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Key indicators

Single-crystal X-ray study
T = 180 K
Mean $\sigma(\text{Cl}-\text{O}) = 0.007 \text{ \AA}$
H-atom completeness 77%
R factor = 0.045
wR factor = 0.111
Data-to-parameter ratio = 13.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Hydronium pentaquacopper(II) triperchlorate

The crystal structure of the double salt hydronium pentaquacopper(II) triperchlorate, $(\text{H}_3\text{O})[\text{Cu}(\text{H}_2\text{O})_5](\text{ClO}_4)_3$, has been determined at 180 K. In space group $P3_221$, the structure contains a square-pyramidal $[\text{Cu}(\text{H}_2\text{O})_5]^{2+}$ moiety with its basal plane capped by one edge of a perchlorate anion, so that Cu^{II} exhibits [5+2] coordination. Both cations and one of the anions lie on twofold rotation axes.

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Comment

The perchlorate salt of Cu^{II} is most commonly isolated as the green-blue hexahydrate $[\text{Cu}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, containing a Jahn–Teller-distorted octahedral hexaaquacopper(II) cation (Mani & Ramaseshan, 1961; Gallucci & Gerkin, 1989). We report here the crystal structure of a double salt, $(\text{H}_3\text{O})[\text{Cu}(\text{H}_2\text{O})_5](\text{ClO}_4)_3$, incorporating pentaquacopper(II) and a hydronium cation. In space group $P3_221$, the axial $\text{Cu}-\text{OH}_2$ vector of the square-pyramidal $[\text{Cu}(\text{H}_2\text{O})_5]^{2+}$ moiety is sited on a crystallographic twofold axis. The opposite face of the basal plane is capped by one edge of the perchlorate anion $[\text{O}8^{\text{i}}$ and $\text{O}8^{\text{ii}}$; symmetry codes: (i) $1 + x, y, z$; (ii) $1 + x - y, -y, \frac{1}{3} - z$], which is also sited on the twofold axis (Fig. 1). This gives rise to two additional $\text{Cu}-\text{O}$ contacts of $3.305(10) \text{ \AA}$, so that the coordination arrangement around Cu^{2+} may be described as [5+2].

[5+2] coordination geometry is rare in Cu^{II} salts. The structures of other reported tetra-, penta- and hexaaquacopper(II) complexes show predominantly distorted octahedral geometry about Cu^{2+} , with either six water ligands or a combination of water ligands and oxo donors from oxoanions (see, for example, Kennard *et al.*, 1985; Manojlovic-Muir *et al.*, 1999; Couldwell *et al.*, 1978). Most notably, the comparable sulfate $[\text{Cu}(\text{H}_2\text{O})_5](\text{SO}_4)$ contains Jahn–Teller-distorted octahedral $[\text{Cu}(\text{H}_2\text{O})_4(\text{O})_2]$ units, in which both axial sites are occupied by vertices of SO_4^{2-} anions that bridge between two octahedral moieties (Beevers & Lipson, 1934; Baur & Rolin, 1972; Bacon & Curry, 1962; Varghese & Maslen, 1985). The fifth water molecule in the formula unit is uncoordinated. It is

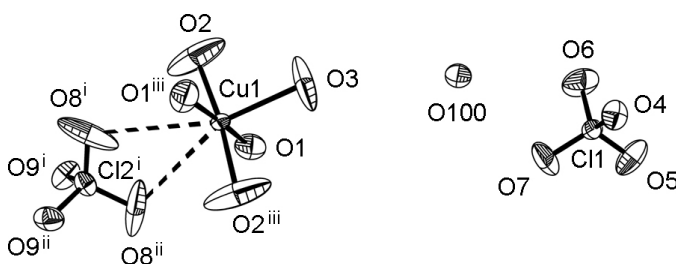


Figure 1

The molecular units in the title compound, showing displacement ellipsoids at the 50% probability level. H atoms are not shown. Symmetry codes (i), (ii) and (iii) are as given in Table 1.

notable in the title compound that the displacement parameters of O8, O2 and O3 suggest some degree of disorder (static or dynamic) towards a distorted octahedral coordination geometry about Cu²⁺. It is possible that the [5+2] geometry is an averaged representation of local distorted octahedral arrangements. Apparent anomalies in the octahedral coordination geometry of Cu²⁺ have been discussed recently by Persson *et al.* (2002).

Experimental

The title compound was isolated as a by-product of an attempted complexation of Cu^{II} by the polyol erythritol. A mixture of 0.2705 g (2.22 mmol) erythritol was dissolved in 8 ml methanol by warming and vigorous stirring. The solution was cooled to room temperature and 0.4114 g (1.11 mmol) Cu(ClO₄)₂·6H₂O was added. A 1 M solution of diethylamine in ethanol was diffused into this solution (vapour diffusion) and blue crystals of the title compound appeared after storage for several months at room temperature.

Crystal data

(H ₃ O)[Cu(H ₂ O) ₅](ClO ₄) ₃	Mo K α radiation
$M_r = 470.99$	Cell parameters from 2728 reflections
Trigonal, $P3_21$	$\theta = 2.3\text{--}26.0^\circ$
$a = 10.1659$ (7) Å	$\mu = 1.99$ mm ⁻¹
$c = 13.1601$ (9) Å	$T = 180$ (2) K
$V = 1177.83$ (14) Å ³	Block, blue
$Z = 3$	$0.30 \times 0.15 \times 0.10$ mm
$D_x = 1.992$ Mg m ⁻³	

Data collection

Bruker SMART 1000 CCD diffractometer	1610 independent reflections
Thin-slice ω scans	1348 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	$R_{\text{int}} = 0.050$
$T_{\text{min}} = 0.646$, $T_{\text{max}} = 0.826$	$\theta_{\text{max}} = 26.4^\circ$
7204 measured reflections	$h = -12 \rightarrow 12$
	$k = -11 \rightarrow 12$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 2.6785P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.111$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.58$ e Å ⁻³
1610 reflections	$\Delta\rho_{\text{min}} = -0.55$ e Å ⁻³
118 parameters	Absolute structure: Flack (1983),
Only coordinates of H atoms refined	671 Friedel pairs
	Flack parameter = 0.02 (3)

Table 1

Selected geometric parameters (Å, °).

Cu1—O2	1.969 (6)	Cu1—O3	2.320 (7)
Cu1—O2 ⁱ	1.969 (6)	Cu1—O8 ⁱⁱ	3.305 (10)
Cu1—O1 ⁱ	2.001 (5)	Cu1—O8 ⁱⁱⁱ	3.305 (10)
Cu1—O1	2.001 (5)		
O2—Cu1—O2 ⁱ	172.9 (8)	O2—Cu1—O8 ⁱⁱ	73.2 (4)
O2—Cu1—O1 ⁱ	89.2 (3)	O2 ⁱ —Cu1—O8 ⁱⁱ	100.0 (4)
O2 ⁱ —Cu1—O1 ⁱ	90.7 (3)	O1 ⁱ —Cu1—O8 ⁱⁱ	104.2 (2)
O1 ⁱ —Cu1—O1	177.3 (3)	O3—Cu1—O8 ⁱⁱ	159.15 (13)
O2—Cu1—O3	93.5 (4)	O8 ⁱⁱ —Cu1—O8 ⁱⁱⁱ	41.7 (3)
O1 ⁱ —Cu1—O3	91.34 (17)		

Symmetry codes: (i) $x - y, -y, \frac{1}{3} - z$; (ii) $1 + x, y, z$; (iii) $1 + x - y, -y, \frac{1}{3} - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1B \cdots O6 ⁱⁱ	0.89 (1)	2.40 (5)	3.184 (8)	148 (7)
O1—H1A \cdots O5 ^{iv}	0.89 (1)	2.34 (3)	3.188 (7)	161 (6)
O2—H2A \cdots O4 ⁱⁱ	0.88 (1)	2.44 (3)	3.299 (10)	165 (11)
O2—H2B \cdots O7 ^v	0.88 (1)	2.58 (7)	3.343 (11)	145 (10)
O3—H3A \cdots O5 ^{vi}	0.87 (1)	2.16 (1)	3.017 (7)	168 (2)

Symmetry codes: (ii) $1 + x, y, z$; (iv) $y, x, -z$; (v) $1 - x, -x + y, \frac{2}{3} - z$; (vi) $1 + x - y, 1 - y, \frac{1}{3} - z$.

H atoms associated with the water molecules of the [Cu(H₂O)₅]²⁺ moiety were located in difference Fourier maps and refined with O—H distances restrained to be 0.88 (1) Å and H \cdots H distances restrained to be 1.44 (1) Å, ensuring a chemically reasonable geometry. Their displacement parameters were constrained so that $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. H atoms associated with the hydronium cation (sited on a twofold axis) were not apparent from difference Fourier maps, and were omitted from the final structure model. The hydronium atom occupies a cavity between eight potential hydrogen-bond acceptors, so that the H atoms are almost certainly disordered.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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