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## Key indicators

Single-crystal X-ray study  
 $T = 170$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å  
H-atom completeness 86%  
Disorder in main residue  
 $R$  factor = 0.031  
 $wR$  factor = 0.079  
Data-to-parameter ratio = 12.1For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

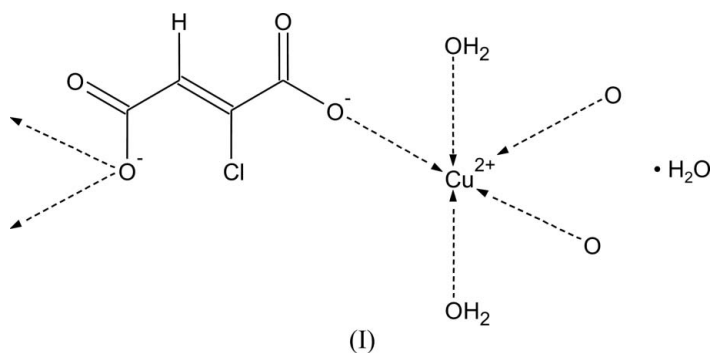
## Copper(II) chlorofumarate trihydrate

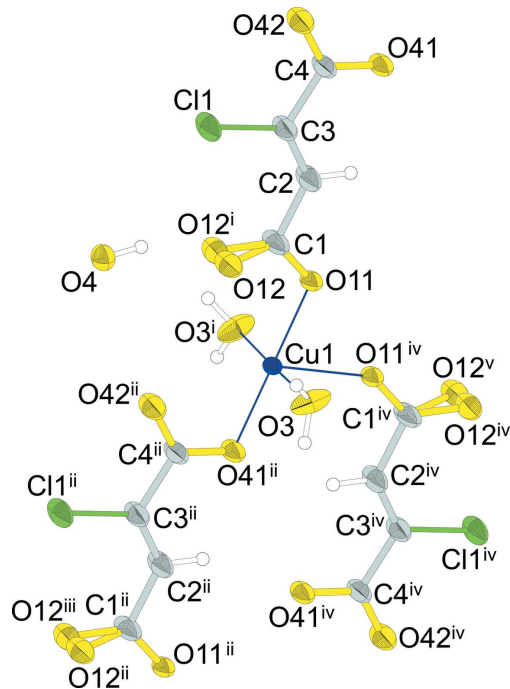
Blue crystals of the title compound, poly[[[diaquacopper(II)- $\mu_3$ -chlorofumarato] monohydrate],  $\{[\text{Cu}(\text{OOC}-\text{CH}=\text{CCl}-\text{COO})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\}_n$ , crystallized unexpectedly from an aqueous solution containing acetylenedicarboxylic acid and  $\text{CuCl}_2$ . Each copper cation is coordinated by five O atoms – three from three fumarate anions and two from two water molecules – in the form of a distorted square pyramid. All atoms of the asymmetric unit, except a carboxylate oxygen and the coordinated water molecule, lie on a mirror plane. These units are connected by the bifunctional anions to form ribbons along [001]. These ribbons are held together by hydrogen bonds, which also involve the third water molecule.

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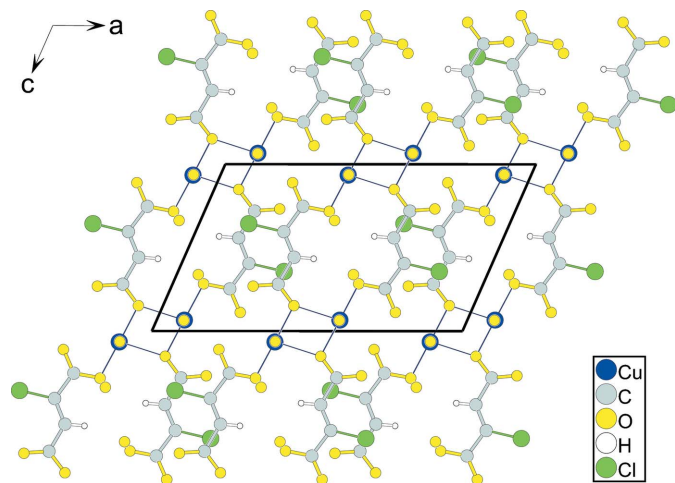
## Comment

During our ongoing studies of coordination polymers based on the dianion of acetylenedicarboxylic acid (*e.g.* Billetter *et al.*, 2004) we unexpectedly obtained blue crystals of the title compound, (I). The crystal structure of (I) is composed of copper ions (Fig. 1) coordinated by five O atoms from three chlorofumarate anions and two water molecules in the form of a square pyramid [ $\text{Cu}-\text{O} = 1.954(2)$ – $1.970(2)$  Å in the square base and  $2.297(3)$  Å for the apical position]. This coordination polyhedron is very similar to that found for  $[\text{Cu}\{\text{C}_2(\text{COO})_2\}(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$  (Billetter *et al.*, 2003). In (I), two such square pyramids share a common edge to form a dimeric unit with  $\text{Cu}\cdots\text{Cu}^{\text{viii}} = 3.268(11)$  Å [symmetry code: (viii)  $2 - x, y, 2 - z$ ]. This is significantly longer than the  $\text{Cu}\cdots\text{Cu}$  distance found in dimeric  $[\text{Cu}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]_2$  ( $\text{Cu}\cdots\text{Cu} = 2.64$  Å; Van Niekerk & Schoening, 1953). The dimeric units are connected by the bifunctional chlorofumarate anions to form a one-dimensional ribbon parallel to [001] (Fig. 2). These ribbons are held together by hydrogen bonds, which also involve the third water molecule.





**Figure 1**  
A view of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H-atom radii are arbitrary. [Symmetry codes: (i)  $x, 1 - y, z$ ; (ii)  $x, y, 1 + z$ ; (iii)  $x, 1 - y, 1 + z$ ; (iv)  $2 - x, y, 2 - z$ ; (v)  $2 - x, 1 - y, 2 - z$ .] Both positions of disordered O12 are shown. The second H atom of water molecule O4 could not be placed in a chemically sensible position and is omitted from the figure.



**Figure 2**  
A view of the crystal structure of (I) in a projection along [010]. H atoms of water molecules have been omitted for clarity.

significantly enlarged displacement ellipsoids perpendicular to this plane. Attempts to place O12 on the mirror plane as well led to a very large parameter  $U_{22}$ . Therefore it was assumed that O12 is disordered and a split position was refined (Fig. 1).

It is surprising that (I) was obtained from a solution containing acetylenedicarboxylic acid and  $\text{CuCl}_2$ . A *trans*

addition of HCl to the triple bond of acetylenedicarboxylic acid must have occurred under the conditions of crystallization. We already observed this unusual reaction in another experiment (Billetter *et al.*, 2005).

### Experimental

Acetylenedicarboxylic acid (0.57 g, 5 mmol) and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.85 g, 5 mmol) were dissolved in deionized water (20 ml). The beaker was sealed with a perforated foil. After approximately one month blue crystals and a green precipitate were obtained. The blue crystals were isolated manually. Analysis calculated (%) for  $\text{C}_4\text{H}_7\text{ClCuO}_7$  (266.09): C 18.06, H 2.65; found: C 18.04, H 2.66. One crystal was selected for the single-crystal X-ray analysis. No yield was determined.

#### Crystal data

$[\text{Cu}(\text{C}_4\text{HClO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$   
 $M_r = 266.09$   
 Monoclinic,  $C2/m$   
 $a = 14.849$  (3) Å  
 $b = 7.1407$  (6) Å  
 $c = 8.7237$  (15) Å  
 $\beta = 113.751$  (13)°  
 $V = 846.7$  (2) Å<sup>3</sup>  
 $Z = 4$

$D_x = 2.087$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 6215 reflections  
 $\theta = 1.5\text{--}32.4^\circ$   
 $\mu = 2.90$  mm<sup>-1</sup>  
 $T = 170$  (2) K  
 Plate, blue  
 $0.2 \times 0.2 \times 0.05$  mm

#### Data collection

Stoe IPDS-II diffractometer  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: numerical  
 The absorption correction (*X-RED*; Stoe & Cie, 2001) was performed after optimizing the crystal shape using *X-SHAPE* (Stoe & Cie, 1999).  
 $T_{\min} = 0.531$ ,  $T_{\max} = 0.847$   
 7365 measured reflections

1109 independent reflections  
 1019 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.048$   
 $\theta_{\text{max}} = 28.0^\circ$   
 $h = -19 \rightarrow 19$   
 $k = -9 \rightarrow 8$   
 $l = -11 \rightarrow 11$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.079$   
 $S = 1.07$   
 1109 reflections  
 92 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 2.1723P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.74$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.66$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0054 (11)

**Table 1**

Selected geometric parameters (Å, °).

Cu1—O11	1.954 (2)	C1—O11	1.274 (5)
Cu1—O41 <sup>ii</sup>	1.962 (3)	C1—C2	1.498 (5)
Cu1—O3 <sup>i</sup>	1.970 (2)	C2—C3	1.322 (6)
Cu1—O3	1.970 (2)	C3—C4	1.511 (5)
Cu1—O11 <sup>v</sup>	2.297 (3)	C3—Cl1	1.726 (4)
Cl1—O12 <sup>i</sup>	1.257 (6)	C4—O42	1.239 (5)
Cl1—O12	1.257 (6)	C4—O41	1.273 (5)
O11—Cu1—O41 <sup>ii</sup>	179.76 (11)	O11—Cu1—O11 <sup>v</sup>	79.79 (10)
O11—Cu1—O3 <sup>i</sup>	89.41 (7)	O41 <sup>ii</sup> —Cu1—O11 <sup>v</sup>	100.44 (10)
O41 <sup>ii</sup> —Cu1—O3 <sup>i</sup>	90.60 (7)	O3 <sup>i</sup> —Cu1—O11 <sup>v</sup>	89.48 (8)
O3 <sup>i</sup> —Cu1—O3	178.54 (16)		

Symmetry codes: (i)  $x, 1 - y, z$ ; (ii)  $x, y, z + 1$ ; (v)  $2 - x, 1 - y, 2 - z$ .

**Table 2**  
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H31 $\cdots$ O4 <sup>vi</sup>	0.84 (1)	1.91 (2)	2.702 (3)	156 (5)
O3—H32 $\cdots$ O4 <sup>vii</sup>	0.85 (1)	1.98 (2)	2.792 (3)	161 (6)
O4—H41 $\cdots$ O12	0.84 (1)	1.91 (3)	2.696 (5)	154 (6)
O4—H41 $\cdots$ O12 <sup>i</sup>	0.84 (1)	1.91 (3)	2.696 (5)	154 (6)

Symmetry codes: (i)  $x, 1 - y, z$ ; (vi)  $\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$ ; (vii)  $\frac{3}{2} - x, \frac{3}{2} - y, 2 - z$ .

The methylene H atom was placed in an idealized position and constrained to ride on its parent atom, with a C—H distance of 0.93 Å and  $U_{\text{iso}}(\text{H})$  values of 0.043 Å<sup>2</sup>. Three H atoms of two water molecules were located in difference Fourier maps and refined, with O—H distances restrained to 0.85 (1) Å. The remaining H atom of water molecule O4 could not be placed in a chemically sensible position which is not close to a symmetry-related H atom. It was therefore omitted from the final refinement. Concerning the disorder of O12 we attempted to refine the crystal structure of (I) in subgroups of  $C2/m$ , *i.e.*  $C2$  and  $Cm$ ; neither refinement led to a significant improvement of the refined parameters and  $R$  values, but the number of variables increases drastically. In  $C2/m$  this atom is disordered equally on each side of the mirror plane

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

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