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# Poly[tetraaquadi-$\mu_6$-citrato-tetracopper(II)]: a redetermination

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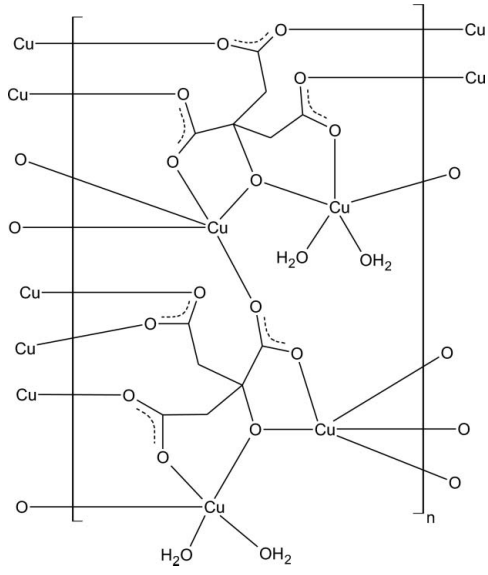
Key indicators: single-crystal X-ray study; $T$ = 120 K; mean $\sigma$(C–C) = 0.004 Å; disorder in main residue; $R$ factor = 0.027; $wR$ factor = 0.069; data-to-parameter ratio = 12.6.

The crystal structure of the title compound, $[Cu_4(C_6H_4O_7)_2(H_2O)_4]_n$, has been reported twice previously, by Mastropaolo, Powers, Potenza & Schugar [(1976). *Inorg. Chem.* **15**, 1444–1449] and Zhang, Yang & Ma [(2006). *Cryst. Growth Des.* **6**, 375–381]. These authors used strong reflections only for the unit-cell determination. The present structure redetermination is based on intensities measured at low temperature (120 K). The new data set (including the intensities of *hkl* with $h = 2n + 1$, omitted in earlier papers) indicates a doubled cell volume and the presence of four pentacoordinated copper cations, two tetra-ionized citrate anions and four water molecules in the asymmetric unit.

## Related literature

For related literature, see: Mastropaolo *et al.* (1976); Zhang *et al.* (2006). For synthesis, see: Henisch (1970).




## Experimental

### Crystal data

$[Cu_4(C_6H_4O_7)_2(H_2O)_4]$
$M_r$ = 702.45
Monoclinic, $P2_1/c$
$a$ = 13.749 (4) Å
$b$ = 9.713 (4) Å
$c$ = 14.471 (6) Å
$\beta$ = 91.56 (3)°
$V$ = 1931.8 (13) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 4.44 mm$^{-1}$
$T$ = 120 (2) K
0.6 × 0.34 × 0.25 mm

### Data collection

Oxford Diffraction KM-4 CCD area-detector diffractometer
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2003)
$T_{min}$ = 0.15, $T_{max}$ = 0.33
11784 measured reflections
3973 independent reflections
3341 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.038

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.069
$S$ = 1.01
3973 reflections
316 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.57 e Å$^{-3}$

**Table 1**
Selected torsion angles (°).

| | | | |
|---|---|---|---|
| O2—C1—C2—C3 | −47.6 (3) | O12—C11—C12—C13 | −54.2 (3) |
| C3—C4—C5—O4 | 44.4 (3) | C13—C14—C15—O14 | −2.3 (3) |
| C2—C3—C6—O6 | 67.7 (3) | C12—C13—C16—O16 | 81.9 (3) |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1$W$—H1$W$1···O7$^{i}$ | 0.84 | 2.33 | 3.130 (3) | 159 |
| O1$W$—H2$W$1···O2$W^{ii}$ | 0.84 | 1.98 | 2.820 (3) | 180 |
| O2$W$—H1$W$2···O17$^{iii}$ | 0.84 | 1.88 | 2.706 (3) | 168 |
| O11$W$—H2$WA$···O17$^{iv}$ | 0.84 | 2.40 | 3.195 (3) | 157 |
| O11$W$—H1$WA$···O12$W^{v}$ | 0.84 | 1.96 | 2.797 (3) | 175 |
| O12$W$—H1$WB$···O7 | 0.84 | 1.88 | 2.715 (3) | 170 |
| O12$W$—H2$WB$···O15$^{iii}$ | 0.84 | 2.40 | 3.152 (3) | 149 |

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) and *WinGX* (Farrugia, 1999); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990) and *XtalDraw* (Downs & Hall-Wallace, 2003); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2275).

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 doi:10.1107/S1600536807039086  

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# supplementary materials

*Acta Cryst.* (2007). E**63**, m2339-m2340 [ **doi:10.1107/S1600536807039086** ]

# Poly[tetraaquadi-$\mu_6$-citrato-tetracopper(II)]: a redetermination

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## Comment

The crystal structure of the title compound (I) has been previously reported by Mastropaolo *et al.* (1976) and Zhang *et al.* (2006). In the first work the complex was obtained by the urea hydrolysis technique, whereas in the second one the crystals were prepared using the hydrothermal conditions. In our studies complex (I) was synthesized using the gel method (Henisch, 1970). However, in all those works not only the preparations differ, the diffraction data sets were collected using different devices. Mastropaolo *et al.* (1976) collected data on an Enraf–Nonius CAD–3 diffractometer with Mo radiation using a small crystal of dimensions 0.27 *x* 0.09 *x* 0.03 mm. The unit-cell parameters were determined from angular values of 11 reflections. In the second report intensities were measured on a Bruker Smart 1000 CCD diffractometer (Mo radiation), and accurate unit-cell parameters were determined by a least-squares fit of 200 strong reflections.

We report here the refinement using the data collected on a KM4 CCD diffracometer with Mo radiation at low temperature(120 K). The unit cell parameters were determined both at room temperature and at 120 K. We found that some reflection groups with h=2n+1 have lower intensities than mean intensity determined for all data. Therefore, the space group must be $P2_1/c$ with unit-cell parameters: a = 13.749 (4), b = 9.713 (4), c = 14.471 (6) Å, β = 91.56 (3)°, whereas the dimensions reported by Mastropaolo *et al.* (1976) (in $P2_1/a$) were a' = 14.477 (9), b' = 9.718 (6), c' = 6.890 (5) Å, β' = 91.27 (5)°, and by Zhang *et al.* (2006) (in $P2_1/c$) were a" = 6.929 (1), b" = 9.762 (1), c" = 14.537 (2) Å, β" = 91.377 (2)°. The structural analysis based on a unit cell having a ≃ 2a"(c') indicated the asymmetric unit to be doubled. Thus, the asymmetric unit has stoichiometry of 4:2:4, *viz*. 4 Cu(II)/2 tetraionized citrate anions/4 $H_2O$ (Fig. 1). Note that Cu1 as well as Cu11 cation are disordered over two positions with the major sof's being 0.955 (5) and minor 0.045 (5), without the change of coordination polyhedra.

The crystal structure is based on dimeric complex with the two subunits $[Cu_2(cit)(H_2O)_2]$ connected by the O7–C6–O6 group. The dinuclear $Cu_2O_9$ moieties, in which one citrate anion is tridentate chelating and second one is bridging (Table 1), create three-dimensional polymeric structure.

In all works, the mode of copper coordination is the same (Fig. 2), however some differences are observed in: (i) respective Cu–O distances within the $CuO_5$ spheres (Table 1), (ii) the citrate C–C–C–O torsion angles (Table 1), and (iii) the hydrogen bond pattern between subunits (Table 2).

## Experimental

The title complex was prepared in a silica-gel medium using the technique described by Henisch (1970). The silica gel was prepared by adding a solution of sodium metasilicate to citric acid. The final pH of the gel was 5.4. After the setting of gel an aqueous solution of $Cu(NO_3)_2$ was carefully poured over it. The crystallization was carried out in the glass tubes in 308 K. After few days green single crystals of $[Cu_4(C_6H_4O_7)_2(H_2O)_4]_n$ appeared in the gel column.

### Refinement

Two of four copper cations are disordered over two positions with the sof's being 0.955 (5) for Cu1 and Cu11, and 0.045 (5) for Cu1A and Cu1B. The H atoms bonded to the citrate C atoms were positioned geometrically. The C—H bonds were set to 1.00 Å. The positions of the water H atoms were found in the difference maps and next the OW—HW distances were fixed at 0.84 Å. The H atoms were included in the refinement in the riding model approximation, with $U_{iso}$(H) = 1.2 $U_{eq}$(C) and $U_{iso}$(H) = 1.5 $U_{eq}$(O).

### Figures

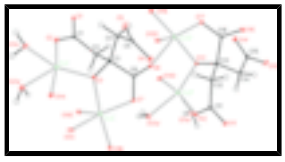

Fig. 1. The atom-numbering of (I). The Cu1 and Cu11 cations with major occupancy factor (0.954) are drawn; displacement ellipsoids are drawn at the 30% probability level. Equivalence between symmetry codes given on figure and Table 1 is as follows: A = i, B = ii, C =iii, D = iv and E = v.

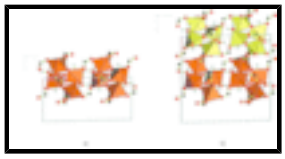

Fig. 2. Polyhedral representation of the crystal packing for the structure (*a*) determined by Zhang *et al.* (2006) and (*b*) determined in the present paper. View along the *b* axis.

### Poly[tetraaquadi-μ$_6$-citrato-tetracopper(II)]

*Crystal data*

| | |
|---|---|
| $[Cu_4(C_6H_4O_7)_2(H_2O)_4]$ | $F_{000}$ = 1392 |
| $M_r$ = 702.45 | $D_x$ = 2.415 Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation<br>λ = 0.71073 Å |
| Hall symbol: -P 2ybc | Cell parameters from 12949 reflections |
| $a$ = 13.749 (4) Å | θ = 2.9–26.6º |
| $b$ = 9.713 (4) Å | μ = 4.44 mm$^{-1}$ |
| $c$ = 14.471 (6) Å | $T$ = 120 (2) K |
| β = 91.56 (3)º | Block, green |
| $V$ = 1931.8 (13) Å$^3$ | 0.6 × 0.34 × 0.25 mm |
| $Z$ = 4 | |

*Data collection*

| | |
|---|---|
| Oxford Diffraction KM-4 CCD area-detector diffractometer | 3973 independent reflections |
| Radiation source: fine-focus sealed tube | 3341 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.038 |
| $T$ = 120(2) K | $\theta_{max}$ = 26.5º |
| ω scans | $\theta_{min}$ = 3.0º |
| Absorption correction: analytical | $h$ = −17→17 |

(CrysAlis RED; Oxford Diffraction, 2003)

$T_{min}$ = 0.15, $T_{max}$ = 0.33

11784 measured reflections

$k$ = −12→10

$l$ = −18→17

*Refinement*

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.027

$wR(F^2)$ = 0.069

$S$ = 1.02

3973 reflections

316 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.043P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 0.55 e Å$^{-3}$

$\Delta\rho_{min}$ = −0.57 e Å$^{-3}$

Extinction correction: none

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Cu1 | 0.46981 (8) | −0.33007 (10) | 0.36000 (4) | 0.00878 (16) | 0.955 (5) |
| Cu2 | 0.34787 (2) | −0.26017 (3) | 0.16600 (2) | 0.00760 (10) | |
| Cu11 | 0.06839 (8) | 0.12127 (10) | 0.15292 (3) | 0.0103 (2) | 0.955 (5) |
| Cu12 | 0.15173 (2) | 0.25321 (3) | 0.33927 (2) | 0.00756 (10) | |
| Cu1A | 0.4490 (14) | −0.3560 (19) | 0.3522 (12) | 0.016 (4)* | 0.045 (5) |
| Cu1B | 0.0381 (14) | 0.1574 (19) | 0.1451 (8) | 0.009 (3)* | 0.045 (5) |
| O1W | 0.58264 (14) | −0.3905 (2) | 0.44238 (13) | 0.0141 (4) | |
| H1W1 | 0.6142 | −0.4585 | 0.4235 | 0.021* | |
| H2W1 | 0.5827 | −0.4048 | 0.4996 | 0.021* | |
| O2W | 0.41608 (14) | −0.5611 (2) | 0.36561 (14) | 0.0168 (5) | |
| H1W2 | 0.3582 | −0.5752 | 0.3481 | 0.025* | |
| H2W2 | 0.4381 | −0.6101 | 0.3232 | 0.025* | |
| O11W | −0.07413 (14) | 0.1233 (2) | 0.07486 (14) | 0.0188 (5) | |
| H1WA | −0.0788 | 0.1173 | 0.0170 | 0.028* | |
| H2WA | −0.1240 | 0.0786 | 0.0885 | 0.028* | |

| | | | | |
|---|---|---|---|---|
| O12W | 0.08871 (13) | −0.08641 (19) | 0.11672 (14) | 0.0146 (4) |
| H1WB | 0.1477 | −0.0962 | 0.1320 | 0.022* |
| H2WB | 0.0529 | −0.1467 | 0.1398 | 0.022* |
| O1 | 0.28209 (13) | −0.19504 (19) | 0.54941 (13) | 0.0117 (4) |
| O2 | 0.39643 (14) | −0.2967 (2) | 0.46885 (13) | 0.0142 (4) |
| O3 | 0.40390 (12) | −0.19572 (18) | 0.28274 (13) | 0.0090 (4) |
| O4 | 0.44720 (13) | 0.1186 (2) | 0.24013 (13) | 0.0131 (4) |
| O5 | 0.55877 (13) | 0.0951 (2) | 0.35529 (14) | 0.0165 (4) |
| O6 | 0.22539 (13) | 0.06961 (19) | 0.26405 (13) | 0.0130 (4) |
| O7 | 0.28046 (13) | −0.08570 (19) | 0.16685 (13) | 0.0101 (4) |
| C1 | 0.31930 (19) | −0.2243 (3) | 0.47378 (19) | 0.0100 (6) |
| C2 | 0.26865 (18) | −0.1671 (3) | 0.38848 (18) | 0.0091 (5) |
| H2A | 0.2201 | −0.1006 | 0.4065 | 0.011* |
| H2B | 0.2355 | −0.2411 | 0.3554 | 0.011* |
| C3 | 0.34105 (18) | −0.0973 (3) | 0.32411 (18) | 0.0079 (5) |
| C4 | 0.40083 (18) | 0.0091 (3) | 0.37832 (18) | 0.0091 (5) |
| H4B | 0.3574 | 0.0778 | 0.4029 | 0.011* |
| H4C | 0.4337 | −0.0360 | 0.4302 | 0.011* |
| C5 | 0.47510 (18) | 0.0793 (3) | 0.32053 (19) | 0.0091 (5) |
| C6 | 0.27838 (19) | −0.0288 (3) | 0.24731 (19) | 0.0088 (5) |
| O11 | 0.22315 (13) | 0.29627 (19) | −0.04781 (13) | 0.0109 (4) |
| O12 | 0.13140 (14) | 0.16551 (19) | 0.03933 (13) | 0.0136 (4) |
| O13 | 0.09871 (13) | 0.29247 (18) | 0.21706 (12) | 0.0083 (4) |
| O14 | 0.01121 (14) | 0.5506 (2) | 0.25088 (14) | 0.0162 (4) |
| O15 | −0.04164 (15) | 0.6468 (2) | 0.11897 (14) | 0.0187 (5) |
| O16 | 0.23375 (14) | 0.60134 (18) | 0.22896 (14) | 0.0150 (4) |
| O17 | 0.22314 (13) | 0.42411 (19) | 0.32481 (13) | 0.0110 (4) |
| C11 | 0.19406 (19) | 0.2596 (3) | 0.03031 (18) | 0.0082 (5) |
| C12 | 0.23525 (18) | 0.3348 (3) | 0.11400 (18) | 0.0079 (5) |
| H12B | 0.2776 | 0.4082 | 0.0941 | 0.010* |
| H12C | 0.2738 | 0.2715 | 0.1518 | 0.010* |
| C13 | 0.15300 (18) | 0.3959 (3) | 0.17203 (18) | 0.0081 (5) |
| C14 | 0.08611 (19) | 0.4857 (3) | 0.11149 (19) | 0.0100 (6) |
| H14B | 0.1256 | 0.5493 | 0.0770 | 0.012* |
| H14C | 0.0515 | 0.4274 | 0.0672 | 0.012* |
| C15 | 0.01295 (18) | 0.5668 (3) | 0.16499 (19) | 0.0096 (5) |
| C16 | 0.20629 (18) | 0.4841 (3) | 0.24588 (19) | 0.0095 (5) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0099 (3) | 0.0103 (3) | 0.0061 (2) | 0.0030 (2) | 0.00042 (19) | 0.00081 (19) |
| Cu2 | 0.00742 (17) | 0.00875 (18) | 0.00656 (19) | 0.00170 (12) | −0.00111 (13) | −0.00171 (12) |
| Cu11 | 0.0150 (4) | 0.0100 (3) | 0.0060 (2) | −0.0046 (3) | 0.00202 (17) | −0.00110 (17) |
| Cu12 | 0.00874 (17) | 0.00843 (18) | 0.00547 (19) | −0.00169 (12) | −0.00062 (13) | 0.00043 (12) |
| O1W | 0.0151 (9) | 0.0176 (11) | 0.0094 (10) | 0.0012 (8) | −0.0012 (8) | 0.0015 (8) |
| O2W | 0.0140 (10) | 0.0202 (11) | 0.0159 (11) | −0.0032 (8) | −0.0042 (8) | −0.0019 (9) |
| O11W | 0.0141 (10) | 0.0286 (12) | 0.0138 (11) | 0.0006 (9) | −0.0023 (8) | 0.0009 (9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O12W | 0.0094 (9) | 0.0131 (10) | 0.0212 (12) | −0.0025 (8) | −0.0024 (8) | 0.0003 (8) |
| O1 | 0.0109 (9) | 0.0124 (10) | 0.0117 (11) | 0.0008 (8) | −0.0001 (8) | 0.0010 (8) |
| O2 | 0.0165 (10) | 0.0180 (10) | 0.0084 (10) | 0.0070 (8) | 0.0023 (8) | 0.0024 (8) |
| O3 | 0.0084 (9) | 0.0095 (9) | 0.0090 (10) | 0.0020 (7) | −0.0009 (7) | −0.0022 (8) |
| O4 | 0.0123 (9) | 0.0177 (10) | 0.0094 (10) | −0.0054 (8) | −0.0001 (8) | 0.0022 (8) |
| O5 | 0.0118 (9) | 0.0199 (11) | 0.0175 (11) | −0.0071 (8) | −0.0056 (8) | 0.0083 (9) |
| O6 | 0.0166 (10) | 0.0133 (10) | 0.0091 (10) | 0.0065 (8) | −0.0007 (8) | −0.0013 (8) |
| O7 | 0.0124 (9) | 0.0119 (9) | 0.0058 (10) | 0.0024 (7) | −0.0026 (7) | −0.0023 (8) |
| C1 | 0.0124 (13) | 0.0068 (13) | 0.0108 (15) | −0.0038 (10) | 0.0030 (11) | 0.0013 (11) |
| C2 | 0.0075 (12) | 0.0103 (13) | 0.0096 (14) | −0.0008 (10) | 0.0011 (10) | −0.0007 (11) |
| C3 | 0.0082 (12) | 0.0085 (13) | 0.0071 (14) | 0.0010 (10) | 0.0019 (10) | 0.0004 (10) |
| C4 | 0.0095 (12) | 0.0115 (13) | 0.0062 (14) | −0.0004 (10) | 0.0012 (10) | −0.0004 (11) |
| C5 | 0.0099 (12) | 0.0060 (12) | 0.0116 (15) | 0.0003 (10) | 0.0005 (11) | −0.0020 (11) |
| C6 | 0.0100 (12) | 0.0073 (12) | 0.0091 (14) | −0.0020 (10) | 0.0002 (10) | 0.0001 (11) |
| O11 | 0.0121 (9) | 0.0127 (10) | 0.0079 (10) | −0.0013 (8) | 0.0007 (8) | 0.0010 (8) |
| O12 | 0.0203 (10) | 0.0136 (10) | 0.0071 (10) | −0.0064 (8) | 0.0023 (8) | −0.0011 (8) |
| O13 | 0.0114 (9) | 0.0084 (9) | 0.0052 (10) | −0.0018 (7) | 0.0010 (7) | 0.0006 (7) |
| O14 | 0.0216 (10) | 0.0187 (11) | 0.0083 (11) | 0.0100 (9) | 0.0022 (8) | 0.0017 (8) |
| O15 | 0.0209 (10) | 0.0255 (11) | 0.0097 (11) | 0.0161 (9) | 0.0024 (8) | 0.0035 (9) |
| O16 | 0.0221 (10) | 0.0102 (10) | 0.0128 (11) | −0.0081 (8) | 0.0032 (8) | −0.0005 (8) |
| O17 | 0.0128 (9) | 0.0129 (10) | 0.0070 (10) | −0.0037 (8) | −0.0027 (7) | 0.0001 (8) |
| C11 | 0.0099 (12) | 0.0083 (13) | 0.0063 (14) | 0.0044 (10) | 0.0012 (10) | 0.0012 (10) |
| C12 | 0.0093 (12) | 0.0082 (13) | 0.0062 (14) | −0.0002 (10) | −0.0007 (10) | 0.0001 (10) |
| C13 | 0.0090 (12) | 0.0081 (13) | 0.0073 (14) | 0.0006 (10) | 0.0029 (10) | 0.0004 (10) |
| C14 | 0.0106 (12) | 0.0116 (13) | 0.0079 (14) | 0.0000 (10) | 0.0010 (10) | 0.0014 (11) |
| C15 | 0.0101 (12) | 0.0079 (13) | 0.0110 (15) | −0.0004 (10) | 0.0023 (10) | 0.0015 (11) |
| C16 | 0.0077 (12) | 0.0105 (13) | 0.0105 (14) | −0.0008 (10) | 0.0030 (10) | −0.0019 (11) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cu1—O2 | 1.921 (2) | O11W—H2WA | 0.8399 |
| Cu1—O3 | 1.929 (2) | O12W—H1WB | 0.8399 |
| Cu1—O4$^{i}$ | 1.934 (2) | O12W—H2WB | 0.8402 |
| Cu1—O1W | 2.018 (2) | O1—C1 | 1.253 (3) |
| Cu1—O2W | 2.365 (2) | O2—C1 | 1.276 (3) |
| Cu1—Cu1A | 0.40 (2) | O3—C3 | 1.431 (3) |
| Cu2—O7 | 1.932 (2) | O4—C5 | 1.273 (3) |
| Cu2—O5$^{i}$ | 1.934 (2) | O5—C5 | 1.252 (3) |
| Cu2—O3 | 1.941 (2) | O6—C6 | 1.230 (3) |
| Cu2—O1$^{ii}$ | 1.942 (2) | O7—C6 | 1.290 (3) |
| Cu2—O16$^{iii}$ | 2.276 (2) | C1—C2 | 1.507 (4) |
| Cu11—Cu1B | 0.55 (2) | C2—C3 | 1.539 (4) |
| Cu11—O12 | 1.927 (2) | C2—H2A | 0.9700 |
| Cu11—O13 | 1.944 (2) | C2—H2B | 0.9700 |
| Cu11—O14$^{iv}$ | 1.921 (2) | C3—C4 | 1.524 (4) |
| Cu11—O11W | 2.235 (2) | C3—C6 | 1.539 (4) |
| Cu11—O12W | 2.105 (2) | C4—C5 | 1.501 (4) |
| Cu12—O17 | 1.943 (2) | C4—H4B | 0.9700 |

| | | | |
|---|---|---|---|
| Cu12—O15$^{iv}$ | 1.943 (2) | C4—H4C | 0.9700 |
| Cu12—O13 | 1.932 (2) | O11—C11 | 1.261 (3) |
| Cu12—O11$^{v}$ | 1.944 (2) | O12—C11 | 1.265 (3) |
| Cu12—O6 | 2.335 (2) | O13—C13 | 1.420 (3) |
| Cu1A—O2 | 1.942 (17) | O14—C15 | 1.254 (3) |
| Cu1A—O3 | 1.945 (17) | O15—C15 | 1.258 (3) |
| Cu1A—O4$^{i}$ | 1.997 (17) | O16—C16 | 1.226 (3) |
| Cu1A—O2W | 2.05 (2) | O17—C16 | 1.298 (3) |
| Cu1A—O1W | 2.250 (19) | C11—C12 | 1.511 (4) |
| Cu1B—O11W | 1.854 (17) | C12—C13 | 1.545 (4) |
| Cu1B—O13 | 1.858 (10) | C12—H12B | 0.9700 |
| Cu1B—O14$^{iv}$ | 1.964 (12) | C12—H12C | 0.9700 |
| Cu1B—O12 | 2.025 (12) | C13—C14 | 1.527 (4) |
| O1W—H1W1 | 0.8400 | C13—C16 | 1.540 (4) |
| O1W—H2W1 | 0.8400 | C14—C15 | 1.508 (4) |
| O2W—H1W2 | 0.8400 | C14—H14B | 0.9700 |
| O2W—H2W2 | 0.8400 | C14—H14C | 0.9700 |
| O11W—H1WA | 0.8400 | | |
| O2—Cu1—O3 | 96.44 (8) | H1W1—O1W—H2W1 | 101.8 |
| O2—Cu1—O4$^{i}$ | 172.54 (8) | H1W2—O2W—H2W2 | 92.6 |
| O3—Cu1—O4$^{i}$ | 91.02 (8) | H1WA—O11W—H2WA | 99.1 |
| O2—Cu1—O1W | 88.69 (9) | H1WB—O12W—H2WB | 112.9 |
| O3—Cu1—O1W | 151.76 (11) | O1—C1—O2 | 122.2 (3) |
| O4$^{i}$—Cu1—O1W | 84.71 (9) | O1—C1—C2 | 116.2 (2) |
| O2—Cu1—O2W | 87.73 (9) | O2—C1—C2 | 121.6 (2) |
| O3—Cu1—O2W | 121.32 (9) | C1—C2—C3 | 111.5 (2) |
| O4$^{i}$—Cu1—O2W | 88.40 (8) | C1—C2—H2A | 109.3 |
| O1W—Cu1—O2W | 86.53 (8) | C3—C2—H2A | 109.3 |
| O7—Cu2—O5$^{i}$ | 163.60 (9) | C1—C2—H2B | 109.3 |
| O7—Cu2—O3 | 83.72 (8) | C3—C2—H2B | 109.3 |
| O5$^{i}$—Cu2—O3 | 97.10 (8) | H2A—C2—H2B | 108.0 |
| O7—Cu2—O1$^{ii}$ | 89.43 (8) | O3—C3—C4 | 110.2 (2) |
| O5$^{i}$—Cu2—O1$^{ii}$ | 89.67 (8) | O3—C3—C6 | 108.6 (2) |
| O3—Cu2—O1$^{ii}$ | 173.11 (8) | C4—C3—C6 | 111.2 (2) |
| O7—Cu2—O16$^{iii}$ | 100.36 (8) | O3—C3—C2 | 111.5 (2) |
| O5$^{i}$—Cu2—O16$^{iii}$ | 95.85 (8) | C4—C3—C2 | 109.6 (2) |
| O3—Cu2—O16$^{iii}$ | 95.96 (8) | C6—C3—C2 | 105.6 (2) |
| O1$^{ii}$—Cu2—O16$^{iii}$ | 84.58 (8) | C5—C4—C3 | 112.8 (2) |
| O14$^{iv}$—Cu11—O12 | 167.41 (8) | C5—C4—H4B | 109.0 |
| O14$^{iv}$—Cu11—O13 | 94.50 (9) | C3—C4—H4B | 109.0 |
| O12—Cu11—O13 | 96.95 (8) | C5—C4—H4C | 109.0 |
| O14$^{iv}$—Cu11—O12W | 85.42 (9) | C3—C4—H4C | 109.0 |
| O12—Cu11—O12W | 86.31 (9) | H4B—C4—H4C | 107.8 |
| O13—Cu11—O12W | 155.57 (10) | O5—C5—O4 | 125.5 (3) |

| | | | |
|---|---|---|---|
| O14$^{iv}$—Cu11—O11W | 81.98 (9) | O5—C5—C4 | 117.6 (2) |
| O12—Cu11—O11W | 88.58 (9) | O4—C5—C4 | 116.9 (2) |
| O13—Cu11—O11W | 114.05 (10) | O6—C6—O7 | 122.6 (2) |
| O12W—Cu11—O11W | 90.17 (8) | O6—C6—C3 | 121.1 (2) |
| O13—Cu12—O15$^{iv}$ | 96.43 (8) | O7—C6—C3 | 116.1 (2) |
| O13—Cu12—O17 | 84.95 (8) | O11—C11—O12 | 122.0 (2) |
| O15$^{iv}$—Cu12—O17 | 152.67 (9) | O11—C11—C12 | 117.5 (2) |
| O13—Cu12—O11$^{v}$ | 170.95 (8) | O12—C11—C12 | 120.5 (2) |
| O15$^{iv}$—Cu12—O11$^{v}$ | 89.26 (9) | C11—C12—C13 | 110.9 (2) |
| O17—Cu12—O11$^{v}$ | 93.24 (8) | C11—C12—H12B | 109.5 |
| O13—Cu12—O6 | 83.21 (7) | C13—C12—H12B | 109.5 |
| O15$^{iv}$—Cu12—O6 | 95.17 (8) | C11—C12—H12C | 109.5 |
| O17—Cu12—O6 | 112.06 (8) | C13—C12—H12C | 109.5 |
| O11$^{v}$—Cu12—O6 | 89.28 (7) | H12B—C12—H12C | 108.0 |
| O2—Cu1A—O3 | 95.2 (7) | O13—C13—C14 | 110.6 (2) |
| O2—Cu1A—O4$^{i}$ | 155.3 (12) | O13—C13—C16 | 108.8 (2) |
| O3—Cu1A—O4$^{i}$ | 88.7 (7) | C14—C13—C16 | 110.4 (2) |
| O2—Cu1A—O2W | 96.7 (8) | O13—C13—C12 | 112.3 (2) |
| O3—Cu1A—O2W | 139.2 (11) | C14—C13—C12 | 110.2 (2) |
| O4$^{i}$—Cu1A—O2W | 96.1 (7) | C16—C13—C12 | 104.5 (2) |
| O2—Cu1A—O1W | 81.8 (7) | C15—C14—C13 | 113.8 (2) |
| O3—Cu1A—O1W | 131.5 (11) | C15—C14—H14B | 108.8 |
| O4$^{i}$—Cu1A—O1W | 77.4 (6) | C13—C14—H14B | 108.8 |
| O2W—Cu1A—O1W | 88.8 (6) | C15—C14—H14C | 108.8 |
| Cu11—Cu1B—O11W | 127.5 (14) | C13—C14—H14C | 108.8 |
| Cu11—Cu1B—O13 | 90.5 (12) | H14B—C14—H14C | 107.7 |
| O11W—Cu1B—O13 | 141.9 (14) | O14—C15—O15 | 125.1 (3) |
| O11W—Cu1B—O14$^{iv}$ | 91.5 (5) | O14—C15—C14 | 118.3 (2) |
| O13—Cu1B—O14$^{iv}$ | 95.9 (5) | O15—C15—C14 | 116.6 (2) |
| O11W—Cu1B—O12 | 97.3 (5) | O16—C16—O17 | 123.0 (2) |
| O13—Cu1B—O12 | 96.5 (5) | O16—C16—C13 | 121.4 (2) |
| O14$^{iv}$—Cu1B—O12 | 147.0 (13) | O17—C16—C13 | 115.5 (2) |
| O1—C1—C2—C3 | 131.5 (2) | O11—C11—C12—C13 | 124.4 (2) |
| O2—C1—C2—C3 | −47.6 (3) | O12—C11—C12—C13 | −54.2 (3) |
| C1—C2—C3—O3 | 69.1 (3) | C11—C12—C13—O13 | 69.7 (3) |
| C1—C2—C3—C4 | −53.2 (3) | C11—C12—C13—C14 | −54.1 (3) |
| C1—C2—C3—C6 | −173.1 (2) | C11—C12—C13—C16 | −172.6 (2) |
| O3—C3—C4—C5 | 55.5 (3) | O13—C13—C14—C15 | 64.1 (3) |
| C6—C3—C4—C5 | −65.0 (3) | C16—C13—C14—C15 | −56.3 (3) |
| C2—C3—C4—C5 | 178.6 (2) | C12—C13—C14—C15 | −171.2 (2) |
| C3—C4—C5—O5 | −135.9 (2) | C13—C14—C15—O14 | −2.3 (3) |
| C3—C4—C5—O4 | 44.4 (3) | C13—C14—C15—O15 | 177.3 (2) |
| O3—C3—C6—O6 | −172.5 (2) | O13—C13—C16—O16 | −158.0 (2) |
| C4—C3—C6—O6 | −51.1 (3) | C14—C13—C16—O16 | −36.5 (3) |
| C2—C3—C6—O6 | 67.7 (3) | C12—C13—C16—O16 | 81.9 (3) |
| O3—C3—C6—O7 | 11.6 (3) | O13—C13—C16—O17 | 24.7 (3) |

| | | | |
|---|---|---|---|
| C4—C3—C6—O7 | 133.0 (2) | C14—C13—C16—O17 | 146.1 (2) |
| C2—C3—C6—O7 | −108.2 (3) | C12—C13—C16—O17 | −95.4 (3) |

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1/2; (ii) *x*, −*y*−1/2, *z*−1/2; (iii) *x*, *y*−1, *z*; (iv) −*x*, *y*−1/2, −*z*+1/2; (v) *x*, −*y*+1/2, *z*+1/2.

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1W—H1W1···O7$^{i}$ | 0.84 | 2.33 | 3.130 (3) | 159 |
| O1W—H2W1···O2W$^{vi}$ | 0.84 | 1.98 | 2.820 (3) | 180 |
| O2W—H1W2···O17$^{iii}$ | 0.84 | 1.88 | 2.706 (3) | 168 |
| O11W—H2WA···O17$^{iv}$ | 0.84 | 2.40 | 3.195 (3) | 157 |
| O11W—H1WA···O12W$^{vii}$ | 0.84 | 1.96 | 2.797 (3) | 175 |
| O12W—H1WB···O7 | 0.84 | 1.88 | 2.715 (3) | 170 |
| O12W—H2WB···O15$^{iii}$ | 0.84 | 2.40 | 3.152 (3) | 149 |

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1/2; (vi) −*x*+1, −*y*−1, −*z*+1; (iii) *x*, *y*−1, *z*; (iv) −*x*, *y*−1/2, −*z*+1/2; (vii) −*x*, −*y*, −*z*.

**Fig. 1**

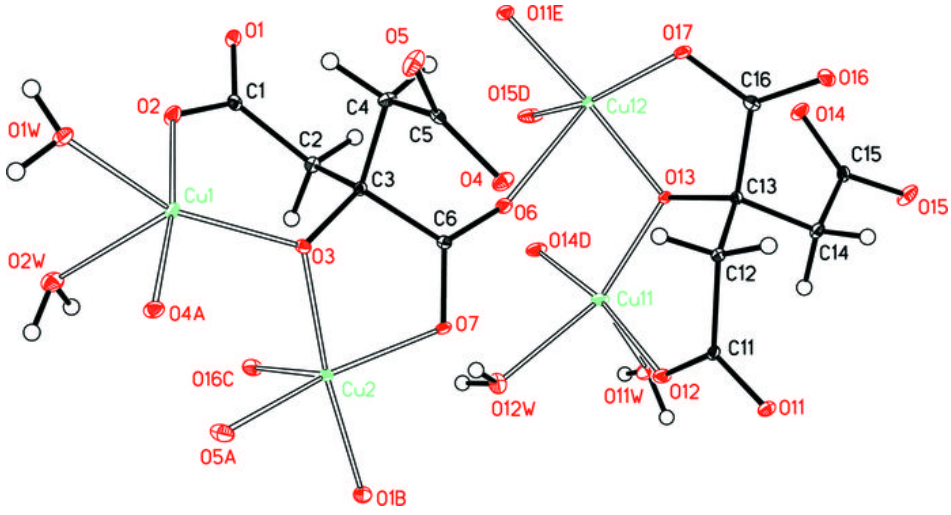
O11E
O17
O1
O5
C16
O16
O15D
Cu12
C1
O2
C4
O14
O1W
C2
C5
C15
C3
O4
O13
C13
O15
Cu1
C6
O6
O14D
O2W
O3
C12
C14
Cu11
O4A
O7
C11
O16C
Cu2
O12W
O11W
O12
O11
O5A
O1B

**Fig. 2**