Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Aquamalonato(1,10-phenanthroline)-copper(II) sesquihydrate

Madina Diallo,[a] Moussa Dieng,[a] Mohamed Gaye,[a]* Abdou Salam Sall,[a] Aliou Hamady Barry[b] and Beghidja Chahrazed[c]

[a]Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Senegal, [b]Département de Chimie, Faculté des Sciences, Université de Nouakchott, Nouakchott, Mauritania, and [c]Université Louis Pasteur, Laboratoire DECMET, UMR CNRS 7513, 4 Rue Blaise Pascal, 6700 Strasbourg, France
Correspondence e-mail: mlgayeastou@yahoo.fr

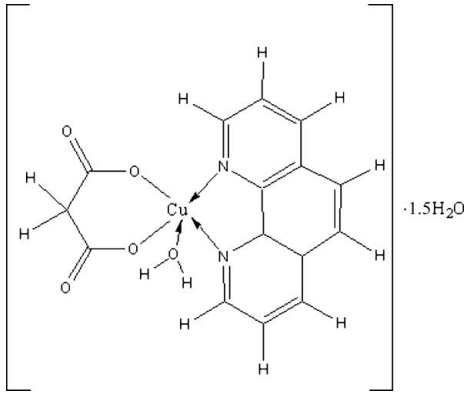
Received 26 April 2007; accepted 11 May 2007

Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.004 Å; R factor = 0.045; wR factor = 0.124; data-to-parameter ratio = 20.2.

In the title compound, $[Cu(C_3H_4O_4)(C_{12}H_8N_2)(H_2O)]\cdot 1.5H_2O$, there are two complex molecules and three uncoordinated water molecules in the asymmetric unit. In both complex molecules, the Cu atom is five-coordinated by one bidentate 1,10-phenanthroline molecule, one bidentate malonate dianion and one water molecule, resulting in a distorted square-based pyramidal CuN_2O_3 chromophore. The structure is stabilized by O—H···O hydrogen bonds involving both the coordinated and uncoordinated water molecules.

Related literature

For related structures: see Anitolini *et al.* (1985); Ivanovic-Burmazovic *et al.* (1998); Chawla *et al.* (2004). For related literature, see: Addison *et al.* (1984).



Experimental

Crystal data

$[Cu(C_3H_4O_4)(C_{12}H_8N_2)(H_2O)]\cdot 1.5H_2O$
M_r = 390.84
Triclinic, $P\overline{1}$
a = 11.5591 (2) Å
b = 11.7450 (2) Å
c = 12.5081 (2) Å
α = 92.177 (1)°
β = 105.457 (1)°
γ = 109.1821 (8)°
V = 1531.06 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.47 mm^{-1}
T = 173 (2) K
0.10 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
21966 measured reflections
8939 independent reflections
6592 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.124
S = 1.07
8939 reflections
442 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.74 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—O2	1.9061 (18)	Cu2—O3	1.9114 (16)
Cu1—O1	1.9270 (16)	Cu2—O7	1.9246 (16)
Cu1—N4	1.989 (2)	Cu2—N1	2.017 (2)
Cu1—N3	2.0298 (19)	Cu2—N2	2.0260 (18)
Cu1—O9	2.293 (2)	Cu2—O10	2.2643 (18)

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

D—H···A	D—H	H···A	D···A	D—H···A
O9—H29···O4	0.91	2.08	2.961 (3)	161
O9—H30···O12	0.96	1.85	2.769 (3)	158
O10—H27···O5	0.87	1.91	2.720 (3)	154
O10—H28···O8^{i}	0.91	1.92	2.824 (3)	172
O11—H25···O8^{ii}	0.99	1.99	2.983 (3)	174
O11—H26···O5	0.86	1.99	2.831 (3)	167
O12—H23···O13^{iii}	0.95	1.86	2.800 (3)	168
O12—H24···O4^{iv}	0.90	1.89	2.780 (3)	169
O13—H21···O6	0.96	1.96	2.915 (3)	177
O13—H22···O6^{iii}	0.94	2.06	2.952 (3)	156

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Nonius, 1998); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors thank the Agence Universitaire de la Francophonie for financial support (AUF-PSCI No. 6301PS48).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2396).

  doi:10.1107/S160053680702332X

References

Addison, A. W., Rao, T. N., Reedijk, J., Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Anitolini, L., Marcotrigiano, G., Menabue, L., Pellacani, G. C., Salaini, M. & Sola, M. (1985). *Inorg. Chem.* **24**, 3621–3626.

Chawla, S. K., Arora, M., Nattinen, K., Rissanen, K. & Yakhmi, J. V. (2004). *Polyhedron*, **23**, 3007–3019.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Ivanovic-Burmazovic, I., Bacchi, A., Pelissi, G., Leovac, V. & Andjelkovic, K. (1998). *Polyhedron*, **18**, 119–127.

Nonius (1998). *COLLECT* and *DENZO*. Nonius BV, Delft, The Netherlands.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

Acta Cryst. (2007). E**63**, m1810-m1811 [**doi:10.1107/S160053680702332X**]

Aquamalonato(1,10-phenanthroline)copper(II) sesquihydrate

M. Diallo, M. Dieng, M. Gaye, A. S. Sall, A. H. Barry and B. Chahrazed

Comment

The title compound, (I), consists of a mononuclear Cu(II) complex with two neutral molecules in the asymmetric unit (Fig. 1). The Cu(II) ion displays a five coordinated-geometry where the Cu atom is coordinated by two nitrogen atoms of one 1,10-phenanthroline ligand, two oxygen atoms of one non-bridging dicarboxylate group and one oxygen atom of a water molecule (Table 1). Furthermore the largest angles around the Cu(II) centers (β:N1—Cu2—O7=168.67 (8)° and β: N4—Cu1—O2=172.50 (8)°) are slightly larger than the second-largest ones (α: N2—Cu2—O3=164.80 (8)° and α: N3—Cu1—O1=164.14 (9)°). Since the distortion value of the coordination polyhedron, τ=(β-α)/60 is evaluated by the two largest angles in the five coordinated geometry (Addison *et al.* 1984), the values of τ=0.14 for Cu1 and τ=0.06 for Cu2 which can be compared with the ideal values of 1 for a trigonal-bipyramidal and 0 for a square-pyramidal seem to indicate a distorted square pyramidal geometry around the two Cu centers. Atoms [O1, O2, N4 and N3] and [O3, O7, N1 and N2] consist of a square planar geometry with some deviation from perfect square plane. The apical positions are occupied by O6 and O10 respectively. The malonate ligand afforded two deprotonated carboxylate groups leading to a dinegative charge on the ligand. The structure of (I) is stablisied by O—H···O hydrogen bonds (Table 2).

This structure is comparable to that of [Cu(*L*-glu)(phen)(H_2O)] (Anitolini *et al.* 1985) in which the Cu ions also have distorted square-pyramidal coordination geometry comprised of a bidentate phenanthroline ligand and an O,*N*-bidentate glutamate dianion and an apical coordination water O atom. The Cu—O_{water} lengths are 2.303 (2) and 2.268 (2) Å in the two molecules, slighly shorter than the value of 2.332 (4) Å observed for Cu—O_{water} Å in the complex [Cu(Hdapsox)(H_2O)](ClO_4) where H_2dapsox is 2',2'''-(2,6-pyridindiyldiethylidene) dioxamohydrazide (Ivanovic-Burmazovic *et al.* 1998) but similar to that observed in the complex $[Cu_2(mal)_2(IX)(H_2O)_6]_n$ (Chawla *et al.* 2004) where IX is 1,4-bis(imidazole-1-yl-methylene)benzene) (2.277 Å).

Experimental

Into an aqueous solution (5 ml) of $Cu(NO_3)_2$ $3H_2O$ (0.3011 g, 1.25 mmol) was poured 1.5 ml of a molar solution of Na_2CO_3. The mixture was stirred for 5 minutes and centrifuged. The solid which was isolated was added into a methanolic solution (10 ml) of 1,10-phenanthroline monohydrate (0.2478 g, 1.25 mmol) and malonic acid (0.1301 g, 1.25 mmol). The resulting mixture was heated at 343 K for thirty minutes. The green solution was filtered and then allowed to evaporate slowly in an open atmosphere. After one week, green crystals of (I) were obtained. The crystals were separated, washed with cold methanol and dried (yield: 65%, based on $Cu(NO_3)_2$ $3H_2O$); Anal. Calc. for $C_{30}H_{30}Cu_2N_4O_{13}$: C, 46.10; H, 3.87; N, 7.17%. Found: C, 46.06; H, 3.85; N, 7.19%.

Refinement

The O-bound H atoms were located in a difference map and refined as riding in their as found relative positions with a fixed U_{iso} of 0.062 Å^2. The C-bound H atoms were placed geometrically (C—H = 0.950.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

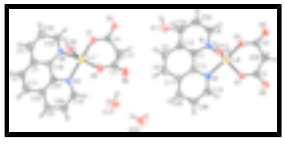


Fig. 1. View of the asymmetric unit of (I) with displacement ellipsoids plotted at the 50% probability level (arbitrary spheres for the H atoms).

Aquamalonato(1,10-phenanthroline)copper(II) sesquihydrate

Crystal data

$[Cu(C_3H_4O_4)(C_{12}H_8N_2)(H_2O)]\cdot 1.5H_2O$	$Z = 4$
$M_r = 390.84$	$F_{000} = 800$
Triclinic, $P\overline{1}$	$D_x = 1.696$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
$a = 11.5591$ (2) Å	Cell parameters from 12012 reflections
$b = 11.7450$ (2) Å	$\theta = 1.0$–30.0º
$c = 12.5081$ (2) Å	$\mu = 1.47$ mm^{-1}
$\alpha = 92.177$ (1)º	$T = 173$ (2) K
$\beta = 105.457$ (1)º	Prism, green
$\gamma = 109.1821$ (8)º	0.10 × 0.10 × 0.05 mm
$V = 1531.06$ (5) Å^3	

Data collection

Nonius Kappa CCD diffractometer	6592 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.044$
Monochromator: graphite	$\theta_{max} = 30.0$º
$T = 173(2)$ K	$\theta_{min} = 1.7$º
ω and φ scans	$h = -16\rightarrow16$
Absorption correction: none	$k = -16\rightarrow15$
21966 measured reflections	$l = -17\rightarrow17$
8939 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.124$

$S = 1.07$

8939 reflections

442 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2 + 0.2273P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.58$ e Å^{-3}

$\Delta\rho_{min} = -0.74$ 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 $F^2 > 2$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}
Cu1	0.83061 (3)	0.35565 (3)	0.64500 (2)	0.03168 (9)
Cu2	0.71496 (3)	0.06782 (3)	0.97437 (2)	0.02830 (9)
O1	0.86279 (19)	0.36223 (17)	0.80482 (13)	0.0398 (4)
O2	0.7194 (2)	0.4471 (2)	0.62900 (14)	0.0491 (5)
O3	0.71195 (19)	0.03964 (18)	0.82197 (13)	0.0404 (4)
O4	0.7521 (2)	−0.03321 (19)	0.67820 (14)	0.0474 (5)
O5	0.84700 (18)	0.42129 (17)	0.96762 (13)	0.0387 (4)
O6	0.6375 (2)	0.5720 (2)	0.68385 (17)	0.0643 (7)
O7	0.78901 (17)	−0.05295 (16)	1.02331 (13)	0.0362 (4)
O8	0.88860 (19)	−0.18133 (18)	1.01234 (15)	0.0441 (5)
O9	0.67258 (18)	0.16762 (18)	0.58759 (15)	0.0442 (5)
O10	0.90425 (16)	0.22466 (16)	1.03827 (13)	0.0348 (4)
O11	0.7673 (2)	0.5795 (2)	1.08301 (16)	0.0530 (5)
O12	0.4202 (2)	0.1567 (2)	0.52647 (18)	0.0660 (6)
O13	0.6054 (2)	0.6153 (2)	0.45161 (19)	0.0718 (7)
N1	0.60609 (19)	0.17145 (19)	0.92857 (15)	0.0289 (4)
N2	0.66727 (19)	0.08302 (19)	1.11745 (15)	0.0300 (4)
N3	0.8475 (2)	0.38116 (18)	0.48948 (15)	0.0307 (4)
N4	0.95203 (19)	0.26891 (19)	0.64407 (15)	0.0302 (4)
C1	0.5672 (2)	0.2071 (2)	1.01363 (18)	0.0281 (5)
C2	1.0673 (3)	0.1905 (3)	0.4113 (2)	0.0458 (7)
H1	1.1170	0.1460	0.3941	0.055*

C3	0.4628 (3)	0.3173 (3)	1.0999 (2)	0.0411 (6)
H2	0.4183	0.3729	1.0956	0.049*
C4	0.8381 (2)	0.4326 (2)	0.86825 (18)	0.0294 (5)
C5	0.8384 (2)	−0.1090 (2)	0.97004 (19)	0.0303 (5)
C6	0.7621 (2)	−0.0238 (2)	0.77940 (18)	0.0310 (5)
C7	1.0521 (3)	0.1971 (2)	0.5215 (2)	0.0374 (6)
C8	0.5733 (2)	0.2109 (2)	0.8310 (2)	0.0361 (6)
H3	0.5992	0.1861	0.7708	0.043*
C9	0.4924 (3)	0.2704 (3)	1.1961 (2)	0.0411 (6)
H4	0.4671	0.2926	1.2577	0.049*
C10	0.4974 (2)	0.2848 (2)	1.0038 (2)	0.0347 (5)
C11	0.7124 (3)	0.5173 (2)	0.7043 (2)	0.0367 (6)
C12	0.4645 (3)	0.3256 (3)	0.8995 (2)	0.0433 (6)
H5	0.4170	0.3788	0.8888	0.052*
C13	1.0119 (3)	0.2465 (3)	0.3323 (2)	0.0444 (7)
H6	1.0219	0.2393	0.2596	0.053*
C14	0.7998 (3)	0.5366 (2)	0.82237 (19)	0.0387 (6)
H7	0.7580	0.5632	0.8731	0.046*
H8	0.8795	0.6053	0.8276	0.046*
C15	0.5996 (2)	0.1581 (2)	1.11580 (18)	0.0277 (5)
C16	0.7976 (3)	0.4437 (2)	0.41560 (19)	0.0360 (6)
H9	0.7485	0.4872	0.4355	0.043*
C17	0.5615 (2)	0.1877 (2)	1.20699 (19)	0.0332 (5)
C18	0.9751 (2)	0.2590 (2)	0.54358 (18)	0.0296 (5)
C19	0.6969 (3)	0.0339 (3)	1.2106 (2)	0.0376 (6)
H10	0.7440	−0.0192	1.2130	0.045*
C20	0.5945 (3)	0.1345 (3)	1.3033 (2)	0.0404 (6)
H11	0.5706	0.1519	1.3674	0.048*
C21	1.1090 (3)	0.1438 (3)	0.6107 (2)	0.0528 (8)
H12	1.1634	0.1013	0.6006	0.063*
C22	0.8396 (3)	−0.0902 (3)	0.8508 (2)	0.0403 (6)
H13	0.9302	−0.0474	0.8542	0.048*
H14	0.8134	−0.1721	0.8086	0.048*
C23	1.0055 (3)	0.2159 (3)	0.72536 (19)	0.0384 (6)
H15	0.9886	0.2208	0.7953	0.046*
C24	0.9179 (2)	0.3201 (2)	0.45969 (18)	0.0293 (5)
C25	0.9382 (2)	0.3168 (2)	0.35420 (19)	0.0341 (5)
C26	0.8837 (3)	0.3834 (3)	0.27801 (19)	0.0396 (6)
H16	0.8943	0.3841	0.2052	0.048*
C27	0.8157 (3)	0.4470 (3)	0.3094 (2)	0.0407 (6)
H17	0.7804	0.4938	0.2589	0.049*
C28	0.6612 (3)	0.0576 (3)	1.3048 (2)	0.0434 (7)
H18	0.6832	0.0204	1.3696	0.052*
C29	0.5015 (3)	0.2878 (3)	0.8138 (2)	0.0430 (6)
H19	0.4788	0.3137	0.7426	0.052*
C30	1.0856 (3)	0.1536 (3)	0.7115 (2)	0.0517 (8)
H20	1.1236	0.1181	0.7718	0.062*
H21	0.6133	0.5993	0.5272	0.062*
H22	0.5357	0.5415	0.4228	0.062*

H23	0.3996	0.2283	0.5323	0.062*
H24	0.3640	0.1262	0.4584	0.062*
H25	0.8137	0.6589	1.0626	0.062*
H26	0.7833	0.5224	1.0522	0.062*
H27	0.9093	0.2935	1.0132	0.062*
H28	0.9674	0.2114	1.0153	0.062*
H29	0.6825	0.1033	0.6230	0.062*
H30	0.5809	0.1432	0.5701	0.062*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.04086 (18)	0.04053 (19)	0.02340 (14)	0.02651 (15)	0.00992 (12)	0.00430 (12)
Cu2	0.03470 (17)	0.03519 (18)	0.02483 (14)	0.02200 (14)	0.01212 (12)	0.00651 (11)
O1	0.0572 (12)	0.0509 (12)	0.0259 (8)	0.0380 (10)	0.0119 (8)	0.0046 (7)
O2	0.0648 (13)	0.0685 (14)	0.0297 (9)	0.0510 (12)	0.0057 (8)	−0.0006 (8)
O3	0.0582 (12)	0.0535 (12)	0.0259 (8)	0.0391 (10)	0.0142 (8)	0.0092 (8)
O4	0.0661 (13)	0.0620 (14)	0.0255 (8)	0.0366 (11)	0.0141 (8)	0.0055 (8)
O5	0.0548 (11)	0.0444 (11)	0.0273 (8)	0.0286 (9)	0.0146 (8)	0.0074 (7)
O6	0.0869 (17)	0.0887 (18)	0.0454 (11)	0.0738 (15)	0.0117 (11)	0.0028 (11)
O7	0.0535 (11)	0.0428 (11)	0.0302 (8)	0.0336 (9)	0.0194 (8)	0.0108 (7)
O8	0.0596 (12)	0.0521 (12)	0.0445 (10)	0.0422 (10)	0.0240 (9)	0.0190 (9)
O9	0.0456 (11)	0.0453 (12)	0.0398 (9)	0.0166 (9)	0.0079 (8)	0.0119 (8)
O10	0.0359 (9)	0.0394 (10)	0.0352 (8)	0.0191 (8)	0.0124 (7)	0.0093 (7)
O11	0.0723 (14)	0.0597 (14)	0.0483 (11)	0.0393 (12)	0.0308 (10)	0.0139 (10)
O12	0.0638 (15)	0.0736 (16)	0.0508 (12)	0.0323 (13)	−0.0077 (10)	0.0003 (11)
O13	0.0708 (16)	0.0746 (18)	0.0614 (14)	0.0227 (14)	0.0070 (12)	0.0268 (12)
N1	0.0306 (10)	0.0342 (11)	0.0268 (9)	0.0164 (9)	0.0098 (8)	0.0056 (8)
N2	0.0332 (10)	0.0361 (11)	0.0286 (9)	0.0183 (9)	0.0138 (8)	0.0070 (8)
N3	0.0363 (11)	0.0318 (11)	0.0268 (9)	0.0160 (9)	0.0085 (8)	0.0055 (8)
N4	0.0347 (11)	0.0371 (12)	0.0251 (9)	0.0193 (9)	0.0104 (8)	0.0059 (8)
C1	0.0257 (11)	0.0308 (13)	0.0301 (11)	0.0123 (10)	0.0094 (9)	0.0030 (9)
C2	0.0519 (17)	0.0580 (19)	0.0436 (14)	0.0297 (15)	0.0270 (13)	0.0059 (13)
C3	0.0392 (14)	0.0419 (16)	0.0520 (15)	0.0245 (13)	0.0170 (12)	0.0007 (12)
C4	0.0324 (12)	0.0333 (13)	0.0254 (10)	0.0152 (11)	0.0084 (9)	0.0033 (9)
C5	0.0332 (12)	0.0314 (13)	0.0314 (11)	0.0172 (11)	0.0104 (10)	0.0045 (9)
C6	0.0352 (13)	0.0354 (14)	0.0255 (10)	0.0151 (11)	0.0106 (9)	0.0030 (9)
C7	0.0396 (14)	0.0447 (16)	0.0376 (12)	0.0224 (12)	0.0174 (11)	0.0051 (11)
C8	0.0380 (14)	0.0429 (16)	0.0326 (12)	0.0196 (12)	0.0112 (10)	0.0095 (10)
C9	0.0387 (14)	0.0477 (17)	0.0447 (14)	0.0216 (13)	0.0184 (11)	−0.0056 (12)
C10	0.0323 (13)	0.0347 (14)	0.0424 (13)	0.0175 (11)	0.0125 (10)	0.0041 (10)
C11	0.0455 (15)	0.0423 (15)	0.0332 (12)	0.0267 (13)	0.0145 (11)	0.0088 (11)
C12	0.0421 (15)	0.0402 (16)	0.0566 (16)	0.0257 (13)	0.0145 (13)	0.0131 (12)
C13	0.0512 (17)	0.0552 (18)	0.0359 (13)	0.0210 (14)	0.0248 (12)	0.0052 (12)
C14	0.0581 (17)	0.0343 (14)	0.0293 (11)	0.0244 (13)	0.0114 (11)	0.0045 (10)
C15	0.0268 (11)	0.0265 (12)	0.0307 (11)	0.0099 (10)	0.0097 (9)	0.0015 (9)
C16	0.0438 (15)	0.0357 (14)	0.0313 (11)	0.0193 (12)	0.0085 (10)	0.0069 (10)
C17	0.0308 (12)	0.0386 (14)	0.0313 (11)	0.0117 (11)	0.0127 (10)	−0.0009 (10)

C18	0.0310 (12)	0.0304 (13)	0.0287 (11)	0.0117 (10)	0.0102 (9)	0.0030 (9)
C19	0.0392 (14)	0.0465 (16)	0.0356 (12)	0.0238 (12)	0.0130 (11)	0.0120 (11)
C20	0.0413 (14)	0.0526 (17)	0.0312 (12)	0.0175 (13)	0.0167 (11)	0.0019 (11)
C21	0.0603 (19)	0.074 (2)	0.0484 (15)	0.0495 (18)	0.0222 (14)	0.0155 (15)
C22	0.0518 (16)	0.0550 (17)	0.0331 (12)	0.0365 (14)	0.0200 (11)	0.0131 (11)
C23	0.0467 (15)	0.0491 (16)	0.0290 (11)	0.0278 (13)	0.0123 (11)	0.0101 (11)
C24	0.0323 (12)	0.0289 (12)	0.0260 (10)	0.0098 (10)	0.0089 (9)	0.0022 (9)
C25	0.0360 (13)	0.0369 (14)	0.0271 (11)	0.0084 (11)	0.0114 (10)	0.0019 (10)
C26	0.0432 (15)	0.0462 (16)	0.0261 (11)	0.0096 (13)	0.0119 (10)	0.0084 (10)
C27	0.0456 (15)	0.0421 (16)	0.0314 (12)	0.0149 (13)	0.0060 (11)	0.0141 (11)
C28	0.0482 (16)	0.0593 (19)	0.0282 (12)	0.0228 (14)	0.0139 (11)	0.0153 (11)
C29	0.0451 (15)	0.0505 (17)	0.0422 (14)	0.0262 (14)	0.0132 (12)	0.0196 (12)
C30	0.064 (2)	0.069 (2)	0.0434 (15)	0.0492 (18)	0.0163 (14)	0.0184 (14)

Geometric parameters (Å, °)

Cu1—O2	1.9061 (18)	C3—C10	1.440 (3)
Cu1—O1	1.9270 (16)	C3—H2	0.9500
Cu1—N4	1.989 (2)	C4—C14	1.513 (3)
Cu1—N3	2.0298 (19)	C5—C22	1.519 (3)
Cu1—O9	2.293 (2)	C6—C22	1.514 (3)
Cu2—O3	1.9114 (16)	C7—C18	1.392 (3)
Cu2—O7	1.9246 (16)	C7—C21	1.415 (4)
Cu2—N1	2.017 (2)	C8—C29	1.401 (4)
Cu2—N2	2.0260 (18)	C8—H3	0.9500
Cu2—O10	2.2643 (18)	C9—C17	1.436 (4)
O1—C4	1.273 (3)	C9—H4	0.9500
O5—C4	1.235 (3)	C10—C12	1.408 (4)
O2—C11	1.264 (3)	C11—C14	1.511 (3)
O6—C11	1.219 (3)	C12—C29	1.364 (4)
O7—C5	1.272 (3)	C12—H5	0.9500
O8—C5	1.238 (3)	C13—C25	1.432 (4)
O3—C6	1.263 (3)	C13—H6	0.9500
O4—C6	1.237 (3)	C14—H7	0.9900
O9—H29	0.914	C14—H8	0.9900
O9—H30	0.962	C15—C17	1.398 (3)
O10—H27	0.868	C16—C27	1.399 (3)
O10—H28	0.907	C16—H9	0.9500
O11—H25	0.993	C17—C20	1.398 (4)
O11—H26	0.856	C18—C24	1.432 (3)
O12—H23	0.952	C19—C28	1.394 (4)
O12—H24	0.897	C19—H10	0.9500
O13—H21	0.957	C20—C28	1.365 (4)
O13—H22	0.944	C20—H11	0.9500
N1—C8	1.326 (3)	C21—C30	1.367 (4)
N1—C1	1.362 (3)	C21—H12	0.9500
N2—C19	1.333 (3)	C22—H13	0.9900
N2—C15	1.355 (3)	C22—H14	0.9900
N3—C16	1.331 (3)	C23—C30	1.394 (4)

N3—C24	1.357 (3)	C23—H15	0.9500
N4—C23	1.330 (3)	C24—C25	1.402 (3)
N4—C18	1.361 (3)	C25—C26	1.406 (4)
C1—C10	1.391 (3)	C26—C27	1.364 (4)
C1—C15	1.431 (3)	C26—H16	0.9500
C2—C13	1.346 (4)	C27—H17	0.9500
C2—C7	1.438 (3)	C28—H18	0.9500
C2—H1	0.9500	C29—H19	0.9500
C3—C9	1.350 (4)	C30—H20	0.9500
O2—Cu1—O1	94.22 (7)	C17—C9—H4	119.4
O2—Cu1—N4	172.50 (8)	C1—C10—C12	117.3 (2)
O1—Cu1—N4	92.40 (7)	C1—C10—C3	118.3 (2)
O2—Cu1—N3	90.83 (8)	C12—C10—C3	124.3 (2)
O1—Cu1—N3	164.15 (9)	O6—C11—O2	121.6 (2)
N4—Cu1—N3	81.87 (8)	O6—C11—C14	118.5 (2)
O2—Cu1—O9	96.55 (8)	O2—C11—C14	119.9 (2)
O1—Cu1—O9	99.84 (8)	C29—C12—C10	119.2 (2)
N4—Cu1—O9	85.78 (8)	C29—C12—H5	120.4
N3—Cu1—O9	94.49 (7)	C10—C12—H5	120.4
O3—Cu2—O7	94.75 (7)	C2—C13—C25	122.0 (2)
O3—Cu2—N1	89.31 (7)	C2—C13—H6	119.0
O7—Cu2—N1	168.67 (8)	C25—C13—H6	119.0
O3—Cu2—N2	164.81 (8)	C11—C14—C4	119.5 (2)
O7—Cu2—N2	92.39 (7)	C11—C14—H7	107.4
N1—Cu2—N2	81.31 (8)	C4—C14—H7	107.4
O3—Cu2—O10	99.15 (7)	C11—C14—H8	107.4
O7—Cu2—O10	93.79 (7)	C4—C14—H8	107.4
N1—Cu2—O10	96.00 (7)	H7—C14—H8	107.0
N2—Cu2—O10	93.73 (7)	N2—C15—C17	123.3 (2)
C4—O1—Cu1	126.47 (15)	N2—C15—C1	116.27 (19)
C11—O2—Cu1	127.43 (16)	C17—C15—C1	120.4 (2)
C6—O3—Cu2	129.19 (15)	N3—C16—C27	121.8 (2)
C5—O7—Cu2	127.87 (15)	N3—C16—H9	119.1
Cu1—O9—H29	119.3	C27—C16—H9	119.1
Cu1—O9—H30	131.1	C15—C17—C20	117.2 (2)
Cu2—O10—H27	117.8	C15—C17—C9	118.3 (2)
Cu2—O10—H28	112.6	C20—C17—C9	124.6 (2)
H29—O9—H30	98.1	N4—C18—C7	123.6 (2)
H27—O10—H28	98.2	N4—C18—C24	116.0 (2)
H25—O11—H26	110.1	C7—C18—C24	120.4 (2)
H23—O12—H24	94.7	N2—C19—C28	122.4 (2)
H21—O13—H22	92.2	N2—C19—H10	118.8
C8—N1—C1	118.1 (2)	C28—C19—H10	118.8
C8—N1—Cu2	128.98 (16)	C28—C20—C17	119.6 (2)
C1—N1—Cu2	112.87 (15)	C28—C20—H11	120.2
C19—N2—C15	117.8 (2)	C17—C20—H11	120.2
C19—N2—Cu2	129.25 (17)	C30—C21—C7	119.7 (3)
C15—N2—Cu2	112.89 (15)	C30—C21—H12	120.1
C16—N3—C24	118.3 (2)	C7—C21—H12	120.1

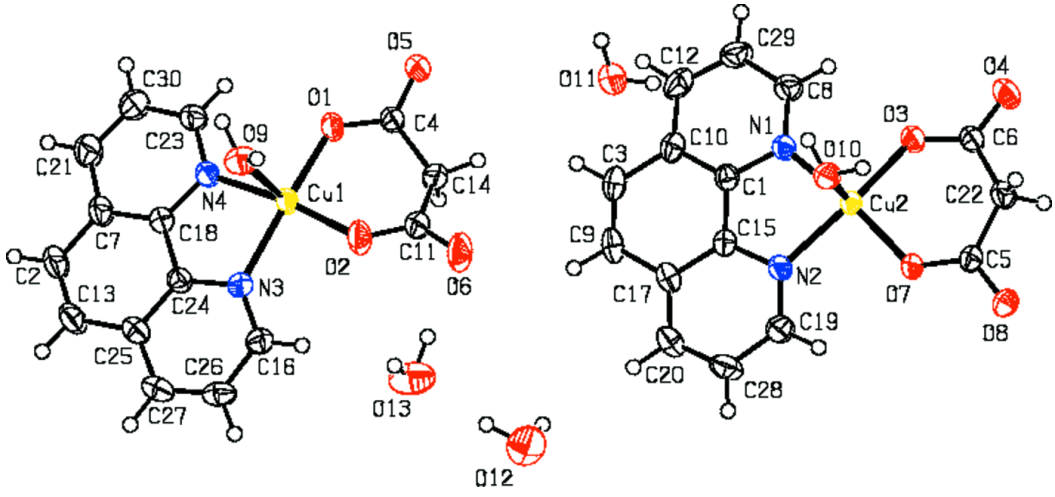
C16—N3—Cu1	129.80 (17)	C6—C22—C5	123.0 (2)
C24—N3—Cu1	111.89 (15)	C6—C22—H13	106.6
C23—N4—C18	118.1 (2)	C5—C22—H13	106.6
C23—N4—Cu1	128.45 (16)	C6—C22—H14	106.6
C18—N4—Cu1	113.33 (15)	C5—C22—H14	106.6
N1—C1—C10	123.3 (2)	H13—C22—H14	106.5
N1—C1—C15	116.3 (2)	N4—C23—C30	122.3 (2)
C10—C1—C15	120.4 (2)	N4—C23—H15	118.8
C13—C2—C7	120.7 (2)	C30—C23—H15	118.8
C13—C2—H1	119.7	N3—C24—C25	123.5 (2)
C7—C2—H1	119.7	N3—C24—C18	116.46 (19)
C9—C3—C10	121.3 (2)	C25—C24—C18	120.1 (2)
C9—C3—H2	119.4	C24—C25—C26	116.8 (2)
C10—C3—H2	119.4	C24—C25—C13	118.0 (2)
O5—C4—O1	122.5 (2)	C26—C25—C13	125.2 (2)
O5—C4—C14	118.1 (2)	C27—C26—C25	119.5 (2)
O1—C4—C14	119.4 (2)	C27—C26—H16	120.2
O8—C5—O7	122.1 (2)	C25—C26—H16	120.2
O8—C5—C22	116.2 (2)	C26—C27—C16	120.2 (2)
O7—C5—C22	121.7 (2)	C26—C27—H17	119.9
O4—C6—O3	121.8 (2)	C16—C27—H17	119.9
O4—C6—C22	117.0 (2)	C20—C28—C19	119.6 (2)
O3—C6—C22	121.23 (19)	C20—C28—H18	120.2
C18—C7—C21	116.6 (2)	C19—C28—H18	120.2
C18—C7—C2	118.7 (2)	C12—C29—C8	119.9 (2)
C21—C7—C2	124.7 (2)	C12—C29—H19	120.1
N1—C8—C29	122.2 (2)	C8—C29—H19	120.1
N1—C8—H3	118.9	C21—C30—C23	119.6 (3)
C29—C8—H3	118.9	C21—C30—H20	120.2
C3—C9—C17	121.3 (2)	C23—C30—H20	120.2
C3—C9—H4	119.4		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9—H29···O4	0.91	2.08	2.961 (3)	161
O9—H30···O12	0.96	1.85	2.769 (3)	158
O10—H27···O5	0.87	1.91	2.720 (3)	154
O10—H28···O8^{i}	0.91	1.92	2.824 (3)	172
O11—H25···O8^{ii}	0.99	1.99	2.983 (3)	174
O11—H26···O5	0.86	1.99	2.831 (3)	167
O12—H23···O13^{iii}	0.95	1.86	2.800 (3)	168
O12—H24···O4^{iv}	0.90	1.89	2.780 (3)	169
O13—H21···O6	0.96	1.96	2.915 (3)	177
O13—H22···O6^{iii}	0.94	2.06	2.952 (3)	156

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

Fig. 1


O5
C30
O1
C23
O9
C4
C21
N4
Cu1
C14
C7
C18
O2
C11
O6
C2
C13
C24
N3
C25
C26
C16
O13
C27
O12
C29
O11
C12
C8
O4
O3
C10
N1
C6
C3
O10
C1
C22
Cu2
C9
C15
C5
C17
N2
O7
O8
C19
C20
C28