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Redetermination of $[HCu_2\{(CH_3HXTA)(H)\}(H_2O)_2]\cdot 4H_2O$ [CH_3HXTA = *N*,*N*′-(2-hydroxy-5-methyl-1,3-xylylene)bis(*N*-carboxymethylglycine)]

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The structure of the title compound, {μ-2-[*N*,*N*-bis(carboxylatomethyl)aminomethyl]-6-[*N*-(carboxylatomethyl)-*N*-(carboxymethyl)aminomethyl]-6-methylphenolato}dicopper(II) tetrahydrate, $[Cu_2(C_{17}H_{17}N_2O_9)(H_2O)_2]\cdot 4H_2O$, which has been published previously [Holz, Brink, Gobena & O'Connor (1994). *Inorg. Chem.* **33**, 6086–6092], has been redetermined. The H atom missing in the earlier study is shown to be associated with a carboxyl group.

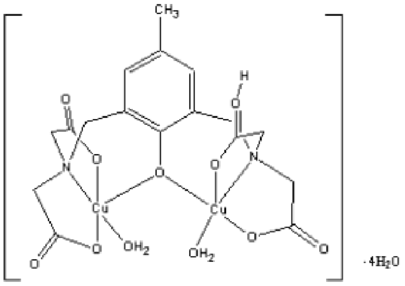
Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.004 Å
R factor = 0.031
wR factor = 0.082
Data-to-parameter ratio = 11.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The crystal structure of the title compound, (I) (Fig. 1), has been published previously (Holz *et al.*, 1994). The present study, also using data collected at low temperature, confirms the earlier structure with improved precision [*e.g.* the standard uncertainties of Holz *et al.* (1994) for the Cu—N bonds are 0.004 Å, compared with 0.002 Å here]. Earlier work on dinucleating ligands and their potential applications as models for dinuclear metallo-biosites has been summarized by Sorrell (1989).



(I)

In the previous study of (I), one H atom was not located, leading to charge imbalance. Here, the additional H atom is attached to the carboxyl atom O5. It is interesting that the C10—O5 distance is 1.301 (3) Å, while the C—O distances for the three unprotonated carboxyl O atoms are in the range 1.223 (3)–1.249 (3) Å. The near-linear hydrogen bond formed by O5—H5···O15^{i} (see Table 2 for symmetry code) is further evidence of the correctness of this formulation.

As shown in Table 2. and illustrated in Fig. 2, a number of intra- and intermolecular hydrogen bonds stabilize the crystal structure. These hydrogen bonds are formed mainly between coordinated water molecule (H-atom donors) and carbonyl O atoms from carboxyl groups (H-atom acceptors) or the uncoordinated water molecules (as H-atom donors or acceptors).

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China, and were used

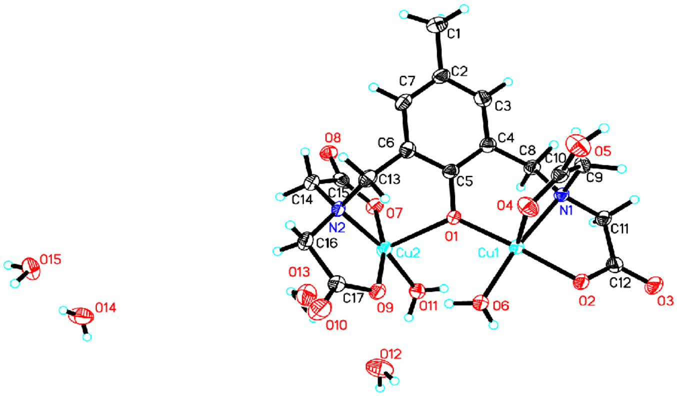


Figure 1
A view of the molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

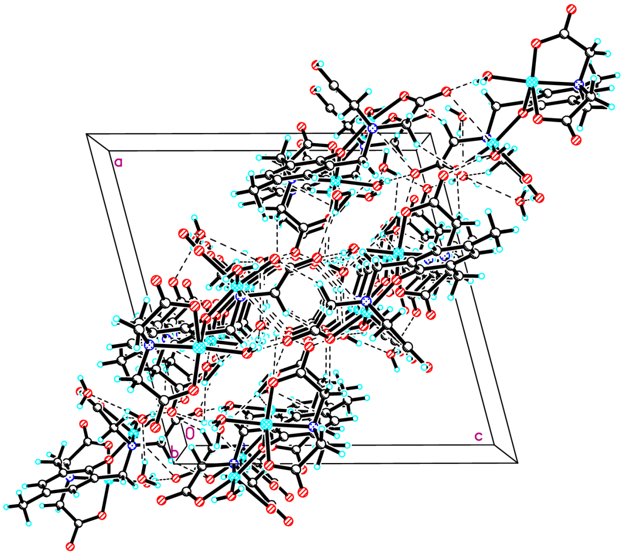


Figure 2
Packing diagram of (I), viewed along the *b* direction. Hydrogen bonds are indicated by dashed lines.

without further purification. The ligand CH_3HXTA was synthesized according to a published procedure (Branum *et al.*, 2001). $CuCl_2 \cdot 2H_2O$ (0.3410 g, 2 mmol) and $Na_4(HXTA)$ (0.486 g, 1 mmol) were dissolved in water (5 ml) and mixed with stirring at 323 K for 3 h. The resulting dark-green solution was filtered and the filtrate was left to stand at room temperature. Dark-green crystals of (I) appeared after a week as a result of slow evaporation of the aqueous solvent.

Crystal data

$[Cu_2(C_{17}H_{17}N_2O_9)(H_2O)_2] \cdot 4H_2O$
$M_r = 629.51$
Monoclinic, $P2_1/n$
$a = 15.0895$ (18) Å
$b = 10.8217$ (13) Å
$c = 15.2048$ (18) Å
$\beta = 104.705$ (2)°
$V = 2401.5$ (5) Å^3
$Z = 4$

$D_x = 1.741$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5375 reflections
$\theta = 2.3$–26.9°
$\mu = 1.85$ mm^{-1}
$T = 183$ (2) K
Plate, dark green
0.40 × 0.40 × 0.20 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.509$, $T_{max} = 0.688$
9615 measured reflections

4221 independent reflections
3623 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 25.0°$
$h = -13 \rightarrow 17$
$k = -11 \rightarrow 12$
$l = -18 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.082$
$S = 1.01$
4221 reflections
378 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9056 (17)	O1—Cu2	2.2288 (17)
Cu1—O2	1.9457 (17)	Cu2—O11	1.947 (2)
Cu1—O6	1.957 (2)	Cu2—O7	1.9624 (18)
Cu1—N1	2.042 (2)	Cu2—O9	1.9866 (18)
Cu1—O4	2.298 (2)	Cu2—N2	2.001 (2)
Cu1···Cu2	3.7194 (6)		
Cu1—O1—Cu2	128.05 (8)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5···O15^{i}	0.82 (4)	1.72 (4)	2.533 (3)	175 (5)
O6—H6A···O8^{i}	0.76 (4)	2.00 (4)	2.734 (3)	163 (4)
O6—H6B···O9	0.81 (3)	1.91 (3)	2.704 (3)	167 (3)
O11—H11C···O3^{ii}	0.75 (4)	1.96 (4)	2.703 (3)	172 (4)
O11—H11D···O12	0.86 (3)	1.80 (3)	2.645 (3)	167 (3)
O12—H12A···O14^{iii}	0.80 (4)	2.04 (4)	2.811 (4)	163 (4)
O12—H12B···O8^{iv}	0.90 (4)	1.89 (4)	2.787 (3)	173 (4)
O13—H13C···O3^{v}	0.73 (4)	2.20 (4)	2.911 (4)	166 (4)
O13—H13D···O12	0.75 (3)	2.43 (3)	3.011 (4)	135 (4)
O14—H14C···O15	0.79 (4)	2.16 (4)	2.896 (4)	156 (4)
O14—H14D···O8^{vi}	0.67 (5)	2.21 (5)	2.807 (3)	149 (5)
O15—H15A···O10^{vii}	0.77 (3)	1.82 (3)	2.574 (3)	165 (3)
O15—H15B···O4^{viii}	0.94 (4)	1.87 (4)	2.790 (3)	165 (3)

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

H atoms attached to C atoms were placed in geometrically idealized positions, with Csp^3—H = 0.96 Å (for methyl), Csp^3—H = 0.97 Å (for methylene) and Csp^2—H = 0.93 Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.5U_{eq}(C)$ (for methyl) and $U_{iso}(H) = 1.2U_{eq}(C)$ (for others). H atoms attached to O atoms were located in difference Fourier maps and refined with a common U_{iso} value. The O—H distances are in the range 0.67 (5)–0.94 (4) Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 2000); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 2000); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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