Table 2. *Distances* (Å) *and angles* (°) *in the* PO_4 *tetrahedron and* $(MoW)O_6$ *octahedra, and* K—O *distances* (Å) *in the* KO_8 *polyhedron*

P(1)	O(2^{i})	O(2^{ii})	O(6)	O(6^{iii})
O(2^{i})	1·515 (6)	2·490 (8)	2·495 (9)	2·402 (9)
O(2^{ii})	110·5 (4)	1·515 (6)	2·402 (9)	2·495 (9)
O(6)	110·8 (3)	104·8 (3)	1·516 (6)	2·561 (9)
O(6^{iii})	104·8 (3)	110·8 (3)	115·3 (2)	1·516 (6)

P(2)	O(3^{iii})	O(4)	O(5^{iv})	O(7)
O(3^{iii})	1·507 (5)	2·540 (7)	2·530 (7)	2·407 (5)
O(4)	115·1 (3)	1·504 (5)	2·427 (7)	2·515 (7)
O(5^{iv})	115·4 (3)	108·4 (3)	1·488 (5)	2·499 (8)
O(7)	101·4 (3)	108·1 (3)	107·9 (4)	1·603 (3)

MoW	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1·880 (1)	2·801 (7)	3·958 (8)	2·793 (7)	2·776 (8)	2·805 (7)
O(2)	91·8 (3)	2·018 (6)	2·923 (8)	4·038 (8)	2·779 (8)	2·917 (8)
O(3)	176·5 (3)	91·0 (2)	2·079 (5)	2·794 (7)	2·853 (7)	2·898 (8)
O(4)	91·2 (3)	174·8 (2)	85·8 (2)	2·024 (5)	2·847 (7)	2·899 (8)
O(5)	90·3 (3)	86·6 (2)	87·9 (2)	89·1 (2)	2·032 (5)	4·051 (8)
O(6)	91·9 (3)	92·5 (3)	90·0 (2)	91·6 (2)	177·6 (2)	2·020 (6)

K—O(7^{v})	2·742 (9)	K—O(6^{vii})	3·037 (7)
K—O(2^{ii})	2·762 (6)	K—O(3^{i})	3·172 (6)
K—O(2^{vi})	2·762 (6)	K—O(3^{viii})	3·172 (6)
K—O(6)	3·037 (7)	K—O(1^{ii})	3·273 (8)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, 0{\cdot}5+y, z$; (iii) $x, 0{\cdot}5-y, -z$; (iv) $1-x, 0{\cdot}5+y, z$; (v) $-x, y-0{\cdot}5, z$; (vi) $-x, 0{\cdot}5-y, 0{\cdot}5-z$; (vii) $x, y, 0{\cdot}5-z$; (viii) $-x, -y, 0{\cdot}5+z$.

been expected from the structure of $KMo_2P_3O_{12}$ which is characterized by a double cell with two equivalent sites for molybdenum. The difficulty in obtaining $KW_2P_3O_{12}$, containing only tungsten, is probably due to the great tendency of tungsten to form oxides characterized by electron delocalization. This is indeed the case for the phosphate tungsten bronzes, which exhibit a large homogeneity range and may have greater stability than the molybdenum-type phosphates whose valence electrons are localized.

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Structure of Copper(II) Perchlorate Hexahydrate

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Abstract. $Cu(ClO_4)_2.6H_2O$, $M_r = 370{\cdot}54$, monoclinic, $P2_1/c$, $a = 5{\cdot}137\,(1)$, $b = 22{\cdot}991\,(3)$, $c = 13{\cdot}849\,(2)$ Å, $\beta = 90{\cdot}66\,(1)°$, $V = 1635{\cdot}4\,(4)$ Å^3, $Z = 6$, $D_x = 2{\cdot}26$ g cm^{-3}, $\lambda(\text{Mo }K\bar{\alpha}) = 0{\cdot}71069$ Å, $\mu = 26{\cdot}44$ cm^{-1}, $T = 296$ K, $F(000) = 1122$, 2911 unique reflections having $I > \sigma_I$, $R = 0{\cdot}030$. Each of the two inequivalent copper ions is coordinated by six water-molecule O atoms in a significantly distorted octahedral arrangement. Each of the three inequivalent but geometrically quite similar perchlorate groups is slightly distorted from regular tetrahedral geometry. The overall observed mean Cl—O distance is 1·429 (5) Å while the overall observed mean perchlorate O—O distance is 2·333 (8) Å. Both the Cu–O complexes and the perchlorate ions were tested and found to behave as rigid bodies. The perchlorate-ion parameters corrected for rigid-body motion are: overall mean Cl—O distance, 1·453 (6) Å; overall mean perchlorate O—O distance, 2·372 (8) Å. Location and refinement of the 18 H atoms gave a detailed account of hydrogen bonding, which occurs between oxygen octahedra, between oxygen octahedra and perchlorate groups, and, more weakly, within oxygen octahedra.

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Introduction. Through interest in the structure of barium perchlorate trihydrate (Gallucci & Gerkin, 1988), we have become interested in the structures of a number of other perchlorate hydrates. A previous report on the structure of copper perchlorate hexahydrate by Mani & Ramaseshan (1961) was based on data obtained using photographic methods. We undertook the present study in an attempt to provide a complete determination of the structure including the hydrogen coordinates.

Experimental. Crystals of greenish-blue copper(II) perchlorate hexahydrate were produced by slow evaporation at room temperature from a solution formed from G. F. Smith reagent copper(II) perchlorate hexahydrate and $\sim 1M$ perchloric acid. A crystal whose shape approximated a rectangular rod was cut perpendicular to its long axis to yield the experimental crystal with approximate dimensions $0{\cdot}42 \times 0{\cdot}27 \times 0{\cdot}31$ mm. Since the crystal appeared to become somewhat clearer and of darker blue color upon approach of a hand, it was judged to be potentially too hygroscopic to permit data collection. Accordingly, it was coated with a thin layer of epoxy cement. The crystal was analyzed at 296 K with a Rigaku AFC-5S diffractometer, utilizing graphite-monochromated Mo $K\bar{\alpha}$ radiation.

Unit-cell parameters were obtained from a least-squares fitting of the setting angles for 25 well centered reflections with $29 \leq 2\theta \leq 30°$. Intensity data were measured for 4304 reflections (exclusive of the standards) with $+h$, $+k$, $\pm l$ indices ($h_{\max} = 6$; $k_{\max} = 29$; $l_{\max} = 18$) and 2θ values in the range $4 \leq 2\theta \leq 55°$. The ω–2θ scan technique was employed with scan widths $(1{\cdot}20 + 0{\cdot}35\tan\theta)°$ in ω, and a background/scan time ratio of 0·5. Uncertainties were assigned to each reflection using the formula $\sigma_I^2 = \sigma_{cs}^2(I) + (0{\cdot}02I)^2$ where σ_{cs} is based on counting statistics and I is the integrated intensity. Six standard reflections ($13\bar{1}$, 120, 113, $2,12,\bar{4}$, 159, 374) were measured after every 150 reflections, and exhibited a maximum relative intensity variation of $\pm 3{\cdot}6\%$. Accordingly, no decay correction was applied. The data were corrected for Lorentz and polarization effects. A ψ-scan absorption correction was applied based on ψ-scan data obtained at the conclusion of intensity-data collection; the range of transmission factors was 0·949–1·000, with an average value 0·977.

The crystal was found to have the space group $P2_1/c$. Since there are six Cu atoms in the cell, four are expected to be at general positions and the remaining two at special positions. Accordingly, Cu(1) was placed at $x = 0$, $y = 0$, $z = 0$ and, consistent with the Patterson map, Cu(2) was placed in a general position at $x \simeq 0{\cdot}53$, $y \simeq 0{\cdot}33$, $z \simeq 0{\cdot}00$. The Cl atoms were then located using Fourier methods in conjunction with the Patterson map. The O atoms, and subsequently the H atoms, were then located using Fourier methods. Full-matrix least-squares refinement was performed using *TEXSAN* (Molecular Structure Corporation, 1987) to minimize the function $\sum \sigma_F^{-2}(|F_o| - |F_c|)^2$, in which $\sigma_F = \sigma_I/2F\mathrm{Lp}$. Neutral-atom scattering factors and anomalous-dispersion factors were taken from Cromer & Waber (1974) for Cu, Cl and O; scattering factors for H were taken from Stewart, Davidson & Simpson (1965).

Following refinement to the isotropic stage for all atoms except H using the data having $I > 3\sigma_I$, the ψ-scan absorption correction was applied, the data were averaged ($R_{\text{int}} = 0{\cdot}007$ for 412 pairs of reflections), and refinement proceeded to the anisotropic stage for all atoms except H and to the isotropic stage for H atoms. At this stage eight intense reflections for which $(|F_c| - |F_o|)/\sigma_F > 10$ (102, $13\bar{1}$, $03\bar{3}$, 060, $10\bar{4}$, $0\bar{6}\bar{6}$, 0,12,0 and 162) were rejected and all other unique reflections with $I > \sigma_I$ were included.

The results for the final refinement cycle were: 2911 independent observations having $I > \sigma_I$; 304 variables; $R = 0{\cdot}030$; $wR = 0{\cdot}034$; $S = 1{\cdot}78$; $(\Delta/\sigma)_{\max} = 0{\cdot}02$. Maximum and minimum peaks on the final electron density difference map had values $+0{\cdot}49$ and $-0{\cdot}53$ e Å^{-3}, respectively. The maximum peak was located at $x = 0{\cdot}01$, $y = 0{\cdot}31$, $z = 0{\cdot}35$, $\sim 0{\cdot}8$ Å from O(14); the minimum peak was located at $x = 0{\cdot}18$, $y = 0{\cdot}17$, $z = 0{\cdot}17$, $\sim 0{\cdot}5$ Å from Cl(1). (For the final refinement cycle for 2763 independent observations having $I > 3\sigma_I$: $R = 0{\cdot}027$; $wR = 0{\cdot}033$; $S = 1{\cdot}79$. Similarly, for the 3776 independent observations having $I > 0$: $R = 0{\cdot}052$; $wR = 0{\cdot}034$; $S = 1{\cdot}56$.)

The final atomic coordinates, equivalent isotropic and isotropic thermal parameters and their uncertainties are given in Table 1.* Selected interatomic distances and angles in the coordination polyhedra around copper, in the perchlorate ions and in the water molecules are given in Table 2 together with their uncertainties. Hydrogen bonds involving each of the nine water-molecule O atoms and its associated protons are delineated in Table 3, as discussed in detail below.

Rigid-body analysis of the Cu–O complexes and the perchlorate ions was performed using the program *THMA*11 (Trueblood, 1986). The average magnitude of the differences in the mean-square displacement amplitudes (MSDA) for the ten unique atom pairs of perchlorate ion (1) was found to be $20\,(18) \times 10^{-4}$ Å^2; for perchlorate ion (2), $11\,(19) \times 10^{-4}$ Å^2; and for perchlorate ion (3), $22\,(20) \times$

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* Lists of structure factors, anisotropic thermal parameters and material relating to the rigid-body analysis have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51808 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters and equivalent isotropic and isotropic thermal parameters, B_{eq}/B (Å^2), for copper*(II) *perchlorate hexahydrate at* 296 K

E.s.d.'s are given within parentheses.

	x	*y*	*z*	B_{eq}*/*B*
Cu(1)	0	0	0	1·64 (2)
Cu(2)	0·53325 (6)	0·33277 (2)	0·00040 (3)	1·70 (1)
Cl(1)	0·31225 (13)	0·16918 (3)	0·16317 (5)	1·88 (3)
Cl(2)	0·80370 (13)	0·16378 (3)	0·83605 (5)	1·88 (3)
Cl(3)	0·80963 (14)	0·00159 (3)	0·33611 (5)	2·00 (3)
O(1)	0·2460 (5)	0·0533 (1)	−0·0586 (2)	2·7 (1)
O(2)	−0·1868 (5)	0·0643 (1)	0·0622 (2)	2·4 (1)
O(3)	0·3003 (5)	−0·0075 (1)	0·1317 (2)	2·4 (1)
O(4)	0·7248 (5)	0·3970 (1)	0·0617 (2)	2·6 (1)
O(5)	0·7803 (5)	0·2791 (1)	0·0602 (2)	2·7 (1)
O(6)	0·2882 (5)	0·3862 (1)	−0·0608 (2)	2·9 (1)
O(7)	0·3388 (5)	0·2689 (1)	−0·0600 (2)	2·3 (1)
O(8)	0·2428 (5)	0·3267 (1)	0·1331 (2)	2·5 (1)
O(9)	0·8206 (5)	0·3418 (1)	−0·1324 (2)	2·6 (1)
O(10)	0·5903 (4)	0·1714 (1)	0·1554 (2)	3·4 (1)
O(11)	0·1950 (5)	0·1791 (1)	0·0701 (2)	3·6 (1)
O(12)	0·2272 (5)	0·2133 (1)	0·2286 (2)	3·4 (1)
O(13)	0·2319 (5)	0·1138 (1)	0·1978 (2)	3·4 (1)
O(14)	1·0800 (4)	0·1641 (1)	0·8494 (2)	3·6 (1)
O(15)	0·7155 (5)	0·2182 (1)	0·7992 (2)	3·8 (1)
O(16)	0·6807 (5)	0·1522 (1)	0·9264 (2)	3·5 (1)
O(17)	0·7357 (5)	0·1190 (1)	0·7690 (2)	3·7 (1)
O(18)	1·0866 (4)	0·0038 (1)	0·3418 (2)	3·7 (1)
O(19)	0·7259 (5)	−0·0530 (1)	0·2986 (2)	3·6 (1)
O(20)	0·7027 (6)	0·0097 (1)	0·4297 (2)	4·7 (2)
O(21)	0·7174 (5)	0·0471 (1)	0·2733 (2)	3·8 (1)
H(1)	0·369 (9)	0·041 (2)	−0·084 (3)	5·4 (13)
H(2)	0·216 (7)	0·084 (2)	−0·075 (3)	3·9 (11)
H(3)	−0·206 (8)	0·091 (2)	0·037 (3)	4·6 (13)
H(4)	−0·165 (11)	0·072 (3)	0·113 (4)	8·9 (19)
H(5)	0·265 (8)	−0·029 (2)	0·171 (3)	4·3 (11)
H(6)	0·335 (9)	0·021 (2)	0·154 (3)	5·3 (13)
H(7)	0·721 (9)	0·425 (2)	0·041 (3)	4·8 (13)
H(8)	0·696 (8)	0·401 (2)	0·113 (3)	5·0 (13)
H(9)	0·906 (8)	0·291 (2)	0·079 (3)	3·6 (10)
H(10)	0·734 (11)	0·253 (3)	0·087 (4)	9·9 (21)
H(11)	0·160 (8)	0·373 (2)	−0·083 (3)	4·3 (11)
H(12)	0·304 (8)	0·413 (2)	−0·070 (3)	3·6 (12)
H(13)	0·302 (8)	0·243 (2)	−0·031 (3)	4·5 (12)
H(14)	0·383 (9)	0·263 (2)	−0·108 (3)	5·8 (14)
H(15)	0·207 (10)	0·360 (3)	0·164 (4)	8·6 (17)
H(16)	0·274 (10)	0·311 (2)	0·168 (4)	5·8 (17)
H(17)	0·779 (8)	0·363 (2)	−0·179 (3)	4·5 (11)
H(18)	0·843 (8)	0·317 (2)	−0·158 (3)	3·0 (10)

* The form of the equivalent isotropic thermal parameter is:

$$B_{eq} = \tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

10^{-4} Å^2. Further, the average magnitude of the differences in the MSDA for the six unique atom pairs of the Cu(1)–O complex was found to be 43 (17) × 10^{-4} Å^2; and for the 21 unique atom pairs of the Cu(2)–O complex, 39 (19) × 10^{-4} Å^2. On the basis of these values, we concluded that Hirshfeld's rigid-bond test, as described by Dunitz, Schomaker & Trueblood (1988), is satisfied, and have applied corrections for the rigid-body motion in each of the two Cu–O complexes and each of the three perchlorate ions. The corrected bond lengths are given in Table 2; the corrected angles differed typically from the observed angles by less than their standard deviations and were therefore not tabulated.

Discussion. This structure consists of two inequivalent types of copper ions each coordinated by six water-molecule O atoms in significantly distorted octahedral arrangements and three inequivalent but geometrically quite similar tetrahedral perchlorate groups which just fail to be regular within the experimental uncertainty.

The distorted octahedral coordination of Cu^{II} by six water O atoms found in this salt is quite normal. The Cu(1) octahedron manifests three different pairs of Cu—O distances while the Cu(2) octahedron (which may by symmetry exhibit six different Cu—O distances) also exhibits three pairs of distances. The mean corrected values of these pairs are 1·953 (1), 1·970 (4) and 2·388 (2) Å. Thus, two of the three pairs of distances are almost equal while the third is substantially larger and the Cu^{II} ions in this crystal display the so-called (4 + 2) type of coordination that has often been observed and which is consistent with the Jahn–Teller effect. For comparison with the present results, some previously published examples are listed in Table 4. Taken as a group, these examples suggest that '(4 + 2)' is somewhat a misnomer and that '(2 + 2 + 2)' more aptly describes the distorted coordination octahedra about Cu^{II} in these salts.

The perchlorate-group bond distances also fall easily into the normal range. The overall observed average Cl—O bond length, 1·429 (5) Å, is very similar, for example, to the corresponding observed average bond length in $Ba(ClO_4)_2.3H_2O$, 1·433 (6) Å, as recently reported by Gallucci & Gerkin (1988). The mean corrected values of the Cl—O distances in the inequivalent perchlorate groups are 1·452 (5), 1·452 (4) and 1·454 (5) Å with an overall mean corrected value 1·453 (6) Å, which is in very good agreement with the value of 'about 1·46 Å' cited by Dunitz *et al.* (1988) for perchlorate-ion bonds corrected for rigid-body motion. Correspondingly, the mean corrected O—O distances are 2·372 (9), 2·371 (8) and 2·373 (5) Å with an overall mean corrected value 2·372 (8) Å.

Concerning the water-molecule geometries we note that the observed H—O—H angles (Table 2) ranged from 98–116° with an average value 108° and e.s.d. of ~5°. These values compare favorably with the values for water-molecule H—O—H angles determined by neutron diffraction and tabulated by Chiari & Ferraris (1982): for class D inorganic hydrates, the range is 103–113° with an average value 109·5°; for all classes of inorganic hydrates, the range is 101–114° with an average value 107·2°.

The presence of two inequivalent and distorted octahedra of water O atoms whose H atoms can interact with potential hydrogen-bond-acceptor O atoms in these two distorted octahedra and in the three inequivalent perchlorate groups leads to a great diversity of hydrogen-bonding interactions. Our analysis of these interactions and their geometries is based partially upon treatments of hydrogen bonding by Jeffrey (1987) and Chiari & Ferraris (1982).

Table 2. *Bond lengths* (Å) *and angles* (°) *for copper*(II) *perchlorate hexahydrate*

E.s.d.'s in parentheses.

Coordination polyhedron (1); rigid body (1)

	Observed	Rigid-body corrected		Observed	Rigid-body corrected		Observed	Rigid-body corrected
Cu(1)—O(1)	1·945 (2)	1·952	O(1)—O(1$^{\text{i}}$)	3·890 (5)	3·905	O(1)—O(2)	2·810 (4)	2·819
Cu(1)—O(2)	1·967 (2)	1·973	O(2)—O(2$^{\text{i}}$)	3·934 (5)	3·946	O(1)—O(3)	2·993 (4)	3·001
Cu(1)—O(3)	2·381 (2)	2·387	O(3)—O(3$^{\text{i}}$)	4·761 (5)	4·775	O(2)—O(3)	3·140 (4)	3·145

O(1)—Cu(1)—O(1$^{\text{i}}$)	180	O(1)—Cu(1)—O(2)	91·8 (1)
O(2)—Cu(1)—O(2$^{\text{i}}$)	180	O(1)—Cu(1)—O(3)	87·0 (1)
O(3)—Cu(1)—O(3$^{\text{i}}$)	180	O(2)—Cu(1)—O(3)	92·0 (1)

Coordination polyhedron (2); rigid body (2)

	Observed	Rigid-body corrected		Observed	Rigid-body corrected		Observed	Rigid-body corrected
Cu(2)—O(4)	1·961 (2)	1·968	O(4)—O(5)	2·725 (4)	2·735	O(5)—O(9)	3·040 (4)	3·049
Cu(2)—O(5)	1·948 (2)	1·956	O(4)—O(6)	2·807 (4)	2·818	O(6)—O(7)	2·709 (4)	2·719
Cu(2)—O(6)	1·946 (3)	1·954	O(4)—O(7)	3·920 (3)	3·933	O(6)—O(8)	3·025 (4)	3·034
Cu(2)—O(7)	1·959 (2)	1·965	O(4)—O(8)	3·127 (4)	3·133	O(6)—O(9)	3·093 (4)	3·105
Cu(2)—O(8)	2·385 (3)	2·392	O(4)—O(9)	3·018 (4)	3·030	O(7)—O(8)	3·032 (4)	3·045
Cu(2)—O(9)	2·380 (2)	2·387	O(5)—O(6)	3·894 (4)	3·909	O(7)—O(9)	3·161 (4)	3·168
			O(5)—O(7)	2·808 (4)	2·818	O(8)—O(9)	4·765 (4)	4·778
			O(5)—O(8)	3·147 (4)	3·159			

O(4)—Cu(2)—O(5)	88·4 (1)	O(5)—Cu(2)—O(9)	88·7 (1)
O(4)—Cu(2)—O(6)	91·9 (1)	O(6)—Cu(2)—O(7)	87·9 (1)
O(4)—Cu(2)—O(7)	179·4 (1)	O(6)—Cu(2)—O(8)	88·0 (1)
O(4)—Cu(2)—O(8)	91·5 (1)	O(6)—Cu(2)—O(9)	90·7 (1)
O(4)—Cu(2)—O(9)	87·5 (1)	O(7)—Cu(2)—O(8)	88·0 (1)
O(5)—Cu(2)—O(6)	179·3 (2)	O(7)—Cu(2)—O(9)	93·0 (1)
O(5)—Cu(2)—O(7)	91·9 (1)	O(8)—Cu(2)—O(9)	178·4 (1)
O(5)—Cu(2)—O(8)	92·6 (1)		

Water molecules

O(1)—H(1)	0·78 (5)	O(1)—H(2)	0·75 (4)	H(1)—O(1)—H(2)	112 (4)
O(2)—H(3)	0·72 (5)	O(2)—H(4)	0·73 (6)	H(3)—O(2)—H(4)	105 (5)
O(3)—H(5)	0·77 (4)	O(3)—H(6)	0·74 (5)	H(5)—O(3)—H(6)	109 (5)
O(4)—H(7)	0·70 (5)	O(4)—H(8)	0·73 (4)	H(7)—O(4)—H(8)	107 (5)
O(5)—H(9)	0·74 (4)	O(5)—H(10)	0·75 (7)	H(9)—O(5)—H(10)	113 (5)
O(6)—H(11)	0·78 (4)	O(6)—H(12)	0·62 (4)	H(11)—O(6)—H(12)	114 (5)
O(7)—H(13)	0·74 (4)	O(7)—H(14)	0·71 (5)	H(13)—O(7)—H(14)	116 (5)
O(8)—H(15)	0·90 (6)	O(8)—H(16)	0·62 (5)	H(15)—O(8)—H(16)	100 (6)
O(9)—H(17)	0·84 (5)	O(9)—H(18)	0·68 (4)	H(17)—O(9)—H(18)	98 (4)

Perchlorate ion (1); rigid body (3)

	Observed	Rigid-body corrected		Observed	Rigid-body corrected		Observed	Rigid-body corrected
Cl(1)—O(10)	1·434 (2)	1·456	O(10)—O(11)	2·345 (3)	2·384	O(11)—O(12)	2·336 (3)	2·372
Cl(1)—O(11)	1·435 (2)	1·459	O(10)—O(12)	2·340 (3)	2·376	O(11)—O(13)	2·326 (3)	2·362
Cl(1)—O(12)	1·432 (2)	1·454	O(10)—O(13)	2·348 (3)	2·379	O(12)—O(13)	2·326 (3)	2·360
Cl(1)—O(13)	1·422 (2)	1·442						

	Observed	Rigid-body corrected		Observed	Rigid-body corrected
Cl(1)—O(mean)	1·431 (5)	1·452	O—O(mean)	2·337 (9)	2·372

O(10)—Cl(1)—O(11)	109·6 (2)	O(11)—Cl(1)—O(12)	109·1 (2)
O(10)—Cl(1)—O(12)	109·4 (1)	O(11)—Cl(1)—O(13)	109·0 (2)
O(10)—Cl(1)—O(13)	110·5 (1)	O(12)—Cl(1)—O(13)	109·1 (1)

Perchlorate ion (2); rigid body (4)

	Observed	Rigid-body corrected		Observed	Rigid-body corrected		Observed	Rigid-body corrected
Cl(2)—O(14)	1·429 (2)	1·456	O(14)—O(15)	2·345 (2)	2·384	O(15)—O(16)	2·332 (3)	2·363
Cl(2)—O(15)	1·422 (2)	1·443	O(14)—O(16)	2·338 (3)	2·380	O(15)—O(17)	2·322 (4)	2·361
Cl(2)—O(16)	1·433 (2)	1·454	O(14)—O(17)	2·324 (3)	2·368	O(16)—O(17)	2·330 (3)	2·368
Cl(2)—O(17)	1·428 (2)	1·454						

	Observed	Rigid-body corrected		Observed	Rigid-body corrected
Cl(2)—O(mean)	1·428 (4)	1·452	O—O(mean)	2·332 (8)	2·371

O(14)—Cl(2)—O(15)	110·7 (2)	O(15)—Cl(2)—O(16)	109·5 (2)
O(14)—Cl(2)—O(16)	109·6 (2)	O(15)—Cl(2)—O(17)	109·1 (2)
O(14)—Cl(2)—O(17)	108·9 (2)	O(16)—Cl(2)—O(17)	109·1 (2)

Perchlorate ion (3); rigid-body (5)

	Observed	Rigid-body corrected		Observed	Rigid-body corrected		Observed	Rigid-body corrected
Cl(3)—O(18)	1·425 (2)	1·452	O(18)—O(19)	2·339 (3)	2·378	O(19)—O(20)	2·322 (4)	2·365
Cl(3)—O(19)	1·423 (2)	1·445	O(18)—O(20)	2·334 (4)	2·383	O(19)—O(21)	2·328 (4)	2·364
Cl(3)—O(20)	1·426 (3)	1·455	O(18)—O(21)	2·333 (3)	2·376	O(20)—O(21)	2·332 (4)	2·376
Cl(3)—O(21)	1·437 (3)	1·462						

Table 2 (*cont.*)

	Observed	Rigid-body corrected		Observed	Rigid-body corrected
Cl(3)—O(mean)	1·428 (5)	1·454	O—O(mean)	2·332 (5)	2·373

O(18)—Cl(3)—O(19)	110·4 (2)	O(19)—Cl(3)—O(20)	109·2 (2)
O(18)—Cl(3)—O(20)	109·9 (2)	O(19)—Cl(3)—O(21)	109·0 (2)
O(18)—Cl(3)—O(21)	109·2 (2)	O(20)—Cl(3)—O(21)	109·1 (2)

	Observed	Rigid-body corrected		Observed	Rigid-body corrected
Overall mean Cl—O	1·429 (5)	1·453 (6)	Overall mean O—O	2·333 (8)	2·372 (8)

Code for symmetry-related atoms: (−) x, y, z; (i) $-x, -y, -z$.

Table 3. *Hydrogen-bond parameters for copper*(II) *perchlorate hexahydrate*

E.s.d.'s in parentheses. See text for details.

Water oxygen—acceptor oxygen	Distance (Å)	Proton—acceptor oxygen	Observed distance (Å)	Neutron-adjusted distance (Å)	Observed O—H—O angle (°)
O(1)—O(2^{i})	2·723 (4)	H(1)—O(2^{i})	2·62 (5)	2·63	89 (4)
O(1)—O(3^{vi})	2·761 (4)	H(1)—O(3^{vi})	1·99 (5)	1·81	173 (5)
O(1)—O(14^{v})	2·969 (4)	H(2)—O(14^{v})	2·23 (4)	2·04	167 (4)
O(1)—O(16^{iv})	3·194 (4)	H(1)—O(16^{iv})	3·01 (5)	3·00	96 (4)
		H(2)—O(16^{iv})	2·86 (4)	2·79	110 (4)
O(2)—O(16^{v})	2·838 (4)	H(3)—O(16^{v})	2·15 (5)	1·93	160 (5)
O(2)—O(21^{ii})	2·996 (4)	H(4)—O(21^{ii})	2·38 (6)	2·20	143 (6)
O(2)—O(10^{ii})	3·013 (4)	H(3)—O(10^{ii})	2·68 (5)	2·61	111 (4)
		H(4)—O(10^{ii})	2·67 (6)	2·60	111 (5)
O(2)—O(13)	3·058 (4)	H(4)—O(13)	2·53 (6)	2·38	131 (5)
O(3)—O(17^{vii})	2·915 (4)	H(5)—O(17^{vii})	2·22 (4)	2·06	151 (4)
O(3)—O(13)	2·959 (4)	H(6)—O(13)	2·28 (5)	2·10	151 (5)
O(3)—O(18^{ii})	3·132 (4)	H(5)—O(18^{ii})	2·65 (4)	2·55	123 (4)
		H(6)—O(18^{ii})	2·93 (5)	2·91	99 (4)
O(3)—O(21)	3·149 (4)	H(6)—O(21)	2·62 (5)	2·49	130 (4)
O(4)—O(20^{x})	2·820 (4)	H(7)—O(20^{x})	2·16 (5)	1·92	159 (5)
O(4)—O(17^{x})	2·894 (4)	H(8)—O(17^{x})	2·21 (4)	2·01	155 (5)
O(4)—O(18^{ix})	2·955 (4)	H(7)—O(18^{ix})	2·63 (5)	2·54	112 (4)
		H(8)—O(18^{ix})	2·69 (5)	2·65	104 (4)
O(4)—O(19^{viii})	3·245 (4)	H(8)—O(19^{viii})	2·72 (4)	2·57	131 (4)
O(5)—O(4)	2·725 (4)	H(9)—O(4)	2·62 (4)	2·63	90 (3)
O(5)—O(8^{iii})	2·794 (4)	H(9)—O(8^{iii})	2·05 (4)	1·83	177 (4)
O(5)—O(10)	2·975 (4)	H(10)—O(10)	2·23 (7)	2·00	175 (7)
O(5)—O(11^{iii})	3·135 (4)	H(9)—O(11^{iii})	2·97 (4)	2·95	96 (4)
		H(10)—O(11^{iii})	2·93 (6)	2·94	99 (5)
O(6)—O(7)	2·709 (4)	H(11)—O(7)	2·58 (4)	2·59	91 (3)
O(6)—O(9^{ii})	2·782 (4)	H(11)—O(9^{ii})	2·00 (4)	1·82	177 (4)
O(6)—O(18^{xi})	3·042 (4)	H(12)—O(18^{xi})	2·53 (4)	2·29	141 (5)
O(6)—O(20^{x})	3·207 (5)	H(12)—O(20^{x})	2·72 (4)	2·48	138 (5)
O(7)—O(11)	2·842 (4)	H(13)—O(11)	2·11 (4)	1·89	171 (5)
O(7)—O(15^{iv})	2·998 (4)	H(14)—O(15^{iv})	2·38 (5)	2·19	145 (5)
O(7)—O(12^{x})	3·004 (4)	H(14)—O(12^{x})	2·46 (5)	2·30	135 (5)
O(7)—O(14^{v})	3·016 (4)	H(13)—O(14^{v})	2·70 (4)	2·64	108 (4)
		H(14)—O(14^{v})	2·81 (5)	2·78	100 (4)
O(8)—O(12)	2·925 (4)	H(16)—O(12)	2·42 (5)	2·16	142 (6)
O(8)—O(19^{viii})	2·927 (4)	H(15)—O(19^{viii})	2·09 (6)	2·04	154 (5)
O(8)—O(14^{xi})	3·127 (4)	H(15)—O(14^{xi})	2·72 (6)	2·70	109 (4)
		H(16)—O(14^{xi})	2·78 (5)	2·63	119 (6)
O(9)—O(21^{x})	2·916 (4)	H(17)—O(21^{x})	2·19 (5)	2·09	145 (4)
O(9)—O(15^{iv})	3·042 (4)	H(18)—O(15^{iv})	2·43 (4)	2·20	150 (4)
O(9)—O(12^{xii})	3·124 (4)	H(18)—O(12^{xii})	2·63 (4)	2·46	131 (4)
O(9)—O(10^{x})	3·169 (4)	H(17)—O(10^{x})	2·60 (4)	2·53	126 (4)
		H(18)—O(10^{x})	2·89 (4)	2·82	108 (4)

Code for symmetry-related atoms: (−) x, y, z; (i) $-x, -y, -z$; (ii) $x-1, y, z$; (iii) $x+1, y, z$; (iv) $x, y, z-1$; (v) $x-1, y, z-1$; (vi) $1-x, -y, -z$; (vii) $1-x, -y, 1-z$; (viii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ix) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$; (x) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (xi) $x-1, \frac{1}{2}-y, -\frac{1}{2}+z$; (xii) $x+1, \frac{1}{2}-y, -\frac{1}{2}+z$.

Table 4. Cu^{II}—O *distances in some distorted oxygen octahedra in hexahydrated copper*(II) *salts*

Substance	Longest Cu—O distance (Å)	Intermediate Cu—O distance (Å)	Shortest Cu—O distance (Å)	Reference
$(NH_4)_2\{Cu(H_2O)_6\}$-$(CuSO_3)_4$	Cu (1) 2·329 (8) Cu (2) 2·339 (8)	2·005 (6) 2·006 (6)	1·980 (7) 1·965 (7)	Nyberg (1978)
$Cu(NH_4)_2(SeO_4)_2.6H_2O$	2·237 (5)	2·031 (5)	1·990 (5)	Monge & Gutierrez-Puebla (1981)
$Cu(H_2O)_6(SbF_4)_2$	2·410 (3)	1·990 (3)	1·963 (3)	Shchegoleva, Iskhakova, Ovanesyan, Shakhnazaryan & Trunov (1983)
$Cu(ClO_4)_2.6H_2O$	Cu(1) 2·381 (2) Cu(2) 2·382 (3)	1·967 (2) 1·960 (2)	1·945 (2) 1·947 (3)	This work

To account for the foreshortening of the water O—H bond distance as determined by X-ray diffraction, the position of each water proton was adjusted along the corresponding O—H bond direction (as determined by the X-ray data) until the O—H bond distance was 0·96 Å, the mean value for the O—H bond distance as determined by neutron diffraction in inorganic hydrated crystals of class D (Chiari & Ferraris, 1982; Ferraris & Franchini-Angela, 1972) to which this salt belongs. The resulting adjusted proton coordinates were then used to calculate distances and angles involving potential hydrogen-bond-acceptor O atoms. Since the adjusted O(water)—H—O(acceptor) angles typically differed from the observed angles (calculated directly from the X-ray-determined coordinates) by less than one standard deviation, only the observed angles are tabulated together with observed O(water)—O(acceptor) distances and observed and neutron-adjusted H—O(acceptor) distances in Table 3. In the following material, the neutron-adjusted H—O(acceptor) distance is taken to be the hydrogen-bond length.

As can be seen from Table 3, each of the 18 inequivalent H atoms is involved in at least one hydrogen bond if we go to an H—O(acceptor) distance of 2·29 Å: four of these hydrogen bonds are in the range 1·80–1·89 Å; two 1·90–1·99 Å; six 2·00–2·09 Å; three 2·10–2·19 Å; and three 2·20–2·29 Å. We take these results to be consistent with the 'maximum' H—O(acceptor) value from neutron studies of class D hydrates as tabulated by Chiari & Ferraris (1982), namely 2·176 Å. Of these 18 hydrogen bonds, the three shortest are to water-oxygen acceptors and have observed O—H—O angles of 173, 177, and 177°; the remainder are to perchlorate-oxygen acceptors and have observed O—H—O angles ranging from 141 to 175°. In addition we have tabulated nine weaker hydrogen bonds in the range 2·30–2·63 Å (of which three involve water-oxygen acceptors) and 16 bifurcated hydrogen bonds (see Jeffrey, 1987) to perchlorate-oxygen acceptors in the range 2·53–3·00 Å and which involve all protons except the two bonded to water oxygen O(6). We note that only four of the O(water)—O(acceptor) distances involved exceed the 'maximum' value cited by Jeffrey (1987) and Chiari & Ferraris (1982) for hydrogen-bond formation in inorganic hydrates (3·15 Å), the longest being 3·245 Å.

Concerning the three strong hydrogen bonds to water-oxygen acceptors we note that one is from O(1) [~1·94 Å Cu(1)—O distance] of one Cu(1) complex to O(3) [~2·38 Å Cu(1)—O distance] of another Cu(1) complex while, similarly, two are from O(5) and O(6) [~1·95 Å Cu(2)—O distance] of one Cu(2) complex to O(8) and O(9) [~2·38 Å Cu(2)—O distance], respectively, of two other Cu(2) complexes. For the three weaker hydrogen bonds involving water-oxygen acceptors, we note that they all occur within single complexes and involve only O atoms with the shorter Cu—O distances: O(1) and O(2^i) for the Cu(1) complex and O(5)—O(4) and O(6)—O(7) for the Cu(2) complex.

Considering the hydrogen bonding from the viewpoint of the perchlorate-oxygen acceptors we observe that each of these 12 inequivalent O atoms is involved in one or more of the strong hydrogen bonds (length 2·29 Å or less). If both the weaker hydrogen bonds involving perchlorate-oxygen acceptors and the bifurcated bonds (all of which involve perchlorate-oxygen acceptors) are included, each of the 12 inequivalent perchlorate O atoms is involved in two or more hydrogen bonds.

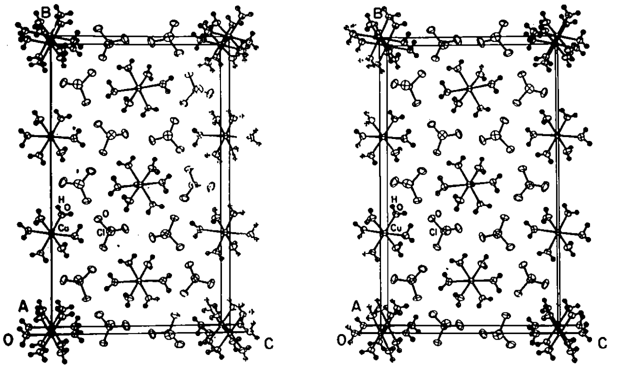

Fig. 1. Stereoview of a portion of the copper(II) perchlorate hexahydrate structure prepared using *ORTEP*II (Johnson, 1971). Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

We note finally that the 18 strongest hydrogen bonds alone form a three-dimensional network in this structure. Thus, inclusion of the weaker and bifurcated hydrogen bonds merely elaborates further the three-dimensional character of this network.

A view of the structure is presented in Fig. 1.

The structure for $Cu(ClO_4)_2.6H_2O$ presented by Mani & Ramaseshan (1961) on the basis of limited photographic data, although generally concordant with the present structure qualitatively, is superseded in all quantitative details by the present determination.

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