[Contribution from the Department of Chemistry, Washington University]

The Crystal Structure of Cesium Chlorocuprate, Cs_2CuCl_4, and the Spectrum of the Chlorocuprate Ion

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A structure determination of Cs_2CuCl_4 has been made in order to establish the configuration of the chlorocuprate ion. The crystal space group is D_{2h}^{16} -Pnma. and the unit cell dimensions are: $a = 9.70$, $b = 7.60$, $c = 12.35$ Å. In the crystal the configuration found for the ion may be considered as a tetrahedron distorted by a flattening that removes the threefold symmetry of the tetrahedron but still preserves the fourfold inversion axis. The copper–chlorine distance within the ion is 2.22 Å. Chlorine–chlorine distances within the ion are 3.50 and 3.80 Å., and two values of chlorine–copper–chlorine bond angles are found, 120 and 104°. A comparison of the spectrum of the chlorocuprate ion in solution and in crystalline Cs_2CuCl_4 is made.

The existence of the chlorocuprate ion in solution is well known, this ion being responsible for the yellow color produced upon adding concentrated hydrochloric acid to dilute solutions of cupric ion. Until the time of the present work, however, discrete chlorocuprate ions had not been found in the crystalline state. Since cupric copper shows a strong tendency toward square planar coördination[2] the view has been taken that the chlorocuprate ion should be square planar[3,4] although no direct evidence had been presented for this structure.

In studying the spectrum of complex ions, knowledge of the ion configuration is necessary in an attempt to formulate a theory of the spectrum. The present work provides information for theoretical treatment of the spectrum of the chlorocuprate ion.

Cesium chlorocuprate, a yellowish-orange crystal, was chosen for investigation since it seemed likely that it would contain discrete $CuCl_4^{=}$ groups. The similarity between the color of the crystals and the color of chlorocuprate ion in solution favors this possibility as does the fact that the solid contains no water molecules (water of crystallization) which might displace the chlorine ions from the coördination positions around the copper ions as in $K_2CuCl_4 \cdot 2H_2O$ for example.[2d]

Preparation.—Crystals of cesium chlorocuprate were grown by evaporation at room temperature of an aqueous solution of cesium chloride and cupric chloride in a mole ratio of 2:1.

Physical Properties.—The crystal is dichroic and appears orange when the electric vector is parallel to the b-axis and yellow when perpendicular to the b-axis; density[5] 3.42 g. cm.$^{-3}$. Goniometric examination shows holohedral orthorhombic symmetry, D_{2h}-mmm, with $a/c = 0.786$, $b/c = 0.616$. Refractive indices[5] for the sodium D-line: $\alpha = 1.625$, β 1.648, $\gamma = 1.678$; biaxial positive with $b = \gamma$, $2V = 83° 46'$. No pyroelectric effect is shown.[5] The crystal has a tabular habit whose largest faces are of the form {101}. Bipyramidal forms and the pinacoid {010} terminate the crystal. The crystal is stable in air.

Unit Cell and Space Group.—Cu$K\alpha$ radiation ($\lambda = 1.542$ Å.) was used to obtain equatorial reflections suitable for lattice constant determination. The lattice constants found are compared with those given by Mellor,[6] who carried out a space group and lattice constant determination

	Present work, Å.	Mellor, Å.
a	9.70 ± 0.02	9.69
b	7.60 ± 0.02	7.58
c	12.35 ± 0.03	12.33

Laue pictures were made and showed no evidence requiring a larger unit cell. Using the experimental value of the crystal density one calculates the number of molecules per unit cell, $Z = 3.99 \sim 4$.

Two sets of reflection data were obtained by taking oscillation pictures with filtered Mo $K\alpha$ radiation ($\lambda = 0.709$ Å.), with the beam normal to the a-axis in the first set, to the b-axis in the second. Intensities were estimated visually by the multiple film technique.[7]

For the $0kl$ reflections absorption corrections were computed by graphically integrating exp$(-\mu d)$ over the cross section of the crystal, where d is the path length and μ the linear absorption coefficient. Since a very small crystal of nearly square cross section was used for $h0l$ reflections, Claassen's values for a cylindrical absorber[8] were used in this set. The limiting value of $(\sin \theta)/\lambda$ was 0.58.

Systematic absences of reflections occur as follows: $hk0$ absent when h is odd, $0kl$ absent when $k + l$ is odd. The possible space groups are D_{2h}^{16}-Pnma and C_{2h}^{9}-Pna. Since the face development of the crystal is centrosymmetric, the holohedral space group, Pnam, was chosen. The following atomic positions occur in this space group.

Four-fold (a) $000,\ 0\tfrac{1}{2}0,\ \tfrac{1}{2}0\tfrac{1}{2},\ \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}$ (b) $00\tfrac{1}{2},\ 0\tfrac{1}{2}\tfrac{1}{2},\ \tfrac{1}{2}00,\ \tfrac{1}{2}\tfrac{1}{2}0$
(c) $x\tfrac{1}{4}z;\ \bar{x}\tfrac{3}{4}\bar{z};\ \tfrac{1}{2} - x, \tfrac{3}{4}, \tfrac{1}{2} + z;\ \tfrac{1}{2} + x, \tfrac{1}{4}, \tfrac{1}{2} - z$
Eight-fold (d) $\pm|xyz;\ \tfrac{1}{2} + x, \tfrac{1}{2} - y, \tfrac{1}{2} - z;\ \bar{x}, \tfrac{1}{2} + y, \bar{z};\ \tfrac{1}{2} - x, \bar{y}, \tfrac{1}{2} + z|$

Patterson Functions.—Patterson projections p(v,w), Fig. 1, and p(u,w), Fig. 2, were prepared by using the $0kl$ and $h0l$ reflections. The coördinates

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(2) Square planar coördination has been found in the following: (a) $CuCl_2 \cdot 2H_2O$. D. Harker, *Z. Krist.*, **A93**, 136 (1936); (b) $CuCl_2$. A. F. Wells, *J. Chem. Soc.*, 1670 (1947); (c) $CuBr_2$. L. Helmholz, This Journal, **69**, 886 (1947); (d) $K_2CuCl_4 \cdot 2H_2O$. S. B. Hendricks and R. G. Dickinson, *ibid.*, **49**, 2149 (1927); L. Chrobak, *Z. Krist.*, **88**, 35 (1934); (e) $CsCuCl_3$. A. F. Wells, *J. Chem. Soc.*, 1662 (1947); (f) CuO. G. Tunnell, E. Posnjak and C. J. Ksanda, *Z. Krist.*, **90**, 120 (1935); (g) Copper organo-complexes. E. G. Cox and K. C. Webster, *J. Chem. Soc.*, 713 (1935).

(3) D. P. Mellor, *Chem. Revs.*, **33**, 137 (1943); A. F. Wells, *J. Chem. Soc.*, 1662 (1947).

(4) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 104 ff.

(5) D. P. Mellor, *Z. Krist.*, **95**, 315 (1936).

(6) D. P. Mellor, *ibid.*, **101**, 160 (1939).

(7) J. J. DeLange, J. M. Robertson and I. Woodward, *Proc. Roy. Soc. (London)*, **A171**, 398 (1939).

(8) "Internationale Tabellen für Strukturbestimmung," Gebr. Borntraeger, Berlin, 1935, p. 583.

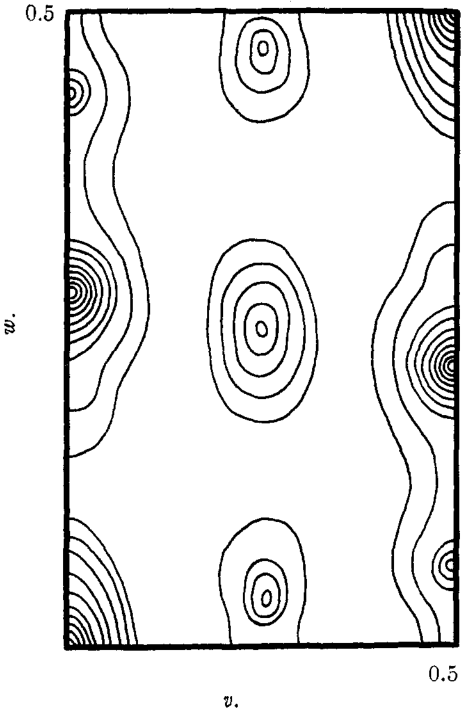

Fig. 1.—Patterson projection on 100.

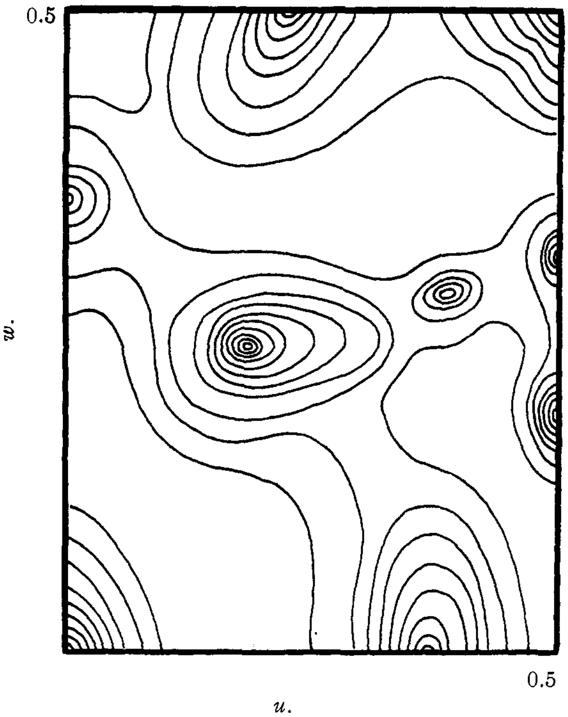

Fig. 2.—Patterson projection on 010.

u,v,w in Patterson space correspond to the x,y,z directions. There is no indication in the projections that atoms are to be placed in the special positions (a) and (b), or that the eight cesium atoms per unit cell are to placed in the eightfold positions, (d).

In these projections one expects the peaks corresponding to cesium–cesium interactions to be the largest, and to lead readily to the location of the cesium atoms. Since in $p(v,w)$ the maximum at $v = 0.00$, $w = 0.28$ is of magnitude comparable to that of the maximum at the origin, a large number of interatomic distances must have these components. It seems reasonable that the cesium atoms be separated in this way.

Assigning four cesium atoms ($\mathrm{Cs_I}$) to the positions (c) with $z = 0.103$[9] gives two cesium–cesium interactions at $v = 0.00$, $w = 0.29$. Assignment of the remaining cesium atoms ($\mathrm{Cs_{II}}$) to positions (c) with $z = 0.675$ contributes two more cesium–cesium interactions at $v = 0.00$, $w = 0.28$ and two at $v = 0.00$, $w = 0.15$. The maximum at $v = 0.00$, $w = 0.43$ also arises from interaction between the two sets of cesium atoms. For a list of all interactions see Table I.

The maxima at $v = 0.25$, $w = 0.033$ and at $v = 0.25$, $w = 0.25$ are probably cesium–chlorine interactions, which means that chlorine atoms lie halfway between layers of cesium atoms, thus in planes $y = 0.00$, $y = 0.50$ and necessarily in eight-fold positions (d) with a y-parameter of 0.00.

It seems likely that, with no further maxima appearing in $p(v,w)$, the z-parameter for the copper atoms (which must be in (c)) might well be close to that of one of the sets of cesium atoms. Giving copper a z-parameter of 0.083 serves to increase the magnitude of the maxima in Fig. 1 to which $\mathrm{Cs_I}$, already located, contributes. Since these are the largest maxima of $p(v,w)$ this choice was made provisionally and later found to be in agreement with further projections.

The Patterson projection $p(u,w)$ was used to establish x-parameters of the cesium atoms. The maximum at $u = 0.00$, $w = 0.35$ suggests that $x(\mathrm{Cs_{II}})$ is close to 0.00. The selection of $x(\mathrm{Cs_I})$ as 0.125 results in good agreement between the expected $\mathrm{Cs_I}$–$\mathrm{Cs_I}$, $\mathrm{Cs_{II}}$–$\mathrm{Cs_{II}}$, $\mathrm{Cs_I}$–$\mathrm{Cs_{II}}$ interactions (see Table I) and $p(u,w)$. In particular the interactions $u = 0.375$, $w = 0.278$ and $u = 0.000$, $w = 0.350$ seem completely resolved.

Since both Patterson projections suffer from serious overlapping of maxima, evaluation of the Patterson sections, $P(u,{}^1/_4,w)$, Fig. 3, and $P(u,0,w)$, Fig. 5, was carried out. These sections were expected to indicate clearly the location of the copper and chlorine atoms. About 330 reflections were used. Comparison of these sections with the projection $p(u,w)$ shows the gratifying resolution obtained.

Interactions of cesium and copper atoms (whose y-parameters are 0.250) with chlorine atoms (whose y-parameter is 0.000) $\mathrm{Cl_I}$ may be expected to appear in $P(u,{}^1/_4,w)$. Maxima in this section indicate that the parameters for the eight chlorine atoms, $\mathrm{Cl_I}$, in (d) are $x = 0.800$, $y = 0.000$, $z = 0.155$. Comparison of $P(u,{}^1/_4,w)$ with the corresponding vector map, Fig. 4, shows reasonable agreement. In addition, it may be seen that the interactions of $\mathrm{Cl_I}$ atoms with the cesium and copper atoms completely accounts for all of the maxima in $P(u,{}^1/_4,w)$.

The maximum in $P(u,{}^1/_4,w)$ at $u = 0.07$, $w = 0.07$ appears to be a copper–chlorine interaction

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[9] For the sake of clarity final parameter values are used in the discussion that follows. It is understood that these values were obtained by refinement of approximate parameters derived from the Patterson functions.

TABLE I

COÖRDINATES OF PATTERSON MAXIMA

The coördinates u, v, w tabulated below are calculated from final parameter values.

$\mathrm{Cs_I{-}Cs_I}$	0.500, 0.000, 0.294	0.250, 0.500, 0.206	0.250, 0.500, 0.500	
$\mathrm{Cs_I{-}Cs_{II}}$	.375, .000, .278	.375, .500, .072	.125, .500, .222	0.125, 0.000, 0.428
$\mathrm{Cs_I{-}Cu}$	.395, .000, .020	.105, .000, .314	.145, .500, .186	.355, .500, .480
$\mathrm{Cs_I{-}Cl_I}$	.325, .250, .052	.175, .250, .242	.075, .250, .258	.425, .250, .448
$\mathrm{Cs_I{-}Cl_{II}}$	.375, .000, .003	.125, .000, .297	.375, .500, .203	.125, .500, .497
$\mathrm{Cs_I{-}Cl_{III}}$	.295, .000, .181	.205, .000, .475	.045, .500, .025	.455, .500, .319
$\mathrm{Cs_{II}{-}Cs_{II}}$	.500, .000, .150	.000, .500, .350	.500, .500, .500	
$\mathrm{Cs_{II}{-}Cu}$	.230, .000, .258	.270, .000, .408	.230, .500, .092	.270, .500, .242
$\mathrm{Cs_{II}{-}Cl_I}$	.300, .250, .020	.200, .250, .170	.300, .250, .330	.200, .250, .480
$\mathrm{Cs_{II}{-}Cl_{II}}$	.000, .000, .275	.500, .000, .425	.000, .500, .075	.500, .500, .225
$\mathrm{Cs_{II}{-}Cl_{III}}$	.330, .000, .097	.170, .000, .247	.330, .500, .253	.170, .500, .403
$\mathrm{Cu{-}Cu}$	.500. .000. .334	.460, .500, .166	.040, .500, .500	
$\mathrm{Cu{-}Cu_I}$	.070, .250, .072	.430, .250, .262	.470, .250, .238	.030, .250, .428
$\mathrm{Cu{-}Cl_{II}}$	.230, .000, .017	.270, .000, .317	.230, .500, .183	.270, .500, .483
$\mathrm{Cu{-}Cl_{III}}$	.100, .000, .161	.400, .000, .495	.440, .500, .005	.060, .500, .339
$\mathrm{Cl_I{-}Cl_I}$	.100, .500, .500	.500, .500, .190	.400, .500, .310	
	.100, .000, .500	.500, .000, .910	.400, .000, .310	.000, .500, .000
$\mathrm{Cl_I{-}Cl_{II}}$	.300, .250, .055	.200, .250, .245	.300, .250, .255	.200, .250, .445
$\mathrm{Cl_I{-}Cl_{III}}$	.370, .250, .077	.130, .250, .267	.030, .250, .233	.470, .250, .423
$\mathrm{Cl_{II}{-}Cl_{II}}$	.500. .000, .300	.000, .500, .200	.500. .500, .500	
$\mathrm{Cl_{II}{-}Cl_{III}}$	.330, .000, .178	.170, .000, .478	.330, .500, .022	.170, .500, .322
$\mathrm{Cl_{III}{-}Cl_{III}}$	.500, .000, .344	.340, .500. .156	.160. .500, .500	

since its magnitude is small and since the interatomic distance corresponding to this maximum is close to the sum the known copper and chlorine radii. This offers two possibilities for x(Cu): $x = 0.730$ or $x = 0.870$, only the former, however, being consistent with the Patterson projection p(u,w) and the Patterson section P(u,0,w).

At this point the cesium, copper and half the chlorine atoms have been located. It is clear that if the copper–chlorine coördination is square planar then the chlorines already located do not lie at the ends of the square diagonal since they are not collinear with the copper atom. The only other possibility, that they are situated on one of the edges of a square, requires the occupation of a second set of eightfold positions by the remaining chlorine atoms in such a way that they are coplanar with the copper atom and $\mathrm{Cl_I}$ atoms. This possibility seems ruled out by steric considerations, and by the fact that eight new maxima would be required in the function P(u,${}^1/_4$,w) due to cesium–chlorine interactions alone, not to mention copper–chlorine interactions. Nevertheless all of the

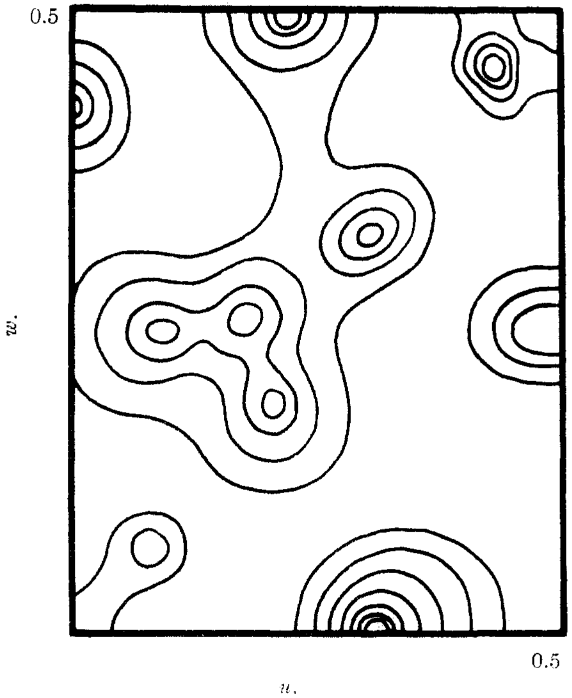

Fig. 3.—Patterson section P(u,${}^1/_4$,w).

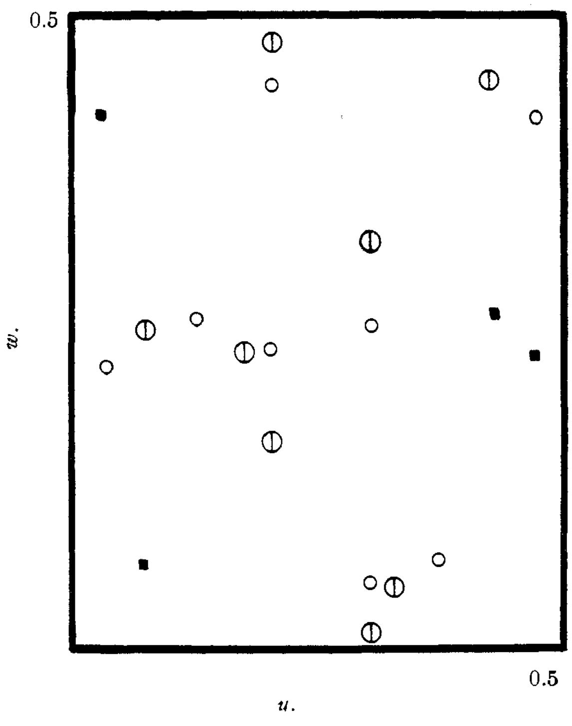

Fig. 4.—Vector map corresponding to P(u,${}^1/_4$,w) (see Fig. 6. for legend.)

maxima in $P(u,{}^1/_4,w)$ have been accounted for without the necessity of introducing the remaining chlorine atoms into further eightfold positions, and the relative magnitudes of peaks appear in reasonably good agreement with what should be expected. Hence the square planar configuration must be abandoned.

TABLE II

CALCULATED AND OBSERVED STRUCTURE FACTORS

The left hand column gives the index, the middle column the observed structure factor, and the right hand column, the calculated structure factor. The calculated structure factors have been multiplied by 0.75

11*l*		
1	<4	4
2	44	−40
3	9	10
4	26	22
5	<5	2
6	<5	1
7	12	−11
8	<8	− 6
9	12	−13
10	11	11
11	<9	1
12	13	−13
13	11	12

21*l*		
1	42	33
2	6	− 7
3	5	− 2
4	24	25
5	7	−16
6	10	15
7	13	22
8	7	−10
9	10	−10
10	10	−15
11	11	−10
12	<9	0

31*l*		
1	25	−32
2	7	− 8
3	<5	7
4	27	27
5	23	28
6	24	−22
7	9	10
8	18	−20
9	9	−10
10	21	22

41*l*		
1	28	31
2	<5	0
3	<5	0
4	<5	1
5	22	−25
6	<6	0
7	8	9
8	<8	1
9	<8	− 4

51*l*		
1	28	18
2	10	11
3	12	− 6
4	36	40
5	19	−17
6	14	−17
7	<6	− 4
8	20	−27
9	9	9
10	10	9

61*l*		
1	18	21
2	<6	3
3	<6	4
4	10	−13
5	<7	− 7
6	<7	− 7
7	17	16
8	13	8

71*l*		
1	<7	9
2	31	−27
3	<7	− 4
4	<8	7
5	<8	10
6	<8	3
7	<9	− 1
8	<9	0
9	10	− 6

81*l*		
1	<9	− 2
2	<9	5
3	18	−25

10*l*		
1	<3	3
2	5	3
3	32	26
4	11	−16
5	32	−35
6	<6	6
7	7	− 4
8	10	17
9	16	20
10	<8	− 7

20*l*		
0	5	8
1	24	−19
2	39	−24
3	56	−42
4	6	3
5	13	−12
6	34	25
7	27	28
8	7	− 9
9	15	17
10	<8	6

30*l*		
1	63	−53
2	53	−48
3	63	54
4	12	−16
5	8	7
6	12	14
7	9	− 4
8	9	11
9	<7	5
10	7	5

40*l*		
0	30	24
1	<4	− 5
2	24	−18
3	12	10
4	<5	2
5	14	19
6	24	31
7	<8	− 9
8	18	−24
9	14	−12
10	10	−10

50*l*		
1	27	−26
2	38	28
3	27	21
4	29	21
5	7	8
6	11	− 8
7	14	10
8	19	−17

60*l*		
0	38	29
1	24	17
2	16	−12
3	12	12
4	14	−11
5	12	−13
6	14	15
7	10	− 9
8	7	−10

70*l*		
1	7	2
2	8	9
3	19	19
4	<4	− 4
5	29	−25
6	10	−12
7	12	−12
8	<8	2
9	14	16

80*l*		
0	39	31
1	<6	− 3
2	<6	− 1
3	<7	0
4	15	−14

00*l*		
2	<3	− 1
4	78	−74
6	6	− 8
8	10	−14
10	12	16
12	15	21
14	6	−11

01*l*		
1	<3	− 3
3	66	−58
5	15	−21
7	44	54
9	<6	6
11	16	−16
13	<7	− 3

TABLE II *Continued*

02*l*		
0	68	−91
2	11	−14
4	41	40
6	23	28
8	18	15
10	23	−28
12	17	−14
14	14	14

03*l*		
1	<3	0
3	51	47
5	12	17
7	47	−47
9	7	− 6
11	12	15
13	<7	2

04*l*		
0	86	91
2	<4	0
4	50	−46
6	<6	− 5
8	<7	− 9
10	12	13
12	13	17

05*l*		
1	<4	0
3	28	−30
5	14	−11
7	32	34
9	8	3
11	12	−12

06*l*		
0	36	−40
2	<5	− 5
4	14	19
6	12	15
8	8	7
10	11	−16

07*l*		
1	<5	0
3	19	19
5	<6	8
7	16	−21
9	<7	− 3

08*l*		
0	27	33
2	<5	0
4	15	−18
6	<6	− 2

2*k*0		
1	39	−33
2	38	−29
3	26	26
4	<4	6
5	14	17
6	12	17
7	8	12

40*k*		
1	<4	0
2	8	11
3	<5	0
4	17	11
5	<6	0
6	<6	5
7	<7	0

6*k*0		
1	16	15
2	30	21
3	12	13
4	23	21

8*k*0		
1	<6	9
2	35	42
3	<8	8
4	19	22

The maxima not yet accounted for in $P(u,0,w)$ Fig. 5, indicate the location of the eight remaining chlorine atoms in two sets of fourfold positions (c). Assignment of one set of four chlorine atoms, Cl_{II}, to (c) with $x = 0.500$, $z = 0.100$, and the other set of four, Cl_{III}, with $x = 0.830$, $z = 0.922$ gives good agreement with the observed maxima, as can be seen by comparing $P(u,0,w)$ with the vector map corresponding to it, Fig. 6.

Approximate parameter values obtained from the Patterson functions were used to calculate structure factors, and small shifts were made to improve the agreement between calculated and ob-

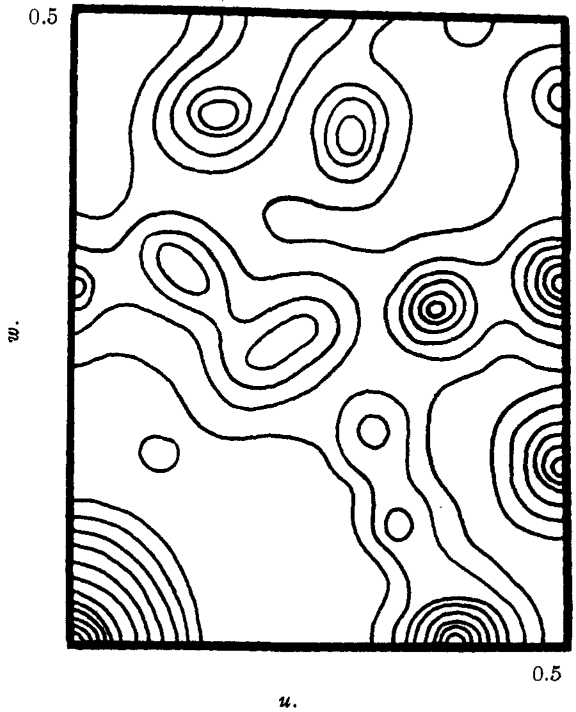

Fig. 5.—Patterson section $P(u,0,w)$.

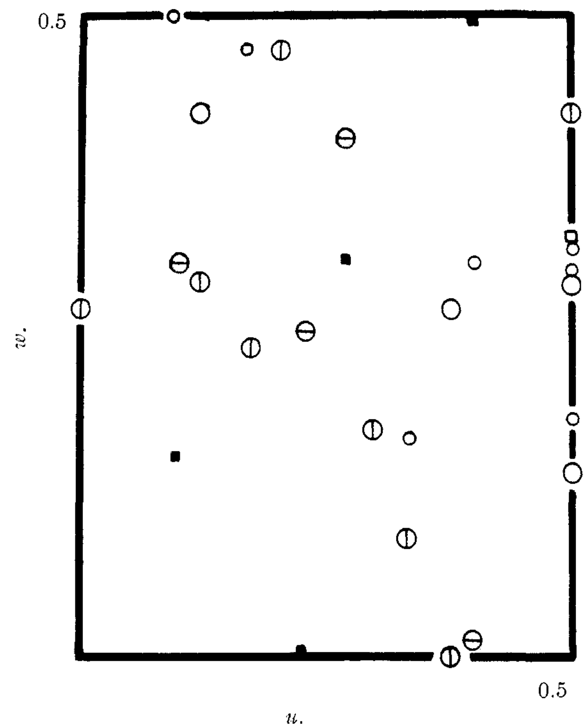

Fig. 6.—Vector map corresponding to P(u,0,w). The points above show interatomic distances calculated from final parameters. Large open circles represent cesium–cesium distances; circles with horizontal diameter, cesium–copper; circles with vertical diameter, cesium–chlorine; open square, copper–copper; solid square, copper–chlorine; small open circles, chlorine–chlorine.

served amplitudes. These are compared in Table II. Atomic scattering factors[10] multiplied by exp-$(-B \sin^2 \theta/\lambda^2)$ were used, with $B = 3.0 \times 10^{-16}$.

The final parameter values found are:

	x	y	z
$\mathrm{Cs_{I}}$	0.125 ± 0.002		0.103 ± 0.002
$\mathrm{Cs_{II}}$	.000 ± .002		.675 ± .002
Cu	.730 ± .003		.083 ± .003
$\mathrm{Cl_{I}}$	.800 ± .005	0.000 ± 0.003	.155 ± .005
$\mathrm{Cl_{II}}$	.500 ± .005		.100 ± .005
$\mathrm{Cl_{III}}$	.830 ± .005		.922 ± .005

The structure factors are much more insensitive to variation of chlorine parameters than to variation of the parameters of the strongly scattering cesium atoms, so that relatively large errors are to be found in the chlorine parameters. The mean fractional deviation of the calculated amplitudes from those observed is 0.19, but this figure does not take into account unobserved reflections, which were uniformly calculated very weak.

There remains no doubt, however, that the essential features of the structure are correct. Three considerations support this contention: First, the order of agreement with the Patterson functions is good; other combinations suggested by considering any one of the Patterson functions result in serious inconsistencies with the other Patterson data. Second, the location of the cesium atoms can be unequivocally established, and simple trial and error calculation shows that in the remaining space there is room for no more than one eightfold set of chlorine atoms. Attempts to fill a second set of eightfold positions give rise to either unreasonably short cesium–chlorine distances or chlorine–chlorine distances. Furthermore it seems impossible to fit calculated and observed structure factors with any

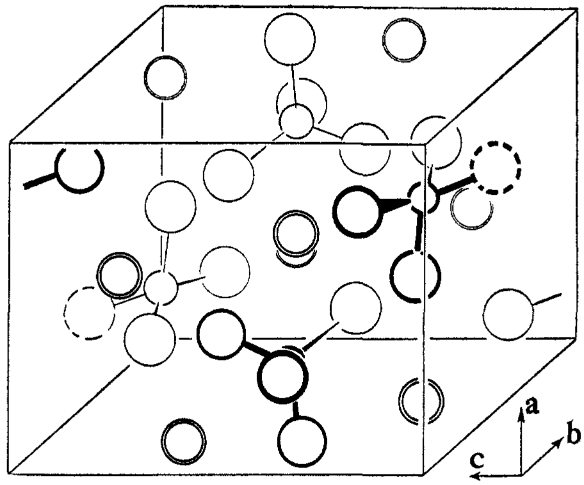

Fig. 7.—Unit cell of cesium chlorocuprate. Large circles are chlorine atoms, small circles are copper atoms, double circles are cesium atoms. Dotted circles indicate that the atom lies outside the unit cell.

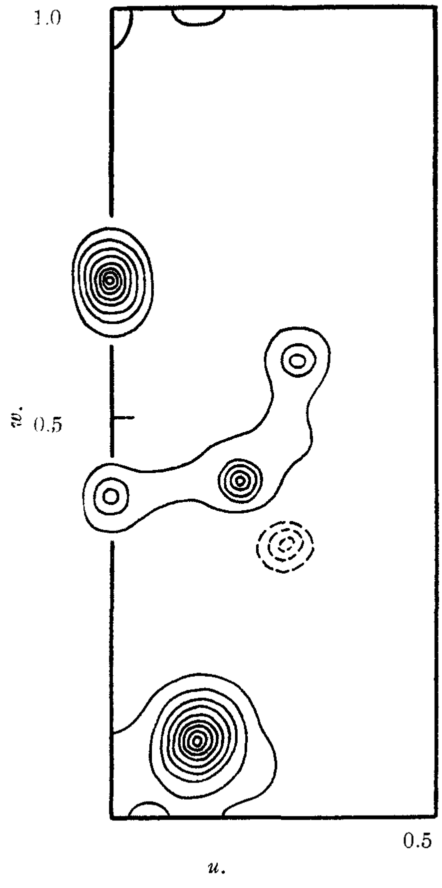

Fig. 8.—Section at $y = 0.25$ from three-dimensional Fourier density function. Dotted maxima indicate the positions in the planes $y = 0.00$, $y = 0.50$ occupied by the eightfold chlorine atoms.

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[10] Values taken from the "Internationale Tabellen," see ref. 8.

variety of arrangements of chlorine atoms all in eightfold positions. Third, the generally good agreement between the observed and calculated structure factors provides justification for the structure found.

Discussion of Structure.—The configuration of the chlorocuprate ion may be seen in Fig. 7 and in the section at $y = 0.25$ from the three-dimensional Fourier density function, Fig. 8. The configuration is shown in Fig. 8 by indicating with dotted lines the location of two of the eightfold chlorine atoms lying in the planes $y = 0.000$ and $y = 0.500$, one above the other. The ion has closely (although not required by the space group) the symmetry of a tetragonal sphenoid, that is fourfold inversion symmetry, and may be considered as either a flattened tetrahedron, or as a square plane deformed by pushing the atoms at the ends of one diagonal up from the plane, those at the ends of the other diagonal down from the plane.

The average copper–chlorine contact distance is 2.22 Å. ($Cu{-}Cl_I$, 2.21 Å.; $Cu{-}Cl_{II}$, 2.24 Å., $Cu{-}Cl_{III}$, 2.21 Å., all ± 0.06 Å.). This is a shortening of nearly 0.1 Å. relative to the copper–chlorine distance found in $CuCl_2$, $CuCl_2 \cdot 2H_2O$, and $K_2CuCl_4 \cdot 2H_2O$, that is, 2.30 Å. Within the ion two chlorine–chlorine distances are found, a long distance of 3.80 Å. between the two Cl_I atoms and between Cl_{II} and Cl_{III}, and a shorter distance of 3.50 Å. between Cl_I and Cl_{II}, and between Cl_I and Cl_{III}. The bond angles $Cl_I{-}Cu{-}Cl_I$ and $Cl_{II}{-}Cu{-}Cl_{III}$ are 120 ± 3°, and the bond angles $Cl_I{-}Cu{-}Cl_{II}$ and $Cl_I{-}Cu{-}Cl_{III}$ are 104 ± 3°.

CESIUM-CHLORINE DISTANCES (IN Å.) AND DISTANCES BETWEEN CHLORINE ATOMS IN DIFFERENT IONS

$Cs_I{-}Cl_I$	3.72	$Cs_{II}{-}Cl_I$	3.49	$Cs_{II}{-}Cl_{III}$	3.42
	3.92		3.43		3.47
$Cs_I{-}Cl_{II}$	3.63	$Cs_I{-}Cl_{III}$	3.72	$Cs_{II}{-}Cl_{II}$	3.40
$Cl_I{-}Cl_I$	5.40	$Cl_I{-}Cl_{II}$	4.06	$Cl_I{-}Cl_{III}$	4.00

Absorption Spectrum.—The molar extinction of chlorocuprate ion is shown in Fig. 9. This was obtained from measurements of solutions containing cupric ion and chloride ion in the ratio of $1:10^5$. The Beckman DU spectrophotometer was used. That the solution contains a saturated chloride complex ion (*i.e.*, four coördinated) was demonstrated by Moeller,[11] and according to Bjerrum[12] all but a few per cent. of the copper in such solutions is accounted for in chlorocuprate ion.

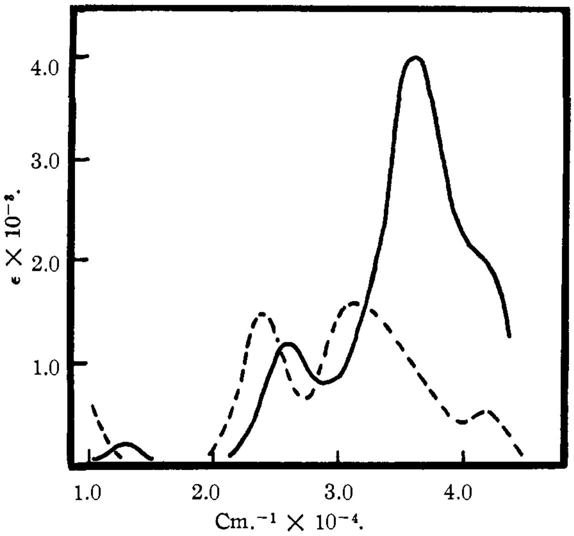

Fig. 9.—Absorption spectrum of chlorocuprate ion. Solid line shows absorption in solution (molar extinction). Broken line shows crystal absorption plotted on an arbitrary extinction scale.

Extinction measurements were made of powdered cesium chlorocuprate suspended in a transparent mineral oil. A thin film of the mineral oil suspension was supported between quartz plates and transmission measurements were made with the Beckman DU spectrophotometer. The absorption is also shown in Fig. 9 plotted on an extinction scale that is arbitrary, since the length of the light path was undetermined.

The appearance of the spectrum in both cases is comparable although the heights of the maxima relative to each other have changed in going from the solution to the crystal. The difference between the two spectra seems to us too large to be accounted for on the basis of crystal perturbations. It seems more likely that the structure of the aqueous ion is not the same as that in the crystal, though the difference would certainly not have to be very great to produce the observed effect.

The moderate birefringence indicates the non-tetrahedral nature of the chlorocuprate ion and since its actual value is smaller than one expects for a planar ion it is consistent with the non-planar structure found.

ST. LOUIS, MISSOURI

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[11] T. Moeller, *J. Phys. Chem.*, **48**, 112 (1944).

[12] J. Bjerrum, *Det. Kgk. Danske Selskab., Mat. Fys. Medd., Bd.* XXII, Nr. 18 (1946).