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Poly[[aqua{μ_4-2-[(carboxymethyl)sulfanyl]nicotinato-$\kappa^4O:O':O'':O'''$}copper(II)] trihydrate]

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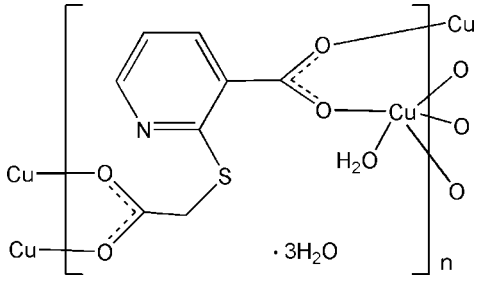
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; R factor = 0.032; wR factor = 0.085; data-to-parameter ratio = 17.3.

In the polymeric title complex, $\{[Cu(C_8H_5NO_4S)(H_2O)]\cdot 3H_2O\}_n$, the Cu^{II} cation is coordinated by one water molecule and four carboxylate O atoms from four 2-[(carboxymethyl)sulfanyl]nicotinate anions in a distorted square-pyramidal geometry. The 2-[(carboxymethyl)sulfanyl]nicotinate anion bridges four Cu^{II} cations, forming a two-dimensional polymeric complex parallel to the *bc* plane. In the crystal, O—H···O, O—H···N and O—H···S hydrogen bonds link the complex molecules and lattice water molecules into a three-dimensional supramolecular architecture.

Related literature

For background to the 2-[(carboxymethyl)sulfanyl]nicotinato ligand, see: Wang & Feng (2010). For related compounds, see: Jiang *et al.* (2012). For metal complexes with 2-mercaptonicotinate ligands, see: Humphrey *et al.* (2006); Sun *et al.* (2011).



Experimental

Crystal data

$[Cu(C_8H_5NO_4S)(H_2O)]\cdot 3H_2O$
M_r = 346.82
Monoclinic, $P2_1/c$
a = 9.940 (7) Å
b = 16.639 (9) Å
c = 7.876 (4) Å
β = 96.28 (5)°
V = 1294.8 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.88 mm^{-1}
T = 296 K
0.25 × 0.09 × 0.06 mm

Data collection

Bruker SMART APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.812, T_{max} = 0.892
20324 measured reflections
2973 independent reflections
2331 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.085
S = 1.04
2973 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—O1	1.958 (2)	Cu1—O4^{iii}	1.9836 (19)
Cu1—O2^{i}	1.9682 (19)	Cu1—O1*W*	2.171 (2)
Cu1—O3^{ii}	1.9687 (19)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O4*W*^{iv}	0.82	1.93	2.747 (4)	174
O1*W*—H1*WB*···O2*W*^{iii}	0.84	2.11	2.899 (4)	156
O2*W*—H2*WA*···O3*W*^{v}	0.83	2.05	2.843 (5)	157
O2*W*—H2*WB*···O4	0.84	2.26	2.911 (4)	135
O2*W*—H2*WB*···N1	0.84	2.56	3.253 (4)	141
O3*W*—H3*WA*···O3^{vi}	0.82	2.40	3.110 (4)	146
O3*W*—H3*WB*···O2*W*	0.83	2.00	2.803 (5)	165
O4*W*—H4*WB*···S1^{vi}	0.85	2.62	3.356 (4)	146

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5692).

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supporting information

Acta Cryst. (2013). E**69**, m268 [https://doi.org/10.1107/S1600536813009604]

Poly[[aqua{μ_4-2-[(carboxymethyl)sulfanyl]nicotinato-$\kappa^4O:O':O'':O'''$}copper(II)] trihydrate]

Wei-Qi Li

S1. Comment

2-Carboxymethylsulfanylnicotinic acid is prepared from 2-mercaptonanicotinic acid (Wang & Feng, 2010). 2-Mercaptonanicotinic acid is a multifunctional ligand, and some complexes containing 2-mercaptonanicotinate ligand have been previously investigated (Humphrey *et al.*, 2006; Sun *et al.*, 2011).

The 2-carboxymethylsulfanylnicotinic acid is an interesting ligand because of its potential versatile coordinate behavior. Recently, only three metal compounds have been reported about 2-carboxymethylsulfanyl nicotinic acid (Jiang *et al.*, 2012). Herein, we report the synthesis and structure of the title compound.

A perspective view of (I) is presented in Fig.1. The asymmetric unit consists of one Cu^{II} ion, one $(C_8H_5NO_4S)^{2-}$ ligands, one coordinated water molecule, and three lattice water molecules. As shown in Fig. 2, each pair of Cu^{2+} ion is μ-linked by four carboxylic groups of the individual $(C_8H_5NO_4S)^{2-}$ ligands with Cu···Cu distances of 2.6524 (15) Å. The $(C_8H_5NO_4S)^{2-}$ ligands bridge adjacent dinuclear units in a head-to-tail fashion to form a two-dimensional layer on the *bc* plane, and further linked into the three-dimensional architecture by O—H···O/N/S hydrogen bonds (Fig.3).

S2. Experimental

2-Carboxymethylsulfanyl nicotinic acid (1.0 mmol) in H_2O (10 ml) was stirred under basic condition in which $NH_3.H_2O$ was needed to keep pH value of 11. $CuCl_2.2H_2O$ was added and stirred for 2 h. The resulting solution was placed for 2 days, and the crystals were filtered off, giving blue crystals of the title compound for X-ray analysis.

S3. Refinement

The carbon-bound H-atoms were positioned geometrically and included in the refinement using a riding model [aromatic C—H 0.93 Å and aliphatic C—H 0.97 Å, U_{iso}(H) = 1.2U_{eq}(C)]. The oxygen-bound H-atoms was located in a difference Fourier maps and refined with the O—H distance restrained to 0.83 (2) Å and U_{iso}(H) = 1.2U_{eq}(O).

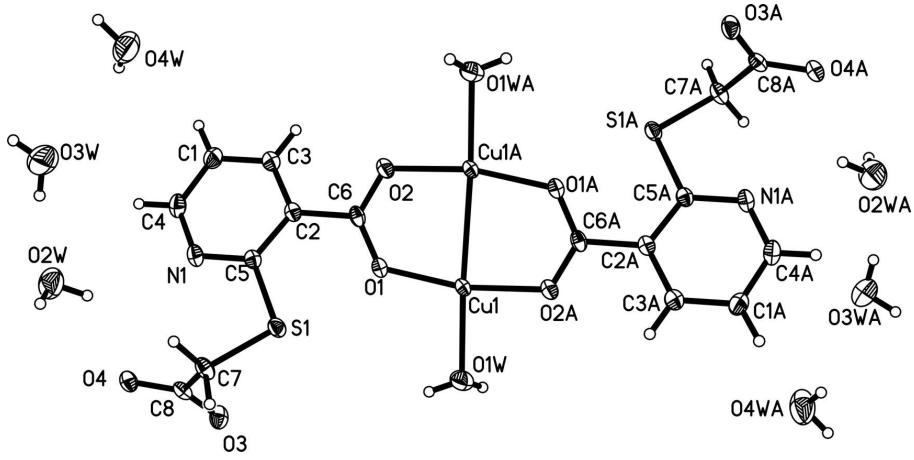

Figure 1

A view of the molecule of (I) showing the atom-labelling scheme with displacement ellipsoids drawn at the 30% probability. Symmetry codes: (A) -*x* + 2,-*y* + 1,-*z* + 1.

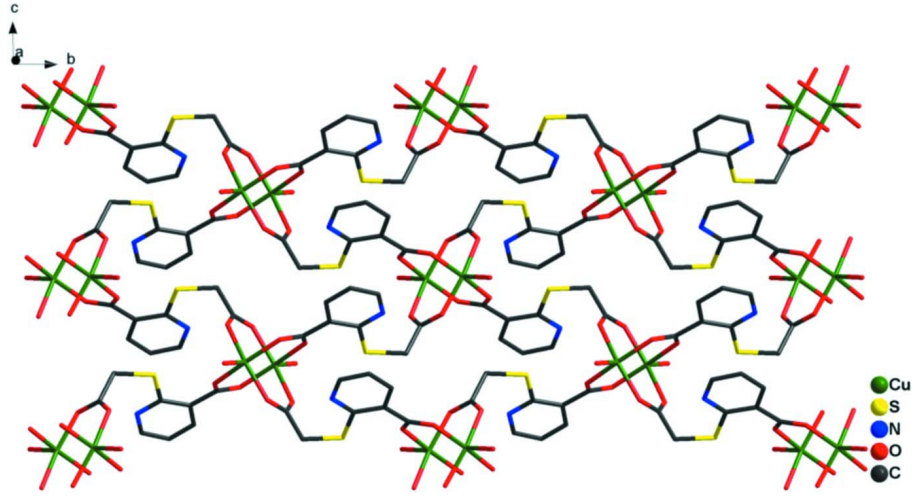

Figure 2

A view of the two-dimensional layer structure of (I).

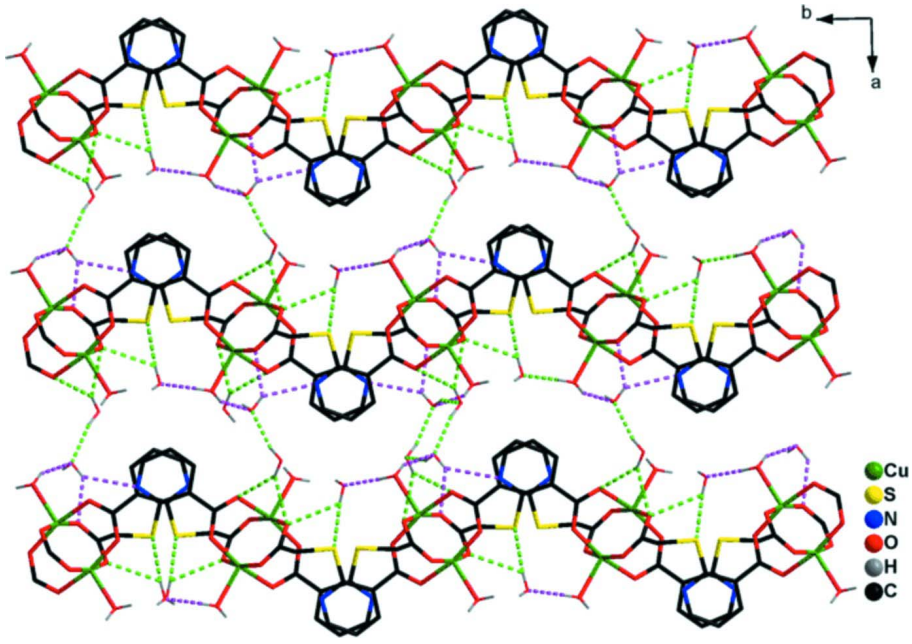

Figure 3

three-dimensional supramolecular architecture of (I). Dashed lines indicate hydrogen bonds.

Poly[[aqua{μ_4-2-[(carboxymethyl)sulfanyl]nicotinato-$\kappa^4O:O':O'':O'''$}copper(II)] trihydrate]

Crystal data

$[Cu(C_8H_5NO_4S)(H_2O)]\cdot 3H_2O$
$M_r = 346.82$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 9.940\ (7)$ Å
$b = 16.639\ (9)$ Å
$c = 7.876\ (4)$ Å
$\beta = 96.28\ (5)°$
$V = 1294.8\ (13)$ Å^3
$Z = 4$
$F(000) = 708$
$D_x = 1.779$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3501 reflections
$\theta = 2.1–27.6°$
$\mu = 1.88$ mm^{-1}
$T = 296$ K
Plate, blue
0.25 × 0.09 × 0.06 mm

Data collection

Bruker SMART APEXII area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.812$, $T_{max} = 0.892$
20324 measured reflections
2973 independent reflections
2331 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 27.6°$, $\theta_{min} = 2.1°$
$h = -11\rightarrow12$
$k = -21\rightarrow21$
$l = -10\rightarrow10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.085$
$S = 1.04$
2973 reflections
172 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map	$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.2317P]$ where $P = (F_o^2 + 2F_c^2)/3$
Hydrogen site location: inferred from neighbouring sites	$(\Delta/\sigma)_{max} = 0.001$
H-atom parameters constrained	$\Delta\rho_{max} = 0.37$ e Å^{-3}
	$\Delta\rho_{min} = -0.32$ e Å^{-3}

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	1.10928 (3)	0.455426 (15)	0.48878 (4)	0.02469 (11)
S1	0.96122 (7)	0.21713 (3)	0.44052 (8)	0.03032 (16)
O1	0.97500 (18)	0.37850 (10)	0.3866 (2)	0.0338 (4)
O1W	1.2932 (2)	0.39085 (12)	0.4498 (3)	0.0473 (5)
H1WA	1.2787	0.3469	0.4037	0.057*
H1WB	1.3419	0.4141	0.3845	0.057*
O2	0.7893 (2)	0.45444 (10)	0.3972 (3)	0.0369 (4)
O3	1.0779 (2)	0.08898 (11)	0.2128 (2)	0.0374 (4)
O4	0.89346 (19)	0.01319 (10)	0.2319 (2)	0.0328 (4)
N1	0.7301 (2)	0.17934 (12)	0.2526 (3)	0.0341 (5)
C1	0.5606 (3)	0.27286 (16)	0.1366 (4)	0.0398 (7)
H1A	0.4768	0.2817	0.0745	0.048*
C2	0.7636 (3)	0.32137 (14)	0.2965 (3)	0.0267 (5)
C3	0.6384 (3)	0.33602 (16)	0.2060 (4)	0.0348 (6)
H3A	0.6068	0.3885	0.1919	0.042*
C4	0.6114 (3)	0.19624 (16)	0.1627 (4)	0.0393 (7)
H4A	0.5600	0.1536	0.1147	0.047*
C5	0.8059 (3)	0.24081 (14)	0.3179 (3)	0.0260 (5)
C6	0.8489 (3)	0.38985 (13)	0.3664 (3)	0.0268 (5)
C7	0.9514 (3)	0.10887 (14)	0.4500 (3)	0.0319 (6)
H7A	1.0178	0.0897	0.5403	0.038*
H7B	0.8626	0.0938	0.4794	0.038*
C8	0.9757 (3)	0.06765 (14)	0.2838 (3)	0.0286 (5)
O2W	0.6123 (3)	−0.00071 (16)	0.2997 (4)	0.0759 (8)
H2WA	0.6385	−0.0244	0.3907	0.091*
H2WB	0.6774	0.0299	0.2886	0.091*
O3W	0.3765 (3)	0.07734 (18)	0.3764 (4)	0.0831 (9)
H3WA	0.3048	0.0589	0.3329	0.100*
H3WB	0.4364	0.0491	0.3424	0.100*
O4W	0.2538 (3)	0.24845 (18)	0.2749 (5)	0.1001 (11)

H4WA	0.2766	0.2280	0.1881	0.120*
H4WB	0.1699	0.2362	0.2691	0.120*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02945 (19)	0.01710 (15)	0.02766 (18)	0.00031 (11)	0.00377 (12)	0.00057 (11)
S1	0.0364 (4)	0.0231 (3)	0.0307 (4)	0.0012 (3)	0.0001 (3)	−0.0052 (2)
O1	0.0335 (11)	0.0208 (8)	0.0472 (12)	−0.0032 (7)	0.0043 (9)	−0.0036 (7)
O1W	0.0429 (12)	0.0403 (11)	0.0603 (14)	0.0085 (9)	0.0123 (10)	−0.0024 (9)
O2	0.0382 (11)	0.0238 (9)	0.0469 (12)	0.0011 (8)	−0.0026 (9)	−0.0080 (8)
O3	0.0434 (12)	0.0363 (10)	0.0337 (10)	−0.0079 (9)	0.0093 (9)	−0.0118 (8)
O4	0.0412 (11)	0.0248 (8)	0.0330 (10)	−0.0010 (8)	0.0066 (8)	−0.0051 (7)
N1	0.0417 (14)	0.0242 (10)	0.0357 (13)	−0.0065 (9)	0.0016 (10)	−0.0041 (9)
C1	0.0335 (16)	0.0393 (15)	0.0444 (17)	−0.0048 (12)	−0.0052 (13)	−0.0017 (12)
C2	0.0320 (14)	0.0234 (12)	0.0254 (13)	−0.0021 (10)	0.0056 (10)	−0.0014 (9)
C3	0.0357 (16)	0.0275 (13)	0.0410 (16)	−0.0008 (11)	0.0027 (12)	0.0011 (11)
C4	0.0424 (17)	0.0338 (14)	0.0403 (16)	−0.0121 (12)	−0.0012 (13)	−0.0045 (12)
C5	0.0308 (14)	0.0242 (11)	0.0238 (12)	−0.0016 (10)	0.0066 (10)	−0.0016 (9)
C6	0.0398 (16)	0.0188 (11)	0.0221 (12)	−0.0042 (10)	0.0039 (11)	0.0023 (9)
C7	0.0499 (17)	0.0225 (12)	0.0234 (13)	0.0016 (11)	0.0039 (12)	−0.0010 (9)
C8	0.0388 (15)	0.0202 (11)	0.0263 (13)	0.0065 (10)	0.0015 (11)	−0.0008 (9)
O2W	0.0679 (18)	0.0680 (17)	0.097 (2)	−0.0153 (14)	0.0337 (15)	−0.0023 (15)
O3W	0.0590 (18)	0.0867 (19)	0.098 (2)	−0.0033 (15)	−0.0178 (15)	−0.0172 (17)
O4W	0.069 (2)	0.090 (2)	0.150 (3)	−0.0265 (17)	0.048 (2)	−0.055 (2)

Geometric parameters (Å, º)

Cu1—O1	1.958 (2)	N1—C5	1.340 (3)
Cu1—O2^{i}	1.9682 (19)	C1—C4	1.379 (4)
Cu1—O3^{ii}	1.9687 (19)	C1—C3	1.382 (4)
Cu1—O4^{iii}	1.9836 (19)	C1—H1A	0.9300
Cu1—O1W	2.171 (2)	C2—C3	1.386 (4)
Cu1—Cu1^{i}	2.6524 (15)	C2—C5	1.410 (3)
S1—C5	1.773 (3)	C2—C6	1.489 (3)
S1—C7	1.806 (3)	C3—H3A	0.9300
O1—C6	1.261 (3)	C4—H4A	0.9300
O1W—H1WA	0.8228	C7—C8	1.521 (3)
O1W—H1WB	0.8384	C7—H7A	0.9700
O2—C6	1.263 (3)	C7—H7B	0.9700
O2—Cu1^{i}	1.9682 (19)	O2W—H2WA	0.8345
O3—C8	1.263 (3)	O2W—H2WB	0.8359
O3—Cu1^{iv}	1.9687 (19)	O3W—H3WA	0.8165
O4—C8	1.258 (3)	O3W—H3WB	0.8253
O4—Cu1^{v}	1.9836 (19)	O4W—H4WA	0.8176
N1—C4	1.337 (4)	O4W—H4WB	0.8547
O1—Cu1—O2^{i}	167.93 (8)	C3—C2—C5	117.9 (2)

O1—Cu1—O3^{ii}	87.44 (9)	C3—C2—C6	119.9 (2)
O2^{i}—Cu1—O3^{ii}	90.03 (9)	C5—C2—C6	122.2 (2)
O1—Cu1—O4^{iii}	90.75 (9)	C1—C3—C2	120.1 (2)
O2^{i}—Cu1—O4^{iii}	89.31 (9)	C1—C3—H3A	119.9
O3^{ii}—Cu1—O4^{iii}	168.14 (8)	C2—C3—H3A	119.9
O1—Cu1—O1W	99.49 (9)	N1—C4—C1	124.1 (3)
O2^{i}—Cu1—O1W	92.56 (9)	N1—C4—H4A	117.9
O3^{ii}—Cu1—O1W	99.18 (9)	C1—C4—H4A	117.9
O4^{iii}—Cu1—O1W	92.69 (9)	N1—C5—C2	122.1 (2)
O1—Cu1—Cu1^{i}	82.33 (7)	N1—C5—S1	117.35 (19)
O2^{i}—Cu1—Cu1^{i}	85.74 (7)	C2—C5—S1	120.48 (19)
O3^{ii}—Cu1—Cu1^{i}	86.50 (7)	O1—C6—O2	125.7 (2)
O4^{iii}—Cu1—Cu1^{i}	81.64 (7)	O1—C6—C2	116.7 (2)
O1W—Cu1—Cu1^{i}	174.09 (6)	O2—C6—C2	117.5 (2)
C5—S1—C7	101.32 (12)	C8—C7—S1	113.56 (17)
C6—O1—Cu1	125.29 (16)	C8—C7—H7A	108.9
Cu1—O1W—H1WA	113.2	S1—C7—H7A	108.9
Cu1—O1W—H1WB	114.3	C8—C7—H7B	108.9
H1WA—O1W—H1WB	103.0	S1—C7—H7B	108.9
C6—O2—Cu1^{i}	120.56 (18)	H7A—C7—H7B	107.7
C8—O3—Cu1^{iv}	120.36 (16)	O4—C8—O3	125.7 (2)
C8—O4—Cu1^{v}	125.43 (17)	O4—C8—C7	116.5 (2)
C4—N1—C5	118.0 (2)	O3—C8—C7	117.8 (2)
C4—C1—C3	117.6 (3)	H2WA—O2W—H2WB	101.8
C4—C1—H1A	121.2	H3WA—O3W—H3WB	106.2
C3—C1—H1A	121.2	H4WA—O4W—H4WB	102.4

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O4*W*^{vi}	0.82	1.93	2.747 (4)	174
O1*W*—H1*WB*···O2*W*^{iii}	0.84	2.11	2.899 (4)	156
O2*W*—H2*WA*···O3*W*^{vii}	0.83	2.05	2.843 (5)	157
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O3*W*—H3*WA*···O3^{viii}	0.82	2.40	3.110 (4)	146
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O4*W*—H4*WB*···S1^{viii}	0.85	2.62	3.356 (4)	146

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