The crystal structure of copper perchlorate hexahydrate, $Cu(ClO_4)_2 : 6H_2O$

By N. V. Mani and S. Ramaseshan

Department of Physics, Indian Institute of Science, Bangalore, India

With 3 figures

Auszug

Die Struktur des Kupferperchlorat-Hexahydrats wurde eingehend untersucht mittels der Fourier-Methode und der Methode der kleinsten Quadrate unter Berücksichtigung chemischer Betrachtungen über Ionenpackungen. Die monoklinen Kristalle der Raumgruppe $P2_1/c$ enthalten sechs Formeleinheiten in der Zelle mit $a = 5{,}14$ Å, $b = 23{,}173$ Å, $c = 14{,}147$ Å und $\beta = 90°$. Die Struktur baut sich aus oktaedrischen Gruppen von Wassermolekülen um das Kupferion und aus tetraedrischen Perchloratgruppen auf. Sowohl das $Cu(H_2O)_6$-Oktaeder mit einem mittleren Cu—O-Abstand von 2,18 Å als das ClO_4-Tetraeder mit einem mittleren Cl—O-Abstand von 1,48 Å sind leicht deformiert. Die durch Wasserstoffionen verbundenen Wasser- und Perchlorat-Sauerstoffatome liegen auf Sechserringen von „Boot"- *und* von „Sessel"-Form. Beim Magnesiumperchlorat-Hexahydrat fand West nur Ringe in „Sessel"-Form. Weil beide Strukturen sonst in jeder Beziehung ähnlich sind, bedarf West's Strukturvorschlag einer Überprüfung.

Abstract

The detailed x-ray analysis of the structure of copper perchlorate hexahydrate has been carried out by Fourier and least-squares methods aided by chemical considerations of ionic packing. The monoclinic crystals, space group $P2_1/c$, have six formula units in a cell of dimensions $a = 5.14$ Å, $b = 23.173$ Å, $c = 14.147$ Å with $\beta = 90°$. The structure consists of octahedral groups of water molecules around the cupric ion, and tetrahedral perchlorate groups. The $Cu\text{-}(H_2O)_6$ octahedron with a mean Cu—O length of 2.18 Å and the ClO_4 tetrahedron with a mean Cl—O length of 1.48 Å are only slightly deformed from the ideal structures. The hydrogen bonds which link the water and perchlorate oxygens are puckered six-membered rings having the 'boat' and 'chair' shapes unlike those in the structure of magnesium perchlorate hexahydrate proposed by West where these rings have always a chair-shaped structure. As the two structures are otherwise similar in all respects, West's analysis may require revision.

Introduction

The investigation of the crystal structure of copper perchlorate hexahydrate described in this paper forms part of the systematic x-ray work done in this laboratory on some perchlorates[1-3].

WEST[4,5], who has made some detailed studies of the structures of some perchlorates (mostly of divalent metals), examined the morphology and crystal character of $Cu(ClO_4)_2 \cdot 6H_2O$ and its isomorph $Cu(BF_4)_2 \cdot 6H_2O$ but did not proceed any further in elucidating their structures. He felt that no simple relation in the atomic arrangements is evident between these cupric salts and the hexagonal structures of other perchlorates worked out by him earlier[5]. Hence it seemed desirable to investigate the structure of this compound and compare it with the structures of other perchlorates.

Experimental

The pale bluish green crystals have a low melting point ($\simeq 60\,°C$) and are extremely hygroscopic. When viewed between crossed polaroids, most of them showed clear signs of twinning but single crystals were carefully chosen and enclosed in Lindemann glass capillaries. As the specimen revealed a marked tendency to deliquesce and become amorphous in the process of grinding, the complete x-ray data had to be confined to measurements in the rotation and Weissenberg photographs about the axis of elongation (a) only.

The crystals have monoclinic symmetry with cell dimensions $a = 5.14 \pm 0.01$ Å, $b = 23.173 \pm 0.008$ Å and $c = 14.147 \pm 0.008$ Å with $\beta = 90° \pm 1°$. The monoclinic angle was estimated by the level-offset method due to BUERGER[6] using higher level a axis Weissenberg photographs. The measured value of the density ϱ (meas.) $= 2.24$ g. cm^{-3} was in fair agreement with the value ϱ (calc.) $= 2.19$ g. cm^{-3}

[1] K. VENKATESAN, The crystal structure of ammonium perchlorate, NH_4ClO_4. Proc. Ind. Acad. Sci. A46 (1957) 134—142.

[2] N. V. MANI, The crystal structure of potassium perchlorate, $KClO_4$. Proc. Ind. Acad. Sci. A46 (1957) 143—151.

[3] N. V. MANI and S. RAMASESHAN, The crystal structure of barium perchlorate trihydrate, $Ba(ClO_4)_2 \cdot 3 H_2O$ and the crystal coordination of Ba^{++} ion. Z. Kristallogr. 114 (1960) 200—214.

[4] C. D. WEST, Crystal structures of some hydrated compounds, I. $LiClO_4 \cdot 3 H_2O$, $LiI \cdot 3 H_2O$, $Ba(ClO_4)_2 \cdot 3 H_2O$. Z. Kristallogr. 88 (1934) 198—204.

[5] C. D. WEST, Crystal structures of hydrated compounds, II. Structure type $Mg(ClO_4)_2 \cdot 6 H_2O$. Z. Kristallogr. 91 (1935) 480—493.

[6] M. J. BUERGER, X-ray crystallography (John Wiley, New York, 1942), p. 375—377.

calculated on the assumption of six formula units in the cell. The space group $P2_1/c$ was consistent with the observed extinctions in the $0k0$ and $h0l$ spectra when k and l are odd respectively. Further, the presence of pseudo-symmetry was also revealed by the occurrence of $0kl$ reflections only when $k = 3n$ and $0k0$ only when $k = 6n$.

The intensities of hkl reflections, with h from 0 through 4, were recorded on multiple-film equi-inclination Weissenberg photographs using $CuK\alpha$ radiation, and their measurements were carried out by visual methods using calibrated strips for comparison. The geometrical corrections for Lorentz and polarisation factors and the physical corrections for absorption in cylinders ($\mu = 81$ cm^{-1} for $CuK\alpha$; $r = 0.028$ cm) were also applied.

The total number of reflections recorded were about 2500; of these, nearly 1920 were definitely measurable and the rest a little below the threshold of observation.

Determination of the structure

From the symmetry of the space group $P2_1/c$ and the number of molecules in the cell (six), it followed that the asymmetric unit contained $1^1/_2$ formula units with three perchlorate groups, nine water molecules and one copper (all in general positions) with the other copper necessarily in a special position (two-fold). The task of evaluating the seventy-five unknown atomic parameters required to define the structure was considerably simplified by the presence of additional symmetry elements. The extinctions in $0kl$ reflections when $k = 3n$ (and $0k0$ when $k = 6n$) clearly revealed the presence of pseudo-glides parallel to (100) with translation components $\pm \frac{1}{3}b$ and one of these at $\frac{1}{4}a$, for example, with component $\frac{2}{3}b$ generates two extra equivalent points $\frac{1}{2} - x, \frac{2}{3} + y, z$ and $x, \frac{1}{3} + y, z$ from each of the points $x\,y\,z$. This reduces the number of unknown parameters to forty only.

1. $0kl$ projection

The derivation of the structure in this projection was straightforward from an $0kl$ Patterson diagram computed using nearly 140 reflexions in this zone. The cupric ion was placed at $0\,0$ and the chlorine at $0\frac{1}{3}$, the coordinates of other coppers and chlorines being derivable from consideration of space group as well as pseudo-symmetry. From the peak heights and their distribution, one of the perchlorate oxygens was placed above each chlorine, the other three of the same ClO_4 group

surrounding it such that the latter displayed a three-fold relationship, with two of them as mirror images of each other across the c axis and the third lying on the axis itself. Likewise, the water oxygens were also assigned co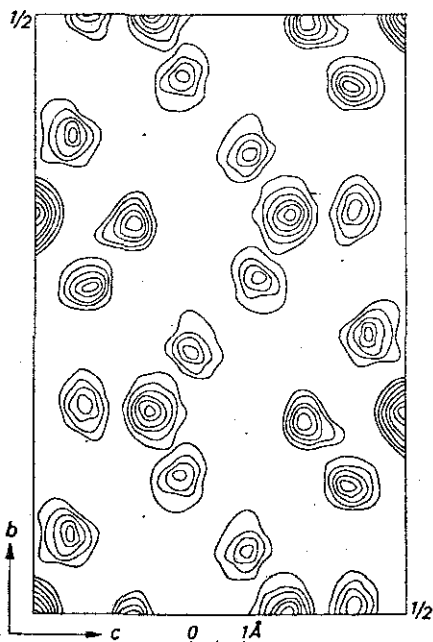ordinates, one being placed on the c axis and the other two on either side of it as before, and with these three inverted across the central copper, we have six water oxygens surrounding the metal ion.

Fig. 1. $Cu(ClO_4)_2 \cdot 6H_2O$. Electron-density projection on (100) with contours drawn at arbitrary intervals. The cupric ions lie along lines parallel to b axis at $c = 0$ and $c = \frac{1}{2}$. The perchlorate groups with an oxygen overlapping on the chlorine in this projection and the water oxygens around the cupric ions can be easily distinguished

With such a disposition, the phases of most of the reflections having $k + l = 2n$ were certain as these obtained contributions from the complete structure whereas, for reflections having $k + l = 2n + 1$, neither the coppers nor the chlorines rendered any contribution. For the latter case, moreover, the calculated values now were exactly zero for the present arrangement because of the spurious reflection symmetry across the c axis. This was gradually obliterated by trial movements of the oxygens, and the structure in projection was refined by subsequent F_o syntheses wherein larger number of structure factors with $k + l = 2n + 1$ were included. Further refinements of these oxygens were effected by series of difference and subtraction Fourier syntheses. The measure of the agreement between the structure factors was evaluated at every stage, the scaling and mean temperature corrections being improved by graphical comparison.

As the movements of the chlorine atom (at $0\frac{1}{2}$) were not so obvious in difference maps, probably because of the overlap, least-squares adjustments[7] of its positional parameters were carried out with $0kl$

[7] E. W. HUGHES, The crystal structure of melamine. J. Amer. Chem. Soc. **63** (1941) 1737—1752.

data. The average shifts after three cycles of treatment were 0.084 and 0.057 Å only in the y and z coordinates when the refinement was stopped.

The F_c values calculated on the basis of the final parameters for an asymmetric unit (and corrected for thermal motion with an isotropic value for $B = 2.38$ Å^2) are compared with the F_o values in Table 1. The ultimate value of the R factor was found to be 0.153,

Table 1. *Comparison between the calculated and observed 0kl structure amplitudes*

0 k l	F_c	F_o	0 k l	F_c	F_o	0 k l	F_c	F_o	0 k l	F_c	F_o
0 0 2	13.0	14.4	0 6 3	− 5.6	4.8	0 12 10	− 9.4	10.0	0 18 12	12.9	15.2
0 0 4	4.1	6.7	0 6 10	− 3.6	9.1	0 12 11	2.2	2.9	0 18 13	− 0.6	< 2.0
0 0 6	48.0	46.1	0 6 11	1.3	2.2	0 12 12	27.9	26.6	0 18 14	11.5	13.4
0 0 8	− 13.9	13.5	0 6 12	35.6	38.7	0 12 13	− 0.4	< 2.0	0 21 1	− 3.2	6.8
0 0 10	3.3	10.6	0 6 13	1.5	2.8	0 12 14	7.0	8.7	0 21 2	5.0	4.8
0 0 12	22.1	28.4	0 6 14	7.7	10.8	0 12 15	0.8	< 2.0	0 21 3	28.2	32.9
0 0 14	17.8	19.8	0 6 15	0	< 2.0	0 12 16	4.2	4.0	0 21 4	3.8	4.2
0 0 16	4.6	7.8	0 6 16	4.6	4.2	0 15 1	14.3	16.1	0 21 5	1.2	< 2.0
0 3 1	7.0	10.2	0 9 1	− 13.9	18.2	0 15 2	5.4	7.2	0 21 6	− 3.2	3.3
0 3 2	1.5	< 2.0	0 9 2	7.0	10.4	0 15 3	36.1	40.3	0 21 7	13.3	10.8
0 3 3*	92.7	68.6	0 9 3	28.4	34.6	0 15 4	1.4	2.3	0 21 8	− 1.0	3.4
0 3 4	4.2	4.5	0 9 4	0.4	2.4	0 15 5	1.5	4.2	0 21 9	22.9	24.5
0 3 5	− 4.9	4.3	0 9 5	39.2	37.8	0 15 6	− 0.8	2.0	0 21 10	− 1.0	< 2.0
0 3 6	− 5.1	5.2	0 9 6	3.2	4.3	0 15 7	10.3	8.2	0 21 11	5.6	7.6
0 3 7	28.7	28.8	0 9 7	15.7	18.1	0 15 8	3.5	5.0	0 21 12	− 2.3	< 2.0
0 3 8	− 7.6	8.2	0 9 8	0.8	5.4	0 15 9	25.1	29.4	0 21 13	− 2.2	2.6
0 3 9	47.3	50.0	0 9 9*	70.8	65.1	0 15 10	− 1.4	< 2.0	0 24 0	22.5	23.7
0 3 10	− 0.6	2.3	0 9 10	3.1	3.9	0 15 11	1.7	< 2.0	0 24 1	0.4	3.9
0 3 11	7.2	8.5	0 9 11	6.7	7.2	0 15 12	1.0	< 2.0	0 24 2	0.4	< 2.0
0 3 12	− 5.2	4.9	0 9 12	− 2.0	4.0	0 15 13	− 0.6	4.6	0 24 3	0	2.7
0 3 13	− 2.4	8.6	0 9 13	− 5.2	6.3	0 15 14	− 3.0	< 2.0	0 24 4	− 1.6	2.6
0 3 14	4.4	3.9	0 9 14	− 1.8	2.0	0 15 15	17.1	17.6	0 24 5	− 3.5	4.0
0 3 15	22.4	24.0	0 9 15	18.9	19.2	0 18 0	54.8	61.8	0 24 6	22.6	22.3
0 3 16	3.0	< 2.0	0 9 16	1.5	2.0	0 18 1	4.0	4.8	0 24 7	1.2	< 2.0
0 3 17	6.4	7.5	0 12 0*	70.9	59.5	0 18 2	4.6	4.8	0 24 8	9.0	11.0
0 6 0*	88.3	63.5	0 12 1	− 2.0	< 2.0	0 18 3	− 2.4	2.6	0 24 9	0.4	< 2.0
0 6 1	0.7	< 2.0	0 12 2	27.9	27.2	0 18 4	3.4	6.4	0 24 10	0.6	< 2.0
0 6 2	13.6	10.5	0 12 3	− 2.5	< 2.0	0 18 5	− 3.4	5.0	0 27 1	0.7	2.1
0 6 3	3.4	3.8	0 12 4	− 12.6	13.2	0 18 6	26.5	30.0	0 27 2	3.3	4.2
0 6 4	− 18.6	22.6	0 12 5	− 1.3	< 2.0	0 18 7	− 3.2	2.5	0 27 3	12.6	14.7
0 6 5	− 8.5	7.6	0 12 6	45.2	48.6	0 18 8	− 1.8	3.5	0 27 4	0.2	2.6
0 6 6*	70.3	55.3	0 12 7	− 1.4	< 2.0	0 18 9	1.6	< 2.0	0 27 5	7.0	6.4
0 6 7	0.5	2.0	0 12 8	11.1	16.7	0 18 10	− 1.6	< 2.0	0 27 6	− 0.6	2.8
0 6 8	27.3	32.8	0 12 9	9.2	9.6	0 18 11	1.2	< 2.0	0 27 7	1.0	< 2.0

omitting a few strong small-angle reflections (marked with an asterisk in the table) probably affected by extinction. The final electron-density projection on (100) is given in Fig. 1 and the corresponding atomic arrangement in Fig. 2.

2. The orientation of perchlorate groups and the derivation of the x coordinates

Owing to difficulties involved in the collection of data for any other axis of crystal rotation, the derivation of the x coordinates was achieved by indirect means. In the first instance this information, to a large extent, was obtained from considerations of ionic packing. The plan of the structure shown in Fig. 2 reveals that the cupric ion has an octahedral environment of water oxygens, with two sets of three on either side of it. As the Cu—Cu distance is 5.14 Å (a translation) and a pair of oxygen triangles are between two cupric ions, it follows from considerations of ionic radii of Cu^{++} and O^{--} that

the water oxygen planes are approximately at heights $\pm \frac{1}{4}$ along a axis. This is similar to the situation encountered in the structure of $Mg(ClO_4)_2 \cdot 6H_2O$ as reported by WEST[5]. It might be pointed out that despite contrary remarks by him, the structures of the orthorhombic Mg salt and monoclinic cupric salt have a close resemblance (for ex. compare Fig. 2 with Fig. 3, p. 484 of WEST's paper[5]).
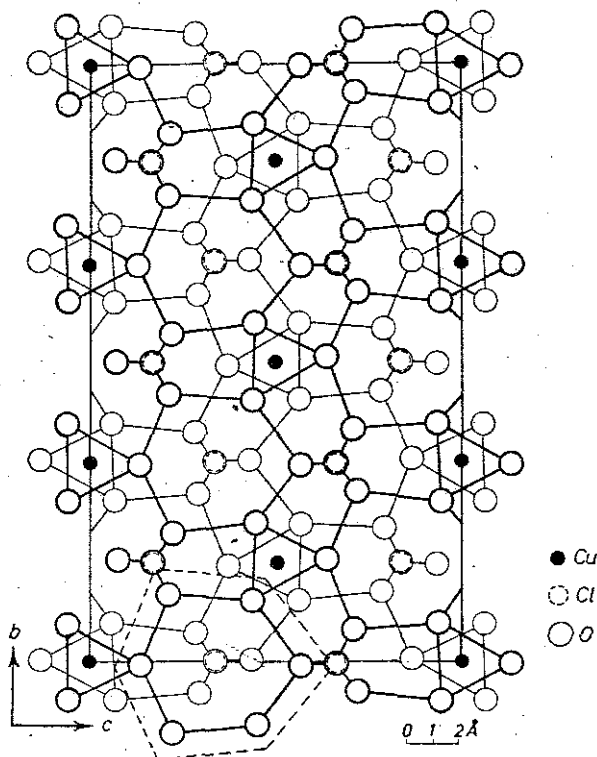

Fig. 2. $Cu(ClO_4)_2 \cdot 6 H_2O$. Projection of the unit cell on (100) showing the tetrahedral ClO_4 and the octahedral $Cu\text{-}(H_2O)_6$ groups. The H bonds between the water and the perchlorate oxygens have been indicated by heavy and light lines, and one ring of these bonds near the origin has been enclosed by broken lines

In addition it was found necessary to have the chlorines also at the same heights as the water oxygens for a satisfactory hydrogen-bonding scheme as represented by the magnesium perchlorate hexahydrate structure. However, neither consideration of packing nor similarity of this structure to the Mg compound could uniquely establish the orientation of the perchlorate groups. For example, with a

Cl at height $\frac{3}{4}a$, the three O atoms associated with it can be at a level 0.66 a (i.e., 0.46 Å lower than chlorine, a value well-known from studies on other perchlorates) or at 0.84 a (0.46 Å above chlorine), the corresponding positions of the fourth oxygen being at 1.04 a or 0.46 a (this represents a mean distance of 1.49 Å to these oxygens from the central chlorine along a). Consequently we were left with four distinct ways of packing the ClO_4 groups in the cell. The effect of these in the six-membered ring of water and perchlorate oxygens was to modify them into four types of 'chair' and 'boat' configurations (two each). This is illustrated graphically in Fig. 3 for atoms at $\frac{3}{4}a$ level enclosed by broken lines in Fig. 2, with figures inside each circle to indicate the heights of each of these atoms in fractions of a translation.

In order to distinguish the exact configuration, the detailed computations of structure factors for $1kl$ and part of $3kl$ reflections (comprising a total of about 1050) for the above four structures were made. It was readily seen that the quality of the overall agreement was definitely better for the third arrangement. In the other
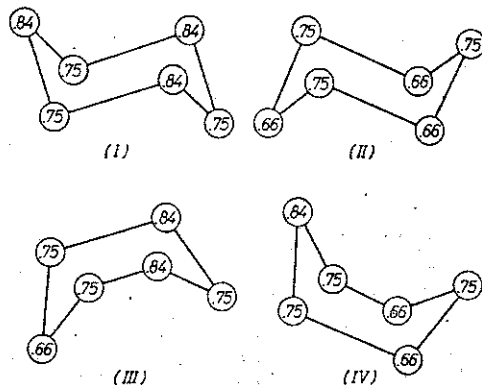

Fig. 3. The four possible structures for the enclosed hexagonal ring in Fig. 2. The figures within the circles denote the heights of the atoms in fractions of the a translation. Note all the water oxygens are at the level $0.75a$

three cases, the discrepancies between the structure factors were so large as to indicate that the corresponding structural arrangements would be improbable. It was hence felt that the third arrangement would lead to the genuine structure and so the structure-factor calculations based on this were completed for the remaining data.

The agreement was found to be consistently good. The R factor for all the hkl reflections with h from 1 to 4 was estimated to be 0.198. Using CRUICKSHANK's method[8], an estimate of the standard deviations in the atomic coordinates was made. The values obtained for the three coordinates were of the same order of magnitude for each

[8] D. W. J. CRUICKSHANK, The accuracy of electron density maps in x-ray analysis with special reference to dibenzyl. Acta Crystallogr. 2 (1949) 65—82.

atom [except, of course, for Cu where only $\sigma(x)$ exists] so that a mean value can be specified. These were as follows:

$\sigma(x) = 0.001$ Å in Cu (II).

$\sigma(x) \simeq \sigma(y) \simeq \sigma(z) = 0.008$ Å in Cl and 0.011 Å in O.

As these were the order of errors involved in the final analyses of many structures, further refinement of the structure was not undertaken as they proved too laborious without adequate computational aids.

Table 2. *Comparison between the calculated and observed h0l structructure amplitudes*

h 0 l	Fc	Fo	h 0 l	Fc	Fo	h 0 l	Fc	Fo	h 0 l	Fc	Fo
1 0 2	63.7	53.4	2 0 6	23.4	27.5	3 0 12	1.3	2.9	4 0 10	−7.7	5.2
1 0 4	−50.7	50.9	2 0 8	36.0	38.4	3 0 14	−11.3	8.3	4 0 12	0.9	<2.0
1 0 6	−2.0	6.6	2 0 10	32.6	40.5	3 0 $\bar{2}$	32.0	30.2	4 0 14	6.0	<2.0
1 0 8	12.2	14.5	2 0 12	8.9	10.0	3 0 $\bar{4}$	−25.3	28.4	4 0 $\bar{2}$	19.7	22.8
1 0 10	12.6	13.0	2 0 14	2.1	<2.0	3 0 $\bar{6}$	−18.5	20.4	4 0 $\bar{4}$	−4.2	6.5
1 0 12	−1.2	3.6	2 0 16	7.6	6.7	3 0 $\bar{8}$	30.7	28.2	4 0 $\bar{6}$	25.5	18.2
1 0 14	14.8	14.9	3 0 2	−13.0	12.5	3 0 $\overline{10}$	0.3	<2.0	4 0 $\bar{8}$	1.7	3.7
1 0 16	3.7	4.1	3 0 4	38.8	34.9	4 0 2	17.5	14.5	4 0 $\overline{10}$	−5.8	4.4
1 0 18	−2.3	3.4	3 0 6	29.3	25.7	4 0 4	−7.9	7.5	4 0 $\overline{12}$	−0.6	<2.0
2 0 2	46.2	44.0	3 0 8	−3.0	6.3	4 0 6	25.1	19.9			
2 0 4	36.1	40.0	3 0 10	11.6	8.3	4 0 8	10.7	10.4			

Table 3. *Comparison between the calculated and observed hk0 structure amplitudes*

h k 0	Fc	Fo	h k 0	Fc	Fo	h k 0	Fc	Fo	h k 0	Fc	Fo
1 1 0	0.4	2.6	1 27 0	−4.2	4.6	2 24 0	4.0	5.2	3 22 0	−8.7	3.7
1 2 0	−22.8	24.8	1 28 0	−6.6	5.7	2 25 0	1.8	<2.0	3 23 0	0	<2.0
1 3 0	−0.6	3.2	1 29 0	0.1	<2.0	2 26 0	0	<2.0	3 24 0	2.0	<2.0
1 4 0	−25.9	24.6	2 1 0	−25.5	25.4	2 27 0	−1.6	<2.0	3 25 0	0.1	<2.0
1 5 0	−0.2	3.6	2 2 0	0.1	<2.0	2 28 0	0	<2.0	4 1 0	4.9	5.8
1 6 0	6.5	4.1	2 3 0	0	<2.0	3 1 0	−0.2	<2.0	4 2 0	−0.1	<2.0
1 7 0	−6.3	2.2	2 4 0	0	<2.0	3 2 0	−26.4	19.7	4 3 0	0	<2.0
1 8 0	−26.9	25.2	2 5 0	8.7	8.2	3 3 0	0.7	<2.0	4 4 0	−0.1	3.6
1 9 0	−5.5	5.2	2 6 0	20.6	18.5	3 4 0	−29.0	16.8	4 5 0	1.0	<2.0
1 10 0	−27.0	25.6	2 7 0	−1.9	2.6	3 5 0	0.1	4.7	4 6 0	31.3	26.9
1 11 0	0.2	<2.0	2 8 0	−0.1	2.3	3 6 0	3.0	7.6	4 7 0	−2.5	3.2
1 12 0	4.6	4.6	2 9 0	−1.0	2.3	3 7 0	0	3.3	4 8 0	−0.1	<2.0
1 13 0	−0.1	<2.0	2 10 0	0.1	<2.0	3 8 0	−10.9	10.1	4 9 0	1.0	<2.0
1 14 0	−15.2	14.9	2 11 0	−2.0	<2.0	3 9 0	1.6	3.3	4 10 0	−0.1	1.8
1 15 0	−2.0	4.2	2 12 0	0.1	<2.0	3 10 0	−10.2	9.0	4 11 0	3.6	2.4
1 16 0	−12.2	11.1	2 13 0	.5	4.4	3 11 0	−0.1	<2.0	4 12 0	35.4	28.2
1 17 0	0	4.0	2 14 0	0.1	2.3	3 12 0	6.1	4.0	4 13 0	−1.2	<2.0
1 18 0	6.4	6.2	2 15 0	0.2	<2.0	3 13 0	−0.1	2.1	4 14 0	0.6	<2.0
1 19 0	−0.2	3.2	2 16 0	−0.2	<2.0	3 14 0	−12.4	9.6	4 15 0	0.4	<2.0
1 20 0	−8.3	7.7	2 17 0	2.6	7.2	3 15 0	2.0	4.1	4 16 0	0.1	2.3
1 21 0	−2.0	<2.0	2 18 0	−13.5	11.8	3 16 0	−9.4	7.7	4 17 0	−5.0	2.6
1 22 0	−13.4	10.8	2 19 0	−5.5	5.4	3 17 0	0.1	<2.0	4 18 0	21.4	18.1
1 23 0	0	<2.0	2 20 0	1.0	5.4	3 18 0	0.9	3.6	4 19 0	3.2	3.6
1 24 0	2.4	<2.0	2 21 0	0.1	<2.0	3 19 0	−0.1	<2.0	4 20 0	0.1	<2.0
1 25 0	−0.2	<2.0	2 22 0	−1.0	<2.0	3 20 0	−10.3	7.2	4 21 0	−0.1	<2.0
1 26 0	−5.7	5.1	2 23 0	2.8	<2.0	3 21 0	2.0	<2.0	4 22 0	−0.1	<2.0

The final comparison between the structure factors in the $h0l$ and $hk0$ zones has been separately shown in Tables 2 and 3. Here attention must be drawn to the fact that these data have been culled out from the general computations of hkl reflections (for h from 1 to 4) and hence the presence of an appreciable scaling correction between the different layers is extremely likely. The assumptions pertaining to thermal motion are suspect also. No attempt was made to allow for anisotropy and a mean isotropic value for $B = 2.38$ Å² has been uniformly

applied for reflections in all the three zones. The structure factors are therefore certain to be in error to some extent. The individual R factors evaluated for the $h0l$ and $hk0$ reflections were found to be 0.163 and 0.198 respectively. The slightly larger value in the latter case obviously arises due to the larger proportion of weak intensities in this zone for which no threshold values have been assigned.

The ultimate coordinates that resulted from our analyses are expressed in fractions of cell edges in Table 4, and the significant interatomic separations and bond angles summarized in Table 5. The Cu—O bond lengths in an octahedral copper and the Cl—O bond in a tetrahedral perchlorate group are correct to 0.018 Å while the estimated errors in the O—Cu—O and O—Cl—O bond angles are of the order of $\pm\, 2\,°$.

Table 4. $Cu(ClO_4)_2 \cdot 6\, H_2O$. Coordinates of the atoms
in an asymmetric unit expressed in fractions of cells edges

Atom	x	y	z
Cu (I)	$^1/_2$	0	0
(II)	0	$^1/_3$	0
Cl (I)	$^1/_4$	0	0.337
(II)	$^3/_4$	0.167	0.163
(III)	$^1/_4$	0.333	0.337
O_2	0.540	0	0.337
(I)	0.16	0.004	0.436
(II)	0.16	0.051	0.283
(III)	0.16	—0.055	0.296
O_2	0.04	0.167	0.163
(I)	0.66	0.171	0.064
(II)	0.66	0.218	0.217
(III)	0.66	0.112	0.204
O_3	0.54	0.333	0.337
(I)	0.16	0.337	0.436
(II)	0.16	0.384	0.283
(III)	0.16	0.278	0.296
$O_1(H_2O)$	$^1/_4$	—0.063	0.067
$O_2(H_2O)$	$^3/_4$	0.004	0.133
$O_3(H_2O)$	$^1/_4$	0.063	0.054
$O_4(H_2O)$	$^3/_4$	0.104	0.433
$O_5(H_2O)$	$^1/_4$	0.163	0.367
$O_6(H_2O)$	$^3/_4$	0.230	0.446
$O_7(H_2O)$	$^1/_4$	0.270	0.067
$O_8(H_2O)$	$^3/_4$	0.329	0.133
$O_9(H_2O)$	$^1/_4$	0.396	0.054

Table 5. *Principal interatomic distances and bond angles in* $Cu(ClO_4)_2 \cdot 6 H_2O$ *

Cu—2 O_1 (H_2O)	2.16₃ Å	$O_1(H_2O)$—Cu—$O_2(H_2O)$	86°53′
Cu—2 O_2 (H_2O)	2.28₁	$O_1(H_2O)$—Cu—$O_3(H_2O)$	86 52
Cu—2 O_3 (H_2O)	2.08₉	$O_2(H_2O)$—Cu—$O_3(H_2O)$	94 12
Mean	2.17₈ Å	Mean	89°19′
		O_1—Cl_1—O_1(I)	108°14′
Cl_1—O_1	1.47	O_1—Cl^1—O_1(II)	107 19
Cl_1—O_1(I)	1.49	O_1—Cl_1—O_1(III)	108 17
Cl_1—O_1(II)	1.48	O_1(I)—Cl_1—O_1(II)	109 55
Cl_1—O_1(III)	1.48	O_1(I)—Cl_1—O_1(III)	109 13
		O_1(II)—Cl_1—O_1(III)	112 52
Mean	1.48 Å	Mean	109° 8′
O_1—O_1(I)	2.41		
(II)	2.41		
(III)	2.40		
O_1(I)—O_1(II)	2.42		
(III)	2.41		
O_1(II)—O_1(III)	2.46		
Mean	2.42 Å		

* The corresponding figures for the other Cu-(H_2O)₆ and ClO_4 groups of the same asymmetric unit are similar as they are related by pseudo-symmetry.

Discussion

1. The perchlorate ion

The structure of this complex ion $(ClO_4)^-$ which has resulted from our x-ray studies on perchlorates shows that it is close-packed and tetrahedral in character. It retains its shape essentially unchanged in different environments as expected since the force acting upon it due to the surrounding cations is generally weaker than those acting within the complex. The great stability of this ion, far exceeding even that of the pyramidal ClO_3^- ion, has been attributed to its tetrahedral symmetry and to the fact that the chlorine atom has all its valence electrons shared. It might be pointed out here that the significant decrease in the Cl—O bond with increasing oxidation number of chlorine (as observed in different 'species') has been cited as a general example of the contraction in size of the complex ion with progressive substitution of electronegative atoms around the central atom[9].

The mean Cl—O and O—O dimensions of one ClO_4 group in this structure are 1.48 and 2.42 Å respectively with the mean tetrahedral

[9] R. B. GILLESPIE, R. A. SPARKS and K. N. TRUEBLOOD, The crystal structure of ammonium chlorite at —35°C. Acta Crystallogr. 12 (1959) 867—872.

Table 6. *Cl—O distances in some perchlorates*

Compound	Average Cl—O distance (Å)	Reference
LiClO$_4$	1.44±0.01	[10]
LiClO$_4$ · 3 H$_2$O	1.46±0.02	[10]
LiClO$_4$ · 3 H$_2$O and Mg(ClO$_4$)$_2$·6H$_2$O	1.50 (assumed)	[4,5]
H$_3$OClO$_4$*	1.42±0.01	[11,9a]
AgClO$_4$ · C$_6$H$_6$	1.48±0.03	[12]
KClO$_4$	1.43±0.01	[10]
	1.46±0.05	[2]
NH$_4$ClO$_4$	1.46±0.03	[1]
Ba(ClO$_4$)$_2$ · 3 H$_2$O	1.44±0.02	[3]
Cu(ClO$_4$)$_2$ · 6 H$_2$O	1.48±0.02	Present investigation

angle O—Cl—O of value 109° 8′. These are comparable with the corresponding figures found for other perchlorates analysed in this laboratory. The actual Cl—O dimensions in some perchlorates recently investigated by x-ray methods are summarized in Table 6.

2. Coordination of Cu^{++} ion

The cupric ion in this compound has six octahedral neighbours of water molecules and these are related centrosymmetrically in pairs about the central copper. The octahedral copper found in this structure is compatible with that observed in other cupric complexes. However, in the vast majority of compounds, the structure consists of four square coplanar bonds and two significantly weaker bonds normal to this plane giving the central ion octahedral surroundings. This is in conformity with the theoretical predictions of the

---

* *Note addet in proof:* Subsequent to corrections for rotational oscillations and anisotropic refinement, the revised value of Cl—O bond length in H$_3$OClO$_4$ is 1.452 ± 0.005 Å[9a].

[9a] M. R. TRUTER, D. W. J. CRUICKSHANK and G. A. JEFFREY, The crystal structure of nitronium perchlorate. Acta Crystallogr. **13** (1960) 855—862.

[10] R. PROSEN, Ph. D. thesis (1955), University of California at Los Angeles as cited in the previous reference.

[11] F. S. LEE and G. B. CARPENTER, The crystal structure of perchloric acid monohydrate. J. Physic. Chem. **63** (1959) 279—282.

[12] H. G. SMITH and R. E. RUNDLE, The silver perchlorate-benzene complex, C$_6$H$_6$ · AgClO$_4$—Crystal structure and charge transfer energy. J. Amer. Chem. Soc. **80** (1958) 5075—5080.

crystal-field theory [13],[14]. In the present structure, despite slightly greater probable errors in the x coordinates, the copper octahedron appears to be very much less distorted than in others.

3. The structure

The structure can be described as consisting of octahedral groupings of water oxygens around the cupric ions, and of tetrahedral perchlorate groups. The plan of the structure down the a axis (shown in Fig. 2) display an approximate three-fold symmetry as shown in the closely analogous structures of $Mg(ClO_4)_2 \cdot 6H_2O$ and $LiClO_4 \cdot 3H_2O$. The coordination groups along the infinite octahedral columns parallel to the a axis at the cell corners have their faces unshared in the structures of the cupric and magnesium compounds unlike those in the $LiClO_4 \cdot 3H_2O$ structure, where the alternate octahedral holes are also filled by Li^+ ions (see, WELLS [15]).

In other words, we have the sequence

$$-3H_2O - Cu - 3H_2O \qquad 3H_2O - Cu - 3H_2O$$

in the cupric (or magnesium) salt as against

$$-3H_2O - Li - 3H_2O - Li - 3H_2O - Li - 3H_2O$$

in the lithium salt giving the ratios $Cu : 6H_2O$ and $Li : 3H_2O$ in the empirical formulas in the two cases.

4. Hydrogen bonds

The linking of the perchlorate oxygens and the water molecules through $O-H \cdots O$ bridges is similar to that found in $Mg(ClO_4)_2 \cdot 6H_2O$ structure. In the present case, however, these bridges directed along puckered hexagonal rings of alternate water and perchlorate oxygens have both the 'boat' and 'chair' configurations whereas in the Mg compound, since WEST has assumed that the ClO_4 groups are all oriented in the same way with Cl atom above the plane of the three

[13] H. A. JAHN and E. TELLER, Stability of polyatomic molecules in degenerate electronic states. Proc. Roy. Soc. [London] A **161** (1937) 220—235.

[14] L. E. ORGEL and J. D. DUNITZ, Stereochemistry of cupric compounds. Nature [London] **179** (1957) 462—465.

[15] A. F. WELLS, Structural inorganic chemistry (Clarendon Press, Oxford, 1950), p. 441.

oxygens, the boat configuration is non-existent. The four probable structures of these hexagonal groups considered in our case have been overlooked in the x-ray analysis of the Mg compound. It appears that more quantitative measurements are required to uniquely establish the structure as proposed by WEST. The O—H $\cdots$ O bonds are apparently too long in our case ($\simeq$ 3 Å) for the formation of strong hydrogen linkages but their formation is presumed more on an analogy of these two structures than on the observed water and perchlorate-oxygen contacts.

Acknowledgement