Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis{(*E*)-2-[2-(2-hydroxybenzoyl)-hydrazono]propanoato-κ^3O,N,O'}-copper(II) trihydrate

Feng Liu, Wang-Ting Wu, Wei-Ping Zhang, Feng-Ying Chen and Shui-Yang He*

Department of Chemistry, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Northwest University, Xi'an, Shaanxi 710069, People's Republic of China
Correspondence e-mail: xdchemistry411@126.com

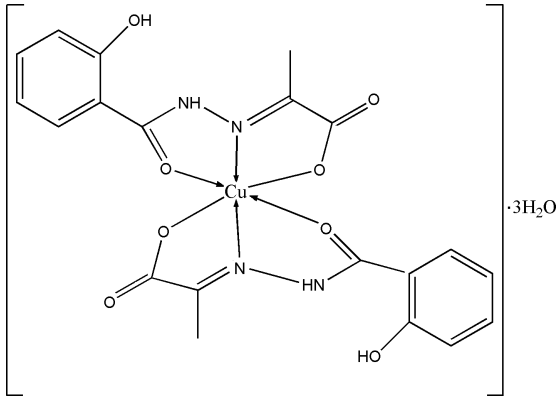
Received 24 July 2007; accepted 17 August 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.045; wR factor = 0.091; data-to-parameter ratio = 11.8.

The title compound, $[Cu(C_{10}H_9N_2O_4)_2]\cdot 3H_2O$, was obtained by evaporation of an aqueous ethanol solution of 2-[2-(2-hydroxybenzoyl)hydrazono]propanoic acid and cupric chloride. Each Cu^{II} atom is six-coordinated in a distorted octahedral geometry by carboxylate and acyl O atoms and imide N atoms from two tridentate ligands in the keto form, forming two five-membered rings sharing one edge for each ligand. N—H···O and O—H···O hydrogen bonds between water molecules and the ligands result in the formation of a three-dimensional network.

Related literature

For related literature, see: Buss *et al.* (2003); He *et al.* (2002); He *et al.* (2003); Rodrguez-Argelles *et al.* (2004);



Experimental

Crystal data

$[Cu(C_{10}H_9N_2O_4)_2]\cdot 3H_2O$
M_r = 559.97
Triclinic, $P\overline{1}$
a = 9.3787 (12) Å
b = 10.7935 (14) Å
c = 11.8795 (15) Å
α = 86.447 (2)°
β = 81.805 (2)°
γ = 79.847 (2)°
V = 1170.8 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.00 mm^{-1}
T = 298 (2) K
0.32 × 0.27 × 0.14 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SAINT-Plus*; Bruker, 2001)
T_{min} = 0.740, T_{max} = 0.871
5974 measured reflections
4104 independent reflections
3173 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.091
S = 0.87
4104 reflections
347 parameters
11 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—N1	1.942 (3)	Cu1—O5	2.208 (3)
Cu1—N3	1.982 (3)	Cu1—O7	2.281 (3)
Cu1—O1	2.047 (2)	O4—C4	1.246 (4)
Cu1—O4	2.092 (3)	O7—C14	1.228 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
O11—H11B···O2^{i}	0.82 (3)	2.11 (5)	2.888 (5)	154 (7)
O9—H9B···O6^{ii}	0.87 (4)	1.99 (6)	2.836 (5)	171 (7)
O11—H11A···O9^{iii}	0.85 (6)	1.91 (6)	2.752 (6)	167 (6)
O9—H9A···O10^{iv}	0.87 (5)	1.86 (5)	2.724 (7)	177 (6)
N2—H2···O11	0.86	2.19	2.830 (5)	131
N2—H2···O3	0.86	2.02	2.623 (4)	126
N4—H4···O8	0.86	1.91	2.573 (4)	133
O8—H8···O1^{v}	0.82	1.77	2.584 (3)	168
O3—H3···O5^{vi}	0.82	1.81	2.605 (3)	162

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

We acknowledge the support of the Natural Science Foundation of Shaanxi Province (grant No. 2007B02).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2076).

References

Bruker (2001). *SMART*, *SAINT-Plus* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Buss, J. L., Arduini, E., Shephard, K. C. & Ponka, P. (2003). *Biochem. Pharmacol.* **65**, 349–360.

  doi:10.1107/S160053680704072X

He, S. Y., Cao, W. K., Chen, J. L., Zhao, J. S. & Shi, Q. Z. (2002). *Chem. J. Chin. Univ.* **23**, 991–995.
He, S. Y., Cao, W. K., Zhao, J. S., Shi, Q. Z., Wang, Z. M. & Yan, C. H. (2003). *Chin. J. Inorg. Chem.* **19**, 699–704.
Rodrguez-Argelles, M. C., Ferrari, M. B., Bisceglie, F., Pelizzi, C., Pelosi, G., Pinelli, S. & Sassi, M. (2004). *J. Inorg. Biochem.* **98**, 313–321.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supplementary materials

Acta Cryst. (2007). E**63**, m2450-m2451 [**doi:10.1107/S160053680704072X**]

Bis{(*E*)-2-[2-(2-hydroxybenzoyl)hydrazono]propanoato-κ^3O,N,O'}copper(II) trihydrate

F. Liu, W.-T. Wu, W.-P. Zhang, F.-Y. Chen and S.-Y. He

Comment

Hydrazones have attracted considerable interest due to their complicated coordination behavior and pharmacological activity. Many of physiologically active hydrazone–metal complexes find applications in the treatment of several diseases such as tuberculosis, tumour and cancer (Buss *et al.*, 2003; Rodrguez-Argelles *et al.*, 2004). The crystal structures of five-coordinated Cu^{II} complexes with the 2-[2-(2-hydroxybenzoyl)hydrazono]propanoate ligand have been studied (He *et al.*, 2002; 2003). However, there are no reports on the crystal structure of six-coordinated Cu^{II} complexes with such a ligand. This paper reports the crystal structure of a new Cu^{II} complexe with 2-[2-(2-hydroxybenzoyl)hydrazono]propanoic acid.

In the title complex, the Cu^{II} atom is six-coordinated by two tridentate ligands through the acyl and carboxyl O atoms and imido N atoms (Fig. 1). Thus two five-membered chelate rings sharing one edge are formed for each ligand. The atoms O1, N1, O4 and N3 are approximately coplanar, forming the equatorial plane, while the other two O atoms occupy the axial sites. The angle of the axial O5—Cu1—O7 is 150.12 (9)°, which deviates from a linear arrangement. These data indicate that the Cu1 atom is in a distorted octahedral geometry. Uncoordinated three water molecules are found in the crystal lattice. Comparing with the distances of C—O (1.42 Å) and C═O (1.23 Å), the bond lengths of O7—C14 and O4—C4 are 1.228 (4) and 1.246 (4)Å (Table 1), respectively, indicating that they are double bonds and the ligand functions in a keto form.

There are abundant hydrogen bonds in the structure (Table 2). The intramolecular hydrogen bonds are observed between imido and hydroxyl groups. At the same time, the intermolecular hydrogen bonds exist between free water molecules and the ligands. These inter- and intramolecular hydrogen bonds result in a three-dimensional network and provide extra stability for the structure.

Experimental

The ligand was prepared according to the literature (He *et al.*, 2002). Pyruvic acid is biochemical reagent and all other chemicals used were of analytical grade.

A solution of 2-[2-(2-hydroxybenzoyl)hydrazono]propanoic acid (0.226 g, 1 mmol) in aqua–ethanol (15 ml, *v*/*v* = 1:2) was added under stirring to a solution of $CuCl_2{\cdot}2H_2O$ (0.088 g, 0.5 mmol) in aqua–ethanol (5 ml, *v*/*v* = 1:2). The resulting solution was refluxed at 353 K for 2 h, then filtered. The filtrate was left to evaporate naturally for about two weeks at room temperature and green prism crystals were obtained. The results of elemental analysis are in good agreement with the title complex.

Refinement

H atoms of the water molecules were located in a difference Fourier map and refined with a restraint of O—H = 0.85 (1)Å and a fixed U_{iso}. The other H atoms were positioned geometrically and refined as riding, with C—H = 0.93Å (CH) and

N—H = 0.86 Å (NH) and U_{iso}(H) = 1.2U_{eq}(C, N), and with C—H = 0.96Å (CH_3) and O—H = 0.82Å (OH) and U_{iso}(H) = 1.5U_{eq}(C, O).

Figures

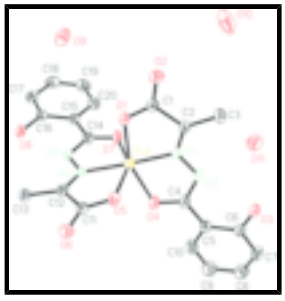


Fig. 1. The molecular structure of the title compoud. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

Bis{(*E*)-2-[2-(2-hydroxybenzoyl)hydrazono]propanoato-κ^3*O*,*N*,*O*'}copper(II) trihydrate

Crystal data

$[Cu(C_{10}H_9N_2O_4)_2]\cdot 3H_2O$	$Z = 2$
$M_r = 559.97$	$F_{000} = 578$
Triclinic, $P\overline{1}$	$D_x = 1.588$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 9.3787$ (12) Å	Cell parameters from 4104 reflections
$b = 10.7935$ (14) Å	$\theta = 1.9$–$25.1°$
$c = 11.8795$ (15) Å	$\mu = 1.00$ mm^{-1}
$\alpha = 86.447$ (2)°	$T = 298$ (2) K
$\beta = 81.805$ (2)°	Block, green
$\gamma = 79.847$ (2)°	0.32 × 0.27 × 0.14 mm
$V = 1170.8$ (3) Å^3	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	4104 independent reflections
Radiation source: fine-focus sealed tube	3173 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.017$
$T = 298(2)$ K	$\theta_{max} = 25.1°$
φ and ω scans	$\theta_{min} = 1.9°$
Absorption correction: multi-scan (SAINT-Plus; Bruker, 2001)	$h = -10\rightarrow11$
$T_{min} = 0.740$, $T_{max} = 0.871$	$k = -12\rightarrow12$
5974 measured reflections	$l = -14\rightarrow8$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.091$	$w = 1/[\sigma^2(F_o^2) + (0.004P)^2 + 3.5P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.87$	$(\Delta/\sigma)_{max} = 0.001$
4104 reflections	$\Delta\rho_{max} = 0.46$ e Å^{-3}
347 parameters	$\Delta\rho_{min} = -0.38$ e Å^{-3}
11 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.96365 (5)	0.75181 (4)	0.26010 (4)	0.04285 (14)
N1	0.9839 (3)	0.7462 (3)	0.4209 (2)	0.0375 (7)
N3	0.9562 (3)	0.7491 (2)	0.0943 (2)	0.0355 (7)
O5	1.1161 (3)	0.8770 (2)	0.1822 (2)	0.0486 (7)
O3	0.8437 (3)	1.0082 (2)	0.6413 (2)	0.0497 (7)
H3	0.8400	1.0384	0.7036	0.075*
O8	0.8088 (3)	0.5336 (2)	−0.0892 (2)	0.0450 (6)
H8	0.8197	0.4948	−0.1478	0.068*
O4	0.8153 (3)	0.9105 (2)	0.3181 (2)	0.0510 (7)
O1	1.1185 (3)	0.5939 (2)	0.2717 (2)	0.0479 (7)
O7	0.7917 (3)	0.6310 (2)	0.2436 (2)	0.0498 (7)
N4	0.8732 (3)	0.6699 (3)	0.0602 (2)	0.0397 (7)
H4	0.8714	0.6592	−0.0106	0.048*
N2	0.8996 (3)	0.8420 (3)	0.4821 (2)	0.0411 (7)
H2	0.9011	0.8481	0.5537	0.049*
C14	0.7938 (4)	0.6088 (3)	0.1432 (3)	0.0386 (8)
O6	1.1890 (3)	0.9618 (2)	0.0119 (2)	0.0526 (7)
C12	1.0356 (4)	0.8087 (3)	0.0209 (3)	0.0373 (8)
C1	1.1542 (4)	0.5673 (3)	0.3714 (3)	0.0410 (9)
C4	0.8137 (4)	0.9265 (3)	0.4213 (3)	0.0392 (8)
C6	0.7345 (4)	1.0711 (3)	0.5872 (3)	0.0406 (8)
C2	1.0792 (4)	0.6613 (3)	0.4607 (3)	0.0381 (8)
O2	1.2374 (3)	0.4751 (3)	0.3998 (2)	0.0646 (8)
C16	0.7262 (4)	0.4758 (3)	−0.0055 (3)	0.0358 (8)
C17	0.6531 (4)	0.3818 (3)	−0.0294 (3)	0.0437 (9)
H17	0.6607	0.3570	−0.1039	0.052*
C13	1.0480 (4)	0.8025 (3)	−0.1052 (3)	0.0441 (9)
H13A	1.1011	0.7217	−0.1284	0.066*

H13B	1.0990	0.8674	−0.1407	0.066*
H13C	0.9521	0.8143	−0.1277	0.066*
C15	0.7146 (4)	0.5144 (3)	0.1066 (3)	0.0376 (8)
C11	1.1221 (4)	0.8899 (3)	0.0752 (3)	0.0399 (8)
C3	1.1214 (5)	0.6499 (4)	0.5772 (3)	0.0527 (10)
H3A	1.2145	0.6759	0.5753	0.079*
H3B	1.1279	0.5638	0.6048	0.079*
H3C	1.0491	0.7025	0.6268	0.079*
C5	0.7198 (4)	1.0345 (3)	0.4785 (3)	0.0384 (8)
C20	0.6267 (4)	0.4558 (4)	0.1915 (3)	0.0486 (10)
H20	0.6165	0.4805	0.2662	0.058*
C10	0.6092 (4)	1.1031 (4)	0.4218 (3)	0.0527 (10)
H10	0.6000	1.0808	0.3491	0.063*
C19	0.5554 (4)	0.3626 (4)	0.1663 (4)	0.0561 (11)
H19	0.4975	0.3247	0.2237	0.067*
C9	0.5136 (5)	1.2027 (4)	0.4704 (4)	0.0628 (12)
H9	0.4402	1.2469	0.4313	0.075*
C7	0.6369 (4)	1.1726 (4)	0.6355 (3)	0.0534 (10)
H7	0.6456	1.1973	0.7075	0.064*
C18	0.5696 (4)	0.3249 (4)	0.0556 (4)	0.0543 (11)
H18	0.5224	0.2608	0.0387	0.065*
C8	0.5277 (5)	1.2365 (4)	0.5776 (4)	0.0626 (12)
H8A	0.4625	1.3033	0.6112	0.075*
O11	0.8000 (4)	0.7508 (3)	0.7027 (3)	0.0812 (10)
O9	0.3526 (4)	0.0972 (4)	0.1281 (4)	0.0952 (12)
O10	0.3972 (5)	0.0687 (7)	0.8498 (4)	0.152 (2)
H11A	0.744 (7)	0.788 (6)	0.758 (4)	0.183*
H9B	0.309 (6)	0.059 (6)	0.086 (6)	0.183*
H10B	0.344 (6)	0.088 (8)	0.796 (4)	0.183*
H11B	0.774 (7)	0.680 (3)	0.696 (6)	0.183*
H9A	0.435 (4)	0.049 (5)	0.136 (6)	0.183*
H10A	0.347 (4)	0.037 (5)	0.906 (4)	0.183*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0542 (3)	0.0390 (3)	0.0353 (3)	−0.0025 (2)	−0.0089 (2)	−0.00926 (19)
N1	0.0452 (18)	0.0367 (16)	0.0308 (15)	−0.0068 (14)	−0.0024 (13)	−0.0107 (13)
N3	0.0411 (17)	0.0307 (15)	0.0368 (16)	−0.0049 (13)	−0.0105 (13)	−0.0081 (13)
O5	0.0694 (18)	0.0443 (15)	0.0376 (15)	−0.0159 (13)	−0.0152 (13)	−0.0087 (12)
O3	0.0675 (18)	0.0472 (15)	0.0355 (14)	−0.0017 (13)	−0.0149 (13)	−0.0144 (12)
O8	0.0606 (17)	0.0456 (15)	0.0311 (13)	−0.0153 (13)	−0.0011 (12)	−0.0125 (11)
O4	0.0654 (18)	0.0534 (16)	0.0326 (14)	0.0010 (14)	−0.0104 (13)	−0.0122 (12)
O1	0.0664 (18)	0.0430 (15)	0.0320 (14)	0.0030 (13)	−0.0106 (13)	−0.0087 (11)
O7	0.0625 (18)	0.0601 (17)	0.0292 (14)	−0.0143 (14)	−0.0053 (12)	−0.0101 (12)
N4	0.0514 (19)	0.0398 (17)	0.0308 (16)	−0.0105 (14)	−0.0093 (14)	−0.0061 (13)
N2	0.0511 (19)	0.0415 (17)	0.0284 (15)	0.0019 (14)	−0.0057 (14)	−0.0098 (13)
C14	0.040 (2)	0.040 (2)	0.034 (2)	0.0002 (16)	−0.0056 (16)	−0.0037 (16)

O6	0.0636 (18)	0.0486 (16)	0.0491 (16)	−0.0199 (14)	−0.0062 (14)	−0.0009 (13)
C12	0.043 (2)	0.0320 (18)	0.037 (2)	0.0011 (16)	−0.0108 (16)	−0.0052 (15)
C1	0.048 (2)	0.036 (2)	0.040 (2)	−0.0056 (17)	−0.0097 (18)	−0.0058 (16)
C4	0.044 (2)	0.042 (2)	0.0331 (19)	−0.0087 (17)	−0.0049 (16)	−0.0085 (16)
C6	0.046 (2)	0.040 (2)	0.037 (2)	−0.0087 (17)	−0.0055 (17)	−0.0036 (16)
C2	0.047 (2)	0.0353 (19)	0.0326 (19)	−0.0075 (16)	−0.0070 (16)	−0.0034 (15)
O2	0.080 (2)	0.0516 (17)	0.0554 (18)	0.0195 (16)	−0.0218 (16)	−0.0109 (14)
C16	0.0342 (19)	0.0338 (18)	0.0368 (19)	0.0013 (15)	−0.0054 (15)	0.0001 (15)
C17	0.041 (2)	0.040 (2)	0.050 (2)	−0.0022 (17)	−0.0102 (18)	−0.0076 (18)
C13	0.054 (2)	0.044 (2)	0.035 (2)	−0.0016 (18)	−0.0127 (17)	−0.0056 (16)
C15	0.039 (2)	0.0374 (19)	0.0353 (19)	−0.0028 (15)	−0.0047 (16)	−0.0036 (16)
C11	0.047 (2)	0.0333 (19)	0.039 (2)	−0.0014 (17)	−0.0079 (17)	−0.0050 (16)
C3	0.065 (3)	0.055 (2)	0.038 (2)	−0.004 (2)	−0.0120 (19)	−0.0066 (18)
C5	0.040 (2)	0.042 (2)	0.0330 (19)	−0.0070 (16)	−0.0025 (16)	−0.0039 (16)
C20	0.049 (2)	0.055 (2)	0.040 (2)	−0.0030 (19)	−0.0065 (18)	0.0032 (18)
C10	0.056 (3)	0.060 (3)	0.041 (2)	0.000 (2)	−0.0130 (19)	−0.0068 (19)
C19	0.049 (2)	0.054 (3)	0.064 (3)	−0.016 (2)	0.000 (2)	0.011 (2)
C9	0.054 (3)	0.066 (3)	0.063 (3)	0.008 (2)	−0.010 (2)	−0.006 (2)
C7	0.060 (3)	0.052 (2)	0.045 (2)	−0.004 (2)	0.003 (2)	−0.0166 (19)
C18	0.047 (2)	0.043 (2)	0.075 (3)	−0.0110 (19)	−0.014 (2)	−0.002 (2)
C8	0.055 (3)	0.058 (3)	0.066 (3)	0.011 (2)	0.003 (2)	−0.015 (2)
O11	0.104 (3)	0.070 (2)	0.069 (2)	−0.025 (2)	0.006 (2)	−0.0090 (18)
O9	0.092 (3)	0.098 (3)	0.101 (3)	−0.034 (2)	0.004 (2)	−0.037 (2)
O10	0.107 (4)	0.260 (7)	0.079 (3)	−0.017 (4)	−0.007 (3)	0.027 (4)

Geometric parameters (Å, °)

Cu1—N1	1.942 (3)	C2—C3	1.485 (5)
Cu1—N3	1.982 (3)	C16—C17	1.385 (5)
Cu1—O1	2.047 (2)	C16—C15	1.404 (5)
Cu1—O4	2.092 (3)	C17—C18	1.370 (5)
Cu1—O5	2.208 (3)	C17—H17	0.9300
Cu1—O7	2.281 (3)	C13—H13A	0.9600
N1—C2	1.281 (4)	C13—H13B	0.9600
N1—N2	1.365 (4)	C13—H13C	0.9600
N3—C12	1.282 (4)	C15—C20	1.402 (5)
N3—N4	1.367 (4)	C3—H3A	0.9600
O5—C11	1.264 (4)	C3—H3B	0.9600
O3—C6	1.346 (4)	C3—H3C	0.9600
O3—H3	0.8200	C5—C10	1.394 (5)
O8—C16	1.361 (4)	C20—C19	1.371 (5)
O8—H8	0.8200	C20—H20	0.9300
O4—C4	1.246 (4)	C10—C9	1.372 (5)
O1—C1	1.279 (4)	C10—H10	0.9300
O7—C14	1.228 (4)	C19—C18	1.382 (6)
N4—C14	1.358 (4)	C19—H19	0.9300
N4—H4	0.8600	C9—C8	1.376 (6)
N2—C4	1.352 (4)	C9—H9	0.9300
N2—H2	0.8600	C7—C8	1.375 (6)

C14—C15	1.481 (5)	C7—H7	0.9300
O6—C11	1.235 (4)	C18—H18	0.9300
C12—C13	1.491 (5)	C8—H8A	0.9300
C12—C11	1.521 (5)	O11—H11A	0.85 (6)
C1—O2	1.213 (4)	O11—H11B	0.85 (4)
C1—C2	1.523 (5)	O9—H9B	0.86 (6)
C4—C5	1.470 (5)	O9—H9A	0.87 (5)
C6—C7	1.394 (5)	O10—H10B	0.86 (5)
C6—C5	1.406 (5)	O10—H10A	0.85 (5)
N1—Cu1—N3	175.97 (12)	O8—C16—C17	121.3 (3)
N1—Cu1—O1	78.90 (11)	O8—C16—C15	118.6 (3)
N3—Cu1—O1	97.23 (10)	C17—C16—C15	120.1 (3)
N1—Cu1—O4	77.76 (11)	C18—C17—C16	120.7 (4)
N3—Cu1—O4	106.09 (10)	C18—C17—H17	119.7
O1—Cu1—O4	156.66 (10)	C16—C17—H17	119.7
N1—Cu1—O5	103.78 (11)	C12—C13—H13A	109.5
N3—Cu1—O5	75.37 (10)	C12—C13—H13B	109.5
O1—Cu1—O5	96.24 (11)	H13A—C13—H13B	109.5
O4—Cu1—O5	89.13 (10)	C12—C13—H13C	109.5
N1—Cu1—O7	106.07 (11)	H13A—C13—H13C	109.5
N3—Cu1—O7	74.94 (10)	H13B—C13—H13C	109.5
O1—Cu1—O7	90.73 (10)	C20—C15—C16	117.9 (3)
O4—Cu1—O7	95.86 (10)	C20—C15—C14	117.2 (3)
O5—Cu1—O7	150.12 (9)	C16—C15—C14	124.8 (3)
C2—N1—N2	124.5 (3)	O6—C11—O5	126.8 (3)
C2—N1—Cu1	119.8 (2)	O6—C11—C12	117.7 (3)
N2—N1—Cu1	115.6 (2)	O5—C11—C12	115.5 (3)
C12—N3—N4	120.6 (3)	C2—C3—H3A	109.5
C12—N3—Cu1	122.3 (2)	C2—C3—H3B	109.5
N4—N3—Cu1	116.7 (2)	H3A—C3—H3B	109.5
C11—O5—Cu1	113.5 (2)	C2—C3—H3C	109.5
C6—O3—H3	109.5	H3A—C3—H3C	109.5
C16—O8—H8	109.5	H3B—C3—H3C	109.5
C4—O4—Cu1	112.8 (2)	C10—C5—C6	118.5 (3)
C1—O1—Cu1	114.6 (2)	C10—C5—C4	117.8 (3)
C14—O7—Cu1	109.9 (2)	C6—C5—C4	123.6 (3)
C14—N4—N3	117.1 (3)	C19—C20—C15	121.2 (4)
C14—N4—H4	121.5	C19—C20—H20	119.4
N3—N4—H4	121.5	C15—C20—H20	119.4
C4—N2—N1	114.8 (3)	C9—C10—C5	121.7 (4)
C4—N2—H2	122.6	C9—C10—H10	119.1
N1—N2—H2	122.6	C5—C10—H10	119.1
O7—C14—N4	120.2 (3)	C20—C19—C18	120.0 (4)
O7—C14—C15	122.8 (3)	C20—C19—H19	120.0
N4—C14—C15	117.0 (3)	C18—C19—H19	120.0
N3—C12—C13	126.1 (3)	C10—C9—C8	119.2 (4)
N3—C12—C11	112.9 (3)	C10—C9—H9	120.4
C13—C12—C11	121.0 (3)	C8—C9—H9	120.4
O2—C1—O1	126.2 (3)	C8—C7—C6	120.5 (4)

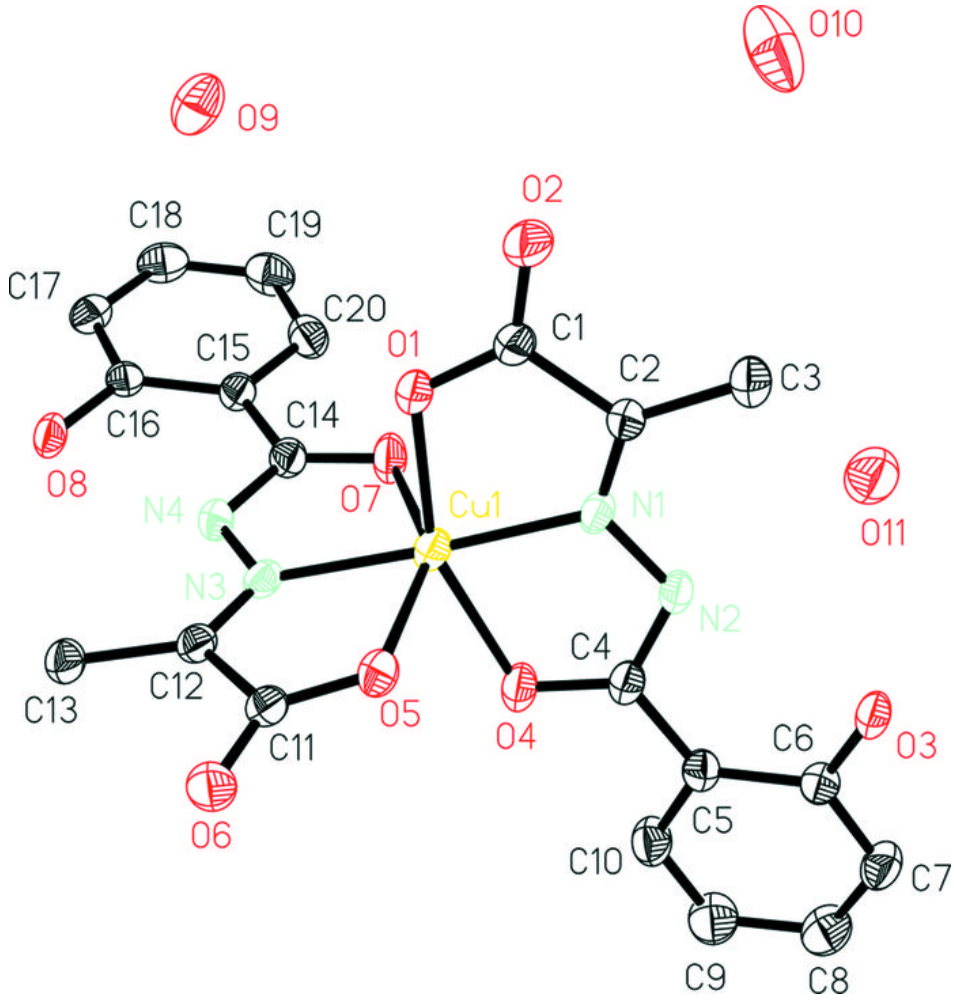
O2—C1—C2	119.1 (3)	C8—C7—H7	119.8
O1—C1—C2	114.7 (3)	C6—C7—H7	119.8
O4—C4—N2	119.1 (3)	C17—C18—C19	120.1 (4)
O4—C4—C5	121.6 (3)	C17—C18—H18	119.9
N2—C4—C5	119.3 (3)	C19—C18—H18	119.9
O3—C6—C7	121.7 (3)	C7—C8—C9	120.8 (4)
O3—C6—C5	119.1 (3)	C7—C8—H8A	119.6
C7—C6—C5	119.2 (4)	C9—C8—H8A	119.6
N1—C2—C3	127.6 (3)	H11A—O11—H11B	108 (6)
N1—C2—C1	111.8 (3)	H9B—O9—H9A	107 (6)
C3—C2—C1	120.6 (3)	H10B—O10—H10A	109 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H11B···O2^{i}	0.82 (3)	2.11 (5)	2.888 (5)	154 (7)
O9—H9B···O6^{ii}	0.87 (4)	1.99 (6)	2.836 (5)	171 (7)
O11—H11A···O9^{iii}	0.85 (6)	1.91 (6)	2.752 (6)	167 (6)
O9—H9A···O10^{iv}	0.87 (5)	1.86 (5)	2.724 (7)	177 (6)
N2—H2···O11	0.86	2.19	2.830 (5)	131
N2—H2···O3	0.86	2.02	2.623 (4)	126
N4—H4···O8	0.86	1.91	2.573 (4)	133
O8—H8···O1^{v}	0.82	1.77	2.584 (3)	168
O3—H3···O5^{vi}	0.82	1.81	2.605 (3)	162

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

Fig. 1


O10
O9
O2
C18
C19
C17
C20
C1
O1
C15
C2
C3
C16
C14
O8
O7
N4
Cu1
N1
O11
N3
N2
C4
C13
C12
O5
O4
C6
O3
C11
C5
O6
C10
C7
C9
C8