

Structure of Tetraaquacopper(II) Chlorate at 296 and 223 K

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Abstract

[Cu(H₂O)₄](ClO₃)₂, $M_r = 302.51$, orthorhombic, *Pbca*, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $Z = 4$, $F(000) = 604$; $T = 296 \text{ K}$, $a = 12.924 (3)$, $b = 9.502 (2)$, $c = 7.233 (1) \text{ \AA}$, $V = 888.3 (3) \text{ \AA}^3$, $D_x = 2.26 \text{ g cm}^{-3}$, $\mu = 31.04 \text{ cm}^{-1}$, $R = 0.041$ for 1174 unique reflections with $I > \sigma(I)$; $T = 223 \text{ K}$, $a = 12.853 (2)$, $b = 9.492 (2)$, $c = 7.216 (2) \text{ \AA}$, $V = 880.4 (3) \text{ \AA}^3$, $D_x = 2.28 \text{ g cm}^{-3}$, $\mu = 31.28 \text{ cm}^{-1}$, $R = 0.033$ for 1279 unique reflections with $I > \sigma(I)$. The single type of copper ion is octahedrally coordinated by four water oxygens and two chlorate ion oxygens; the complex is characterized by three distinct pairs of Cu—O distances (which we have previously described as '2 + 2 + 2' coordination), one of which is substantially larger than the remaining two. The nominal 90° O—Cu—O angles of the complex differ from that value by at most $\pm 1.8^\circ$. The observed structure of the complex is typical for copper(II) and is consistent with the Jahn–Teller effect. The single type of chlorate ion shows the expected trigonal pyramidal geometry, with average Cl—O bond lengths 1.485 (13) and 1.490 (11) Å and average O—Cl—O bond angles 106.8 (13) and 106.8 (13)° for 296 and 223 K, respectively. Location and refinement of the four inequivalent H atoms of the two water molecules permitted detailed analysis of the hydrogen bonding which occurs almost solely between the water hydrogens and chlorate oxygens. Rigid-body analysis showed that while the chlorate ion did not conform to such behavior, the copper ion and the water oxygens (but not the chlorate oxygens) of the octahedral complex did; correction of the relevant bond lengths for the rigid-body effects has been applied. This study is apparently the first which describes the structure of a tetraaquacopper(II) complex.

Introduction

This structural study of tetraaquacopper(II) chlorate was undertaken, on the basis of incomplete information, as an investigation of hexaaquacopper(II) chlorate. The study was planned to test further an earlier

proposal (Gallucci & Gerkin, 1989) that copper(II) octahedral complexes with oxygen typically show three, not two, distinct pairs of Cu—O distances, and thus should be described as manifesting '2 + 2 + 2' (rather than '4 + 2') coordination geometry. Although the crystal phase under investigation was shown to be tetraaquacopper(II) chlorate, a further test of the earlier proposal was nonetheless afforded. As documented below, the initial data collection at room temperature showed large growth and decay of the standard intensities. Although this later proved amenable to correction, it appeared desirable at the time to attempt to reduce growth and decay effects by collecting a data set at lower temperature and this was also accomplished.

Experimental

Crystals of tetraaquacopper(II) chlorate were produced by evaporation at room temperature of a solution formed by metathetical reaction of aqueous analytic reagent grade copper(II) sulfate with a slight excess of saturated aqueous barium chlorate (Alfa Products) followed by filtration of the barium sulfate precipitate. Clear light-blue crystals with approximate principal dimensions 0.19 × 0.27 × 0.31 mm (296 K study) and 0.27 × 0.35 × 0.35 mm (223 K study) were selected and mounted with epoxy cement. Since under room conditions these crystals were hygroscopic, the sample for the room-temperature study was coated with Apiezon L grease. Since both crystals chosen for study were partially rounded, no faces were indexed. The samples were analyzed with a Rigaku AFC5S diffractometer utilizing graphite-monochromated Mo $K\alpha$ radiation and a Molecular Structure Corporation low-temperature apparatus. The stated low temperature was measured continuously during data collection in the cold gas flow just upstream of the crystal; the estimated uncertainty of the crystal temperature is $\pm 2 \text{ K}$.

At room temperature (296 K) unit-cell parameters were obtained from a least-squares fit of the setting angles for 25 centered reflections with $28 < 2\theta < 30^\circ$. Intensity data were measured for 1875 reflections (exclusive of standards) with $+h$, $+k$, $+l$ indices

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($h_{\max} = 14$; $k_{\max} = 19$; $l_{\max} = 10$) and 2θ values in the range $4 \leq 2\theta \leq 65^\circ$. The ω - 2θ scan technique was employed with scan widths $(1.26 + 0.35 \tan \theta)^\circ$ in ω and a background/scan time ratio of 0.5. A standard deviation was assigned to each reflection using the formula $\sigma_I^2 = \sigma_{cs}^2(I) + (0.03I)^2$ where σ_{cs} is based on counting statistics and I is the integrated intensity. Six standard reflections (131, 012, 222, 533, 282 and 424) were measured after every 150 reflections; five of the six showed a significant degree of growth (and subsequently, decay) as the intensity data were collected. Accordingly, growth (or decay) corrections were calculated and applied shell-by-shell (4 – 55° shell: 24.1% mean growth of intensity during collection; 55 – 60° shell: 2.7% mean decay of intensity during collection; 60 – 65° shell: 26.0% mean decay of intensity during collection). The data were corrected for Lorentz and polarization effects. A ψ -scan absorption correction was applied based on ψ -scan data obtained between collection of the 55 and 60° shells of the intensity data; the range of transmission factors was 0.718–1.000, with an average value 0.896.

At low temperature (223 K), unit-cell parameters were obtained from a symmetry-constrained least-squares fit of the setting angles for 25 centered reflections with $29 < 2\theta < 30^\circ$. Intensity data were measured for 1857 reflections (exclusive of standards) with $+h$, $+k$, $+l$ indices ($h_{\max} = 14$; $k_{\max} = 19$; $l_{\max} = 10$) and 2θ values in the range $4 \leq 2\theta \leq 65^\circ$. The ω - 2θ scan technique was employed with scan widths $(1.26 + 0.35 \tan \theta)^\circ$ in ω , and a background/scan time ratio of 0.5. A standard deviation was assigned to each reflection using the formula $\sigma_I^2 = \sigma_{cs}^2(I) + (0.03I)^2$ where σ_{cs} is based on counting statistics and I is the integrated intensity. The standard reflections, chosen to be the same as in the room-temperature data collection, were measured after every 150 reflections; they showed, on average, a maximum non-systematic relative intensity variation of $\pm 2.7\%$. 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 between collection of the 60 and 65° shells of intensity data; the range of transmission factors was 0.856–1.000, with an average value 0.933.

The observed systematic absences ($hk0$, $k = \text{odd}$; $h0l$, $h = \text{odd}$; $0kl$, $l = \text{odd}$) determined the allowed primitive orthorhombic space group uniquely as $Pcab$, a non-standard setting of $Pbca$ (No. 61). The subsequent analyses were carried out following axis transformation to the standard setting.

For the room-temperature structure solution, initial locations of Cu and Cl were obtained from a Patterson map. The O atoms and, subsequently, the H atoms were located from successive electron density difference maps. Full-matrix least-squares

Table 1. Final atomic coordinates and equivalent isotropic and isotropic displacement factors, B_{eq}/B (\AA^2), for tetraaquacopper(II) chlorate at 296 and 223 K

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

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	Temp.	x	y	z	B_{eq}/B
Cu	296	0	0	0	1.75 (2)
	223	0	0	0	1.04 (2)
Cl	296	0.33655 (5)	0.06601 (7)	0.15459 (10)	2.03 (3)
	223	0.33682 (4)	0.06695 (6)	0.15475 (7)	1.25 (2)
O(1)	296	0.11885 (17)	-0.05943 (25)	0.14359 (36)	2.25 (8)
	223	0.12035 (14)	-0.05846 (20)	0.14269 (27)	1.40 (6)
O(2)	296	-0.07698 (21)	-0.17303 (25)	0.06562 (40)	2.78 (10)
	223	-0.07705 (15)	-0.17235 (19)	0.06954 (30)	1.70 (7)
O(3)	296	0.43616 (16)	0.12073 (25)	0.23245 (32)	2.69 (9)
	223	0.43708 (13)	0.12198 (20)	0.23222 (26)	1.71 (6)
O(4)	296	0.28362 (17)	0.19137 (24)	0.07544 (41)	3.26 (12)
	223	0.28370 (14)	0.19274 (19)	0.07432 (32)	2.17 (7)
O(5)	296	0.36095 (25)	-0.02758 (27)	-0.00096 (34)	3.41 (13)
	223	0.36173 (19)	-0.02811 (22)	-0.00072 (27)	2.26 (8)
H(1)	296	0.1254 (41)	-0.0353 (53)	0.2561 (89)	5.5 (13)*
	223	0.1165 (27)	-0.0309 (36)	0.2426 (57)	2.1 (7)*
H(2)	296	0.1512 (32)	-0.1259 (52)	0.1304 (67)	4.3 (11)*
	223	0.1489 (31)	-0.1203 (53)	0.1271 (67)	4.6 (11)*
H(3)	296	-0.1402 (41)	-0.1893 (50)	0.0242 (62)	4.3 (10)*
	223	-0.1373 (39)	-0.1872 (53)	0.0323 (65)	4.9 (11)*
H(4)	296	-0.0429 (41)	-0.2344 (58)	0.0672 (89)	6.1 (14)*
	223	-0.0423 (31)	-0.2396 (46)	0.0824 (64)	4.0 (10)*

* Refined isotropically.

refinement was performed using the *TEXSAN* structure analysis package (Molecular Structure Corporation, 1989) to minimize the function $\sum \sigma_F^{-2} (|F_o| - |F_c|)^2$ in which $\sigma_F = \sigma_I/2FLp$. Neutral-atom scattering factors and anomalous-dispersion factors were taken from Cromer & Waber (1974) for Cu, Cl and O; the scattering factor for H was taken from Stewart, Davidson & Simpson (1965). Following refinement to the isotropic stage for all atoms except hydrogen using the data having $I > 3\sigma_I$, the ψ -scan absorption correction was applied. Then using all the (unique) reflections with $I > \sigma_I$, least-squares refinement [including three scale factors (one for each of the shells given above) and the secondary-extinction coefficient] proceeded to the anisotropic stage for all atoms except hydrogen and to the isotropic stage for the hydrogens. At this stage, five reflections for which $||F_c| - |F_o||/\sigma_F > 10$ (200, 020, 230, 600 and 620) were excluded and refinement continued.

Results for the final refinement cycle were: 1174 independent observations having $I > \sigma_I$; 80 variables; $R = 0.041$; $wR = 0.043$; $w = \sigma_F^{-2}$; $S = 1.59$; $(\Delta/\sigma)_{\max} < 0.01$.* The final refined value of the secondary-extinction coefficient was $2.00(7) \times 10^{-5}$. The maximum and minimum peaks on the final electron

* For the final refinement cycle for 1081 independent observations having $I > 3\sigma_I$; $R = 0.036$; $wR = 0.041$; $S = 1.60$; $(\Delta/\sigma)_{\max} < 0.06$. Similarly, for the final refinement cycle for 1432 independent observations having $I > 0$: $R = 0.056$; $wR = 0.045$; $S = 1.49$; $(\Delta/\sigma)_{\max} < 0.01$. These latter results are for comparison purposes only.

density difference map had values $+0.82$ and -1.38 e \AA^{-3} , respectively. The maximum peak was located at $x = 0.00$, $y = 0.10$, $z = 0.00$, approximately 0.9 \AA from Cu; the minimum peak was located at $x = 0.00$, $y = 0.02$, $z = 0.12$, also approximately 0.9 \AA from Cu. The final atomic coordinates and isotropic and equivalent isotropic displacement parameters with their uncertainties are given in Table 1.*

For the 223 K structure, initial atom locations for the non-H atoms were taken from the room-temperature structure. Otherwise, the procedures were very similar to those just described except that no reflections having $I > \sigma_I$ were excluded. Results for the final refinement cycle were: 1279 independent observations having $I > \sigma_I$; 78 variables; $R = 0.033$; $wR = 0.039$; $w = \sigma_F^{-2}$; $S = 1.57$; $(\Delta/\sigma)_{\max} < 0.03$.† The final refined value of the secondary-extinction coefficient was $1.41(4) \times 10^{-5}$. Maximum and minimum peaks on the final electron density difference map had values $+0.39$ and -0.72 e \AA^{-3} , respectively. The maximum peak was located at $x = 0.04$, $y = 0.07$, $z = -0.01$, approximately 0.9 \AA from Cu; the minimum peak was located at $x = 0.00$, $y = 0.01$, $z = 0.13$, also approximately 0.9 \AA from Cu. The final atomic coordinates and isotropic and equivalent isotropic displacement parameters with their uncertainties are given in Table 1.

Selected interatomic distances and angles in the coordination polyhedron about Cu, in the chlorate ion and in the water molecules are given in Table 2 together with their uncertainties. Hydrogen bonds involving the water molecule oxygens and their protons are delineated in Table 3, as discussed in detail below.

Rigid-body analysis of the copper–oxygen octahedral complex and the chlorate ions was performed using the program *THMA11* (Trueblood, 1986), based on the work of Schomaker & Trueblood (1968). Although the chlorate ion did not conform to a rigid-body model, the average magnitude of the differences in the mean-square displacement amplitudes along the interatomic vectors for the six unique atom pairs of the Cu—O(1)—O(2) portion of the copper–oxygen complex was found to be $16(21) \times 10^{-4} \text{ \AA}^2$ for the 296 K data and $14(11) \times 10^{-4} \text{ \AA}^2$

Table 2. *Interatomic distances (Å) and angles (°) for tetraaquacopper(II) chlorate at 296 and 223 K*

E.s.d.'s in parentheses.				
	Observed distance	Rigid-body corrected distance	Observed angle	
At 296 K				
Coordination polyhedron				
Cu—O(1)	1.938 (2)	1.944	O(1)—Cu—O(1) ^y 180	
Cu—O(2)	1.979 (2)	1.985	O(2)—Cu—O(2) ^y 180	
Cu—O(3) ^m	2.396 (2)		O(3) ^m —Cu—O(3) ^m 180	
O(1)—O(1) ^y	3.876 (4)	3.888	O(1)—Cu—O(2)	91.6 (1)
O(2)—O(2) ^y	3.958 (4)	3.970	O(1)—Cu—O(2) ^y	88.4 (1)
O(3) ^m —O(3) ^m	4.792 (4)		O(1)—Cu—O(3) ^m	91.2 (1)
O(1)—O(2)	2.809 (3)	2.816	O(1)—Cu—O(3) ^m	88.8 (1)
O(1)—O(2) ^y	2.732 (3)	2.739	O(2)—Cu—O(3) ^m	88.2 (1)
O(1)—O(3) ^m	3.113 (4)		O(2)—Cu—O(3) ^m	91.8 (1)
O(1)—O(3) ^m	3.051 (3)			
O(2)—O(3) ^m	3.060 (3)			
O(2)—O(3) ^m	3.155 (3)			
Water molecules				
O(1)—H(1)	0.85 (6)	H(1)—O(1)—H(2)	107 (5)	
O(1)—H(2)	0.76 (5)			
O(2)—H(3)	0.88 (5)	H(3)—O(2)—H(4)	115 (5)	
O(2)—H(4)	0.73 (5)			
Chlorate ion				
Cl—O(3)	1.498 (2)	O(3)—Cl—O(4)	105.18 (12)	
Cl—O(4)	1.488 (2)	O(3)—Cl—O(5)	108.28 (16)	
Cl—O(5)	1.468 (3)	O(4)—Cl—O(5)	106.78 (17)	
O(3)—O(4)	2.372 (3)			
O(3)—O(5)	2.404 (4)			
O(4)—O(5)	2.373 (4)			
Mean Cl—O	1.485 (13)	Mean O—Cl—O	106.8 (13)	
At 223 K				
Coordination polyhedron				
Cu—O(1)	1.939 (2)	1.943	O(1)—Cu—O(1) ^y 180	
Cu—O(2)	1.977 (2)	1.981	O(2)—Cu—O(2) ^y 180	
Cu—O(3) ^m	2.388 (2)		O(3) ^m —Cu—O(3) ^m 180	
O(1)—O(1) ^y	3.878 (4)	3.886	O(1)—Cu—O(2)	91.61 (8)
O(2)—O(2) ^y	3.954 (4)	3.962	O(1)—Cu—O(2) ^y	88.39 (8)
O(3) ^m —O(3) ^m	4.776 (4)		O(1)—Cu—O(3) ^m	91.10 (8)
O(1)—O(2)	2.808 (3)	2.812	O(1)—Cu—O(3) ^m	88.90 (8)
O(1)—O(2) ^y	2.730 (3)	2.738	O(2)—Cu—O(3) ^m	88.46 (7)
O(1)—O(3) ^m	3.105 (3)		O(2)—Cu—O(3) ^m	91.54 (7)
O(1)—O(3) ^m	3.047 (3)			
O(2)—O(3) ^m	3.059 (3)			
O(2)—O(3) ^m	3.141 (3)			
Water molecules				
O(1)—H(1)	0.77 (4)	H(1)—O(1)—H(2)	118 (5)	
O(1)—H(2)	0.70 (5)			
O(2)—H(3)	0.83 (5)	H(3)—O(2)—H(4)	115 (4)	
O(2)—H(4)	0.78 (4)			
Chlorate ion				
Cl—O(3)	1.501 (2)	O(3)—Cl—O(4)	105.13 (10)	
Cl—O(4)	1.493 (2)	O(3)—Cl—O(5)	108.26 (12)	
Cl—O(5)	1.475 (2)	O(4)—Cl—O(5)	107.02 (13)	
O(3)—O(4)	2.378 (2)			
O(3)—O(5)	2.412 (3)			
O(4)—O(5)	2.386 (3)			
Mean Cl—O	1.490 (11)	Mean O—Cl—O	106.8 (13)	

Symmetry code: none x, y, z ; (i) $-x, -y, -z$; (ii) $\frac{1}{2} - x, -y, -\frac{1}{2} + z$; (iii) $-\frac{1}{2} + x, y, \frac{1}{2} - z$.

for the 226 K data. On the basis of these values, we concluded that Hirshfeld's rigid-bond test (Hirshfeld, 1976) is satisfied for the Cu—O(1)—O(2) portion of the copper–oxygen complex and have applied corrections for the rigid-body motion. The corrected bond lengths are given in Table 2; the corrected angles differed from the observed angles by less than one standard deviation and were therefore not tabulated.

* Lists of structure factors, anisotropic displacement parameters and supplementary material relating to the rigid-body analysis have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53810 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† For the final refinement cycle for 1208 independent observations having $I > 3\sigma_I$; $R = 0.030$; $wR = 0.038$; $S = 1.57$; $(\Delta/\sigma)_{\max} < 0.01$. Similarly, for the final refinement cycle for 1468 independent observations having $I > 0$: $R = 0.042$; $wR = 0.040$; $S = 1.50$; $(\Delta/\sigma)_{\max} < 0.01$. These latter results are for comparison purposes only.

Table 3. *Hydrogen-bond parameters (Å, °) for tetraaquacopper(II) chlorate at 296 and 223 K*

E.s.d.'s are given in parentheses. The upper member of a pair of numerical values is for 296 K, the lower member is for 223 K.

Water oxygen acceptor oxygen	Distance	Proton acceptor oxygen	Observed distance	Neutron-adjusted distance	Observed O—H—O angle	Neutron-adjusted angle
O(1)—O(5) ⁱⁱ	2.713 (4)	H(1)—O(5) ⁱⁱ	1.86 (6)	1.75	177 (5)	177
	2.711 (3)		1.96 (4)	1.77	168 (4)	166
O(1)—O(4) ^v	2.727 (3)	H(2)—O(4) ^v	1.97 (5)	1.77	171 (4)	170
	2.710 (3)		2.01 (5)	1.75	174 (5)	173
O(1)—O(3) ⁱⁱⁱ	3.051 (3)	H(1)—O(3) ⁱⁱⁱ	2.86 (5)	2.85	95 (4)	92
	3.047 (3)		2.73 (4)	2.68	107 (3)	103
O(1)—O(3) ^v	3.186 (3)	H(2)—O(3) ^v	2.76 (5)	2.67	118 (4)	114
	3.189 (3)		2.79 (5)	2.67	119 (4)	114
O(2)—O(1) ⁱ	2.732 (3)	H(3)—O(1) ⁱ	2.67 (5)	2.68	84 (3)	83
	2.730 (3)		2.66 (5)	2.67	86 (4)	83
O(2)—O(1)	2.809 (3)	H(4)—O(1)	2.73 (5)	2.74	89 (4)	84
	2.808 (3)		2.74 (4)	2.76	87 (3)	83
O(2)—O(4) ⁱ	2.864 (4)	H(3)—O(4) ⁱ	1.99 (5)	1.91	170 (4)	170
	2.858 (3)		2.03 (5)	1.90	171 (5)	171
O(2)—O(3) ^v	2.934 (4)	H(4)—O(3) ^v	2.29 (6)	2.09	148 (6)	145
	2.906 (3)		2.18 (4)	2.02	155 (4)	152
O(2)—O(5) ⁱⁱ	2.993 (4)	H(3)—O(5) ⁱⁱ	2.70 (5)	2.68	101 (3)	99
	2.992 (3)		2.71 (5)	2.69	102 (4)	99
		H(4)—O(5) ⁱⁱ	2.62 (5)	2.54	114 (5)	109
			2.59 (4)	2.53	113 (3)	110

Symmetry codes: none x, y, z ; (i) $-x, -y, -z$; (ii) $\frac{1}{2}-x, -y, -\frac{1}{2}+z$; (iii) $-\frac{1}{2}+x, y, \frac{1}{2}-z$; (iv) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, -\frac{1}{2}+y, z$; (vi) $-\frac{1}{2}+x, -\frac{1}{2}-y, -z$.

Discussion

The single type of copper ion is at an inversion center in this structure. It is octahedrally coordinated by the two water oxygens, O(1) and O(2), and a chlorate ion oxygen, O(3), and their inversion mates. There are three distinct pairs of copper–oxygen distances in the octahedron with observed values 1.938 (2), 1.979 (2) and 2.396 (2) Å at 296 K, and 1.939 (3), 1.977 (2) and 2.388 (2) Å at 223 K, the largest being the copper–chlorate oxygen distance. Corrected for rigid-body effects the copper–water oxygen distances become 1.944 and 1.985 Å (296 K) and 1.943 and 1.981 Å (223 K), respectively. As required by the symmetry at copper, three of the octahedral O—Cu—O angles are 180° while the remaining angles, which would measure 90° in a regular octahedron, have values ranging from 88.2 to 91.8° at 296 K and from 88.4 to 91.6° at 223 K. Thus, the angles conform more nearly to regular octahedral geometry than do the distances.

The observed pattern of three distinct distances with one substantially different from the other two is consistent with previous results for octahedrally coordinated copper(II) summarized by Gallucci & Gerkin (1989) and designated there as '2 + 2 + 2' coordination. This pattern is also consistent with the Jahn–Teller effect. It may be noted that the three observed Cu—O distances reported here for 296 K are in very good agreement with the corresponding mean values observed for 296 K in hexaaquacopper(II) perchlorate by Gallucci & Gerkin (1989): 1.946, 1.964 and 2.382 Å.

The single type of trigonal pyramidal chlorate ion possesses three inequivalent oxygen atoms: O(3), O(4) and O(5). The observed Cl—O bond lengths

ranged from 1.468 (3) to 1.498 (2) Å with a mean value 1.485 (13) Å at 296 K, and from 1.475 (2) to 1.501 (2) Å with a mean value 1.490 (11) Å at 223 K, while the observed O—Cl—O bond angles ranged from 105.2 (1) to 108.3 (1)° with a mean value 106.8 (13)° at 296 K and from 105.1 (1) to 108.3 (1)° with a mean value 106.8 (13)° at 223 K. These values are in good agreement with the corresponding values reported by Gallucci & Gerkin (1990) for the three-fold symmetric chlorate ion in hexaaquanickel(II) chlorate at 296 K: Cl—O bond distance 1.487 (1) Å and O—Cl—O bond angle 106.45 (6)°. A stereoview of the unit cell of this structure is shown in Fig. 1.

The water molecules have observed H—O—H angles 107 (5) and 115 (5)° at 296 K, 118 (5) and 115 (4)° at 223 K, which are somewhat larger than

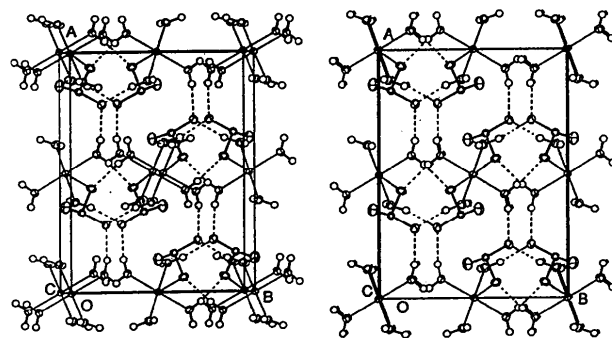


Fig. 1. Stereoview of a unit cell of the tetraaquacopper(II) chlorate structure drawn using ORTEPII (Johnson, 1976). Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. Copper(II) ions occur at the corners and face centers of the orthorhombic unit cell; dashed lines indicate strong hydrogen bonds lying within the unit cell.

those determined by neutron diffraction and tabulated by Ferraris & Franchini-Angela (1972): for class 4 (Chiari & Ferraris, 1982; Ferraris & Franchini-Angela, 1972) to which both waters are assigned, the neutron-based value is 107.6° (from the single example tabulated).

Although there are two types of water molecules, there is only a single type of chlorate ion and copper–oxygen complex in this salt. This leads to a rather simple hydrogen-bonding situation. Our analysis of the hydrogen bonds and their geometries is based partially upon treatments of hydrogen bonding by Jeffrey (1987) and Chiari & Ferraris (1982).

To account for the foreshortening of the water O—H bond distances 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 0.963 \AA , the mean value for the O—H bond distance as determined by neutron diffraction for water molecules of class 4 (Ferraris & Franchini-Angela, 1972). The resulting adjusted proton coordinates were then used to calculate adjusted distances and angles involving potential hydrogen-bonding acceptor O atoms. The observed angles (calculated directly from the X-ray-determined coordinates) and the adjusted angles are tabulated together with observed O(water)—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 shown in Table 3, H(1) and H(2) are involved in hydrogen bonds to chlorate oxygens O(5) and O(4), respectively, in the H—O(acceptor) distance range $1.75\text{--}1.77 \text{ \AA}$ while H(3) and H(4) are involved in hydrogen bonds to chlorate oxygens O(4) and O(3), respectively, in the H—O(acceptor) distance range $1.90\text{--}2.09 \text{ \AA}$. These distances lie near the H—O(acceptor) distance tabulated for class 4 hydrates by Ferraris & Franchini-Angela (1972) and indicate strong hydrogen bonding. H(1) and H(2) are both further involved in weak hydrogen bonding to chlorate oxygen O(3). H(3) and H(4) are both involved in weak hydrogen bonds in the H—O(acceptor) range $2.53\text{--}2.76 \text{ \AA}$, including interactions with the other water oxygen [O(1)] within the same coordination complex and a bifurcated bond (see Jeffrey, 1987) to chlorate oxygen O(5).

Taken together, the four strongest of these hydrogen bonds involve each of the four inequivalent H atoms and each of the three inequivalent chlorate O atoms (not all in the same chlorate ion) and form a three-dimensional network of hydrogen bonds. The three-dimensional character of this network is further developed when the weaker interactions are also considered. We note that the bifurcated bond is somewhat shorter ($2.53\text{--}2.69$ versus $2.75\text{--}2.82 \text{ \AA}$)

than that reported in hexaaquacobalt(II) bromate by Blackburn, Gallucci & Gerkin (1990). Only one of the O(water)—O(acceptor) distances tabulated [O(1)—O(3)^{*}, $\approx 3.19 \text{ \AA}$] exceeds the 'maximum' value cited by Jeffrey (1987) and Chiari & Ferraris (1982) for hydrogen-bond formation in inorganic hydrates (3.15 \AA).

For the H(3)—O(2)—H(4) water molecule, the hydrogen bonding is as shown schematically in Fig. 2. This arrangement of hydrogen bonds was found in hexaaquacobalt(II) bromate (Blackburn, Gallucci & Gerkin, 1990) and is seen also in the hydrates of small biological molecules. It has been described by Jeffrey & Maluszynska (1986) as three-center/bifurcated hydrogen bonding.

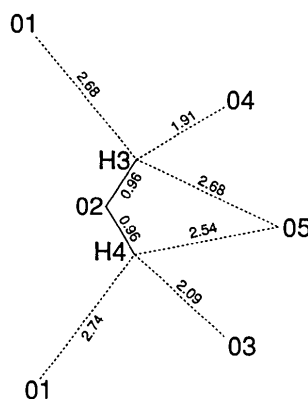


Fig. 2. Schematic drawing of the six hydrogen bonds (dashed lines) involving the H atoms of the water molecule H(3)—O(2)—H(4) in the tetraaquacopper(II) chlorate structure at 296 K. This type of hydrogen bonding has been designated as three-center/bifurcated hydrogen bonding (Jeffrey & Maluszynska, 1986). Bond lengths are given in \AA and are neutron-adjusted (see text).

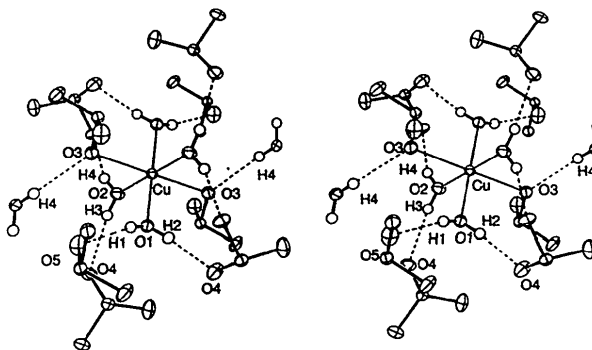


Fig. 3. Stereoview of the near environment of a central Cu ion in the tetraaquacopper(II) chlorate structure drawn using ORTEPII (Johnson, 1976). Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. Strong hydrogen bonds involving atoms in the first coordination shell of the central Cu ion are shown by the dashed lines. The three-dimensional character of the hydrogen-bonding network is readily apparent.

The stereoview presented in Fig. 3 shows a central Cu ion, its coordination complex and the strong hydrogen bonds involving the atoms of the coordination complex.

Considering the hydrogen bonding from the viewpoint of the chlorate oxygen acceptors we observe that O(3) is involved in one strong and two weak bonds; O(4) is involved in two strong bonds; and O(5) is involved in one strong and one bifurcated bond. Thus, each of the inequivalent chlorate oxygens is involved in at least one strong hydrogen bond.

The present study is apparently the first which describes the structure of a tetraaquacopper(II) complex. In this case two additional oxygens from chlorate ions complete a coordination octahedron which is very similar in its dimensions, as shown above, to that formed by six water oxygens in the hexaaquacopper(II) perchlorate structure.

As the analyses above document, the 296 K structure differs but slightly from the 223 K structure and in a manner consistent with the difference in temperature.

In the present investigation the phase commonly crystallizing from aqueous solutions of copper(II) chlorate at room temperature was the tetrahydrate, not the hexahydrate.

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Structure of the α -D-Glucose–Sodium Chloride–Water Complex (2/1/1)

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Abstract

$2\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{NaCl} \cdot \text{H}_2\text{O}$, $M_r = 436.8$, trigonal, $P3_1$ (No. 144), $a = 16.836$ (3), $c = 17.013$ (4) Å, $V = 4176$ (2) Å³, $Z = 9$, $D_m = 1.56$ (by flotation in $\text{CHCl}_3/\text{CCl}_4$), $D_x = 1.563$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 2.9$ cm⁻¹, $F(000) = 2070$, $T = 294$ K, $R = 0.049$ ($wR = 0.065$) for 3530 unique reflections with $I > 3\sigma(I)$. The asymmetric unit has six glucose molecules, three Na⁺ ions, three Cl⁻ and three water

molecules. The glucose molecules all have chair conformations with the C1–O1 groups axial and the remaining substituents equatorial; the mean C1–O1 bond length [1.388 (9) Å] is less than the mean of the other C–O bonds [1.425 (8) Å]. The Na⁺ ions have distorted octahedral coordination [$\text{Na} \cdots \text{O}$ 2.341 (5) to 2.528 (4) Å]; the Cl⁻ ions, water and glucose molecules are linked by an extensive network of hydrogen bonds which utilizes all O–H groups. The corresponding complexes of α -D-glucose monohydrate with sodium bromide and with sodium

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