metal-organic compounds

[Cu{C$_2$(COO)$_2$}(H$_2$O)$_3$]·H$_2$O, the first copper complex of acetylenedicarboxylic acid

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In the title compound, *catena*-poly[[[triaquacopper(II)]-μ-acetylenedicarboxylato-$\kappa^2 O$:O''] hydrate], {[Cu(C$_4$O$_4$)-(H$_2$O)$_3$]·H$_2$O}$_n$, the Cu^{II} ion is coordinated by two monodentate carboxylate groups in *trans* positions and three water molecules, thus forming a fivefold coordination polyhedron that can be described as a distorted square pyramid. All atoms are located on general sites. The polyhedra are connected by bifunctional acetylenedicarboxylate ligands, to form almost linear chains parallel to [001]. Hydrogen bonds involving the non-coordinated water molecule connect these chains to form a three-dimensional framework.

Comment

During our studies of coordination polymers of the acetylenedicarboxylate dianion, C$_2$(COO)$_2$$^{2-}$ (Hohn *et al.*, 2002; Ruschewitz & Pantenburg, 2002), blue crystals of the title compound, (I), were obtained, and its crystal structure is presented here.

(I)
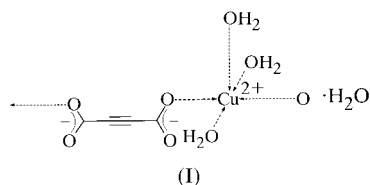
The structure of (I) comprises fivefold coordination polyhedra at the Cu^{II} ions, which are linked by bifunctional acetylenedicarboxylate ligands to form almost linear chains. The coordination polyhedron around the Cu^{II} ion, which can be described as a distorted square pyramid, is formed by two monodentate carboxylate groups in *trans* positions and three water molecules (Fig. 1). As the longest Cu—O distance (Cu1—O6) is about 0.3 Å longer than the second longest Cu—O distance (Cu1—O41^i; Table 1), the Cu coordination can alternatively be described as a slightly distorted square planar
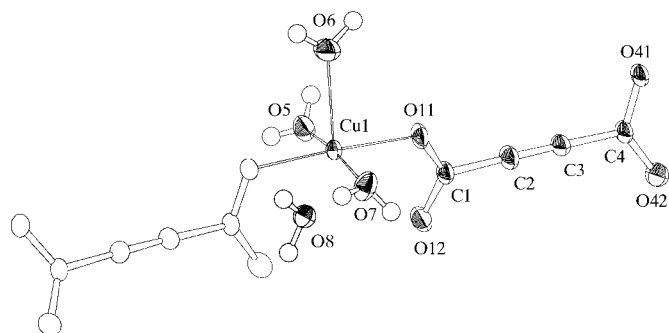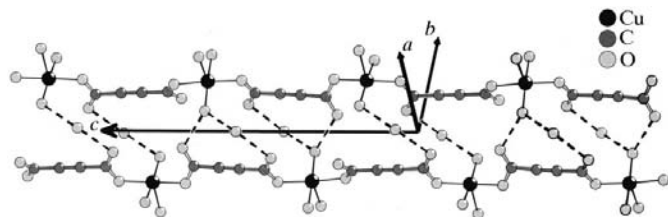

Figure 1
A view of (I), showing the atom-numbering scheme for the asymmetric unit. Displacement ellipsoids are shown at the 50% probability level and H-atom radii are arbitrary.

coordination, with an additional water ligand weakly bonded in an axial position. This coordination of the Cu^{II} ion is similar to that found in [Cu$_2$(CH$_3$COO)$_4$]·2H$_2$O (Cu—O = 1.96–1.99 Å and Cu—OH$_2$ = 2.20 Å; van Niekerk & Schoening, 1953). In contrast to the latter compound, however, where a short Cu—Cu distance (2.64 Å) extends the CuO$_5$ polyhedron to a distorted octahedron, no short Cu—Cu distances are found in (I) [the shortest is Cu1···Cu1^{iv} = 5.246 (12) Å] .

The C—O bond distances of the coordinating O atoms are significantly longer than the C—O distances of the non-coordinating O atoms (Table 1), which indicates that the latter are more characteristic of double bonds and which is consistent with these O atoms having slightly higher U_{eq} values. The C—C distances in the acetylenedicarboxylate dianion are as expected for single (C1—C2 and C3—C4) and triple (C2≡C3) bonds (Table 1). The dianion is almost linear (Table 1), but in contrast to [Cd{C$_2$(COO)$_2$}(H$_2$O)$_3$]·H$_2$O (Ruschewitz & Pantenburg, 2002), the carboxylate groups of the anion are not coplanar. The torsion angles are 26.6 (2) and 25.8 (3)°.

The CuO$_5$ polyhedra are linked by the bifunctional carboxylates to form almost linear chains running parallel to [001] (Fig. 2). A linear polymeric chain structure was also found in [Co{C$_2$(COO)$_2$}(H$_2$O)$_4$]·2H$_2$O (Pantenburg & Ruschewitz, 2002), which is another example of a coordination polymer of acetylenedicarboxylate that crystallizes in a chain structure, with Co^{II} coordinated octahedrally by two monodentate carboxylate groups in *trans* positions and four water

Figure 2
The crystal packing of (I), showing two polymeric chains connected by hydrogen bonds, which involve the non-coordinated H81/O8/H82 water molecule. Three of the four hydrogen bonds around O8 are shown, namely O5···O8, O7···O8 and O42···O8 (see Table 2). H atoms have been omitted for clarity.

molecules. However, in $[Cd\{C_2(COO)_2\}(H_2O)_3]\cdot H_2O$ (Ruschewitz & Pantenburg, 2002), a polymeric zigzag chain is formed.

In all of the compounds mentioned above, the chains are connected by hydrogen bonds that include additional water molecules. In (I), the shortest hydrogen bonds $[O\cdots O = 2.694\,(3)–2.742\,(3)\,\text{Å}]$ connect the polymeric chains to form layers parallel to (100). These layers are connected by slightly longer hydrogen bonds $[O\cdots O = 2.759\,(2)–2.771\,(2)\,\text{Å}]$ to form a three-dimensional network.

Experimental

$CuCl_2\cdot 2H_2O$ (0.85 g, 5 mmol) and acetylenedicarboxylic acid (0.57 g, 5 mmol) were dissolved in de-ionized water (20 ml). After slow evaporation at room temperature, blue crystals of (I) formed. These were filtered off and immediately sealed in a capillary, as the crystals decompose slowly in air forming a black shock-sensitive solid which is amorphous to X-rays. This residue is probably Cu_2C_2 (McCormick *et al.*, 2001). No decomposition of the single crystal was observed during the X-ray analysis.

Crystal data

$[Cu(C_4O_4)(H_2O)_3]\cdot H_2O$	$D_x = 1.936$ Mg m^{-3}
$M_r = 247.64$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 12 049
$a = 6.5261\,(8)$ Å	reflections
$b = 7.0683\,(9)$ Å	$\theta = 1.9–35.3°$
$c = 18.417\,(2)$ Å	$\mu = 2.59$ mm^{-1}
$\beta = 90.418\,(10)°$	$T = 293\,(2)$ K
$V = 849.54\,(18)$ Å^3	Polyhedron, blue
$Z = 4$	$0.2 \times 0.1 \times 0.1$ mm

Data collection

Stoe IPDS-II diffractometer	2468 independent reflections
Oscillation φ and ω scans	1766 reflections with $I > 2\sigma(I)$
Absorption correction: numerical	$R_{int} = 0.066$
(X-$SHAPE$ and X-RED; Stoe &	$\theta_{max} = 30.0°$
Cie, 2001)	$h = -9 \rightarrow 9$
$T_{min} = 0.296$, $T_{max} = 0.541$	$k = -9 \rightarrow 9$
23 355 measured reflections	$l = -25 \rightarrow 25$

Table 1
Selected geometric parameters (Å, °).

Cu1—O7	1.9396 (18)	C1—O11	1.273 (2)
Cu1—O11	1.9555 (15)	C1—C2	1.472 (3)
Cu1—O5	1.9588 (17)	C2—C3	1.191 (3)
Cu1—O41^i	1.9677 (14)	C3—C4	1.469 (3)
Cu1—O6	2.2961 (19)	C4—O42	1.233 (2)
C1—O12	1.231 (3)	C4—O41	1.270 (3)
O7—Cu1—O11	86.92 (8)	O41^i—Cu1—O6	92.24 (7)
O7—Cu1—O5	169.60 (10)	O12—C1—O11	125.76 (19)
O11—Cu1—O5	92.34 (7)	O12—C1—C2	118.93 (18)
O7—Cu1—O41^i	89.79 (8)	O11—C1—C2	115.31 (18)
O11—Cu1—O41^i	176.12 (7)	C3—C2—C1	178.6 (3)
O5—Cu1—O41^i	90.52 (8)	C2—C3—C4	178.0 (2)
O7—Cu1—O6	96.66 (9)	O42—C4—O41	125.28 (19)
O11—Cu1—O6	90.19 (7)	O42—C4—C3	119.17 (19)
O5—Cu1—O6	93.72 (9)	O41—C4—C3	115.55 (17)

Symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H51$\cdots$O11^{ii}	0.78 (4)	2.00 (4)	2.771 (2)	171 (4)
O5—H52$\cdots$O8^{iii}	0.73 (4)	2.02 (4)	2.742 (3)	170 (3)
O7—H71$\cdots$O12^{iv}	0.79 (4)	1.91 (4)	2.694 (3)	171 (4)
O7—H72$\cdots$O8	0.77 (4)	1.95 (4)	2.696 (3)	164 (4)
O8—H81$\cdots$O42^{iv}	0.85 (5)	1.87 (5)	2.722 (3)	174 (4)
O8—H83$\cdots$O41^v	0.63 (4)	2.13 (4)	2.759 (2)	177 (4)

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.069$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.93$	$\Delta\rho_{max} = 0.38$ e Å^{-3}
2468 reflections	$\Delta\rho_{min} = -0.42$ e Å^{-3}
151 parameters	Extinction correction: $SHELXL$97
All H-atom parameters refined	Extinction coefficient: 0.0072 (8)

H atoms were identified from difference Fourier maps and refined freely. Compound (I) crystallizes in a monoclinic unit cell with β close to 90°. A symmetry check using *PLATON* (Spek, 2003) suggests a smaller orthorhombic unit cell with a short c axis ($c' = \frac{1}{2}c$). However, inspection of the diffraction data and the refinement results (see Fig. 2) confirms that the larger monoclinic unit cell is correct.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL*97.

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Brandenburg, K. (2001). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.
Hohn, F., Pantenburg, I. & Ruschewitz, U. (2002). *Chem. Eur. J.* **8**, 4536–4541.
McCormick, B. J., Siemer, C., Afroz, F., Wasson, J. R., Eichhorn, D. M., Scott, B., Shah, S., Noffsinger, K. & Kahol, P. K. (2001). *Synth. Met.* **120**, 969–970.
Pantenburg, I. & Ruschewitz, U. (2002). *Z. Anorg. Allg. Chem.* **628**, 1697–1702.
Ruschewitz, U. & Pantenburg, I. (2002). *Acta Cryst.* C**58**, m483–m484.
Sheldrick, G. M. (1997). *SHELXL*97. Release 97-2. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Stoe & Cie (1999). *X-SHAPE*. Version 1.06. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (2001). *X-RED* (Version 1.22) and *X-AREA* (Version 1.15). Stoe & Cie, Darmstadt, Germany.
Van Niekerk, J. N. & Schoening, F. R. L. (1953). *Acta Cryst.* **6**, 227–232.