-367
12	552	-548
13	246	-248
14	621	-597
15	227	-216
16	340	-339
17	109	-75
18	203	-219
19	90	-101
20	427	-404
21	-49	-95
H= 1, K= 3		
0	370	356
1	522	478
2	1395	-1491
3	808	-825
4	255	-283
5	94	-124
6	434	-447
7	201	-176
8	482	-468
9	319	-310
10	555	-535
11	754	-757
12	355	-381
13	394	-378
14	140	-179
15	-50	-75
16	470	-451
17	659	-647
18	-50	-19
19	152	-174
20	-50	-96
21	213	-253
H= 1, K= 4		
0	293	-307
1	687	-721
2	-45	54
3	344	298
4	333	295
5	249	-294
6	146	145
7	547	-536
8	582	-569
9	214	-195
10	120	118
11	179	-142
12	-45	-103
13	170	-138
14	-45	5
15	-45	-1
16	236	-230
17	-45	4
18	-45	-35
19	-45	-97
20	119	-204
H= 1, K= 5		
0	917	-1058
1	177	210
2	772	-831
3	413	431
4	863	-947
5	-43	-15
6	139	92
7	188	-178
8	561	-603
9	134	-169
10	697	-745
11	-43	128
12	-43	83
13	380	391
14	97	-104
15	-43	-25
16	-43	-71
17	293	-297
18	177	-182
19	-43	-29
20	78	123
H= 1, K= 6		
0	-45	74
1	899	-983
2	77	87
3	335	-372
4	541	552
5	1233	-1389
6	124	-153
7	559	-576
8	142	-148
9	588	-599
10	-45	16
11	178	-158
12	435	429
13	715	-740
14	-45	-26
15	-45	-62
16	-45	-98
17	-45	-102
18	-45	33
19	178	-200
H= 1, K= 7		
0	406	-419
1	230	-219
2	627	-417
3	-45	-39
4	902	-955
5	197	-206
6	190	-152
7	-45	11
8	343	-335
9	-45	-102
10	375	-368
11	156	-206
12	-45	-31
13	-43	9
14	119	-133
15	-45	-108
16	119	-128
17	-45	91
18	-45	34
H= -1, K= 0		
2	332	383
4	282	-300
6	673	665
8	549	575
10	1015	1073
12	299	-289
14	673	693
16	349	322
18	116	142
20	349	322
22	282	271
H= -1, K= 1		
1	-51	-10
2	644	700
3	390	-418
4	401	-321
5	1010	1165
6	484	473
7	145	154
8	357	311
9	432	389
10	393	375
11	815	742
12	104	120
13	432	379
14	-51	-51
15	-51	56
16	-51	-25
17	207	181
18	-51	-36
19	752	704
20	126	138
21	-51	50
22	-51	-91
H= -1, K= 2		
1	576	931
2	-49	37
3	74	-88
4	164	150
5	452	-464
6	172	-112
7	1146	1116
8	924	877
9	-49	12
10	276	278
11	186	137
12	127	130
13	-49	21
14	460	430
15	254	247
16	438	417
17	-49	-98
18	246	237
19	109	104
20	282	265
21	-49	11
22	313	363
H= -1, K= 3		
1	638	-636
2	645	675
3	555	570
4	844	846
5	490	480
6	929	806
7	605	516
8	380	402
9	-50	-30
10	380	376
11	703	622
12	713	648
13	878	808
14	249	225
15	-50	53
16	442	414
17	563	594
18	170	173
19	404	355
20	-50	82
21	297	327
H= -1, K= 4		
1	1004	1068
2	289	295
3	557	534
4	229	-222
5	73	129
6	117	-118
7	638	639
8	806	854
9	502	502
10	-45	24
11	344	321
12	247	255
13	520	534
14	-45	68
15	168	172
16	564	624
17	-45	94
18	-45	76
19	-45	110
20	91	201
21	109	112
H= -1, K= 5		
1	282	-298
2	376	387
3	748	-786
4	1273	1378
5	784	-711
6	240	240
7	186	163
8	231	229
9	134	-141
10	727	752
11	-43	-30
12	362	343
13	488	-478
14	-43	70
15	219	-201
16	-43	-8
17	212	201
18	280	271
19	-43	55
20	-43	-112
H= -1, K= 6		
1	1466	1459
2	267	251
3	117	103
4	458	-460
5	693	759
6	-45	-29
7	550	606
8	287	247
9	774	794
10	350	339
11	122	-170
12	368	-362
13	343	330
14	-45	-64
15	137	148
16	146	137
17	-45	37
18	-45	49
19	148	140
H= -1, K= 7		
1	235	217
2	263	258
3	199	-187
4	880	884
5	471	452
6	370	353
7	-45	-21
8	183	154
9	214	196
10	439	424
11	-45	45
12	-45	11
13	108	106
14	-45	-61
15	221	189
16	163	153
17	-45	-54
18	-45	76
19	-45	87
H= 2, K= 0		
0	2637	-3552
2	465	520
4	1015	-1073
6	1089	-1070
8	1064	-1007
10	436	-426
12	339	-338
14	262	-281
16	253	261
18	267	-270
20	-52	5
H= 2, K= 1		
0	1530	1918
1	1576	-1719
2	552	490
3	673	-666
4	415	420
5	268	-276
6	-52	-66
7	457	-627
8	615	556
9	1297	-1236
10	274	252
11	-52	-45
12	207	194
13	147	-156
14	-52	-37
15	239	-209
16	-52	59
17	-52	-36
18	-52	76
19	-52	73
20	-52	55
H= 2, K= 2		
0	793	-710
1	97	51
2	287	-318
3	150	-165
4	419	-429
5	397	-368
6	867	-853
7	-49	-17
8	115	-77
9	-49	-13
10	254	-227
11	107	-86
12	432	-423
13	195	202
14	254	-241
15	-49	-69
16	-49	-71
17	-49	95
18	-49	-72
19	-49	25
20	-49	-62
H= 2, K= 3		
0	136	-132
1	697	-730
2	-50	6
3	927	-941
4	233	266
5	291	261
6	-50	-17
7	530	-501
8	132	125
9	297	-273
10	128	169
11	362	-360
12	287	291
13	112	132
14	-50	11
15	370	-386
16	412	410
17	100	-146
18	241	215
19	-50	24
20	142	165
H= 2, K= 4		
0	-45	8
1	395	370
2	456	-404
3	108	112
4	-45	61
5	109	126
6	388	-405
7	375	385
8	-45	-33
9	175	162
10	113	-121
11	373	380
12	465	-489
13	219	238
14	240	221
15	234	213
16	-45	-55
17	86	117
18	-45	-61
19	263	348
H= 2, K= 5		
0	240	-224
1	265	-240
2	219	182
3	591	-615
4	-43	35
5	202	196
6	279	259
7	81	-90
8	-43	72
9	177	-166
10	742	743
11	465	-477
12	-43	74
13	120	-117
14	121	130
15	113	105
16	261	271
17	-43	46
18	347	357
19	-43	-33
H= 2, K= 6		
0	189	-160
1	480	484
2	-45	33
3	187	-148
4	281	-253
5	400	364
6	-45	9
7	429	448
8	108	151
9	399	361
10	216	-197
11	153	167
12	306	-295
13	505	492
14	-45	12
15	465	464
16	182	205
17	-45	63
18	144	-127
19	409	375
H= 2, K= 7		
0	186	-163
1	83	76
2	98	91
3	266	241
4	395	393
5	165	-175
6	150	155
7	384	403
8	214	213
9	-45	-70
10	415	418
11	199	218
12	172	205
13	-45	15
14	290	271
15	85	90
16	246	259
17	-45	44
18	154	205
H= -2, K= 0		
2	1743	-2282
4	407	-468
6	193	-179
8	1006	-1126
10	965	-920
12	141	-167
14	474	-527
16	-52	91
18	-52	64
20	-52	-104
22	207	-163
H= -2, K= 1		
1	1004	-1178
2	584	-601
3	284	-266
4	297	-234
5	991	-1043
6	399	-374
7	112	-101
8	401	-385
9	661	-663
10	642	-582
11	507	-498
12	303	285
13	276	-251
14	264	-229
15	-51	10
16	307	298
17	295	-260
18	-51	99
19	-51	-36
20	-51	109
H= -2, K= 2		
1	427	-347
2	740	-728
3	989	1044
4	109	82
5	468	-463
6	319	-351
7	313	279
8	1005	-936
9	-49	87
10	221	-210
11	454	441
12	203	-191
13	109	119
14	303	-249
15	-49	90
16	254	-234
17	589	598
18	109	-85
19	-49	89
20	211	-211
21	352	335
22	-49	-48
H= -2, K= 3		
1	341	317
2	120	77
3	878	-880
4	271	265
5	500	-567
6	112	-129
7	496	-515
8	-50	32
9	-50	-71
10	205	183
11	878	-868
12	893	838
13	170	-150
14	-50	-2
15	-50	-41
16	-50	-76
17	176	-178
18	325	332
19	102	-113
20	386	393
21	-50	54
H= -2, K= 4		
1	384	326
2	1180	-1235
3	302	275
4	-45	-32
5	183	160
6	421	-413
7	82	-55
8	348	-362
9	604	610
10	417	-442
11	502	489
12	436	-454
13	370	370
14	278	-282
15	381	374
16	-45	-25
17	247	232
18	146	147
19	256	244
20	170	-243
21	142	268
H= -2, K= 5		
1	219	-200
2	-43	23
3	509	-517
4	291	286
5	322	-291
6	866	857
7	80	-88
8	-43	-43
9	200	-176
10	474	486
11	500	-523
12	493	478
13	122	-146
14	601	629
15	139	-155
16	-43	36
17	-43	-12
18	404	421
19	109	-95
20	337	427
H= -2, K= 6		
1	323	291
2	-45	-24
3	-45	20
4	213	-156
5	104	130
6	88	91
7	-45	106
8	-45	-23
9	631	664
10	-45	100
11	-45	98
12	-45	-34
13	265	-239
14	216	-196
15	557	544
16	191	190
17	256	250
18	-45	102
19	157	167
H= -2, K= 7		
1	250	244
2	197	-166
3	-45	-40
4	-45	54
5	147	-98
6	522	500
7	424	440
8	210	211
9	-45	-43
10	188	171
11	181	149
12	221	210
13	185	-175
14	384	360
15	241	267
16	114	154
17	-45	-4
18	303	330
19	125	150
20	188	248
H= 3, K= 0		
0	274	300
2	-52	-102
4	332	-294
6	815	765
8	403	410
10	224	220
12	183	184
14	339	346
16	-52	-45
18	357	370
H= 3, K= 1		
0	-52	-95
1	289	-260
2	563	559
3	-52	22
4	145	-146
5	301	289
6	199	181
7	293	243
8	135	158
9	405	409
10	-52	-68
11	295	294
12	241	217
13	120	115
14	-52	-56
15	359	340
16	234	246
17	257	263
18	-52	-51
19	170	230
H= 3, K= 2		
0	-49	63
1	213	202
2	240	252
3	603	564
4	137	127
5	-49	51
6	423	435
7	544	552
8	274	268
9	107	-129
10	248	236
11	589	569
12	568	556
13	-49	113
14	350	394
15	148	151
16	152	192
17	190	163
18	223	264
H= 3, K= 3		
0	388	400
1	237	-261
2	772	779
3	422	398
4	277	-246
5	-50	-43
6	215	208
7	-50	60
8	440	419
9	422	407
10	251	232
11	291	285
12	-50	11
13	-50	39
14	-50	63
15	124	130
16	241	210
17	327	362
H= 3, K= 4		
0	491	471
1	317	327
2	348	-333
3	-45	28
4	-45	-1
5	584	565
6	-45	-57
7	219	200
8	381	384
9	216	211
10	99	-145
11	-45	47
12	-45	53
13	-45	-24
14	-45	-93
15	-45	-3
16	-45	79
17	-45	71
H= 3, K= 5		
0	931	953
1	127	-123
2	544	537
3	177	168
4	354	378
5	235	233
6	219	212
7	209	189
8	645	646
9	266	266
10	310	305
11	-43	-70
12	-43	-141
13	-43	-41
14	299	302
15	116	151
16	-43	60
17	254	251
H= 3, K= 6		
0	-45	-52
1	426	424
2	178	-147
3	599	615
4	191	-197
5	906	980
6	252	256
7	149	147
8	-45	-27
9	435	428
10	97	-92
11	435	418
12	167	-154
13	501	481
14	-45	74
15	-45	-67
16	-45	19
H= 3, K= 7		
0	740	745
1	205	230
2	707	751
3	108	-109
4	660	642
5	-45	47
6	343	327
7	-45	20
8	544	533
9	-45	26
10	297	309
11	-45	107
12	255	233
13	195	-200
14	279	302
H= -3, K= 0		
2	-52	-41
4	282	-277
6	-52	-50
8	-52	-4
10	965	-977
12	103	94
14	224	-206
16	457	-424
18	436	-402
20	116	-130
22	191	-207
H= -3, K= 1		
1	393	-390
2	578	-579
3	393	379
4	228	228
5	717	-769
6	528	-552
7	426	-416
8	174	-167
9	268	-301
10	340	-336
11	455	-408
12	114	-135
13	582	-552
14	-51	2
15	270	-270
16	-51	-30
17	-51	-3
18	116	150
19	650	-604
20	122	-130
21	274	-281
22	99	143
H= -3, K= 2		
1	501	-480
2	188	-197
3	352	-380
4	229	-251
5	223	211
6	162	133
7	621	-627
8	370	-354
9	227	-261
10	715	-678
11	336	-322
12	103	-137
13	221	168
14	113	-132
15	254	-204
16	321	-309
17	211	198
18	305	-298
19	-49	-95
20	158	-186
21	-49	7
22	260	-276
H= -3, K= 3		
1	269	244
2	150	-113
3	112	115
4	349	-376
5	-50	-28
6	603	-644
7	745	-792
8	319	-305
9	-50	-19
10	185	-184
11	-50	-83
12	450	-399
13	639	-595
14	227	-216
15	197	-190
16	114	-76
17	305	-277
18	183	-176
19	293	-299
20	-50	-77
21	331	-366
H= -3, K= 4		
1	619	-651
2	-45	-43
3	982	-1014
4	-45	-54
5	687	-680
6	210	186
7	502	-452
8	701	-694
9	612	-647
10	89	-78
11	366	-352
12	370	-359
13	756	-741
14	-45	60
15	381	-360
16	637	-660
17	164	-205
18	245	-262
19	91	-128
20	119	-130
H= -3, K= 5		
1	254	222
2	122	-107
3	217	203
4	858	-875
5	655	636
6	536	-559
7	258	-237
8	317	-308
9	-43	69
10	388	-321
11	95	-99
12	507	-515
13	-43	2
14	219	-215
15	118	136
16	-43	-16
17	156	-187
18	286	-303
19	-43	-68
H= -3, K= 6		
1	874	-503
2	166	-159
3	321	-341
4	93	95
5	81	-35
6	-45	43
7	231	-175
8	-45	-63
9	668	-627
10	391	-386
11	-45	75
12	-45	64
13	-45	126
14	-45	39
15	-45	22
16	-45	-84
17	-45	-44
18	-45	-94
19	-45	59
H= -3, K= 7		
1	257	-232
2	362	-374
3	497	456
4	537	-509
5	301	-278
6	535	-517
7	-45	101
8	359	-295
9	150	-153
10	417	-442
11	99	108
12	272	-249
13	99	125
14	-45	82
15	96	-103
16	157	-146
17	85	104
18	181	-195
19	125	-147
H= 4, K= 0		
0	436	440
2	232	-187
4	682	684
6	324	316
8	259	218
10	332	337
12	116	111
14	-52	74
16	-52	-51
H= 4, K= 1		
0	842	-811
1	889	1005
2	-52	69
3	253	248
4	282	-246
5	365	422
6	-52	10
7	588	615
8	503	-467
9	590	657
10	-52	10
11	-52	-19
12	-51	-72
13	311	285
14	-51	65
15	214	182
16	-51	-15
17	-51	-8
H= 4, K= 2		
0	715	732
1	-49	-60
2	438	458
3	-49	6
4	558	562
5	-49	46
6	342	346
7	176	-136
8	299	270
9	180	-151
10	358	401
11	-49	10
12	221	244
13	166	-183
14	-49	49
15	127	112
16	-49	64
H= 4, K= 3		
0	-50	-49
1	494	510
2	120	-103
3	223	208
4	176	-198
5	183	-175
6	-50	57
7	406	415
8	140	-173
9	-50	32
10	114	-144
11	-50	63
12	-50	-126
13	-50	46
14	150	-167
15	116	107
16	193	-223
H= 4, K= 4		
0	84	-75
1	234	-239
2	370	426
3	109	79
4	205	168
5	188	-178
6	236	211
7	219	-191
8	-45	-44
9	99	-91
10	196	174
11	245	-211
12	328	317
13	86	-102
14	159	-170
15	190	-223
16	99	151
H= 4, K= 5		
0	291	262
1	282	256
2	254	-257
3	252	255
4	-43	77
5	193	-141
6	217	-202
7	184	148
8	155	-147
9	-43	26
10	401	-379
11	315	303
12	-43	38
13	-43	-59
14	183	-189
15	81	-107
16	231	-263
H= 4, K= 6		
0	-45	48
1	258	-226
2	-45	-45
3	-45	76
4	119	121
5	238	-230
6	-45	-57
7	290	-288
8	-45	-114
9	137	-143
10	211	212
11	362	-348
12	-45	75
13	297	-294
14	-45	-103
H= 4, K= 7		
0	177	181
1	-45	-3
2	217	-206
3	170	-152
4	185	-185
5	156	116
6	-45	-95
7	313	-323
8	261	-240
9	96	102
10	304	-309
11	148	-157
12	214	-200
13	-45	70
14	192	-218
H= -4, K= 0		
2	744	744
4	474	450
6	257	-226
8	386	387
10	391	336
12	141	126
14	112	111
16	232	214
18	-52	14
20	-52	-30
22	224	209
H= -4, K= 1		
1	916	996
2	573	609
3	338	383
4	168	117
5	548	555
6	243	215
7	374	400
8	128	-121
9	453	441
10	469	447
11	449	437
12	237	-222
13	399	393
14	224	182
15	-51	-71
16	241	-240
17	289	283
18	249	-230
19	176	178
20	145	-141
21	-51	56
22	-51	-50
H= -4, K= 2		
1	705	739
2	814	837
3	607	-637
4	436	430
5	146	149
6	164	181
7	-49	-64
8	595	587
9	-49	70
10	607	598
11	481	-443
12	229	254
13	248	-232
14	227	222
15	113	150
16	113	103
17	485	-463
18	-49	32
19	146	-153
20	152	137
21	205	-199
22	107	129
H= -4, K= 3		
1	253	252
2	319	-310
3	170	176
4	207	-207
5	448	434
6	-50	-94
7	440	449
8	100	-144
9	-50	56
10	-50	-108
11	551	528
12	673	-659
13	279	298
14	321	-295
15	114	103
16	-50	-33
17	-50	-85
18	-50	-81
19	128	180
20	307	-346
21	-50	-69
H= -4, K= 4		
1	249	-210
2	716	757
3	309	-305
4	322	269
5	377	-322
6	432	417
7	124	112
8	318	[illegible]
9	359	[illegible]
10	436	[illegible]
11	630	[illegible]
12	251	[illegible]
13	295	-308
14	295	312
15	278	-287
16	234	239
17	249	-256
18	131	-154
19	291	-336
20	109	145
21	137	-162
H= -4, K= 5		
1	136	112
2	-43	-8
3	258	267
4	136	103
5	188	172
6	425	-459
7	158	171
8	209	-160
9	-43	-3
10	233	-210
11	277	268
12	-43	-35
13	-43	-14
14	491	-567
15	-43	42
16	-43	-83
17	-43	-74
18	207	-188
19	-43	28
20	256	-305
H= -4, K= 6		
1	-45	7
2	-45	35
3	-45	-3
4	126	126
5	429	-346
6	205	-167
7	162	145
8	-45	72
9	375	-363
10	-45	-21
11	216	-237
12	-45	-89
13	97	78
14	-45	82
15	148	-160
16	-45	-63
17	270	-293
18	-45	-105
19	171	-208
H= -4, K= 7		
1	266	-236
2	-45	74
3	108	-85
4	114	127
5	192	185
6	393	-321
7	339	-303
8	384	-351
9	-45	0
10	-45	-85
11	156	-158
12	-45	-62
13	310	299
14	379	-389
15	90	-129
16	195	-218
17	-45	30
18	157	-201
19	99	-102
H= 5, K= 0		
0	-52	42
2	-52	28
4	-52	106
6	524	-539
8	-52	-33
10	174	-148
12	220	-213
14	124	-131
H= 5, K= 1		
0	-51	0
1	116	-111
2	352	-394
3	120	-99
4	85	34
5	103	-92
6	120	-123
7	270	-263
8	-51	-26
9	224	-232
10	114	-86
11	191	-218
12	203	-212
13	128	-140
14	-51	-18
15	293	-278
H= 5, K= 2		
0	107	-102
1	264	-248
2	-49	65
3	401	-405
4	-49	-88
5	-49	63
6	160	-190
7	227	-241
8	113	-132
9	90	-43
10	239	-225
11	319	-343
12	229	-251
13	90	76
14	113	-139
15	82	-108
H= 5, K= 3		
0	392	-385
1	-50	83
2	175	-202
3	160	-151
4	140	115
5	-50	43
6	181	-213
7	-50	-62
8	225	-247
9	269	-283
10	-50	36
11	-50	76
12	-50	57
13	-50	-27
H= 5, K= 4		
0	214	-202
1	274	-275
2	249	259
3	240	-242
4	269	-240
5	311	-333
6	99	-42
7	120	-134
8	263	-243
9	256	-238
10	-45	68
11	-45	0
12	-45	-78
H= 5, K= 5		
0	636	-629
1	-43	55
2	197	-200
3	219	-199
4	255	-244
5	-43	-80
6	348	-346
7	167	-154
8	313	-299
9	156	-169
10	-43	-103
11	-43	-26
12	-43	-46
H= 5, K= 6		
0	-45	-23
1	377	-374
2	-45	-19
3	435	-416
4	-45	-47
5	460	-444
6	180	-211
7	-43	-11
8	-45	32
9	384	-387
10	-45	-51
11	278	-271
12	-45	-35
H= 5, K= 7		
0	571	-547
1	-45	-84
2	384	-375
3	185	162
4	384	-364
5	-45	-54
6	366	-364
7	-45	-16
8	333	-329
9	-45	47
10	199	-200
11	-45	36
12	232	-261
H= -5, K= 0		
2	320	-292
4	291	300
6	170	173
8	274	-248
10	486	533
12	187	146
14	116	123
16	116	127
18	503	557
20	199	183
H= -5, K= 1		
1	338	319
2	224	259
3	193	-179
4	-51	-104
5	249	238
6	255	237
7	257	217
8	-51	80
9	357	342
10	170	167
11	-51	130
12	-51	75
13	295	301
14	-51	-63
15	357	375
16	-51	51
17	-51	93
18	-51	-92
19	316	329
20	-51	81
21	214	295
H= -5, K= 2		
1	282	277
2	105	102
3	335	334
4	237	230
5	109	127
6	170	160
7	369	292
8	-49	79
9	137	155
10	423	456
11	376	389
12	358	354
13	-49	-101
14	-49	54
15	135	146
16	166	196
17	121	-154
18	223	235
19	-49	69
20	203	215
H= -5, K= 3		
1	-50	-23
2	321	286
3	-50	1
4	130	155
5	374	-390
6	454	453
7	492	476
8	136	139
9	175	197
10	181	192
11	-50	3
12	197	190
13	110	120
14	249	234
15	156	180
16	-50	-97
17	116	117
18	-50	11
19	-50	93
H= -5, K= 4		
1	285	290
2	133	-161
3	476	470
4	-45	35
5	692	640
6	95	-123
7	375	340
8	348	343
9	439	412
10	-45	17
11	155	186
12	295	301
13	439	437
14	95	-97
15	351	335
16	289	304
17	126	159
18	274	261
19	93	100
20	115	120
H= -5, K= 5		
1	97	-119
2	97	122
3	139	111
4	413	404
5	87	-95
6	380	331
7	326	278
8	439	432
9	155	152
10	97	72
11	97	103
12	348	344
13	343	333
14	256	239
15	139	138
16	-43	30
17	186	211
18	232	251
H= -5, K= 6		
1	377	345
2	97	-81
3	532	473
4	-45	-16
5	-45	46
6	-45	18
7	-45	25
8	-45	-53
9	435	425
10	97	150
11	153	138
12	-45	35
13	-45	4
14	-45	39
15	-45	-127
16	-45	4
17	119	194
H= -5, K= 7		
1	199	205
2	444	435
3	384	-369
4	313	300
5	-45	1
6	313	283
7	157	-129
8	352	310
9	-45	39
10	295	287
11	-45	-111
12	362	357
13	268	-250
14	-45	29
15	76	-85
16	72	97
17	156	-191
18	166	164
H= 6, K= 0		
0	-52	-123
2	187	-164
4	320	-300
6	-52	-55
8	128	-127
10	299	-291
H= 6, K= 1		
0	-51	109
1	380	-401
2	120	-181
3	-51	-83
4	-51	61
5	357	-359
6	-51	-38
7	276	-290
8	151	158
9	224	-244
10	116	-95
H= 6, K= 2		
0	401	-388
1	-49	-28
2	289	-302
3	-49	87
4	276	-275
5	-49	107
6	186	-181
7	164	161
8	278	-352
9	160	179
10	145	-180
H= 6, K= 3		
0	199	225
1	181	-208
2	-50	45
3	134	-118
4	-50	85
5	-50	-13
6	-50	-21
7	249	-299
8	215	236
H= 6, K= 4		
0	-45	-26
1	-45	46
2	295	-311
3	-45	-63
4	-45	-69
5	106	99
6	-45	-32
7	-45	62
H= 6, K= 5		
0	-43	-71
1	139	-156
2	237	238
3	-43	-68
4	116	-118
5	-43	9
6	211	191
H= 6, K= 6		
0	-45	-1
1	-45	66
2	-45	-5
3	-45	-18
H= 6, K= 7		
0	-45	-104
1	-45	-56
2	141	135
3	81	98
H= -6, K= 0		
2	-52	-38
4	416	-394
6	166	170
8	262	-253
10	187	-162
12	224	-222
14	-52	96
16	116	-162
18	249	-304
20	-52	40
H= -6, K= 1		
1	465	-452
2	147	-147
3	328	-332
4	-51	62
5	224	-232
6	-51	-38
7	228	-239
8	191	183
9	270	-274
10	-51	-60
11	241	-239
12	189	190
13	326	-376
14	-51	-30
15	-51	89
16	-51	67
17	128	-155
18	124	163
19	145	-162
20	87	143
H= -6, K= 2		
1	507	-528
2	568	-595
3	113	158
4	423	-426
5	-49	10
6	280	-251
7	-49	79
8	213	-190
9	113	-146
10	423	-461
11	225	219
12	333	-304
13	295	266
14	233	-198
15	119	-92
16	90	-84
17	152	153
18	-49	37
19	141	145
H= -6, K= 3		
1	442	-484
2	160	195
3	112	-152
4	181	211
5	197	-239
6	-50	34
7	362	-382
8	140	166
9	140	-125
10	110	103
11	333	-329
12	422	380
13	211	-220
14	247	225
15	261	-290
16	215	209
17	110	151
H= -6, K= 4		
1	-45	56
2	295	-295
3	196	184
4	99	-100
5	260	259
6	271	-258
7	-45	2
8	99	-116
9	-45	80
10	291	-286
11	370	371
12	-45	-9
13	252	248
14	86	-105
15	97	135
16	177	-188
17	91	137
H= -6, K= 5		
1	-43	-71
2	97	86
3	-43	-73
4	118	-56
5	-43	-69
6	-43	59
7	-43	-117
8	116	86
9	-43	2
10	268	236
11	-43	-24
12	95	-115
13	-43	52
14	286	262
15	-43	18
16	113	105
H= -6, K= 6		
1	-45	-2
2	-45	26
3	216	-214
4	153	-157
5	377	357
6	-45	86
7	-45	-30
8	-45	-39
9	131	129
10	-45	-20
11	124	134
12	-45	20
13	137	168
14	-45	-35
15	84	113
16	-45	-14
17	139	184
H= -6, K= 7		
1	-45	90
2	-45	22
3	127	115
4	127	-106
5	-45	-47
6	-45	160
7	-45	92
8	275	258
9	-45	6
10	137	148
11	118	134
12	-45	-10
13	163	-198
14	210	242
15	-45	1
16	154	229
H= 7, K= 0		
0	135	-114
2	106	124
4	-52	-4
6	278	261
8	-52	-35
H= 7, K= 1		
0	-51	59
1	193	176
2	189	186
3	-51	0
4	-51	0
5	-51	46
6	-51	0
7	185	188
8	-51	59
H= 7, K= 2		
0	-49	-2
1	146	143
2	123	-92
3	217	193
4	-49	68
5	-49	-88
6	-49	52
7	97	126
8	-49	96
H= 7, K= 3		
0	146	171
1	-50	-51
2	96	101
3	-50	33
4	-50	52
5	-50	11
6	150	155
7	-50	89
8	100	104
H= 7, K= 4		
0	-45	43
1	208	201
2	84	-104
3	157	151
4	225	227
5	155	153
6	-45	17
7	133	142
8	109	137
H= 7, K= 5		
0	324	343
1	-43	-15
2	-43	107
3	75	89
4	176	196
5	-43	59
6	192	220
H= 7, K= 6		
0	-45	-10
1	265	295
2	-45	47
3	151	166
4	93	83
5	158	206
H= 7, K= 7		
0	199	182
1	-45	-37
2	-45	98
H= -7, K= 0		
2	137	171
4	-52	-52
6	237	-241
8	158	119
10	212	-204
12	99	-117
14	245	-236
16	-52	-19
H= -7, K= 1		
1	143	-116
2	-51	-73
3	-51	40
4	-51	50
5	-51	-81
6	-51	-100
7	-51	0
8	-51	33
9	251	-253
10	-51	-93
11	-51	-107
12	-51	-5
13	-51	-89
14	-51	45
15	226	-231
16	-51	20
17	158	-179
H= -7, K= 2		
1	170	-171
2	-49	-11
3	188	-134
4	-49	-57
5	217	-203
6	109	-113
7	152	-136
8	-49	-105
9	-49	-34
10	168	-165
11	246	-272
12	282	-269
13	-49	15
14	-49	-49
15	105	-100
16	78	-127
H= -7, K= 3		
1	-50	42
2	261	-278
3	201	-169
4	130	-126
5	291	271
6	317	-331
7	128	-133
8	104	-85
9	142	-169
10	98	-159
11	94	-132
12	90	-114
13	-50	20
14	175	-194
15	-50	-53
H= -7, K= 4		
1	177	-157
2	89	81
3	108	-157
4	-45	8
5	247	-244
6	-45	-5
7	197	-183
8	174	-150
9	190	-177
10	-45	10
11	84	-89
12	190	-198
13	-45	-108
14	-45	1
15	106	-121
H= -7, K= 5		
1	-43	86
2	122	-127
3	-43	-15
4	226	-216
5	-43	-40
6	115	-96
7	198	-211
8	348	-351
9	113	-134
10	-43	-50
11	-43	-41
12	156	-149
13	191	-213
14	156	-158
15	167	-218
H= -7, K= 6		
1	93	-133
2	113	146
3	344	-343
4	-45	57
5	222	-208
6	-45	-62
7	-45	-46
8	-45	19
9	265	-269
10	-45	-5
11	184	-187
12	-45	1
13	180	-229
H= -7, K= 7		
1	159	-174
2	235	-221
3	139	138
4	206	-192
5	-45	45
6	81	-92
7	114	95
8	157	-178
9	-45	-45
10	118	-107
11	-45	61
12	183	-233
H= 8, K= 0		
0	224	187
2	232	187
4	124	131
H= 8, K= 1		
0	-51	6
1	97	149
2	64	106
3	-51	56
4	-51	-27
H= 8, K= 2		
0	166	133
1	-49	47
2	146	125
H= 8, K= 3		
0	164	-162
1	-50	64
H= -8, K= 0		
2	-52	-24
4	295	288
6	-52	-27
8	135	143
10	124	127
12	270	264
H= -8, K= 1		
1	137	136
2	-51	-48
3	199	210
4	-51	-77
5	128	119
6	-51	-72
7	116	86
8	-51	-80
9	145	157
10	-51	-20
11	116	117
12	106	-136
13	218	252
H= -8, K= 2		
1	156	175
2	299	294
3	-49	-50
4	246	254
5	-49	-15
6	217	184
7	109	-143
8	-49	77
9	-49	53
10	213	212
11	-49	-102
12	225	240
13	156	-169
H= -8, K= 3		
1	370	346
2	-50	3
3	191	198
4	96	-124
5	80	113
6	-50	0
7	189	217
8	-50	-71
9	80	122
10	-50	-59
11	185	199

labelling scheme given in Table 6. The labelling of atoms in the Figs. 2 and 3 and the interatomic distances and angles in Table 5 are in accordance with this scheme.

Table 5. *Interatomic distances* (Å) *and angles* (°) *besides those given in Fig.* 4.

Estimated standard deviations are given in parentheses.

Bond lengths and angles involving copper atoms

Cu–Cu(i)	3·567 (2)	Cu(i)–Cu–Cu(ii)	147·10 (2)
Cu–Cu(ii)	3·686 (2)		

Bond lengths involving hydrogen atoms

N(1)–H(1)	0·91	C(6)—H(10)	1·10
N(7)–H(2)	1·10	N(9)—H(11)	0·86
N(7)–H(3)	1·12	N(9)—H(12)	0·91
N(2)–H(4)	0·84	N(5)—H(13)	0·96
N(8)–H(5)	1·56	N(10)–H(14)	1·14
N(8)–H(6)	0·82	N(10)–H(15)	0·88
C(5)–H(7)	0·96	N(6)—H(16)	0·95
C(5)–H(8)	1·05	O(1)—H(17)	0·86
C(6)–H(9)	1·07	O(1)—H(18)	1·09

Contacts involving chloride ions (probable hydrogen bonds)

Cl(1) (v)–N(5)	3·20 (1)	Cl(2) (vii)–O(1) (vii)	3·18 (1)
Cl(1) (v)–N(7) (iii)	3·27 (1)	Cl(2) (vii)–N(10) (vii)	3·31 (1)
Cl(1) (v)–N(8) (vi)	3·26 (1)	Cl(2) (vii)–N(8) (i)	3·29 (1)
Cl(1) (v)–O(1) (vii)	3·25 (1)	Cl(2) (vii)–N(6) (ix)	3·35 (1)
Cl(1) (v)–N(9)	3·29 (1)		
Cl(1) (v)–N(10) (v)	3·43 (1)		

Angles subtended at Cl(1) (v) by

N(5), N(8) (vi)	125·5 (5)	N(7) (iii), O(1) (vii)	81·9 (5)
N(5), N(7) (iii)	110·5 (5)	N(7) (iii), N(8) (vi)	110·8 (5)
N(5), N(9)	41·1 (5)	N(7) (iii), N(10) (v)	106·7 (5)
N(5), O(1 (vii)	79·1 (5)	N(7) (iii), N(9)	72·3 (5)
N(5), N(10) (v)	133·4 (5)	N(8) (vi), N(10) (v)	61·1 (5)
N(9), N(8) (vi)	159·4 (5)	N(8) (vi), O(1) (vii)	73·4 (5)
N(9), O(1) (vii)	88·8 (5)	N(10) (v), O(1) (vii)	133·9 (5)
N(9), N(10) (v)	138·5 (5)		

Angles subtended at Cl(2) (vii) by

N(8) (i), O(1) (vii)	82·5 (5)	N(6) (ix), O(1) (vii)	109·2 (5)
N(8) (i), N(6) (ix)	167·8 (5)	N(6) (ix), N(10) (vii)	115·8 (5)
N(8) (i), N(10) (vii)	62·0 (5)	N(10) (vii), O(1) (vii)	106·6 (5)

Contacts involving oxygen (probable hydrogen bonds)

O(1) (vii)–N(7) (i)	3·01 (2)	O(1) (vii)–Cl(1) (v)	3·25 (1)
O(1) (vii)–N(2) (i)	3·14 (2)	O(1) (vii)–Cl(2) (vii)	3·18 (1)
O(1) (vii)–N(9) (viii)	3·18 (2)		

Angles subtended at O(1) (vii) by

N(7) (i), Cl(1) (v)	97·6 (6)	N(9) (viii), Cl(1) (v)	103·0 (6)
N(7) (i), Cl(2) (vii)	124·1 (6)	N(9) (viii), Cl(2) (vii)	131·6 (6)
N(7) (i), N(9) (viii)	77·1 (8)	N(9) (viii), N(2) (i)	117·9 (8)
N(7) (i), N(2) (i)	44·0 (7)	Cl(2) (vii), Cl(1) (v)	114·3 (5)
N(2) (i), Cl(1) (v)	88·2 (7)	Cl(2) (vii), N(2) (i)	81·4 (5)

Interbond angles for the hydrogen bonded contacts (Subtended by atoms other than hydrogen)

C(1) (i)——N(2) (i) ·····H···O(1) (vii)	97·6 (7)
C(2) (i)——N(2) (i) ·····H···O(1) (vii)	136·5 (7)
C(3)———N(5) ·······H···Cl(1) (v)	103·9 (6)
C(4)———N(5) ·······H···Cl(1) (v)	125·3 (6)
Cu(ix)——N(6) (ix) ····H···Cl(2) (vii)	112·1 (5)
C(4) (ix)—N(6) (ix) ····H···Cl(2) (vii)	121·0 (6)
C(1) (iii)—N(7) (iii) ····H···Cl(1) (v)	135·9 (6)
C(1) (i)——N(7) (i) ·····H···O(1) (viii)	104·8 (7)
C(2) (i)——N(8) (i) ·····H···Cl(2) (vii)	126·4 (6)
C(2) (vi)—N(8) (vi) ····H···Cl(1) (v)	143·8 (6)
C(3)———N(9) ·······H···Cl(1) (v)	100·5 (7)
C(3) (viii)–N(9) (viii) ···H···O(1) (viii)	138·3 (8)
C(4) (v)——N(10) (v) ···H···Cl(1) (v)	118·6 (5)
C(4) (vii) –N(10) (vii)···H···Cl(2) (vii)	108·6 (6)
Cl(1) (v)—O(1) (vii) ···H···Cl(2) (vii)	114·3 (5)

Table 5 (*cont.*)

Other close intermolecular contacts

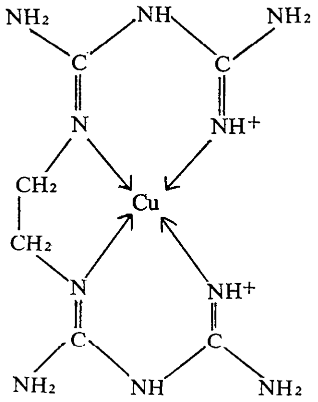
C(3) (i)—N(7)	3·27 (2)	C(4) (ii)—N(8)	3·32 (2)
C(4) (i)—N(2)	3·42 (2)	N(10) (ii)-N(8)	3·40 (2)
N(6) (i)—N(2)	3·31 (2)	N(5) (ii)—N(2)	3·48 (2)
N(6) (i)—C(2)	3·40 (2)	N(9) (ii)—N(7)	3·70 (2)
Cl(1) (v)-Cl(2)	3·874 (4)	Cl(1)——Cl(2)	4·253 (4)

Table 6. *Code for identification of equivalent atoms*

x	y	z	None
$\bar{x}$	$\bar{y}$	$\bar{z}$	i
$1-x$	$\bar{y}$	$\bar{z}$	ii
x	$1+y$	z	iii
$1-x$	$1+y$	z	iv
$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	v
x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	vi
$-1+x$	y	z	vii
$\bar{x}$	$1-y$	$\bar{z}$	viii
$\bar{x}$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	ix

The molecule of ethylenebidiguanide acts as a tetradentate ligand and forms two covalent and two coordinate bonds through its four nitrogen atoms with one Cu(II) ion in an approximately square planar configuration. This results in the formation of one five-membered and two six-membered rings in the chelate compound. The two biguanide residues are independently planar (see Table 7) but their normals make an angle of 4·6° with each other. The non-planarity of the two biguanide residues can be explained as resulting from the strain in the five-membered ring containing the two ethylene groups.

The Cu–N distances which vary between 1·933–1·989 Å are significantly longer than the average Cu–N peptide bond of 1·90 Å (Freeman, Robinson & Schoone, 1964). The C–N bond lengths vary between 1·292–1·419 Å. With a slight increase in the apparent standard deviations of the bond lengths, the C–N bond lengths can be classified into two groups of 1·32 and 1·40 Å. The shorter C–N bonds have, therefore, a considerable double bond character and so the structure of the copper complex ion can be written as follows:



The location of hydrogen atoms in the above structure is in agreement with the positions of hydrogen atoms obtained from the final difference Fourier synthesis.

Although the dimensions of free ethylenebidiguanine are not available for comparison, the structure of guanidium hydrochloride has been determined (Haas, Harris & Mills, 1965) and so the dimensions of the free guanidium ion can be compared with the bond lengths and bond angles of the guanine residue in the copper ethylenebidiguanide complex ion. The average C–N bond lengths and N–C–N angles in the free guanidium ion are 1·323 Å and 120° respectively. There is a considerable deviation from these values in the copper complex ion. This is probably due to the formation of rings in the chelate compound.

The approximately planar complex ions are packed in layers parallel to (100) (Fig. 3). These layers are held together by a network of hydrogen bonds, through

Table 7. *Least-squares planes and out-of-plane distances of the plane determining atoms*

Each plane is represented by

$$lX+mY+nZ+p=0\,.$$

X, Y, Z are cartesian coordinates in Å, referred to the orthogonal axes. The copper ethylenedibiguanide complex ion is not exactly planar. The two halves of the molecule, one containing the atoms Cu, N(1), C(1), N(2), C(2), N(3), C(7), N(8) and the other containing Cu, N(4), C(3), N(5), C(4), N(6), N(9), N(10) are independantly planar; the normals to these planes make an angle of 4·6°.

Plane	Atoms included	Coefficients of the plane			
1	Cu, N(1), C(1), N(2), C(2), N(3), C(7), N(8)	0·9585	−0·1927	0·2099	1·579
2	Cu, N(4), C(3), N(5), C(4), N(6), N(9), N(10)	0·9766	−0·1822	0·1318	1·622

Out-of-plane distances in Å of plane determining atoms in plane No. 1 are

N(1)	C(3)	N(2)	C(2)	N(3)	Cu	N(7)	N(8)
−0·113	0·053	−0·007	0·037	0·020	−0·044	0·019	0·090

Out-of-plane distances in Å of plane determining atoms in plane No. 2 are

N(4)	C(3)	N(5)	C(4)	N(6)	Cu	N(9)	N(10)
0·046	−0·063	0·022	0·031	−0·037	0·051	−0·0218	0·009

the eight chlorine ions and four oxygen atoms of the water molecules. The packing is such that the copper atoms are stacked in rows parallel to the *b* axis (Fig.2). Each copper atom has two other copper neighbours in nearly opposite directions at a distance of Cu–Cu(i) = 3·657 ± 0·002 Å and Cu–Cu(ii) = 3·686 ± 0·002 Å.

In addition to the four Cu–N bonds in a given layer each Cu is bonded to N(1) (i) of the copper complex ion in the lower layer, while as a result of symmetry the Cu(i) atom in the lower layer forms a bond with N(1). The bond length Cu–N(1) is equal to 3·168 Å. This is probably significant because in the mean plane describing all atoms of the complex ion, the deviation of N(1) in the direction of copper in the adjacent layer is considerable (see Table 7). The weakly bonded N(1) lies on the apex of a pyramid with an approximately square planar base of which the corners are occupied by strongly bonded nitrogen atoms, the copper atoms being in the centre of the square planar base.

The packing of the chlorine ions can be seen in Fig. 2. The distances of the neighboring atoms from chlorine are given in Table 5. The shortest distance is Cl(2) (vii)–O(1) (vii) = 3·18 ± 0·01 Å. These two distances correspond to presence of hydrogen bonds between the two pairs of atoms. The other probable hydrogen bond distances are listed in Table 5.

Among the atoms which surround oxygen of the water molecule, only the distance of O(1) (vii)–N(7) (i) = 3·01 ± 0·015 Å can be considered as a hydrogen bond distance. The distances of the remaining atoms and the angles they subtend at O(1) are listed in Table 5.

The authors wish to thank Mr Wayne Wilson for writing programs for calculating structure factors and Fourier analysis on the IBM 7040 computer. Thanks are also due to Dr C. Calvo of the McMaster University for supplying the least-squares program and to the National Research Council for financial support.

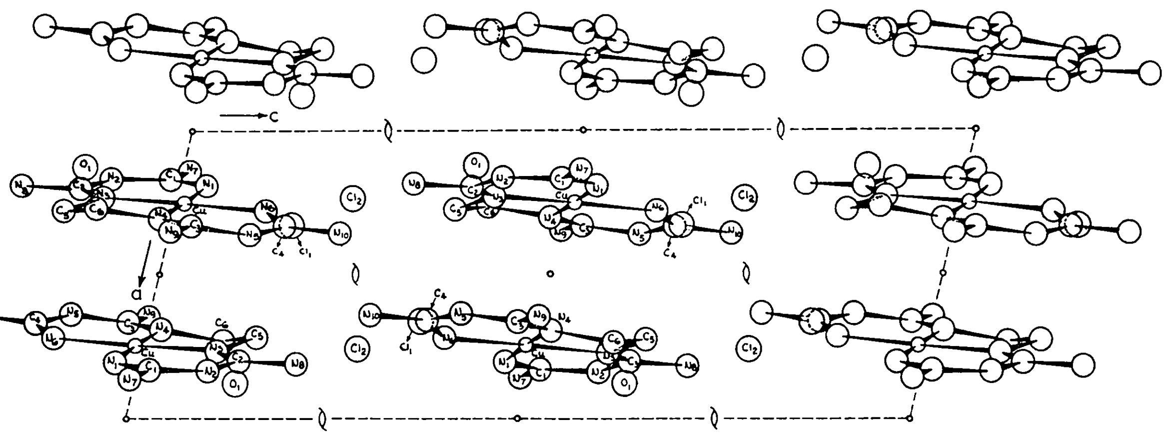


Fig. 3. A projection of the structure along the *b* axis. Distances are given in Å.

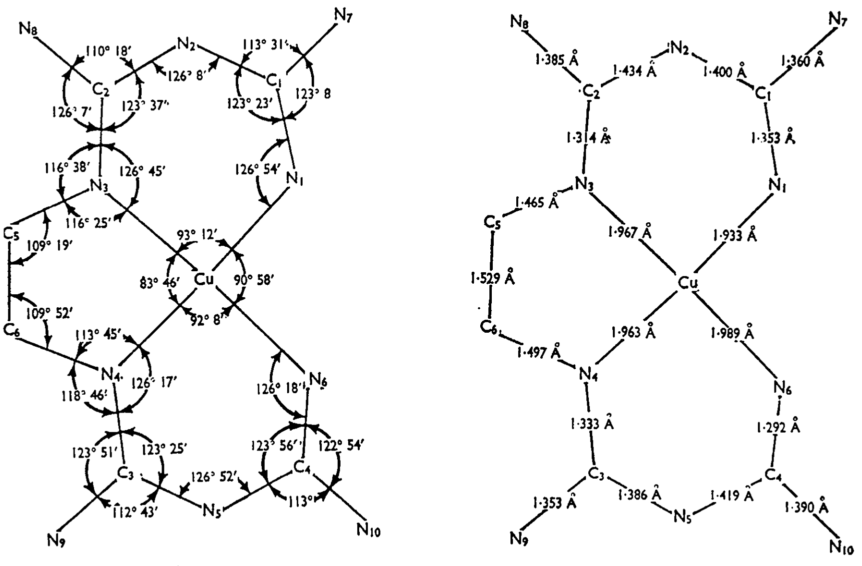


Fig. 4. Dimensions of the copper ethylenebidiguanide complex ion.

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *A Fortran Crystallographic Least-Squares Program.* Oak Ridge National Laboratory, Oak Ridge, Tennessee.

CHAKRAVORTY, K. & RAY, P. (1944). *J. Indian Chem. Soc.* **21**, 41.

DAWSON, B. (1960). *Acta Cryst.* **13**, 403.

FREEMAN, A. J. (1959). *Acta Cryst.* **12**, 261.

FREEMAN, H. C., ROBINSON, G. & SCHOONE, J. C. (1964). *Acta Cryst.* **17**, 719.

HAAS, D. J., HARRIS, D. R. & MILLS, H. H. (1965). *Acta Cryst.* **19**, 676.

LEY, H. & MÜLLER, F. (1907). *Ber. dtsch. Chem. Ges.* **40**, 2950.

RAY, P. & SAHA, H. (1937). *J. Indian Chem. Soc.* **14**, 670.

SLOTTA, K. H. & TSCHESCHE, R. (1929). *Ber. dtsch. Chem. Ges.* **62**, 1390.

TRÄUBE, W. & GLAUBITTE, G. (1930). *Ber. dtsch. Chem. Ges.* **63**, 2094.

TSCHUGAEFF, L. (1907). *Ber. dtsch. Chem. Ges.* **40**, 1975.

WATSON, R. E. & FREEMAN, A. J. (1961). *Acta Cryst.* **14**, 231.

Acta Cryst. (1970). B**26**, 2062

The Crystal Structure of the Sulfate and Selenate Monohydrates of Bis-(1,3-propanediamine)copper(II)[*]

BY B. MOROSIN AND J. HOWATSON[†]

Sandia Laboratories, Albuquerque, New Mexico 87115

(*Received* 15 *July* 1969 *and in revised form* 24 *November* 1969)

The crystal structures of bis-(1,3-propanediamine)copper(II) sulfate monohydrate,

$$Cu[NH_2(CH_2)_3NH_2]_2SO_4.H_2O,$$

and the corresponding isomorphic selenate have been refined by the full-matrix least-squares method using three-dimensional Mo $K\alpha$ intensity data to reliability indices below 0·07. The lattice constants are: $a_0=11·747$, $b_0=15·841$, and $c_0=7·164$ and $a_0=11·998$, $b_0=15·702$ and $c_0=7·352$ Å for the sulfate and selenate respectively; $Z=4$ in space group *Pnam*. The copper ion is surrounded by four nitrogen atoms ($\sim$2·0 Å) in a planar arrangement and by two more distant oxygen atoms (at unequal Cu–O distances of 2·57 and 3·34 Å for the sulfate and 2·52 and 3·52 Å for the selenate) forming a weak chain-like arrangement.

Introduction

The low temperature magnetic and thermal properties of several nitrogen coordinated copper compounds have been interpreted as those of substances containing a magnetic linear chain structure (Griffiths, 1964; Lowndes, 1968; Bonner, 1968); the first such material studied was $Cu(NH_3)_4SO_4.H_2O$ (hereafter CTASUL). Nasanen, Luukkonen & Virtamo (1967) (hereafter NLV) reported the lattice constants for bis(1,3-propanediamine)copper(II) sulfate monohydrate, $Cu[NH_2(CH_2)_3NH_2]SO_4.H_2O$, (hereafter CUPSUL); from their values, it appeared that there might be a close structural resemblance between CTASUL and CUPSUL. Preliminary structural results and specific heat measurements indicated a good fit to the expression $J=ar^{-n}$, where J is the exchange constant, r the interionic Cu–Cu separation and n an exponent with the value 10·9, could be obtained for several of these materials, including CUPSUL, which contain linear chains (Lowndes, Finegold, Rogers & Morosin, 1969). We report here our structure results on CUPSUL and the corresponding isomorphous selenate compound (CUPSEL).

Experimental

Crystals of CUPSUL and CUPSEL were prepared by the method of NLV. The complexes are prepared by dropwise addition of a saturated methanol solution of copper sulfate (or selenate) to a methanol solution of the amine. The resulting blue precipitates of the corresponding anhydrous complexes were converted to the very soluble, purple monohydrates by addition of water.

The quality of the crystals used for data collection was checked optically and by X-ray photographic techniques to insure the absence of twinning. The space group, $Pna2_1$ or *Pnam* was determined on the basis of extinctions observed on these photographs (for $0kl$, $k+l=2n+1$ absent, for $h0l$, $h=2n+1$ absent and for $00l$, $l=2n+1$ absent).

A piezoelectric effect was detected for both CUPSUL and CUPSEL using a circuit similar to that of Robin-

---

[*] This work supported by the U.S. Atomic Energy Commission.

[†] AWU Faculty Professor. Permanent address: Department of Chemistry, University of Wyoming, Laramie, Wyoming.